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ORIGINAL ARTICLE

A survey of Total Petroleum Hydrocarbons (TPH) pollutants and heavy metals, Nickel (NI), Cobalt (CO), Chrome (Cr), Vanadium (V) and Cadmium (Cd) in the north of Qeshm Island

Farnaz Irandoost[1*], Seyed Mohammad TaghiSadati Pour[1], Hossein Ghafoorian[1]
[1]Department of marine pollution, Faculty of marine science and technology, Branch, north of Tehran, Islamic Azad University, Tehran, Iran.
[*]Corresponding Author Email: Farnaz.irandoost@yahoo.com

ABSTRACT
This study evaluated the pollution of northern region of Qeshm Island in terms of heavy and toxic metals and aliphatic and aromatic compounds. Multi-state processes were done by EKMAN method to prepare the samples. The samples analysis was done by spectrophotometer Atomic Absorption HPLC and GC/MS. The results showed that by comparison and analysis of two major groups of pollutants, heavy metals with TPH, the highest pollution is dedicated to Cobalt. The highest pollution of metals group is associated to Chrome.
Keywords: *Qeshm, Heavy metals, Aliphatic and Aromatic compounds, Ekman, Pollution*

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INTRODUCTION

Pollution is transferring or direct or indirect including of materials or energy by human being to environment and harmful effects are imposed via imposing risk to environmental resources, danger for human health, creating barriers for marine activities including fishery, the damages of using sea water and reduction of recreational resources [1].
The source of pollution is classified into two groups:

(1) Point source is a type of pollution and its source is tracing such as wastage of factories (industrial waste) [2].
(2) Non-point source: It is another type of pollution and its source is diffuse and it is hard to control this type of pollution as agricultural runoff [3].

One of the dangerous pollutants for environment is Trace ORGANIC Pollutants. Beside other pollutants as trace elements as Nitrate, Nitrite, Ammonium, Phosphate, silica) create abnormal changes in physical and chemical parameters (e.g. acidity, alkalinity and salinity) and physical features of water (color, odor, taste)in water ecosystems and it is one of the great threats of environment health namely water environment (M. Schnitzer). Trace Organic Pollutants include great volume of various pollutants (Kusha, Hormoz). The pollutions of the resources in land including factories wastage, hot water and extra materials of power plants, wastage of sweet water system utilities, agricultural wastage and agricultural toxics entering the sea via river, livestock waste, urban and home wastewater. The industrial wastage is considered as one of their products and most of them are not environment-friendly. Thus, it can be said, industry is responsible for much environmental pollution [3]. One of them is heavy metals in environment. The influence of physical and chemical pollutants namely polluting resources, Hydrocarbons and heavy metals to marine environments are one of the main factors of destruction of marine ecosystems. Pollutants can have destructive effect on food chain and human health namely in marine products (M.Schnitzer). One of the main adverse effects of pollutants is as:

- The impact of ecosystems namely on water ecosystems
- The adverse effects and unsuitable ecological changes
- The adverse effects on food chains [4].

Heavy metals are the group of metals one of the natural formations of earth crust and their density is above 5. The main problem of these metals is that they are not metabolized in the body. They are stored in tissues after entering the body. Also, they can be replaced by mineral materials of body [5].
Nickel is one of the general metals in surface water and its low value is required for red blood cell of body. As they can be toxic in high values, in long term it can lead to body weight reduction, problems of heart, liver, stimulation and high sensitivity. Nickel can be accumulated in water creatures. Vanadium enters the environment through natural resources and fossil fuels and they remain for a long time in water, soil and air. Vanadium is stable in water environments and it has harmful effect on water organisms in long-term [6]. Cadmium is classified as a pollutant increasing cancer in human being [4].
Diarrhea, Abdominal pains, severe vomiting, bone fragility, infertility and impotency are the symptoms of toxicity with element. Chrome is one of these compounds; if Chrome is eaten it is toxic. When oil is dispersed in sea, it is decomposed and dispersed in sea over time [7].
This dispersion is the result of some of physical and chemical processes and it changes the compound in oil. The processes are considered by weathering, sedimentation, extension, evaporation, photoxidation, dispersion, decomposition is the stages of this process [8]. Decomposition is a technical factor establishing a specific relation between great parts of variables irrelevant to each other [9]. The difference of this technique and multiple regression is as first the variables don't appear in the structure of communication model, second the number of factors as linear combination of main variables and showing specific feature of variables relation are less than the number of main variables.
Thus, one of the main goals of factor analysis technique is reducing the dimension of data. The main assumption in using this technique is a fundamental model with specific model to determining complex relation concepts between the variables [10]. This relation is manifested in the form of a factor in this assumed model. Generally, the implementation of factor analysis has four different stages:

1- The matrix of correlation coefficients between the variables is calculated.
2- The second stage is extracting the factors; this stage indicates determining the number and method of calculating factors. The model fitting is computed in this stage.
3- Applying specific conversion on factors, if necessary and for better interpretation of relations among the data is done in the third stage.
4- The score of each factor for each observation is calculated. These scores can be used as the basis of various analyses [11].

Clustering (clustering analysis) is raised for problem solving in which by a sample of n observations and measuring P variables on each observation, we can classify the observations in clusters as similar observations are inside one class. This method should be completely numerical and its classes shouldn't be determined before [12].
The present study evaluated the presence of heavy metals and Aliphatic and Aromatic compounds in coastal area of Qeshm Island. Based on the application of factor analysis technique by Principal Component Analysis method, at first we should explain the above method to reduce the data dimension and prioritization of variables and factors.

MATERIAL AND METHOD

The study population of this study is coasts and sediment of the north of Qeshm Island.
5 sampling stations were selected based on environmental features and existing ecosystems in the region and sampling was performed in 5 areas of each station and separation of heavy metals and hydrocarbons was investigated.
The sampling of sediment is done after determining five various stations by GRAB sampler and EKMAN model with size 1.5*1.5 [13]. The sediment sample by Grab is leveled on a surface and it is divided into 6 equal parts and of each part, 1 to 2grm is separated and all the separated sediments are re-collected and it is including the evaluated sediment by analysis systems. At first, the frozen samples are exposed to air to be melted, and then it is dried in the oven at 70°C. Then, they are passed from sieve and the particles less than 62micron are separated and are powdered in *Agate Mortar, then 0.5g of the sample is weighted and it is prepared by total digestion method for injection to system.* Anton paar –multiwave3000 is used for samples digestion. To determine the metals, spectrophotometer Atomic Absorption is applied. The preparation stages of sample include extraction, Freeze Dry, Desulfurization by copper powder, condensation, separation and re-condensation. The measurement of aliphatic compounds is done by injecting 5 microliter f1 condensed fraction by GC/FID by capillary column CP Si18 and aromatic compound measurement is done by injecting condense F2 fraction to HPLC or GC/MS according to MOOPAM method. The results are analyzed by SPSS software and numerical analysis method. Finally, the received output is the evaluation criterion of many pollutants and pollution load in the region.

RESULTS AND DISCUSSION

Figures 1 to 6 show heavy metals and TPH of five measured stations. As it is observed, Chrome and Cobalt are less than other materials.

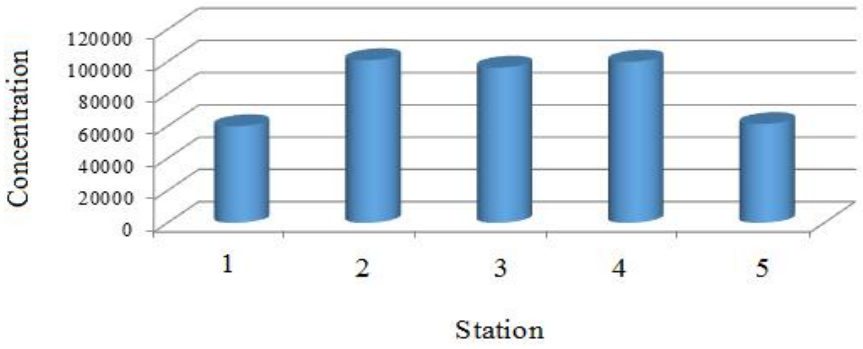

Figure 1- Nickel amount in five main stations (unit per billion ppb)

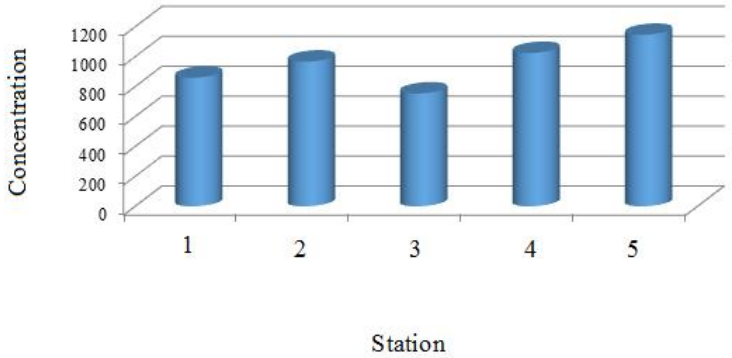

Figure 1- Cadmium amount in five main stations (unit per billion ppb)

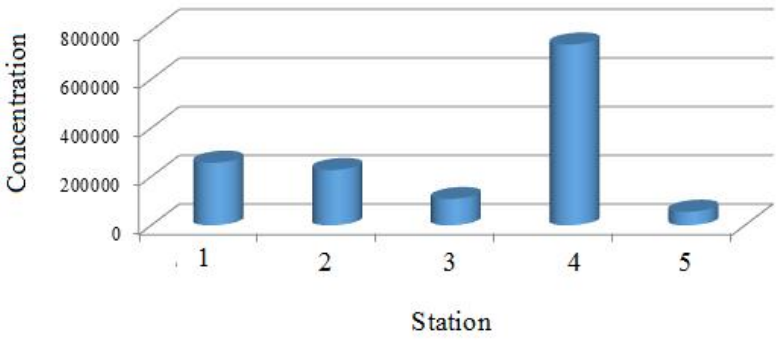

Figure 3- Chrome amount in five main stations (unit per billion ppb)

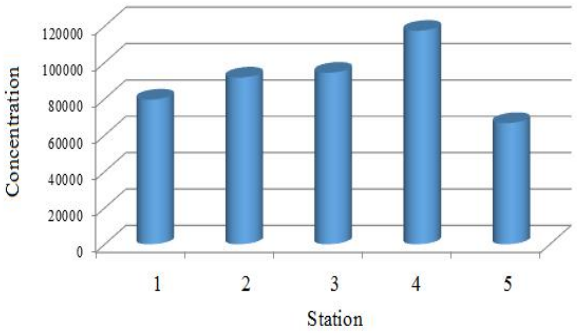

Figure 4- Vanadium amount in five main stations (unit per billion ppb)

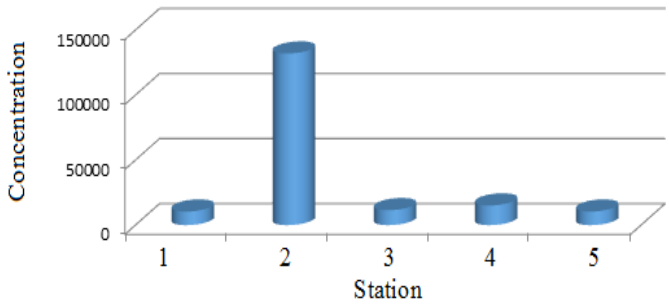

Figure 5-Cobalt amount in five main stations (unit per billion ppb)

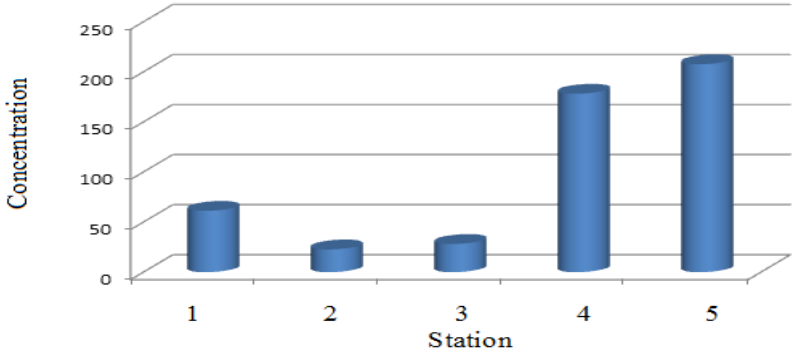

Figure 6 TPH amount based on existing mean in five man stations

Figure 6 indicates TPH based on existing mean in five main stations. Stations 4, 5 have the highest amount of these compounds. By the data of figures 1-6, we can analyze the data of these regions.

The matrix of correlation coefficients presents some criteria to determine the validity of factors analysis. The above part of matrix is dedicated to paired correlation coefficients of variables and diameter elements are 1. The more the elements outside the diameter approach 1, the good evaluation of factor analysis are increased. The correlation coefficients range between 1, -1. If approach -1, it indicates the inverse change of variables and if it is close to 1, it indicates the same direction of variables and if it approaches zero, it indicates the independence of variables. For example, correlation coefficient of Ni, Cd is -0.25 and it indicates relatively low correlation and inverse direction of these two variables.

The lower part of matrix is about one-way significance level for null hypothesis H_0:P_{ij}=0 (P_{ij}s, correlation coefficients) calculated corresponding with the correlation coefficients matrix. For example, significance level of first and second variables is 0.11 and this indicates the support of null hypothesis and we have $P_{S_1,S_2}=0$. In other words, two mentioned variables are independent from each other.

Determinant indicates the determinant of correlation coefficients matrix, the less this value, the higher the validity of factor analysis. The lowest value of this Determinant is zero. In correlation coefficient matrix, determinant value is zero and it indicates factor analysis validity.

Table 1- Correlation Matrix

Correlation Matrix[a]

		Ni	Cd	Cr	Co	V	Tph
Correlation	Ni	1.000	-.255	.298	.804	.815	-.261
	Cd	-.255	1.000	.261	.155	-.210	-.822
	Cr	.298	.261	1.000	.727	.706	-.176
	Co	.804	.155	.727	1.000	.909	-.436
	V	.815	-.210	.706	.909	1.000	-.045
	Tph	-.261	-.822	-.176	-.436	-.045	1.000
Sig. (1-tailed)	Ni		.110	.074	.000	.000	.104
	Cd	.110		.104	.230	.157	.000
	Cr	.074	.104		.000	.000	.201
	Co	.000	.230	.000		.000	.015
	V	.000	.157	.000	.000		.415
	Tph	.104	.000	.201	.015	.415	

a. Determinant = 2.36E-006

Table 2 indicates the data of KMO and Bartlett's Test. KMO and Bartlett's Test is total MSA. The values of 0.9 of this quantity show the very suitable factor analysis about 0.8 as suitable, 0.7 balanced, 0.6 average, 0.5 little and less than 0.5 as unsuitable. As KMO=0.653, the factor analysis model is average. Bartlett's Test of Sphericity tests the unit matrix assumption of correlation coefficients matrix. The support of this test means that all variables act independently. The output of 0.000 rejects the equality of unified matrix with correlation coefficients matrix and variables are not independent from each other.

Table 2- KMO and Bartlett's Test

Kaiser-Meyer-Olkin Measure of Sampling Adequacy.		.653
Bartlett's Test of Sphericity	Approx. Chi-Square	174.227
	df	15
	Sig.	.000

Table 3- Communalities table shows the share of variables in selected factors, Extraction is computed after determining model, for example Ni, 76% of the changes are determined by selected factors.

Table 3 Communalities

Metals	Extraction
Ni	.757
Cd	.976
Cr	.587
Co	.985
V	.980
Tph	.868

.

Table 4 shows Eigen value, variance percent and cumulative percent of factors variance. As shown, variance percent of the first factor is 54.443 and it means the first factor includes 54% of the changes or information of variables. Two factors are selected and they included 86% of the data information.

Table 4- Total Variance Explained

Component	Extraction Sums of Squared Loadings		
	Total	% of Variance	Cumulative %
1	3.267	54.443	54.443
2	1.887	31.446	85.889

Extraction Method: Principal Component Analysis.

Table 5 is coefficients matrix of variables in factors. To determine the belonging of each variable to relevant factor, we should select the biggest coefficient of each variable in factors and variable can be associated to it. For example, the biggest coefficient of first variable is 0.817 in the first factor and the first variable is associated to first factor with coefficient 0.817. The table of factors, variables and scoring of variables are calculated by this method.

Table 5 Component Matrix

Metals	Component	
	1	2
Ni	.817	.298
Cd	.126	-.980
Cr	.760	-.098
Co	.992	-.031
V	.925	.353
Tph	-.408	.838

Extraction Method: Principal Component Analysis.

a. 2 components extracted.

Table 6- Factors, variables and scoring of variables

Factor number	Percent of variance of factors	Variables	Coefficients of variables in factor	Score of variables (Variance percent*variables coefficients)
First	54.443	CO	0.992	54.0075
		V	0.925	50.3598
		Ni	0.817	44.4799
		Cr	0.76	41.3767
Second	31.446	Cd	0.98	30.8171
		Tph	0.838	26.3517

Finally, after multiplication of the coefficient of each variable by variance percent of the same factor, the variables score is calculated and sorting is done in the final table and the variables and prioritization of their effect is achieved (Table 6).

Table 7- Variables and ranking their importance and effect

Rank	Variables	Variables score
1	CO	54.0075
2	V	50.3598
3	Ni	44.4799
4	Cr	41.3767
5	Cd	30.8171
6	Tph	26.3517

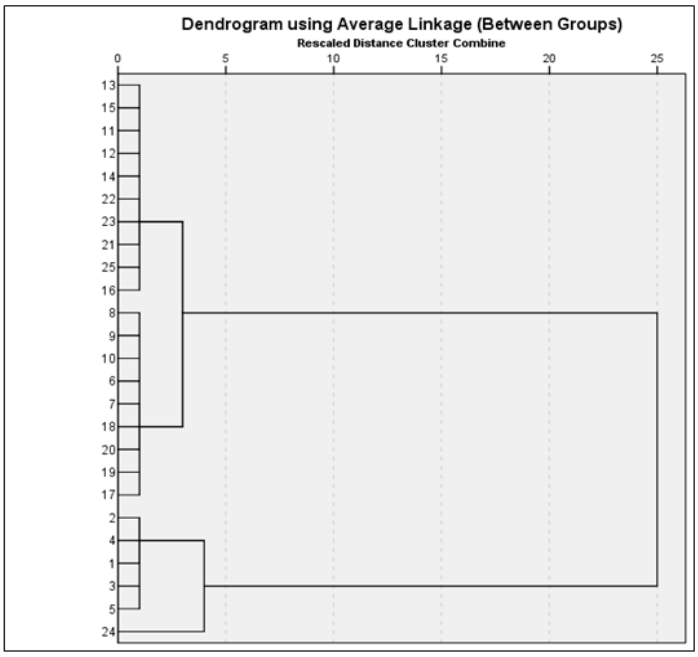

Figure 7- Cluster chart (Tree)

As shown in Figure 7, the data of 25 stations are investigated as variable and based on the quality of variables and their classification, 4 main clusters are determined as the internal variance of clusters is minimum and variance of between clusters is maximum. It means that the stations in one cluster have close variance. By hierarchy clustering method, the stations are clustered in four main clusters with maximum variance to each other.

In a higher level as hierarchy, 4 clusters are determined in the form of 2 great clusters as clusters 1, 2 are in a group and clusters 3, 4 are in another group.

The heavy metals in various stations have different values. By calculation of the mean of each of heavy metals in each of the stations, the highest amount of metals based on the stations is as:

- The highest amount of Nickel (Ni) in station 5 is 100834.5 ppb.
- The highest amount of Cadmium (Cd) in station 3 is 1145.84 ppb.
- The highest amount of Chrome (Cr) in station 4 is 743306.8 ppb.
- The highest amount of Cobalt (Co) in station 5 is 10456.36 ppb.

- The highest amount of Vanadium (V) in station 4 is 117435 ppb.
-

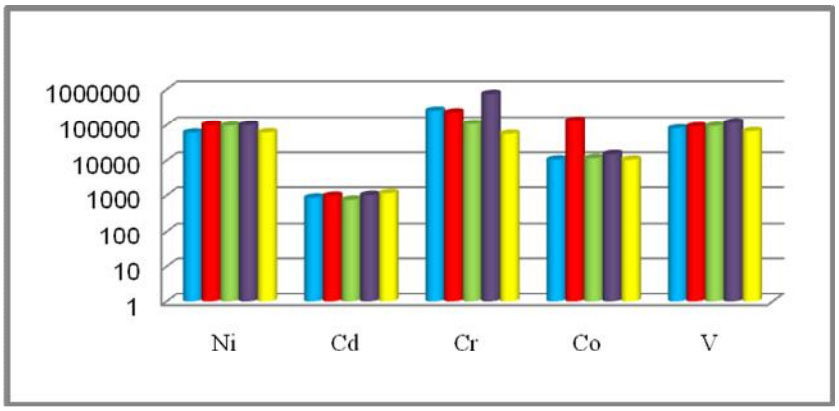

Figure 8- The comparison chart of the mean of heavy metals in 5 main stations based on the metals and stations

By investigation of the sum of means of heavy metals in each of the stations, the comparison table of total pollution based on the stations is achieved as:
Figure 9 indicates that station 4 with the highest heavy metals (976841.2 ppb) has the polluted situation in the required area and station 3 has the least pollution (195620 ppb).

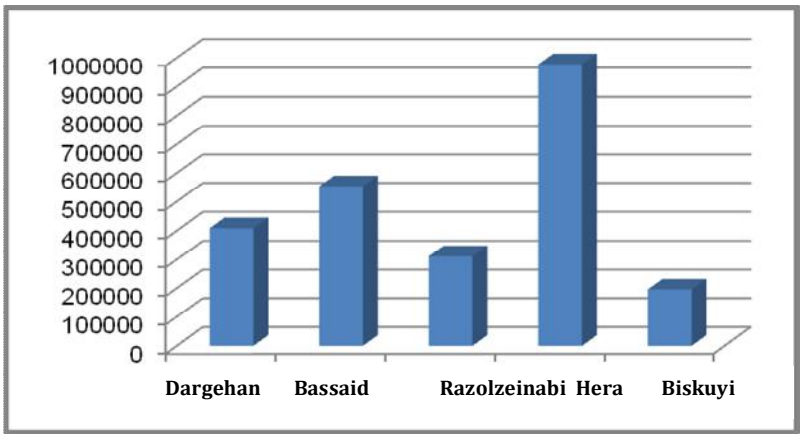

Figure 9- The comparison chart of the total heavy metals in each station
As shown in Figure 10, by sampling of 5 stations (North of Qeshm), the highest amount of this heavy metal is Chrome (Cr) as 1392860 ppb and lowest heavy metals is dedicated to Cadmium (Cd) as 4751.72 ppb.

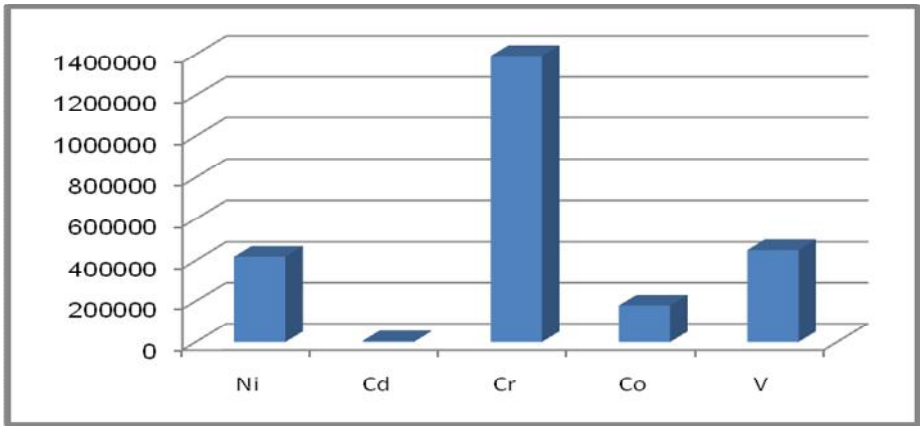

Figure 10- Comparison of the highest amount of metal in north of Qeshm (5 stations)
The evaluation of TPH in required stations and the mean of TPH in each station show that station 1 with 207.64 mg/kg has the highest TPH and station 5 with 28.17 mg/kg has the least TPH (Figure 11).

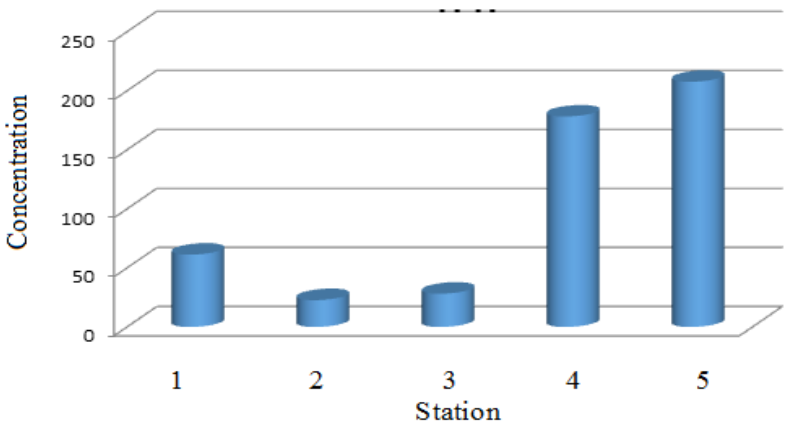

Figure 11- The comparison chart of TPH amount based on existing mean in five main stations

As shown in Chapter 4, by numerical analysis techniques, the values and data of samples, two factors of heavy metals and TPH are evaluated at the same time and by the mentioned technique, ranking of the importance and effect of two factors are considered. It can be said, the values of two main factors are normalized by numerical analysis and then ranking is done. The results of the analysis showed that among two main factors and six variables, Cobalt metal with score 54.0075 is the most important and effective pollutant in the required environment and TPH with score 26.3517 is the least important variable with little effect in the required environment (Figure 12).

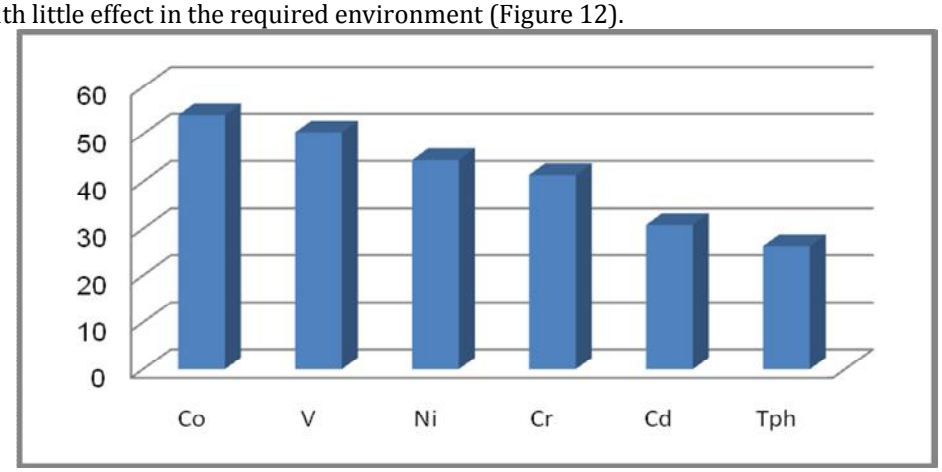

Figure 12- The comparative chart of variables and ranking their importance and effect

CONCLUSION

The amount of heavy metal pollution and TPH can be investigated in the stations of north of Qeshm. At the beginning of this chapter, it was found that the highest pollution is dedicated to metals and Chrome and in comparison and analysis of two major pollutant groups, heavy metals with TPH, the highest pollution is dedicated to Cobalt. The investigations showed that the most polluted station in heavy metals is in station 4 and the highest pollution in TPH is about station 1.

The investigated stations in this study include 5 stages, NO.1, No. 2, NO. 3, No. 4 and No. 5.Dergehan region is located in the north east of Island and it is with sediment coast, made of gravel and sand and it has the major population and highest pollution due to the major industries and focus on industrial townships. There are major industries including oil company of Qeshm on the northeast of Qeshm, Kave port and ship making workshop are working. This region is located on proximity to Kave Wharf No. 2 with two mud coast and single sand and a part of this coast is made of rock due to the presence of some hills.

The northern region of Qeshm has heavy and light industries including electricity plant, oil and gas refinery, ship making, aluminum, zinc and copper industry and all are centers of producing pollution on the north of Island. The pollution in the north of Island is east to west. Thus, this section is the entrance of pollution to forests 4 located in the south of forests No. 4 and then Kave wharf and Laft wharf, Soheili and Tabl and NO. 5 wharfs extending to the west. As it was said, the northern mud coasts and in some regions the mixture of sand and mud or rock and mud and on the north west, there is no considerable pollution source and the only pollution is due to the leaking of the existing fuels in boats and motor fishery boats in

this region. Wharf No. 5 is a fishery wharf and it is a small center of producing pollution in the west of island and due to the open space, pollution is dispersed.
Old wharf No. 5 is used to keep broken boats and it is not used anymore now. Also, it is a fishery port in which fishery boats work and the bottom of this region is rock and the places made of gravel, is very loos and swamp.
Briefly, the reasons and resources of pollution in stations include the followings:

a. No. 1:
1- Proximity to Qeshm city and urban wastewater and sweet water system of Qeshm city
2- The long industrial township and the pollutions of industrial and chemical wastage of this township
3- Position of fishery boats and leakage of their fuel
4- The mud, gravel and sand structure of the coasts in this region and absorption of pollutants
5- The marine flow from the north east to southwest of Island and transferring the pollution
6- The major industries in the upstream of Island

b. No2
1- Kave wharf and floater position
2- The activity of oil company of Qeshm and producing its industrial wastage
3- Boat making factory
4- The marine flows from north east to south west of Island and transferring the pollution

c. No. 3
1- Proximity to industrial township of Kaveh
2- Gas square of Gorzin in the proximity of this region
3- The sediment structure of the coasts of this region and absorption of pollutants
4- Marine flows from the north east to southwest of Island and transferring pollution

d. NO. 4
1- Upstream industry in the southern coast of Bandarabas
2- Laft Wharf
3- Establishing and construction of Khalij Fars bridge
4- Pahl port and electricity industry in region
5- Position of ships in northern coast of NO. 4 and small boats in the south of No. 4 and leakage of fuel of these boats
6- The mud and swamp structure of this region and absorption of pollutants
7- Marine flows from northeast to southwest of Island and transferring pollution

e. No. 5
1- Fishery wharf
2- The proximity to rural residential areas and fuel utilities as gas station
3- The marine flows from northeast to southeast of Island and transferring pollutions
4- The rock structure of the coasts of this region and in mud, loos and swamp regions and absorption of pollutants

Finally, based on the investigations regarding the study of Total Petroleum Hydrocarbons (TPH) and heavy metals, Nickel (Ni), Cobalt (CO), Chrome (Cr), Vanadium (V) and Cadmium (Cd) in the north of Qeshm Island, the following results are achieved:

1- The highest pollution of metals is dedicated to Chrome.
2- Comparing and analysis of two major pollutant groups, heavy metals with TPH showed that highest pollution is dedicated to Cobalt.
3- The investigations showed that the polluted stations in heavy metals are station 4.
4- The highest pollution in TPH is about station 1.

REFERENCES

1. Sina, A, A. (1990). Economic resources of Persian Gulf. The articles of Persian Gulf. Political and international studies office.
2. Abasi, Farshad. Sr (1996). Dispersion of heavy and toxic metals in surface sediment around Qeshm- Hormoz, Lark Island and Hengam.
3. Ahmadi F, Mohammad A, Dey (2000). An introduction to analysis and atomic absorption analysis of nuclear research center of atomic energy organization, Iran.
4. Baghdasarian, Y, (2005). Measuring heavy metals and oil hydrocarbons in water and sediment of Qeshm coast regions.
5. Shushtari, S M. (1990). Economic resources of Persian Gulf. The articles of Persian Gulf. Political and international studies office.
6. Mohammad Sadiq (1992). Toxic metal chemistry in marine environments marcel Dkker, Inc, Us, p250- 303

7. Mazaheri, Shahrzad. Tir 1998. The study of mercury, Arsenic, Vanadium, Nickel in bed sediment, root, stem and leaf of plants, No. 4 in north west of Qeshm Island. p. 55, 73.
8. Salahi Alayi, Zahra. (1978). MA thesis. Measuring heavy metals in trees, NO. 4, Sediment of Islamic Azad University of science and techniques.
9. B.H.Purse (1973).The Persian Gulf. 90.
10. Kashefifard, Kambiz. (2000). The study of pollutant resources of Persian Gulf, Hormozgan province with emphasis on Bandarabas city. BA thesis.
11. W.C.Ghirose and H.L. Ehrlich, (1999). Effects of seawater cation and temperature on manganese dioxide – reductase activity in a marine.89-109
12. Sharmad, Tarane. (2000). The study of the literature of Chabahar Gulf via geochemical studies and organic volatile sediment. MA thesis.
13. Leep.N.W (1998): Effect of heavy metal pollution on plants (vol.1). Applica science publication London.
14. M.Schnitzer and Shamat. (2001). U.Khan, Humic substances in environment, Marcel Dekker, INC. Newyork,N.Y.21.

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