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## **ESTIMATION OF CONTAMINATION WITH VANADIUM AND ARSENIC IN COASTAL SEDIMENTS OF BANDAR ABBAS (PERSIAN GULF, IRAN) ON THE BASIS OF GEOCHEMICAL-ENVIRONMENTAL FACTORS**

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### **Abstract**

In the present research, the intensity of contamination with heavy elements Vanadium (V) and Arsenic (As) in the coastal sediments of Bandar Abbas is gauged and rated using the method of Atomic Absorption Spectroscopy. All processes of sampling and assimilation of sediments are performed according to the guideline of the Manual of Oceanographic Observations and Pollutant Analyses Methods (MOOPAM) Standard issued by the Regional Organization for the Protection of the Marine Environment (RAPMI). The Mean concentrations of V and As in the sediments are of  $102.42 \pm 15.21$  and  $2.57 \pm 0.09 \mu\text{g/g}$  dry weight of sediment, respectively. Statistical analysis showed that the mean concentrations of V and As existing in the channel sediments are meaningfully different with each other, with a confidence coefficient of  $P < 0.05$ . On the basis of the Muller Geochemical Factor and Geoaccumulation Factor, such contamination is classified within The Zero Contamination Class, and on the basis of the standard of contamination factor, such a matter is classified within the low contamination level. Through statistical tests and calculations and considering the coefficient of correlation between V and As, it is distinguished that their source in coastal sediments of Persian Gulf should be similar.

**Key words:** Bandar Abbas, coastal sediments, geochemical factors, heavy elements, Persian Gulf

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### **1. Introduction**

In the Southern side of Iran Plateau, the Persian Gulf is a sea connected to the Indian Ocean, which is one of the most important seas of the world with respect to its aquatic ecosystem and is known as one of the significant resources for supplying energy (Nadim et al., 2008). The special conditions of this region pertaining to the diversity of tropical habitats, various species of aquatics, etc., have endowed a special significance to the environment of the region. Construction of various oil, gas and petrochemical complexes in the region and their environmental consequences, such as creation of petroleum and

chemical sewage, noise pollution, burning of separable gases, accumulation of chemical wastes, garbage disposal represent a great environmental challenge which should be taken into consideration (Regional Organization for the Protection of the Marine Environment, 2003).

Having information about the amount of chemical pollutants in question in the region, and by comparing with international standards through Geochemical-Environmental factors, one may estimate the intensity of the contamination at that area and take remediation actions (Zhang and Liu, 2002). Such information enables one to examine and study the poisonous effects of chemical pollutants on the

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aquatics of the region as compared to their required standards (Pourang et al., 2005). Due to their clayey nature, high electrical load and capacity of cationic exchange, the sediments of the Persian Gulf have a high ability to absorb contaminative elements (Elsagh, 2012a).

Heavy elements, as extensive environmental contaminants, may enter such ecosystems both through natural and anthropogenic processes, such as: soil abrasion, floodwater, circulation of ocean and sea water, burning of oil wells, industrial and urban sewage, discharge and transportation of chemicals, leakage of oil, gas, petroleum hydrocarbons and colored hydrocarbons, radioactive sewage, ship and vessel accidents and discharge of equilibrium water. Heavy elements can accumulate on the bed sediments. Therefore, ecosystems such as ports of industrial seashores, which are faced with a chronic entrance of heavy metals, have the most quantity of contaminated sediments (Demirak et al., 2006; Lado, 2008; Mehran and Sahar, 2017). Due to their toxicity, the bioaccumulation of heavy elements in phytoplankton, bacteria, fungi, and other microorganisms can cause growth inhibition, increased mortality, genetic mutations, and extinction of species in aquatic animals, thereby bringing about dramatic ecological consequences. One of the significant detrimental results of the accumulation of heavy elements is the extensive effects on the food chain. Due to their stability heavy elements can remain and move up in the food chain accumulating to concentrations much more than in water or sediments, thereby leading to potential hazards for the health of humans (Alegria et al., 1990; Jang et al., 2017; Massaro, 1997; Moffat, 2002; Arruda et al., 2010; Yang et al., 2012). For example, the consumption of fish contaminated with heavy metals causes more than 6000 cases of births with defective neurological systems each year in the United States. 6530 cases of hospitalization and 429 deaths due to food contaminated with Mercury were reported in Iraq in 1971-1972 (Davidson et al., 2004).

Vanadium can enter the environment through natural rock weathering, by combustion of fossil fuel and oil products and the leaching of vanadium-rich building materials. Stones made from steel industry residual slags (slag stones) contain rather large amounts of vanadium. The increasing use of these slag stones has also led to increased interest in the toxicity of vanadium to aquatic organisms (Brix et al., 2006). After entering the environment Vanadium remains in the water, soil, and air for a long time. In aquatic environments, Vanadium causes damaging effects on aquatic organisms. Vanadium damages the cardiovascular system and is detrimental to the lungs, liver, neurological system and kidneys (U.S. EPA, 2004; Asadpour et al., 2013). Among the toxic effects of Vanadium is its ability to produce the reactive radicals resulting in DNA damage, lipid peroxidation, carcinogenicity, depletion of protein sulphydryl and other effects (Asadpour et al., 2007).

Arsenic is the twentieth most abundant element, and as such, one of the most important heavy

metals lethal to the environment and living organisms (Hughes et al., 1988). Arsenic contaminations have occurred as a result of both natural geologic processes and the activities of man.

Anthropogenic sources of arsenic include human activities such as mining and processing of ores (Matschullat, 2000). Groundwater may get contaminated by the use of arsenical pesticides, natural mineral deposits or inappropriate disposal of arsenical chemicals (Saha et al., 1999; Mazumder, 2008). Another source includes sedimentary and meta-sedimentary bedrocks (Smedley and Kinniburgh, 2002). Arsenic is prominently toxic and carcinogenic. Extensively available in the form of oxides or sulfides or as a salt of iron, sodium, calcium, copper (Singh et al., 2007).

The toxic effects of Arsenic appear in the form of cardiac damage and loss, shock, amoebiasis, kidney tissue injury, weakening of the central neurological system and disorder of the hematopoiesis system (Guyton and Hall, 2006; Jaishankar et al., 2014). Arsenic can also cause melanoma, lung cancer and osteoporosis (WHO, 2001). Lower levels of arsenic exposure can cause nausea and vomiting, reduced production of erythrocytes and leukocytes, abnormal heartbeat, pricking sensation in hands and legs, and damage to blood vessels (Smith et al., 2000).

Considering the importance of the matter and the dangers that heavy elements pose, the qualitative and quantitative determination of heavy elements in seaboard sediments and offshore and marine ecosystems has been the subject of many studies (e.g., Zhang and Liu, 2002; Soylak and Peker, 2008; Harikumar and Jisha, 2010; Nur et al., 2018). Along these lines, in the present research the stations and canals of Shahid Bahonar Dock, Tavanir Power Plant, Foulad Dock, Oil Refinery, Shahid Rajaei Dock and Persian Gulf Shipbuilding Complex (Fig. 1) are studied to quantify the amount of Arsenic and Vanadium contamination on the basis of geochemical indexes in coastal sediments, and to determine the source of the contamination. Presentation of the results to the relevant organizations, in addition to assisting in the protection of health and hygiene and stable development of the society, can prevent outbreak of some diseases and can be a preface for further research in line with the preparation of a comprehensive identity certificate for regional and national contamination; The minimum result of which shall be the application of the appropriate preventive methods and presentation of applied standards and rules.

## 2. Materials and methods

On the basis of the center for environmental pollution, after selection of the research domain of Bandar Abbas Refinery, the sampling depths, stations, canals of Shahid Bahonar Dock, Tavanir Power Plant, Foulad Dock, Oil Refinery, Shahid Rajaei Dock and Persian Gulf Shipbuilding Complex (shown in Fig. 1), the costal sediments were determined.

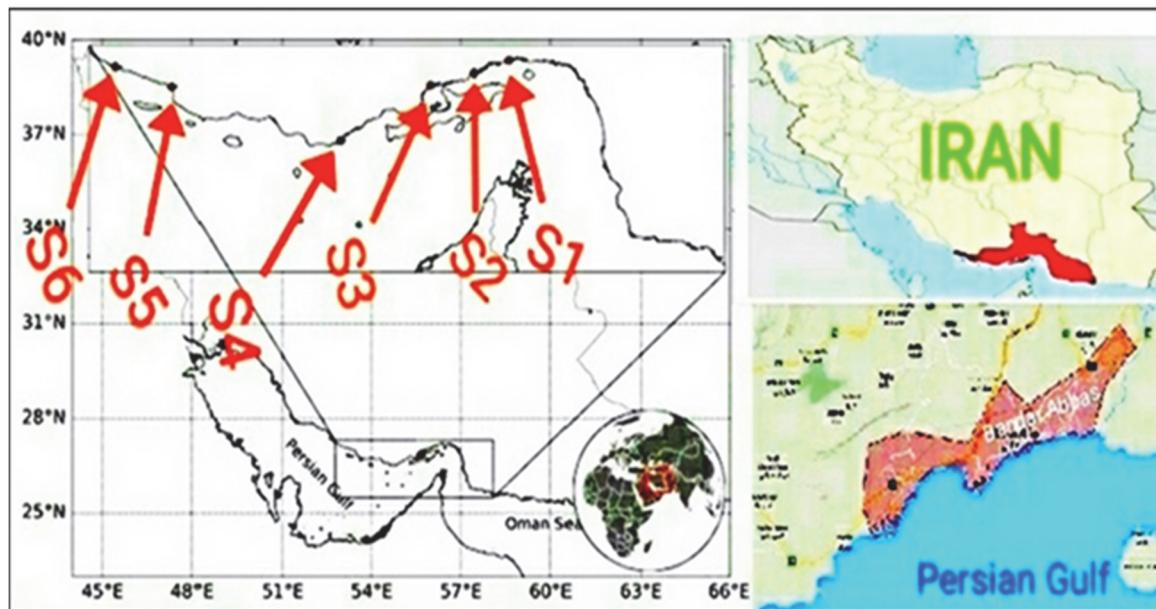


Fig. 1. Coastline of area under study

Table 1. Location of transects for sampling

<i>Transect</i>	<i>Station</i>	<i>Longitude</i>	<i>Latitude</i>
S1	Shahid Bahonar Dock	56° 12' 16"	27° 08' 18"
S2	Tavanir Power Plant	56° 08' 26"	27° 07' 36"
S3	Foulad Dock	56° 07' 06"	27° 06' 10"
S4	Oil Refinery	56° 06' 11"	27° 05' 41"
S5	Shahid Rajaei Dock	56° 04' 36"	27° 04' 11"
S6	Shipbuilding Complex	55° 59' 01"	27° 02' 16"

As the gradient direction of the study area is North to South and the main direction of such a gradient continues in the seabed, the canals (transects) are selected vertical to the seacoast. The sampling was conducted in the summer 2017 according to the map of Fig. 1 and the location of the canals (Table 1). Sampling, preparation and complete assimilation of the sediments are conducted on the basis of MOOPAM (Manual of oceanographic observations and pollutant analyses methods) Standard Guideline published by ROPME in 1999. Considering that the depth of the area under study is often less than 6 m or between 6 m to 10 m, on each transect three stations are selected at the depths of 0-3 m, 3-6 m and 6-9 m and two samples of sediments are taken from each station. Sampling was conducted by Ekman Grub Sampler (with a cross-section area of 15×15 cm<sup>2</sup>), and after bringing up the sediment, it was poured into a polyethylene container (coded) and transferred to the laboratory, where it was dried at a temperature of -40 °C in a Freeze Dryer for 24 hours. Then, the sediments were riddled through a 63-2000µm sieve, and the samples with the size less than 63 microns were turned into powder so that such sediments could pass through a 63µm sieve. Two grams of the dried sediment were poured in a Teflon container and 10 ml of 65% Nitric Acid were added, and put in a greenhouse at a temperature of 90°C for 1 hour, until the completion of the process of assimilation. Then the assimilated

samples were poured into a volumetric flask after rendering and titrated (Anderson and Meyers, 2000). At this stage an Hydride Generation Atomic Absorption Spectrometer (model A400 Buck- scientific Inc.) was used for the measurement of As and a Graphite Furnace Atomic Absorption Spectrometer (model AA240 Varian) was used for the determination of V. For such a purpose, at first, the calibration curves were separately prepared for each element, by the use of the standard solutions with specified concentrations at the maximum wavelengths for each element (Burrows and Whitton, 1983; Yap et al., 2002). The operational indexes of spectrometry are specified in Table 2 (Elsagh, 2012b).

The prepared samples, after mixing and homogenizing of the solution, were injected into the instrument and the absorption and concentration were read (Burrows et al., 1983). The real concentration on the basis of the dry weight of the sample will be calculated from Eq. (1) (Burrows and Whitton, 1983; Elsagh, 2012c).

$$C_r = C_i * V/W \quad (1)$$

where:  $C_r$ : real concentration of the sample based on the dry weight of sample (according to µg/g or mg/kg of dry weight of the sample);  $C_i$ : concentration read from the instrument by the use of a calibration curve (by mg/L).  $V$ : volume of sample (mL) (taking into

account diluting);  $W$ : dry material weight used for assimilation (g).

For testing the accuracy of the procedure, each sample was analyzed three times and its mean was registered. In addition, the method of standard addition and percentage of element retrieval was applied by adding 10 ml of the standard solution of V and As, with a concentration of 1  $\mu\text{g/g}$ , to each sample. It should be noted that for each element, 2 samples with the same specifications and in similar conditions were prepared and the standard solution was only added to one of them. Then the concentration of each solution was separately determined (with the relevant calibration extrapolation) and the percentage of detection of the elements was calculated using the Eq. (2) (Official Method of Analysis, 1980; Elsagh, 2012d).

$$R = 100(A_2 - A_1) * A_S \quad (2)$$

where:  $R$ : detection percentage;  $A_1$ : concentration of non-standard sample ( $\mu\text{g/g}$ );  $A_2$ : concentration of sample containing standard ( $\mu\text{g/g}$ );  $A_S$ : concentration of standard solution ( $\mu\text{g/g}$ ).

Results from the addition of the standard to the samples and detection percentage of the elements are presented in Table 3. According to the percentages of elements retrieved (Table 3), we may conclude that the method used for extraction and determination of the elements is trustworthy enough. All chemicals used, are from the kind Analytical Indicators produced by Merck. All research samples are prepared by the double-distilled water. In order to remove any contamination, all containers were washed with nitric acid 1:1 and distilled water and were dried for 4 hours at a temperature of 60°C, before the experiment. The normalization of the data captured was analyzed and

examined through the Kolmogorov-Smirnov Statistical Test, and the statistical analysis under the Parametric Tests Method was conducted using SPSS/24 Software (Zar, 2019).

### 3. Results

The mean concentration  $\pm$  standard error of V and As were  $102.42 \pm 15.21$  and  $2.57 \pm 0.09$  ( $\mu\text{g/g}$  of dry weight of sediment), respectively. The mean concentration  $\pm$  standard error of Vanadium and Arsenic in the samples, and in the earth's crust and shale (Turekian and Wedepohl, 1961; Satyanarayana et al., 1994; Mico et al., 2006) and the correlation coefficient of the elements in the samples are given in the Tables 4 to 6.

The mean concentrations of V and As in the selected stations, with the confidence level of 95%, using Tukey Statistical Test, Duncan Test and ANOVA Test were compared to each other, and existence or non-existence of meaningful difference at the level of 0.05% was determined (Zietara et al., 2019). The assumption of equality of the means for the mean quantity of V and As in various stations is rejected, and there is a meaningful statistical difference among the mean amount of V and As in all stations ( $P < 0.05$ ).

According to the present test, as it is observed in Figs. 2-4, the maximum amount of V is in the Oil Refinery Station, and after that, in Shahid Bahonar Dock Station, Shahid Rajaei Dock, Tavanir Power Plant, Shipbuilding Complex and Foulad Dock, respectively. Also, the maximum amount of As is observed in the Oil Refinery Station and after that, in Shahid Bahonar Station, Shipbuilding Complex, Shahid Rajaei Dock, Tavanir Power plant, and Foulad Dock, respectively (Asadpour et al., 2013).

**Table 2.** Device condition to measure elements

Element	Wavelength (nm)	Fission width (nm)	Flow (mA)	Method	Optimal concentration range ( $\text{mgKg}^{-1}$ )
V	318.5	0.2	20	GFAAS	1 - 200
As	193.7	0.5	10	HGAAS	3 - 150

GFAAS: Graphite Furnace Atomic Absorption Spectroscopy; HGAAS: Hydride Generation Atomic Absorption Spectroscopy

**Table 3.** Standard addition and reclaim percentage of metals

Element	Concentration of non-standard sample ( $\mu\text{g/g}$ )	Concentration of standard added ( $\mu\text{g/g}$ )	Concentration of sample after adding standard ( $\mu\text{g/g}$ )	Retrieval percentage
V	90.6	1	91.51	91
As	2.95	1	3.87	92

**Table 4.** Regions under study and the mean concentration of V and As in dry samples of sediments, for the depths of 0-3, 3-6 and 6-9

Transect	Station	Vanadium $\mu\text{g/g}$	Arsenic $\mu\text{g/g}$
S1	Shahid Bahonar Dock	$134.67 \pm 1.71$	$2.70 \pm 0.16$
S2	Tavanir Power Plant	$84.83 \pm 3.86$	$2.48 \pm 0.22$
S3	Foulad Dock	$67.50 \pm 2.68$	$2.18 \pm 0.17$
S4	Oil Refinery	$160.33 \pm 2.00$	$2.68 \pm 0.24$
S5	Shahid Rajaei Dock	$96.00 \pm 2.68$	$2.62 \pm 0.23$
S6	Shipbuilding Complex	$71.17 \pm 3.40$	$2.77 \pm 0.30$
N= 6	Mean $\pm$ Standard Error	$102.42 \pm 15.21$	$2.57 \pm 0.09$

**Table 5.** Mean of concentration of V and As in Earth's Crust and Shale's ( $\mu\text{g/g}$ )

Element	V	As
Earth's Crust	130	1.8
Shale/Clay	130	13

**Table 6.** Correlation coefficient between elements

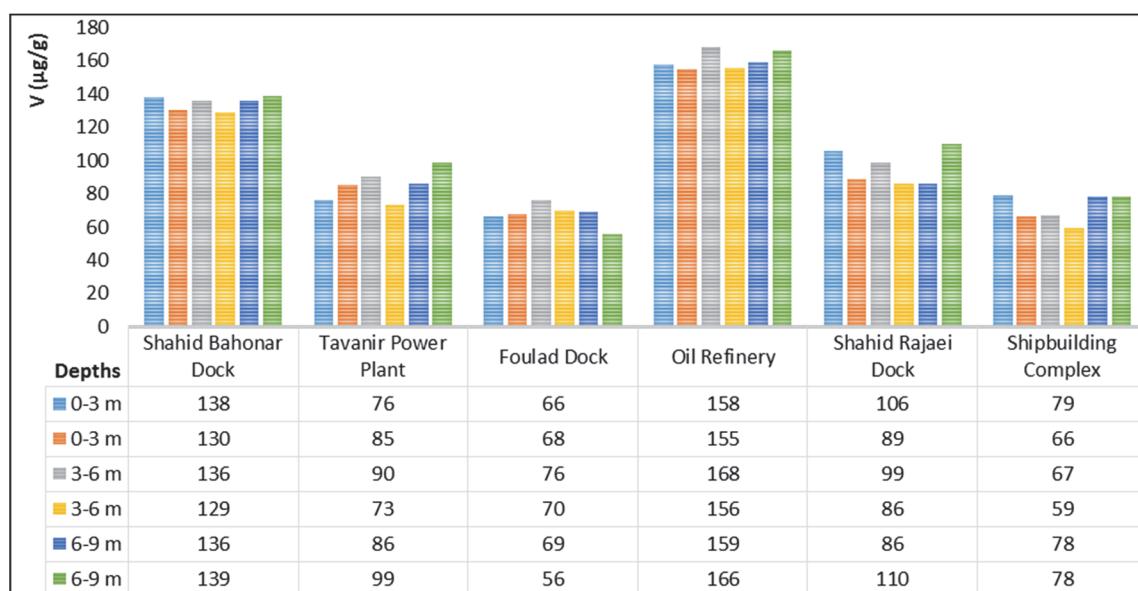
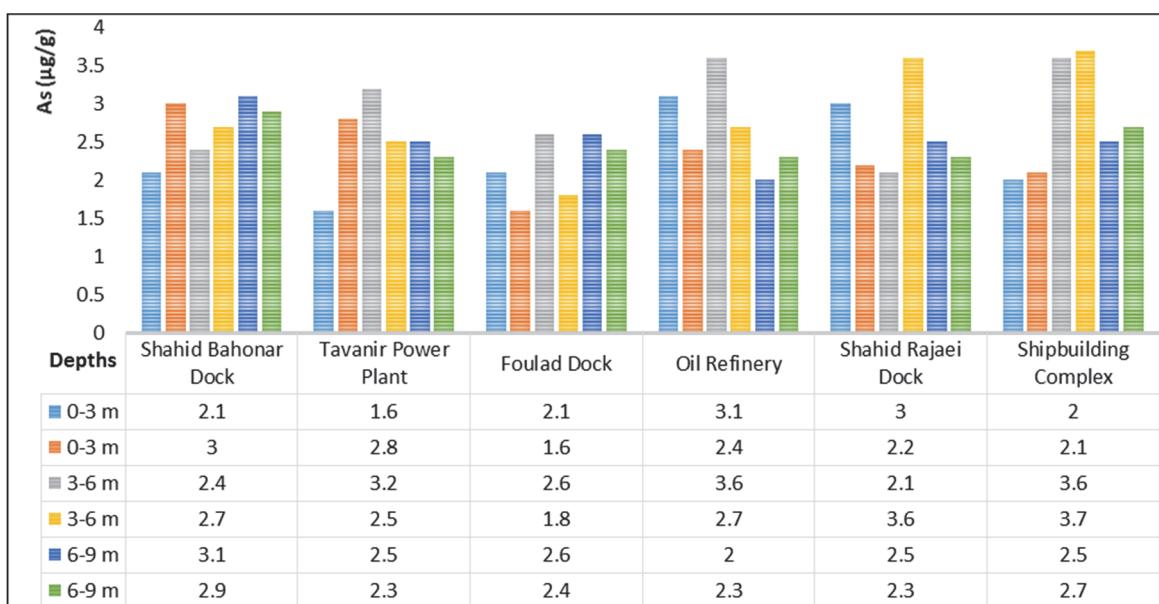
Element	V	As
V	1	0.48
As	0.48	1

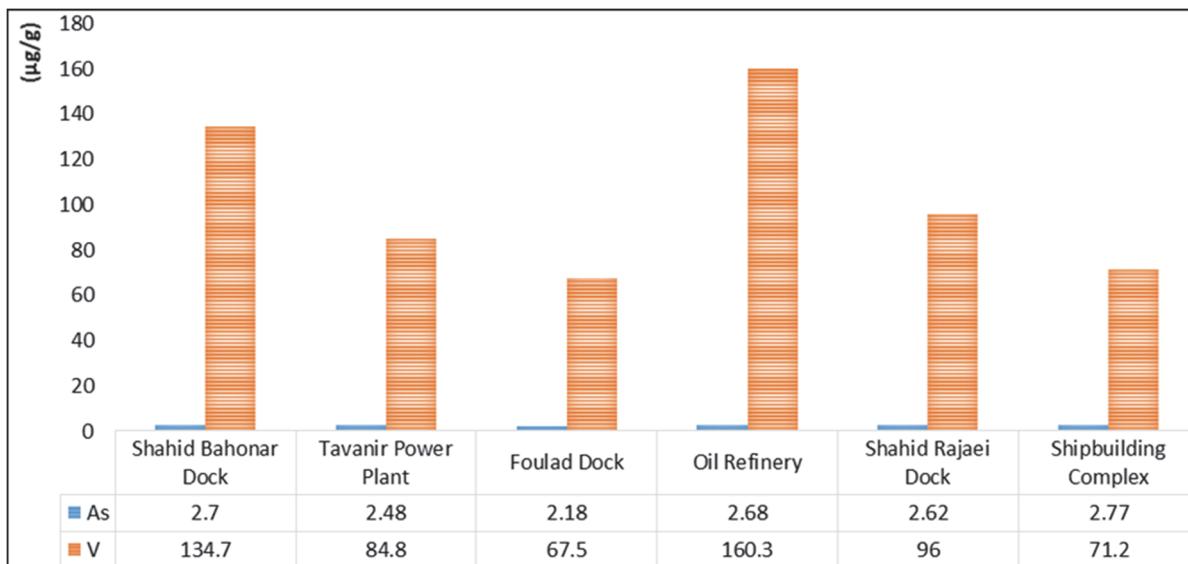
Based on the correlation coefficient and Table 6, for both heavy elements of Vanadium and Arsenic with a positive correlation coefficient of 0.48, it can be concluded that the origin of these metals is the same

in the sediments (Reimann et al., 2008).

#### 4. Discussion

Due to the lack of sufficient information regarding the field concentration of elements in the coastal sediments of Persian Gulf, and also the lack of standards and guidelines for the concentration of elements in the region, the formulas of element enrichment coefficient, geoaccumulation, and contamination index of the sediments were used to obtain a better and more exact analysis of the coastal sediments in the area under study. The enrichment coefficient  $E_f$  is considered as an appropriate criterion for geochemical trends and is used for interregional comparison (Addo et al., 2012).

**Fig. 2.** Mean concentration of V in dry samples of surface sediment in channels**Fig. 3.** Mean concentration of As in dry samples of surface sediments in channels



**Fig. 4.** Comparison of mean concentration of elements in dry samples of surface sediments of channels

A widely applied approach for finding the degree of the contamination properties is the formation of Enrichment Ratios. To evaluate the amount of the contaminants in the environment, the factors related to enrichment, the excess of the species in comparison with that of the materials forming the Earth Crust is calculated. Crust enrichment factors of the elements are, repeatedly and periodically used in the determination of the rate of correction for the component of the sediments (Evren et al., 2018). In the present study, the enrichment factor is used for the purpose of analysis and examination of the level of contamination and human effects in the sediments. The  $E_f$  values indicate that most probably the contaminants sources are related to human activities (Adamo et al., 2005). The enrichment factor is a useful index which reflects the status of environmental contaminants and heavy elements in the components of the aquatic environment and is calculated with Eqs. (3-4) (Sakan et al., 2009; Zalewska et al., 2015; Mohamaden et al., 2017):

In Earth's Crust, in the mentioned sediment:

$$E_f = (X/Fe)_s [1 - (X/Fe)_E] \quad (3)$$

In Earth's Crust, in the Mentioned Sediment:

$$E_f = (X/Al)_s [1 - (X/Al)_E] \quad (4)$$

where:  $X$  is the element under study,  $(X/Fe)_s$  is the ratio of the concentration of  $X$  to Fe in the sample and  $(X/Fe)_E$  is the ratio of the similar source in the surface of the earth's crust.  $(X/Al)_s$  is the ratio of  $X$  to Al in the sediment sample, and  $(X/Al)_E$  is the ratio of the similar source in the earth's crust (Abdol and Hikmat, 2018). Iron and Aluminum which enter the earth's crust from prevailing sources are used for normalization (Eby, 2005; Mashiatullah et al., 2013). In the present research, Iron and Aluminum are applied as the normalization elements for the separation of manmade and natural contaminations (Md et al., 2017).

Iron and Aluminum are the elements which are mostly found in the crust and, are rarely affected by human activities (Guerra-Garcia and Garcia-Gomez, 2005). The enrichment coefficient is an indicator of an accumulating or repellent environment. If the value of  $E_f$  is more than 1, that environment shows the accumulation of the elements and if it is less than 1, it indicates a repelling environment. An  $E_f$  equal to 1 shows a natural environment (Harikumar and Jisha, 2010; Bonnail et al., 2016). Tables 7 and 8 determine the enrichment coefficient of the heavy elements of Vanadium and Arsenic in the coastal sediments of Persian Gulf.

Contamination intensity on the basis of  $E_f$ :

Without Absorption and Enrichment: <1

Slight Absorption and Enrichment: 1-3

Mean Absorption and Enrichment: 3-5

Relatively Intense Absorption and Enrichment: 5-10

Intense Absorption and Enrichment: 10-25

Very Intense Absorption and Enrichment: 50

Critical Absorption and Enrichment: >

**Table 7.** Enrichment coefficient  $E_f$

Element	V	As
Classification	0.75	1.38
Degree of contamination	Very Low Absorption (Without Contamination)	Slight Absorption (Low Contamination)

$E_f$ : Enrichment Factor

**Table 8.** Enrichment coefficient  $E_f$

Element	V	As
Classification	0.943	1.68
Degree of contamination	Very Low Absorption (Without Contamination)	Slight Absorption (Low Contamination)

$E_f$ : Enrichment Factor

Using the Geochemical Formula of the Geoaccumulation index ( $I_{geo}$ ) (Muller, 1979), described below, one can classify the Geochemical index of the contamination from 0 to more than 5 (Eq. 5) (Mohamaden et al., 2017; Raj et al., 2017).

$$I_{geo} = (\log_2 [C_n / (1/5B_n)]) \quad (5)$$

where the factors are described as follows:

$I_{geo}$ : contamination intensity index in sediments;  $C_n$ : element concentration in sediments under study with diameter less than 63 microns;  $B_n$ : field concentration of element in sediment, shale, previous concentration of element.

Coefficient 1/5: For possible variables of the background which are introduced to the lithology because of the related changes.

To determine the contamination rate of the heavy elements of Vanadium and Arsenic in the sediments The Muller Formula (Mico et al., 2016; Fangjian et al., 2018) is applied with the measured concentration of the elements as  $C_n$  and the concentrations of Table 6 as  $B_n$ ,

Very Intense Contamination: >5

Intense Contamination: 4-5

High Contamination: 3-4

Mean Contamination: 2-3

Low Contamination: 1-2

Without Contamination: <0-1

As it is observed in Table 9, on the basis of the geochemical index suggested by Muller, the quality of the sediments of the regions are classified in the 0 class with respect to the amount of heavy elements of Vanadium and Arsenic.

Table 9. Geochemical Index  $I_{geo}$

Element Name	V	As
Enrichment Coefficient	-0.92898	-2.92363
Contamination Intensity	Without Contamination	Without Contamination

$I_{geo}$ : Geochemical Accumulation I

The contamination level of sediments with respect to an element is often expressed in the form of the Contamination Index  $C_f$  as follows (Eq. 6) (Dabiri et al., 2017; Nijole et al., 2018):

$$C_f = (X_s / X_r) \quad (6)$$

In which  $X$  is the element under study,  $X_s$  is the mean concentration of the element in the sediment and  $X_r$  is the mean concentration of the element in shale (Satyanarayana et al., 1994; Anbuselvan et al., 2018).

Low Contamination:  $C_f < 1$

Mean Contamination:  $1 \leq C_f < 3$

Noticeable Contamination:  $2 \leq C_f < 6$

Very High Contamination:  $6 \leq C_f$

Table 10 shows the amounts obtained from the above equation for the elements of Iron, Aluminum and Calcium in coastal sediments of Persian Gulf.

Table 10. Contamination factor  $C_f$

Element	V	As
$C_f$	0.787846	0.197692
Contamination level	Low contamination	Low contamination

$C_f$ : Contamination Factor

Based on the correlation coefficient and Table 6, for both heavy elements of Vanadium and Arsenic with a positive correlation coefficient of 0.48, it can be concluded that the origin of these metals is probably the same in the sediments (Reimann et al., 2008).

## 5. Conclusions

The results of the present research show that the surface sediments of the Persian Gulf, are gradually affected by man-made contaminants. Through the statistical test of Correlation Coefficient and taking into consideration the results of Table 7, for two heavy elements of V and As with positive correlation coefficient, it is determined that the source of such metals in sediments is identical.

Man-made sources and origins for these metals is mostly the abrasion of soil in the coastal domains and contamination arising from oil, and industrial, agricultural and urban resources in stations and channels. Statistical analysis (ANOVA: single factor) also indicates that the mean concentrations of Vanadium and Arsenic existing in the sediment of channels have a meaningful statistical difference with each other ( $P < 0.05$ ). The maximum amount of vanadium may be found in the sediments of the Oil Refinery channel and the minimum amount is found in the channel of Foulad Dock. Considering the amount obtained and the mean concentration of Vanadium in the Earth's crust and the results of the statistical correlation coefficient test, such a matter may be because of transfer of crude oil and petroleum components. As to Arsenic, the maximum amount is found in the sediments of the Channels and the Shipbuilding Complex, which may be due to unloading and loading of minerals and painting the vessels and ships, and the minimum amount is found in channels of Foulad Production Dock. Therefore, the oil refinery contains the maximum amount of these metals and Foulad Dock contains the minimum amount. As a result, the most important source of such elements is the petrochemical and industrial activities in the coasts of the Persian Gulf.

The results of the present research exhibit appropriate information regarding the distribution of the heavy elements (Vanadium and Arsenic) in Persian Gulf Coasts, which may help the processes of protection and evaluation of the sediments in the. Also, through an integration of the three mentioned indices and factors, it is possible to generate the index

of constant development for recognition of environmental contamination.

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