

## Research Article

# Spatial trends of Total Petroleum Hydrocarbons, related heavy metals and sediment characteristics in South Caspian Sea: Effect of depth and temporal dispersions

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Received: August 2017

Accepted: November 2017

### Abstract

In this study, Amirabad Special Economic was used as the study area, the distribution and tracing possible sources TPH, nickel, lead, vanadium, TP and TN were analysed in coastal sediments of 5 transects. According to our results the inner part of the 2 ports, are going to be slightly contaminated with TPH and heavy metals; meaning the contents of all the sites were lower than the background values. Based on physico-chemical parameters of water and according to dbRDA, the separation of offshore and river area was observed. Based on TOM, TPH and sediment nutrients, PCoA separated river and Sadra port transects. Finally, it seems high inter-annual water MVDISP values, reflecting highly temporal dynamic condition, influence the transportation of sediments along a depth gradient proved by nMDS, and the consecutive resuspension of sediments to open water is strong enough to keep the contaminants from rising to very high levels.

**Keywords:** Caspian Sea, TPH, Ni, Pb, Amirabad area, Sediment.

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## Introduction

Caspian Sea is the largest and most important lake in the world from ecological, political and natural resources points of view. The south coastlines also provide a lot of fish for human consumption each year and it is used for tourist purposes. Therefore, Caspian Sea is of great importance to the social, economic and daily life of the local residents and its watershed.

As a land-locked system, pollutants discharged into the Caspian Sea remain trapped within the basin and are exposed to increasing population pressure, urbanization of the coastal zone, and nutrient and sediment run-off from agriculture and forestry, oil exploitation, and production activities. An overwhelming chronic inputs of chemical contaminants such as hydrocarbons and trace metals from focal points along with nonpoint disturbances within and in the vicinity of long coastlines of this lake may all greatly affect natural resources through large-scale and chronic impacts, modification of habitats by influencing the health of benthic organisms, and finally overall quality of the aquatic environments with potential long term risks for human health and the ecosystem (Zaghden *et al.*, 2005; Marchand *et al.*, 2006). The effects of oil hydrocarbons, alone or in combination with heavy metals, depend on factors such as volume discharged, chemical characteristics, proximity to other sources of pollution and their interaction with local and natural environmental variables (Ye *et al.*, 2007; Pinedo *et al.*, 2014).

Since marine sediments are more stable environment than the aqueous phase, they can act as a sink and carrier for pollutants in the aquatic environment. Therefore, sediments are sensitive indication of the quality of aquatic ecosystems (Long *et al.*, 1995) and sediments analysis is important for evaluating pollution status, management, and regulation of marine to protect aquatic ecosystems. However, some sediments-bounded heavy metals may be released back to the overlying water column through re-suspension processes in near-coastal environments via temporal changing of the environmental conditions (Eggerton, 2004; Kalnejais and Bothner, 2010). Finally, in coastal zones, the duration and intensity of resuspension and quantities of contaminants released from sediments depend on properties of sediments and overlying water such as variations in temperature, dissolved oxygen, and hydrodynamic condition (Cantwell and Kester, 2002; Atkinson and Simpson, 2007). Moreover, few studies have been conducted on the accumulation of contaminants in different coastal environmental media, like different depths or temporal dispersion; this has limited the understanding of transport and sources of contaminants in coastal regions.

Special Economic Zone of the Amirabad Port is located in southeast coast of the Caspian Sea, is a multiple economic, industrial, and tourist spot together with the Miyankale protected zone. Miyankale wetland is one of the international conservation areas globally. The other industrial site in this

area is Sadra transportation hub, with jetties and platforms of oil exploration industries. In addition to these, Neka oil terminal port is another industrial site in the area that handles the loading and unloading of fuel cargo with special calm basin.

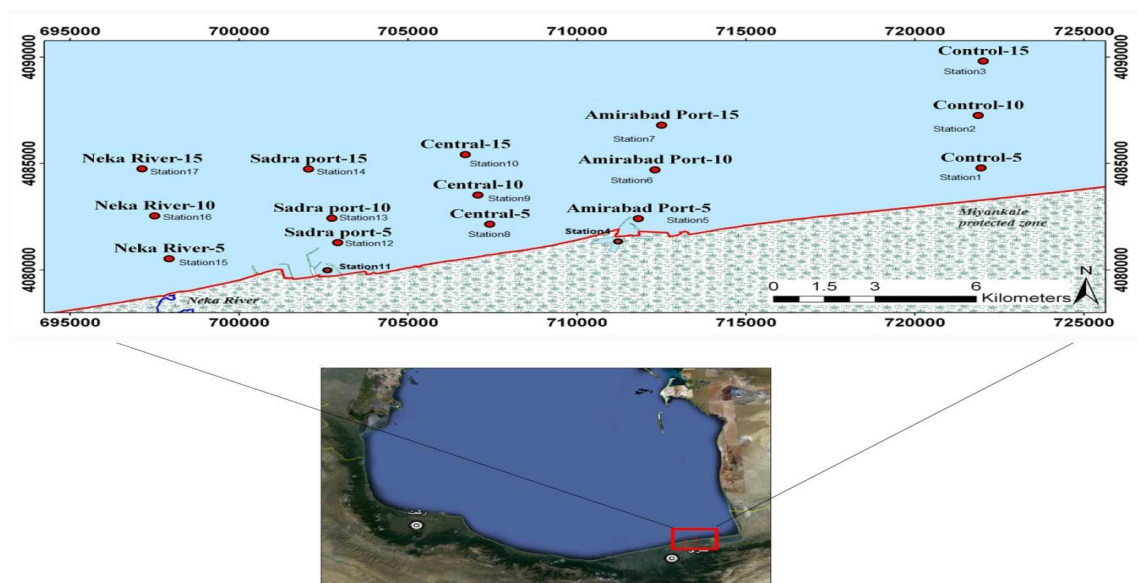
#### Study area

The study area is located between 53/30° East and 36/52° North of

Control transect up to 53/13° East and 36/50° North of River transect. The initial monitoring was done in 13 transects and finally in 5 transects with a focus on industrial coastal operations selected. In each transect, samples were collected from three depths of 5, 10 and 15 m. In addition, samples from ports calm basins have also been collected (Fig. 1 and Table 1).

**Table 1: Geographic positions of sampling transects.**

Transects	Position
1-Control Transects	E= 53.39725 N= 36.86638
2-Amirabad port Transects	E=53.39332 N=36.87108
3-Central Transects	E= 53.32683 N= 36.8625
4-Sadra port Transects	E= 53.27617 N= 36.85567
5-River Transects	E= 53.23267 N=36.851



**Figure 1: Map showing the locations of transects and stations on the study area. dots indicate sampling sites along transects: stations 1,2,3: Control Transect, 4,5,6,7: Amirabad, 8,9,10: Central Transect, 11,12,13,14: Sadra Port, 15 ,16,17: Neka River Transect.**

#### Materials and methods

Sediment samples were collected by Van Veen Grab (0.04 m<sup>2</sup> of the surface area). Sampling for physical and chemical factors such as sediments grain size, total organic matter (TOM), total phosphorus and nitrogen in sediments, heavy metals (Vanadium,

Nickel and Lead), and TPH were performed on each sample. After collection, all samples were kept in plastic containers; except the samples for TPH which collected using wooden spoon and were stored in aluminium containers. All samples were stored in thermal insulated containers and on top

of ice, and were later transferred to the laboratory.

To determine the grading contents, approximately one tablespoon amount of sediment deposits was moved into the Petri dish and heated for 8 h at 70 to 80°C in the oven till it got dry. 25 g of deposits were dried, weighed and dissolved in a beaker with 250 cm<sup>3</sup> tap water and 10 cm<sup>3</sup> solution of sodium hexane meta phosphate 6.2 g L<sup>-1</sup> was added (to remove sediment), and then it was shaken for about 15 min, and was left in a quiet place for 8 h; then the solid materials were deposited, beaker content was stirred again for 15 min and then dried in the oven. The dried deposits were graded by standard sieves (4, 2, 1, 0.5, 0.25, 0.125, and 0.063 mm). Sediment remaining on each sieve was weighed and the percentage of each one was calculated (difference between the total mass of the residue remaining on each sieve and the main deposition of 25 g are the particles of silt and clay, which must be calculated (Buchanana, 1984).

To measure TOM, dry sediments weight percentage was measured and the mean was calculated. For this purpose, the sediment sample was dried in the oven for 8 h at 70 to 80°C then the dried sample was transferred to electric furnace at a temperature of 500 to 600°C for 8 h and finally TOM value was estimated based on Eleftheriou, 2005.

ASTM standard method was used to analyse heavy metal compounds. First frozen samples were weighed and then the dried samples. Then samples were ground to powder and were prepared

for acid digestion. Based on ASTM method, digestive process includes using hydrochloric, hydrofluoric (to digest components of silicate deposits), perchloric, and nitric acid, and finally digested samples were prepared for injection into atomic absorption (ASTM, 2013).

The 3550C EPA standard method (extraction with ultrasonic device) and SW-846 method 8015B were used for the analysis of total petroleum hydrocarbon compounds (TPHs). After weighing sediments' samples and drying with Na<sub>2</sub>SO<sub>4</sub>, samples were prepared for extraction. It should be noted that the drying process can also be done using freeze dryer. In this method, Surrogate Standards (1, 3-Dimethyl-2-nitrobenzene at 250 µg ml<sup>-1</sup> in Methyl tert-Butyl Ether) and solvent mixture of 1: 1 dichloromethane/acetone were used. Then, ultrasonic machine was used to extract organic samples. Finally, the solvent was extracted and concentration of the sample was prepared and injected into a Gas Chromatography-Flame Ionization Detector (GC FID) (EPA, 1996).

Adverse biological effects were assessed by using ERM quotient method (Long *et al.*, 1995). Pollutant concentrations were measured using the ERM. The samples obtained were assessed for adverse biological effects using the m ERM. With this challenge in mind, the mean ERM quotient (mERM) method was used to determine the adverse biological effects of coexisting contaminants (Long *et al.*, 1998) as follows:

$$m\text{ ERM} = \sum (C_i/\text{ERM})/n$$

Accordingly, if the  $m\text{ ERM}$  is less than 0.1, then there is potential for corrupting influence of biological factors in the environment. If  $m\text{ ERM}$  would be between 0.1 and 0.5, there is potential to destroy the biological environment, while if the amount of  $m\text{ ERM}$  is between 0.5 and 1.5 it represents the corrupting medium influence of the biological factors and if it is more than 1.5 then it represents a clear environmental impact (Long *et al.*, 2000).

#### *Data analysis*

In order to compare the selected sampling sites (concentration of selected water parameters, sediment parameters and sediment, TPH, Ni, V, and Pb), one way analysis of variance (ANOVA) was used. Pearson's correlation coefficients were used to examine relationships between heavy metals and TPH in the sediment and between levels of each environmental factor in water and sediment. Also, to better understand the relationship between these variables and identify their origins, Principal Component Analysis (PCA) was used. In cases where the differences were significant, Turkey test was used to determine the difference between group means (SPSS version 19).

In addition, based on physico-chemical parameters, relationships

between samples were examined using distance-based redundancy analysis (dbRDA) which is the best lineal model to explain the spatial distribution of water parameters across sites. Principal Coordination Analysis (PCoA) and non-metric multidimensional scaling (nMDS) were used to examine the environmental variables in sediments across sampling sites, and finally Multivariate Dispersion (MVDISP) was used to determine the degree of dispersion of the samples from the 5 different transects using PRIMER V6.

#### **Results**

Sediment grain size was not different between transects, but was extremely different among sites (54-98%). In general, there were more coarse-grained away on transects 3 sediments. The opposite pattern appears to take place on transects 4 and 5 inside of Sadra port and River estuary, with finer grained sediments. TOM was used to measure 17 sampling sites; the highest recorded average value was in site No. 10 with  $3.26\text{ mg kg}^{-1}$  and the lowest was  $0.98\text{ mg kg}^{-1}$  in site No. 1. TOM was also highly different with no obvious gradient but higher concentrations tend to occur on transects 3 and 4, particularly in transect 4, and gradient increases from shore to depth (Fig. 2).

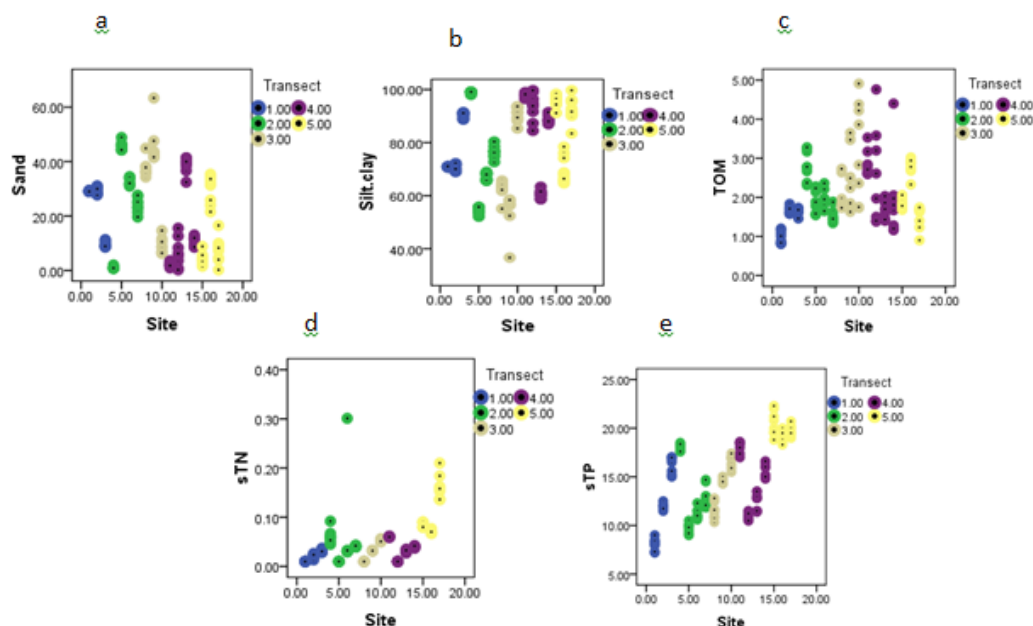


Figure 2: Spatial distributions of a) Sand, b) Silt-clay, c) TOM and, d & e) sediment nutrients.

The measured metal concentrations varied greatly as follows: V, 27-54 mg kg<sup>-1</sup>, the highest 48.6±2.39 mg kg<sup>-1</sup> measured in Amirabad transect at depth of 15 m; Ni, 13-37 mg kg<sup>-1</sup>, the highest 26.13±3.44 mg kg<sup>-1</sup> measured in transect 1 at the depth of 15 m; and Pb, 3.2-32 mg kg<sup>-1</sup>, the highest 31.16±35.77 mg kg<sup>-1</sup> measured in Sadra port at depth of 10 m. No special distribution pattern was observed for petroleum related heavy metals, but the highest concentrations tend to be in the middle or deeper sediments. Metal concentrations were highly different both between and within transects, but were generally higher in the inner port transects (Fig. 3). In particular, Pb with regard to anthropogenic contamination

was again higher at the Port sites (transects 2 and 4).

TPH concentrations also varied between sites and transects (0.41-5.1 μg g<sup>-1</sup>, the highest 3.56±0.74 μg g<sup>-1</sup> measured at entrance of Sadra Port) with a trend of higher concentrations at the inner sites of ports (and depth 5), in particular Sadra port, and in sites of transect 3 (Fig. 3), but it was uniformly low on transects 1 and 5.

Table 2 shows the correlation coefficient matrix for sediment properties, TPH and metal concentrations. A significant positive correlation was observed between TOM, Silt-clay and TPH, V, Pb, and Ni.

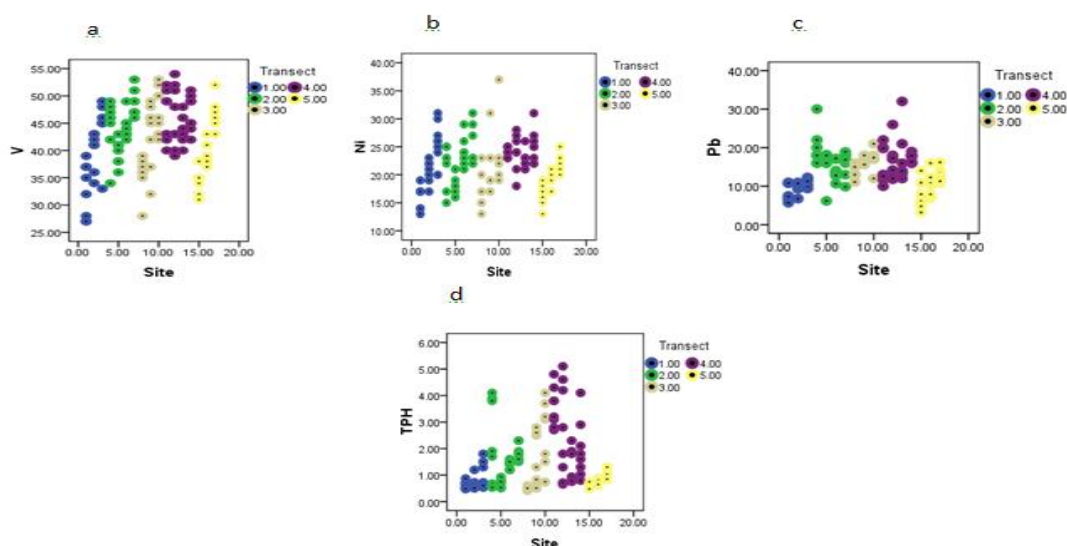


Figure 3: Spatial distributions of a) V, b) Ni, c) Pb and d) TPH in surface sediments of the study area.

Table 2: Pearson's correlation matrix for the measured sediment variables.

	n	TOM	Silt.clay	Sand	TPH	V	Ni	Pb	sTP	sTN
TOM	136	1	<b>0.2<sup>b</sup></b>	<b>-0.2<sup>b</sup></b>	<b>0.7<sup>a</sup></b>	<b>0.5<sup>a</sup></b>	<b>0.3<sup>a</sup></b>	<b>0.4<sup>a</sup></b>	<b>0.3<sup>a</sup></b>	0.032
Silt. Clay	136		1	<b>-0.99</b>	<b>-0.4<sup>a</sup></b>	<b>0.3<sup>a</sup></b>	<b>0.3<sup>a</sup></b>	-0.01	<b>0.6<sup>a</sup></b>	<b>0.6<sup>a</sup></b>
Sand	136			1	<b>0.4<sup>a</sup></b>	<b>-0.3<sup>a</sup></b>	<b>0.3<sup>a</sup></b>	0.02	<b>-0.6<sup>a</sup></b>	<b>-0.4<sup>a</sup></b>
TPH	136				1	<b>0.7<sup>a</sup></b>	<b>0.6<sup>a</sup></b>	<b>0.4<sup>a</sup></b>	0.17	0.05
V	136					1	<b>0.7<sup>a</sup></b>	<b>0.4<sup>a</sup></b>	<b>0.2<sup>b</sup></b>	<b>0.2<sup>b</sup></b>
Ni	136						1	<b>0.2<sup>b</sup></b>	<b>-0.2<sup>b</sup></b>	0.1
Pb	136							1	0.1	-0.1
s.TP	136								1	<b>0.6<sup>a</sup></b>
s.TN	136									1

<sup>a</sup> Level of significance:  $p < 0.01$ , <sup>b</sup> Level of significance:  $p < 0.05$ .

PCA was done on the main sediment properties and heavy metals were measured to better understand the relationship between these variables and identify their origins. As shown in Table 3, the first two principal components with eigenvalues greater than 1 accounted for 66.3% of the total variance. The results demonstrated that the first principal components (PC1) accounted for 43.157% of the total variance and had high loadings of TPH,

V, Ni, TOM and lower loading of Pb. The second PC (PC2) accounted for 23.128% of the total variance, with positive loading on silt-clay, TP, and TN. The close relationship between nutrients (Total Phosphorus (TP) and Total Nitrogen (TN)) with silt-clay suggested that TP and TN are well correlated with municipal wastewater and sewage in river transect.

**Table 3: Total variance explained and component matrices for sediment properties and metal concentrations (principal component analysis with varimax rotation).**

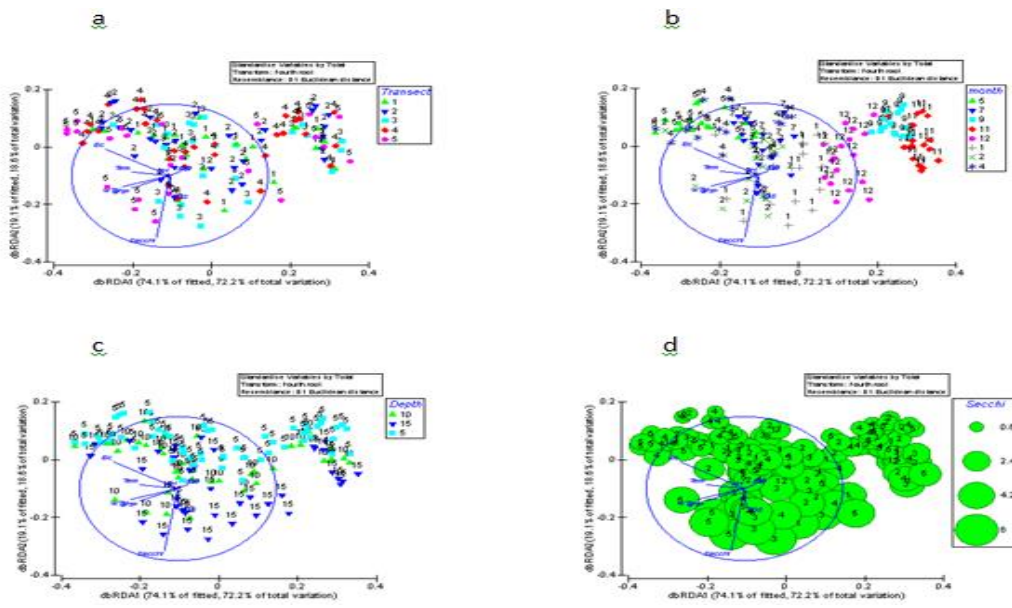
Total Variance Explained						
Component	Initial Eigen values			Rotation Sums of Squared Loadings		
	Total	% of Variance	Cumulative %	Total	% of Variance	Cumulative %
1	3.884	43.157	43.157	3.071	34.121	34.121
2	2.082	23.128	66.285	2.895	32.165	66.285
3	.909	10.100	76.386			
4	.835	9.276	85.661			
5	.654	7.270	92.931			
6	.341	3.790	96.722			
7	.172	1.911	98.633			
8	.122	1.359	99.992			
9	.001	.008	100.000			

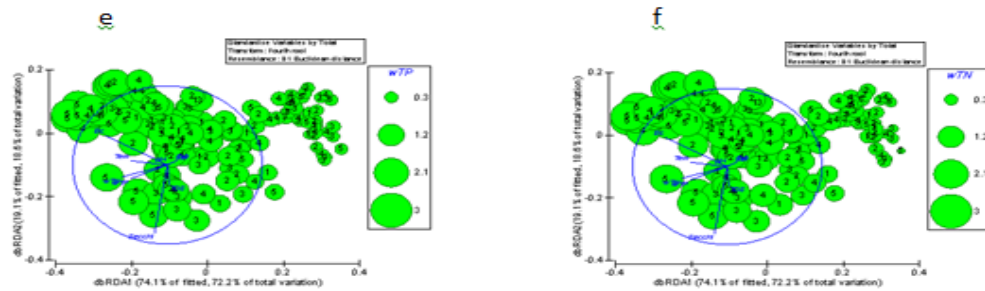
variable	Component	
	1	2
TPH	.883	.192
V	.837	.213
Ni	.735	.212
Pb	.632	-.211
Silt.	.245	.873
Clay		
TOM	.719	.110
sTP	.085	.832
sTN	-.077	.704
Sand	-.249	-.872

Results of the dbRDA showed that all dbRDA axes together explained 94% of the overall variability in the water data (Fig. 4).

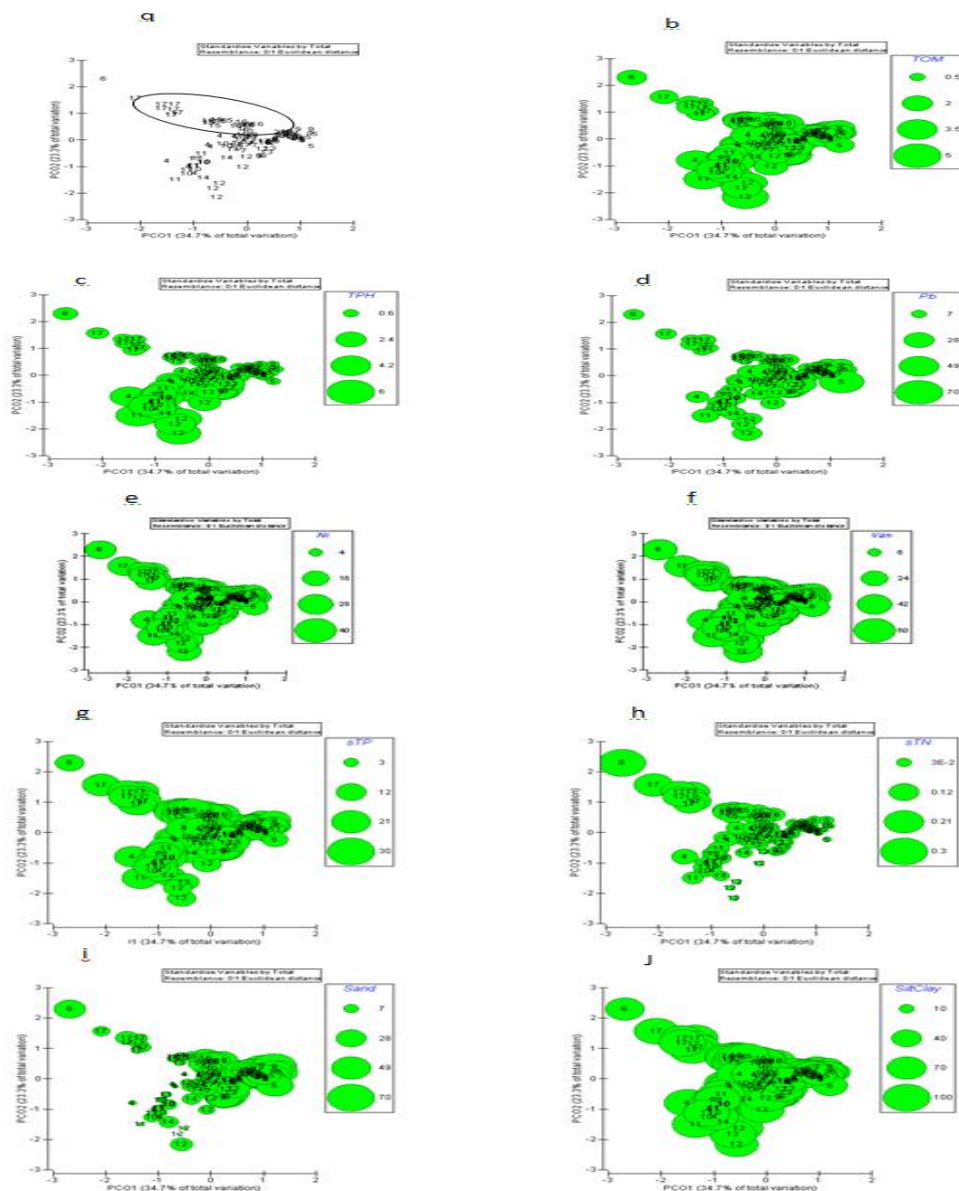
The PCoA for sediment metals, TPH, and nutrients showed a clear spatial gradient (Fig. 5).







**Figure 4:** Distance-based redundancy analysis (dbRDA) of the water data based on results from the distance-based linear model (DstLM) : Bubble plot of d) Secchi depth that better explained the ordination of b) Months of sampling also bubble plots of water TP and f) water TN that better explained the ordination of, a) Transects over b) month and c) Depth of samples.

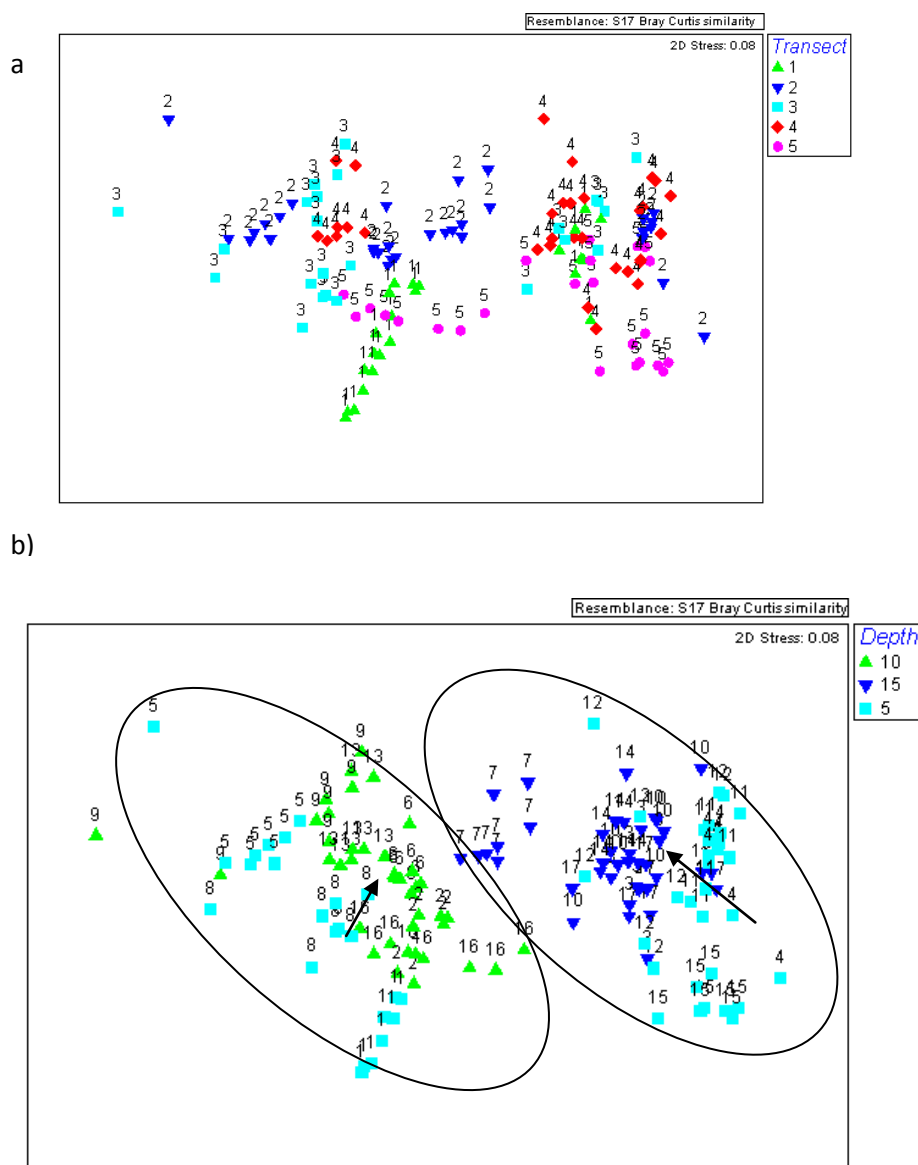


**Figure 5:** Principal coordinates analysis (PCoA) for centroids of standardized sediment variables in the sediments across sampling sites.

PCO Bubble plots of: b) TOM, c) TPH, d) Pb, e) Ni, f) Van, g) sTP, h) sTN, i) Sand and j) Silt Clay superimposed on the transects (a).

In the MDS plot, based on sediment parameters, it was found that all the samples of transects 4 and 5, transects 1 and 2, were separated from each other, and transect 3 was different from all other transects. In particular, sites in

transects 2, 3 and 4 could be separated, as one group is mainly covered by 88 samples for sites 4 to 14. And finally in the MDS plot based on depth factor level, all samples in depth 10 and 15 were separated (Fig. 6).



**Figure 6:** a) Transect and b) Depth MDS ordination plots according to the sediments physico-chemical parameters (Legends: coloured symbols correspond to depth, numbers represent sites).

However, in defining the variability within a group of samples, it can be misleading to use the inter-sample distances on the MDS ordination itself. Despite the stress is near zero, this two-

dimensional view of the higher dimensional data will undergo some distortion. So the apparent differences in variation is within and between transects quantified more precisely

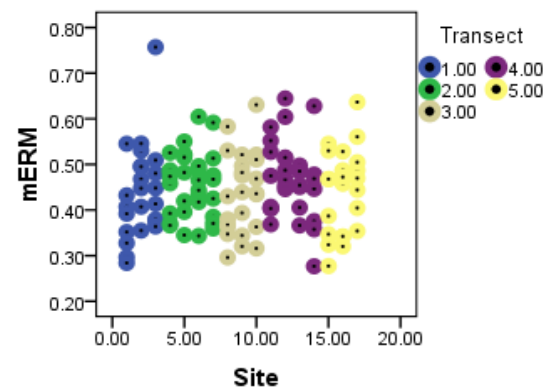
using MVDISP, as described in (Somerfield, 1997). According to MVDISP, the degree of scatter of the bimonthly sediment samples was far greater at transects 3 and 2 than at transect 1 (Table 1). This result reveals that intra-group variability is high and

greatest in transect 3 and depth 5 and least in transect one and depth 15 (Table 4). Such intra-group sequential changes were more obvious for water parameters ranging between 0.59 and 1.38.

**Table 4: Dispersion values for ordination plots: a) sediment parameters and b) water parameters in different transects and depths.**

a) Sediment parameters Global Analysis	
Transect	Dispersion
1	0.837
5	0.919
4	0.973
2	1.098
3	1.115
Global Analysis	
Depth	Dispersion
15	0.678
10	0.784
5	1.273
b) Water parameters Global Analysis	
Transect	Dispersion
2	0.959
1	0.96
3	0.962
4	1.047
5	1.067
Time	Dispersion
7	0.589
1	0.705
4	0.926
11	0.937
5	0.971
9	1.169
12	1.326
2	1.377

To determine Adverse Biological Effects of the two metals, nickel and lead, the following results were obtained based on Effects Range Median. Studies on concentration of TPH and associated heavy metals showed that there is no high level risk for oil pollution in this area.



**Figure 7: Spatial distributions of mERM in the study area.**

## Discussion

The Caspian Sea is the largest lake in the world and also one of the most sensitive aquatic ecosystems through biological values. This ancient sea which supported nation's through centuries now became a research destination for lots of researchers in the world. The preservation of this ecosystem is the most important matter in all researches. On the other hand, increase in population and industrial facilities, is an ongoing challenge for this ecosystem. According to studies conducted, oil pollution in the environment of the Caspian Sea is increasing. Just a comparison between the data obtained from previous years shows that concentrations of TPH increased more than 4 times in this region (Mirzaee *et al.*, 2014).

In the present study, the values of Amirabad zone water indices (temperature, DO, salinity, EC, Secchi depth) and particularly concentration of nutrients clearly changed depending on the season. In the biplot of the first 2 dbRDA axes, variation in water parameters correlated with the first axis separating stormy-windy season (Fig. 4b), while Secchi depth was strongly correlated with the second axis, a separation of "offshore areas" were modelled over a gradient across 3 increasing distances during warm-calm season (Fig. 4c).

According to the results, the surface sediments of the area mainly have a sandy silt texture with a higher proportion of silt-clay grains in the river area. Conversely, sites farther away had sandy texture which reflects the

sediment dynamics prevalent in this coastal marine region which prevent the deposition of predominantly fine-silt-clay sediments (Fig. 5i- j).

Considerable differences having found in the distribution and content of TOM in the sediments of the study area, with higher concentrations in Sadra port and lower concentrations in river transect (Fig. 5b). This is possibly due to different hydrodynamic conditions and hydro chemicals of river inputs. According to (Tissot, 1984) and Demaison (Demaison and Moore, 1980), the relatively high percentages of organic material in the sediments may have resulted from the coastal lagoons and other coastal water bodies that enrich the adjacent sea. It has been reported that over 90% of Miyankale wetland in the middle part of our study area, is covered by macrophytes showing that nitrogen primarily comes from organic matter and is likely present in organic form.

Principal coordinate analysis done on sediment parameters and dbRDA on water parameters showed that the spatial pattern of sediment TN and TP was partly similar to that of the water (Figs. 4 and 5). With a total of 60% of the total variance explained by PCO1 and PCO2 for sediment parameters, samples in Sadra port (sites 11 and 12) and river transect (site 17) are consistently different from the combination of all the samples and all other sites regardless of the season (Fig. 6a). These results showed that Sadra port and Neka River have been the most important chronic source for the input of TOM, TPH and TP, TN along the

southeast coast of Caspian Sea, respectively (Fig. 5 b, c, g and h). Unlike TOM, however, TP showed a higher affinity for the silt-clay fraction (Fig. 5 g and i). Similar to the TP case, high sediment TN values were also observed in deeper sites of transect 5 (Fig. 2 d and e), which is the lowest in Sadra port. In the other distances, the second component in PCA was composed of silt-clay, TP and TN. The highly positive coefficient of the correlation between sediment TP and TN (0.6) (Table 2) and close relationship between nutrients with silt-clay in PCA (PC2, Table 3) suggested that TP and TN are well correlated with agricultural, municipal wastewater, and sewage from nearby cities and towns via inlet river of Neka. In sediments, the processes of N fixation and P availability are influenced by a variety of environmental factors including water depth, pH, temperature and sediment texture. (Joye, 1995; An, 2001).

According to sediment properties, all transects were primarily composed of fine particles and such sediments have a potential to adsorb contaminants. Also, many studies have shown that sediment properties such as grain size and nutrient values are well correlated with metal concentrations (Vane *et al.*, 2007; Qin *et al.*, 2010). As shown in Figure 5, the distribution and variations of Vanadium were similar to that of Ni and significant positive correlations ( $p < 0.01$ ,  $r = 0.7$ ) were observed between V and Ni (Table 2). Moreover, PC1 in Principal component analysis elucidated a relatively large extent of

the total variances of the TPH, V, Ni, TOM and lower loading of Pb (Table 3). Different to V and Ni, the patch of the highest concentration for Pb appeared in Amirabad port (Fig. 3), showing that V, Ni and Pb might originate from the different pollution sources. Lower loading of Pb in the first component of PCA (Table 3) suggested that Pb has mixed contamination origins which resulted from port and anthropogenic activities (traffic pollution of road nearby the study area, also contributed to their accumulation in sediments via atmospheric deposition). The role of organic matter in the accumulation of heavy metals due to its strong complexing capacity with sediments was presented by Wakida *et al.* (2008).

MDS ordination of sediment parameters from all the samples showed a different pattern that is related to transect. All sites in transects 1 and 5 are different to sites in transects 2, 3 and 4 (Fig. 4b). These two transects also had the softer sediments, lowest TOM, and the lowest Ni, Pb and TPH concentrations and dispersion value (Figs. 1, 2 and Table 4). Also, the present study has demonstrated the highest dispersion value (MVDISP) based on sediment parameters, in depth 5 and transect 5 (River transect). MDS plot, Fig. 6b shows that much of the river sediments in coastal sites of transects 4 and 5 (11, 12 and 15) are highly similar to sites 17, 14 and 10 in depth 15. Also within depth 5, groups variations reflecting sediments deposited at the bottom of the coastal sites 1, 5, and 8 have been transported

and deposited in sites 2, 6, 9, 12 and 16, located in depth 10 (Fig. 6b). Furthermore, MVDISP for water parameters showed a high inter-annual dispersion range between 0.59 and 1.38, consistently showing highly temporal dynamic condition in the area. This result suggested that pollutants accumulated in the shallow near shore sediments might disperse during the windy season in the water column. Also, it is well known that coastal processes, such as bottom shear stresses, strong currents near the bottom layer driven by winter onshore winds, precipitation, and terrestrial runoff, influence dispersal patterns of trace metals and other pollutant compounds. This repeated deposition, resuspension, and transportation of sediments from rivers to the deeper portion of the basin has been reported earlier by Dassenakis *et al.* (2006), Gavriil (2005), Lee *et al.* (2008), Thompson *et al.* (2011).

The PCoA results showed that Sadra port has been the most important chronic source for the input of TPH (Fig. 6c). Higher concentrations of TPH were found along the coast, especially the inner most navigated sites of the

ports, while the spatial variation gradually decreased from the coast to the offshore sites (Figs. 3d and 5c). Total petroleum hydrocarbons concentration for surface sediments of our study area ranged from 0.519 to 5.1  $\mu\text{g g}^{-1}$ , which is significantly lower than background sediment values of 10-64 and 0.93-106.1  $\mu\text{g g}^{-1}$  (Maleki, 2000; Nasrolah Zadeh, 2001; Saeedi and Karbassi, 2006). The finding of the present study showed that the sediments from South Caspian Sea areas were clean in terms of TPH as compared to the marine sediment quality standard. This result was consistent with the work of (Commendatore, 2007), who determined a threshold of 10  $\mu\text{g g}^{-1}$  for non-polluted and non-toxic sediments. The relatively low levels of TPH occurred because this compound was not the dominant contaminant in coastal environments of South Caspian Sea area. These values were lower than concentrations reported for those found in sediments of Europe (e.g. UK) and North America, whereas the values are about the same as Izmir Bay in Turkey (Table 5).

**Table 5: Local and worldwide TPH concentrations in sediments ( $\mu\text{g g}^{-1}$ ).**

study area	TPH concentration in $\mu\text{g g}^{-1}$	Reference
Amir abad area	0.519- 5.1	This study
Mazandaran, Golestan	10.6-38.6	(Bazrafshan, 1995)
Mazandaran, Golestan	830-1217	(Bazrafshan, 1996)
Mazandaran, Golestan	0.93-106.1	(Maleki, 2000; Nasrolah Zadeh, 2001)
Mazandaran, Gilan	7.03-921.66	(Mirzaee <i>et al.</i> , 2014)
KSA	5-1300	(Fowler <i>et al.</i> , 1993)
Qatar	28-238	(Fowler <i>et al.</i> , 1993)
Izmir-Turkey	0.45-7.8	(Kucuksezgin, 2006; Guven and Akinci, 2008)
Bohai Bay, China	6.3-535	(Ran Zhou <i>et al.</i> , 2014)
Bay of Bengal, India	1.8-40	(Raj and Jayaprakash, 2008)
North Adriatic Sea, Mediterranean Sea	1520 $\pm$ 76	(Dell'Anno <i>et al.</i> , 2009)

Heavy metal concentrations in Amirabad and Sadra harbor tend to be higher in inner areas as compared to outer sites, but they were all below background sediment values (Saeedi and Karbassi, 2006) of V, 90-140 mg kg<sup>-1</sup>; Ni, 35-67 mg kg<sup>-1</sup>; and Pb, 22-25 mg kg<sup>-1</sup>.

The established empirical sediment quality guidelines (SQGs) often used to assess sediment quality might adversely affect aquatic organisms. Among these, the effects range low (ERL) and effects range median (ERM) developed by US

EPA have been widely used to screen sediment contamination and have been found to be effective predictive tools (Long *et al.*, 1995, 1998, 2000; Agency, 2005). Therefore, toxicity has been determined among samples in which none of the substances was equaled or exceeded the threshold effects levels (TEL) concentrations. Sediments with respect to Pb were grouped below TEL, MET, ERL and ERM at all sites and with respect to Ni were grouped into MET and ERL-ERM range at more than 98% of the samples.

**Table 6: Summary statistics of TPH, Pb, Ni concentrations in surface sediments of our study area, and guide values of empirical sediment quality guidelines.**

	TEL	LEL	MET	ERL	ERM	Minimum	Maximum	Average	STDEV
Pb(mg kg <sup>-1</sup> )	35	31	42	35	110	3.2	32	14	4.63
Ni(mg kg <sup>-1</sup> )	18	16	35	30	50	13	37	21.55	4.24
TPH (µg kg <sup>-1</sup> )	NG	5,000	NG	5,000	10000	410	5100	1440	1130

The results from the analysis of 136 surface sediment samples showed that the metals concentrations in Amirabad zone varied greatly. The mean contents of these metals were lower than the background values showing that metal in the study area suffered from different anthropogenic effects. The sediment of the inner part of 2 ports' values suggested that they are going to be slightly contaminated with TPH and heavy metals, whereas the other sites in the studied areas showed no pollution. The sediment quality was evaluated again on the basis of the ERL and ERM. The results showed that Ni and TPH exceeded their corresponding ERL limits at about 2 and 0.7%, respectively. Moreover, any sites exceeded the ERM thresholds for TPH and heavy metals. This research

will be quite useful for developing strategies for pollution control in Amirabad zone increasingly being under environmental threats and pressures, because of residential, recreational, industrial and agricultural, oil exploitation, production and fishing activities. Possibly, this study may be extended if significant effective strategies of management are not adopted for highly dynamic shallow near shore region.

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