

Sedimentary and Environmental Geochemistry of metals in the surface Sediments of the North-west of Persian Gulf (Boushehr Province Area)

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Abstract

Sediments are generally regarded as the sink for dissolved elements carried out to the sea by rivers. In order to study the source and mechanism of metal transport in sea water, 123 surface sediment samples were taken by using grab sampler in the northwest part of the Persian Gulf in summer. Grain size analysis and geochemical analysis by ICP-OES were carried out on samples after sample preparation. The geochemical results reveal that the mean (and standard deviation) values for trace elements are as follows: V:52 (20.83), Ti:1738 (574.67), Sr:1170 (638.15), Ni:64 (27.68), Mn:366 (104.12), Mo:0.506 (0.27), Fe:21454 (7340.8), Cu:14 (6.19), Cr:80 (26.90), Cd:0.19 (0.07), As:4 (3.35), Al:31876 (11390.6) ppm. Factor analysis and other multivariate statistical methods were used for discrimination of source of the elements. Al, Fe, Cr, Cu, Mn, Ni, Ti and V show strong correlation coefficients and they could be related to a detrital origin out of the sedimentary basin. However, As and Mo are placed in another factor which could be related to agricultural and industrial sources. Ca and Sr fall also in the third component indicating a close relationship and biogenic origin. Based on grain size analysis, fine-grained fraction are also correlated with Al, Cr, Cu, Fe, Ni, Ti, V, As, Mo, Mn, Cd and again Ca and Sr show strong correlation with coarse-grained fraction, i.e. sandy sediments of biogenic origin. The element association indicates the adsorption processes for fine-grained fractions as one of main factor for enrichment of the elements.

Keywords: Persian Gulf, Sediment Geochemistry, Potentially Toxic metals, Source, Statistical Parameters.

1-Introduction

Persian Gulf or Rapme sea environment is a marginal sea in north- west of Indian ocean (Price and Robinson, 1993) that is located at 24° to 30° 30' N and 48° to 56° 25' E (Parsapour, 2006). The Persian Gulf is a shallow, semi - closed basin with the characteristics of poor leaching (Price and Robinson, 1993) and also is the warmest water Basin in the world that have arid to Equatorial arid Weather. An anti-clockwise surficial flow, create a cycle oceanic water in Iranian coast (Hartman *et al.*, 1971). The water salinity ranged from 36.6% in the strait of Hormoz to 40.6% in the North-west

border (Swift and Bower, 2006). Recent sediments of the north part of Persian Gulf include fluvial clastic sediments, biogenic sediment and windy sediments (Lak *et al.*, 2009). Fluvial clastic sediments originate from the Arvand-roud and some other rivers of the northern coast of the basin. The Arvand-roud River flooding, deposited near 90% of its loads in its own Delta and only 10% of its load arrived to the Persian Gulf basin (Milliman and Meade, 1983). The most part of windy sediments originate from the south- west winds that called Shemal (Evans, 1988). Dusty storm move large amount of fine grain clastic sediments from the coastal plan and Northern

and north- western Desert (Iraq) and Arabian Desert (Saudi Arabia) (Al Bakri *et al.*, 1984).

Existence of oil resources in Persian Gulf caused the urbanization and industrial developments and also population increase in this area. Concentration of population and industrial activities in this area caused hazards in the aqueous environment. Garbage dumping, Ship washing, tanker ship traffic, and the refineries waste and oil and commercial wharf firing are causing the pollution and big variation in the Persian Gulf environment that can have irrecoverable effect on biologic species if continue (Zafari, 2008).

The pH, reduction and oxidation potential (redox), and temperature and also bacteriogenic processes affect solubility, mobility and deposition of toxic metals. Some other important factors that affect mobility of heavy metals in environment are: heterogeneous of soil and sediment (for example in size), background of soil and sediment composition (for example mineralogical or amount of organic matter), interaction between particles and fluid or porous water and biological activity. These factors can have big variation from one ecosystem to another and also in different habitats of one ecosystem. Heavy metals reaction and sedimentation, concentrate them correspond with oceanic floor flow direction (Siegel, 2001).

Some elements are mobile in acidic condition and some others are immobile. So, heavy metals solubility affected by pH condition in environment. The average of pH in seawaters is 8.3 and clay minerals and Fe and Mn oxihydroxide in these conditions have negative surficial load (Sarkar, 2002). These particles absorb and precipitate the heavy metals with positive load. In sandy loam when pH decreases under 6 the Cd mobility increase, but Zn mobility increase whenever pH decrease under 5. When pH is 6, Zn and Cd are adsorbed by

clays and free oxide of surficial levels of soils (Scokart *et al.*, 1983).

Sabzalizadeh, (2008) had a study to determine of heavy metals concentration and pollution of basin loads and also assessment of ecological risk index in Lfheh Bosaif (in the west part of KHOR- Mosa Channel). This study shows that elements pollution index for metals at that area have below trend:

$$\text{Pb} > \text{Hg} > \text{Zn} > \text{Ni} > \text{Co} > \text{Cd} > \text{Cu}$$

Based on Spencer and MacLeod (2002), because of negative load of clay particles, sediments are suitable place for element ions accumulation, and if these accumulations don't affect by physical water flow, can become to a stable source of toxic elements in the environment for a long time. In other words because of heavy metals accumulation in sediments and stability of sediments in comparison with water and change in solubility of them in variation of environmental condition, these metals can access by existing part of ecosystem. So studying on heavy metals pollution in sediments for checking probability of contamination is very important (Spencer and MacLeod, 2002).

2–Materials and Methods

The study area is located in the north- western part of Persian Gulf in Bushehr province of Iran waters, between 49° 14' 49'' and 52° 16' 25'' E and 27° 22' 11'' and 30° 10' 12'' N. access to this place is available by Bushehr overland routes and marine way of north- western part of Persian Gulf (Fig. 1).

To find or toxic elements sources in the studied area, 123 samples of surficial sediments of Persian Gulf (Bushehr province area) basin floor was taken by the Islamic Republic of Iran Navy Ship in 2010 summer season. These samples were taken by grape Van Veen sampler of Hydrobios Company from Germany and used echosounder for depth determination. The

samples were taken each 15 Km and packed in plastical bags and moved to Geological Survey of Iran in Karaj laboratory unit. The samples at 48 hours were became dry in laboratory temperature and then sieved for grain size to determination analyze. To determine the type and concentration of elements in sediments, 20 to 25 grams of each sample was analyzed by ICP method in Geological Survey of Iran

laboratory. The elements were chemically analyzed by ICP- OES Variant 735-Es analyzer that was made in United Kingdom. The standard that used in elements analyze are marine carbonate sediments for eastern and central part of study area and also marine clastic sediments for western part of study area. The laboratory results were processed by Arc GIS 9.3, Excel 2007 and SPSS 19.

North_West Persian Gulf

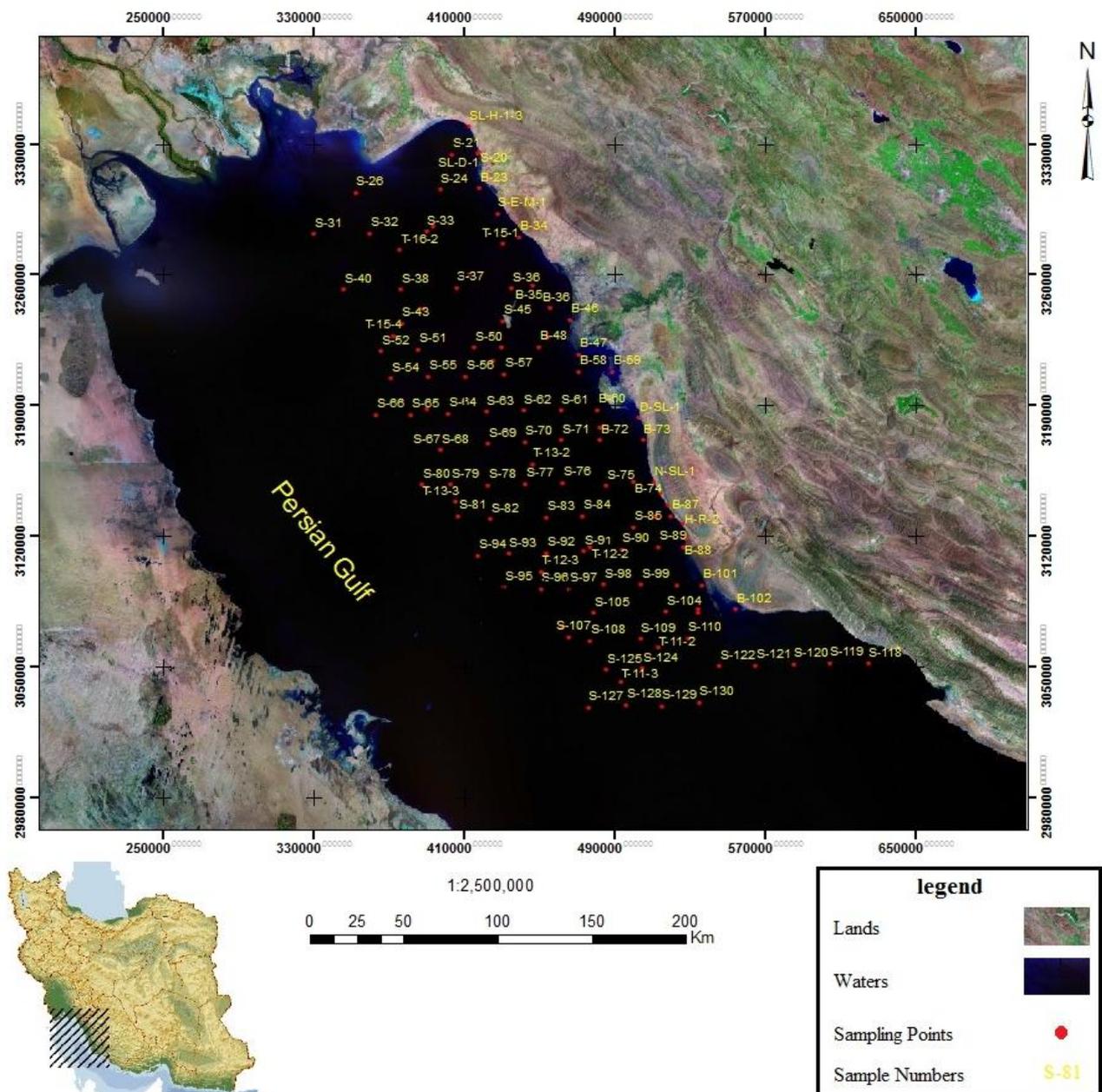


Figure 1) Sampling point positions in the study area (Bushehr province waters).

3–Results and discussion

The maximum, minimum, average and standard deviation of the elements concentration

quantities were calculated by Excel software and its results are shown in Table 1.

Table 1) Statistical parameter for elements concentration in study area.

Elements	Max (ppm)	Min (ppm)	SD	Ave. (ppm)
Al	51464	300	11390.67	31876
Ca	305001	17668	53497	167824
As	25	1	3.3583	4
Cd	0.38	0.05	0.077	0.19
Cr	136	1	26.909	80
Cu	50	1	6.1991	14
Fe	37789	200	7340.8	21454
Mo	2	0.2	0.2766	0.506
Mn	800	1	104.12	366
Ni	123	1	27.688	64
Sr	3700	1	638.15	1170
Ti	2864	50	574.6724	1738
V	101	1	20.831	52

3.1–The Correlation Coefficient

To find element effects on each other, correlation coefficient by Spearman method was calculated for elements. The Spearman method was selected because of non-normal distribution of some elements in sediments and this method is not related to elements distribution. The quantities of correlation coefficient calculation between metals concentration and grain size were provided in Table 2.

The Table 2 checking shows significant relation between Al and some other metals such as: Fe, Cu, Mn, Ni, Ti and V that can be result of these metals participant with clay Aluminum-silicate minerals. Commonly the Al and Fe originate from rocks and soils physic-chemical weathering and this strong relation between them and mentioned metals shows natural sources of them and also clay Aluminum-silicate minerals role on adsorption and transportation of all metals above.

Table 2) correlation coefficient between elements concentration and grain size.

Elements and grain size	Al	As	Ca	Cd	Cr	Cu	Fe	Mo	Mn	Ni	Sr	Ti	V	Clay	Silt	Sand	Gravel
Al	1.00																
As	.299	1.00															
Ca	-.785	-.262	1.00														
Cd	.187	.335	.009	1.00													
Cr	.827	.405	-.555	.498	1.00												
Cu	.813	.309	-.588	.358	.763	1.00											
Fe	.912	.245	-.728	.202	.776	.740	1.00										
Mo	.385	.439	-.128	.404	.595	.310	.326	1.00									
Mn	.580	.511	-.317	.643	.802	.581	.534	.610	1.00								
Ni	.890	.339	-.574	.378	.850	.876	.826	.469	.641	1.00							
Sr	-.682	-.563	.464	-.386	-.700	-.506	-.583	-.555	-.742	-.631	1.00						
Ti	.860	.229	-.580	.399	.896	.789	.806	.507	.805	.842	-.708	1.00					
V	.802	.465	-.432	.587	.883	.807	.743	.591	.793	.923	-.721	.844	1.00				
Clay	.653	-.001	-.435	.193	.526	.630	.592	.091	.287	.656	-.329	.559	.580	1.00			
Silt	.664	.430	-.557	.358	.660	.602	.615	.431	.559	.682	-.536	.633	.679	.312	1.00		
Sand	-.815	-.326	.582	-.369	-.763	-.749	-.729	-.368	-.571	-.837	.584	-.751	-.790	-.754	-.736	1.00	
Gravel	-.636	-.393	.487	-.204	-.642	-.461	-.563	-.432	-.552	-.582	.537	-.592	-.586	-.559	-.521	.688	1.00

Based on Table 2 there is a strong relationship between Fe and Al, Cr, Cu, Ti, Ni and V. also weak relation between Fe with Ca, Sr and As is result of different geochemical features and inexistence of iron oxide in the carbonate minerals network in carbonate sedimentation environment. Dissolved and suspended Mn have strongly affected heavy metals role in water. Fe and Mn can absorb many transition elements from water. This process was done by participation in the crystal structures (Ouddane *et al.*, 1999). The strong relationship between Mn and Mo, Cr, Cd, Ni, Ti and V is result of thus indication. Ca and Al strong negative relationship shows that Al has a non- carbonate source in sediments. Ca discrepancy with Fe and Al is result of Ca property and also its absorption by biological particles and carbonate sands. The Ca can be substituted by Sr in carbonate network and this can be the reason of these elements strong relationship. Therefore the Sr accumulates in carbonates (ATSDR, 2008). Also, Sr have a high solubility in water and the most important matter of this element is that Sr can replace Mg and Ca ions in carbonate minerals network (Byerrum *et al.*, 1974).

Based on correlation coefficient between elements and grain size (Table 2) the elements

distribution in surficial sediments can be divided into two major groups. The first group elements are Al, As, Cd, Mo, Mn, Cr, Cu, Fe, Ni, Ti and V and accumulate in fine grain (silt and clay) part of sediment.

The second groups include Ca and Sr that accumulate in coarse grain (sand and gravel) part of sediments. Since sand and gravel are mainly formed from shells of benthic and plagic organisms, so the Ca and Sr have biogenic sources.

According to results of physic-chemical parameters such as salinity, pH and temperature of water in sampling place, average pH were 8.29 and its close to the pH of seawater (8.13), so the pH can't has significant effect on the elements concentration. But the salinity ranges vary from 39.9 to 40.75% that is higher than seawater (about 33%). The salinity increase cause metal solubility decrease in sea water and it outcome is decrease of bio-availability of toxic elements (Yalcin, 2009).

According to Table 3 the Cd and Sr have direct relation with salinity, so increase (or decrease) of salinity cause increase (or decrease) of these elements concentration.

Table 3) result of correlation coefficient between elements concentration and depth, salinity and temperature of water parameter.

	Al	As	Ca	Cd	Cr	Cu	Fe	Mo	Mn	Ni	Sr	Ti	V
Depth (m)	-0.151	-0.434	-0.181	-0.329	-0.297	-0.072	-0.172	-0.506	-0.453	-0.190	0.508	-0.303	-0.383
Salinity (%)	-0.012	-0.221	0.121	0.409	0.159	-0.188	-0.053	-0.089	-0.291	0	0.403	-0.156	-0.009
Temp. (°C)	-0.221	-0.018	0.085	-0.488	-0.379	-0.094	-0.185	-0.006	0.018	-0.229	-0.171	-0.141	-0.244

The correlation between elements concentration with depth shows that all the elements apart Sr have reverse relationship with depth. So the high concentration of elements is closed to the coastline and decrease by moving to sea. But the Sr increase by away from coast. This increase is related to bio existence and species of deeper area.

3.2–Factor analysis

To determine the source of elements and separating elements by their sources, factor analysis with principal component analysis method was done. Table 4 shows the factors and their classes.

Table 4) Factor analysis value.

	Al	As	Ca	Cd	Cr	Cu	Fe	Li	Mo	Mn	Ni	Sr	Ti	V
Component 1	.895	-.192	-.511	.507	.942	.791	.861	.873	.297	.765	.957	-.636	.956	.921
Component 2	-.163	.758	.383	.364	-.012	-.179	-.102	-.146	.791	.316	-.061	-.191	-.060	.204
Component 3	-.003	-.170	.685	.354	.022	0.184	.061	.209	.155	.219	.101	.381	.081	.132

Factor analysis value shows that all the elements apart from Sr, Ca, As and Mo are in first component and originate from a single similar source (terrestrial origin). The elements originated from rock weathering and transported by rivers into the Persian Gulf basin. The Arsenic and molybdenum are in second component and have a different source in comparison with first component. The negative value of calcium and strontium in first component shows non-clastic origin (biologic source) of them.

3.3–Comparison with other location

3.3.1– Nickel

Nickel and Vanadium are two important sub-elements of petroleum (Ikebe and Tanaka, 1979). Studies show that Ni and V are not mobile in fossil fuels and so their transportation into the aqueous phase is too weak and slow (Bu Olayan and Al Yakoob, 1998; Cantu *et al.*, 2000).

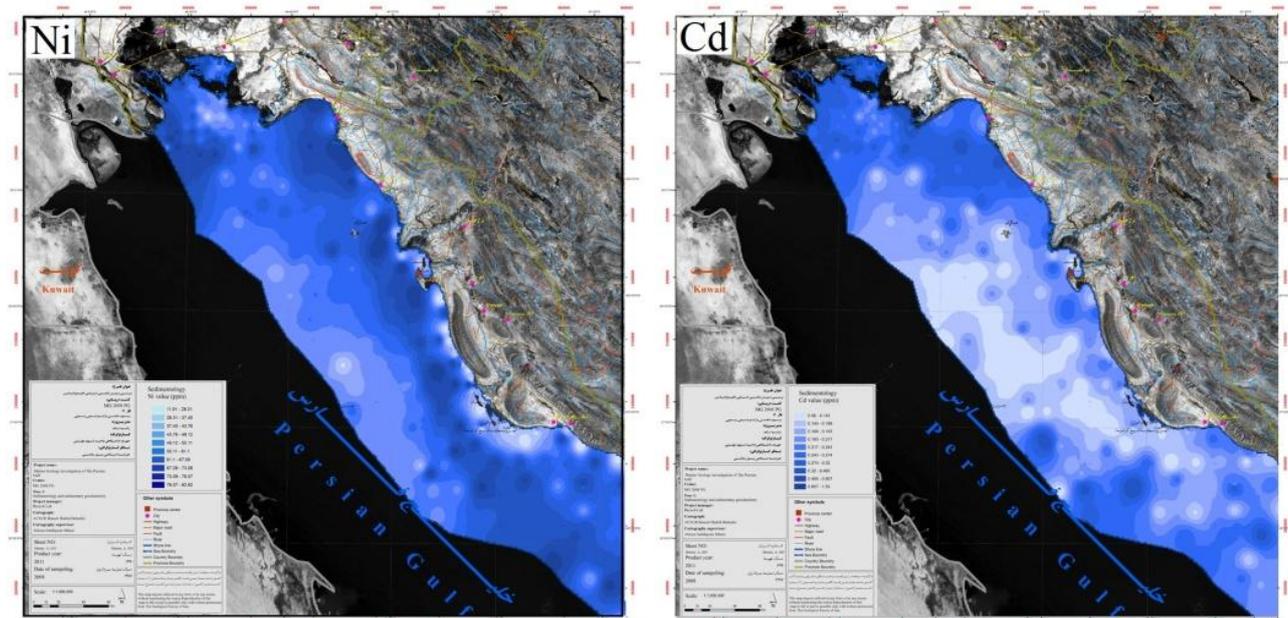


Figure 2) Dispersion of Ni and Cd in north- west of Persian Gulf.

Average of Ni concentration in away coastline sediments of north Alaska vary from 25 to 31 ppm (Sweeny and Naidu 1989). Also the average concentration of this element in shale is 3.3.2– Cadmium

Average concentrations of this element in the earth crust vary from 0.1 to 0.5 ppm and in sea sediment vary from 0.1 to 1 ppm (Alloway and Steinnes, 1999). Cd concentration in shale is 0.3

50 ppm (Turkian and Wedephol, 1964) and its concentration closed to coast of study area is 123 ppm that is higher than shale average.

ppm (Turkian and Wedephol, 1964). Important subject about Cd is that this element in oceanic environment is more mobile than other heavy metals and so it can be very dangerous. Research shows that in Tess Gulf in England the

Cd concentration in winter season is higher than its concentration in summer season. But other heavy metals concentration in sediments in summer season is higher than their concentration in winter season. This matter is caused by seasonal temperature change and its direct influence on pH and oxidation- reduction of elements (Ibhadon *et al.*, 2004). As shown in Figure 2, the cadmium in comparison with other place concentrated in coastal sediments of the Zohreh River and its value is similar to shale average and is about 0.38 ppm. This trend is unlike other elements trend in this area and it can be caused by selective absorption of Cadmium by solutions containing carbonate components.

Cadmium is transported to seawater in different ways including waste of lead and zinc mining,

produce and derivative of phosphate fertilizers, combustion of fossil fuel, plating waste and industrial waste of iron and steel industry (Ibhadon *et al.*, 2004). Natural source of cadmium in seawater is volcanic eruption, forest fire and aerosols.

The distribution of Cd in study area has a sharp difference with Fe, Al and Mg and Ca, Sr and As groups. This difference could be sharper when cadmium correlation compared with other elements of the basin. Also based on Figure 2, cadmium frequency is high in Zohreh estuary that other elements have the lower concentration. So the soluble carbonate could have an important role on cadmium sedimentation.

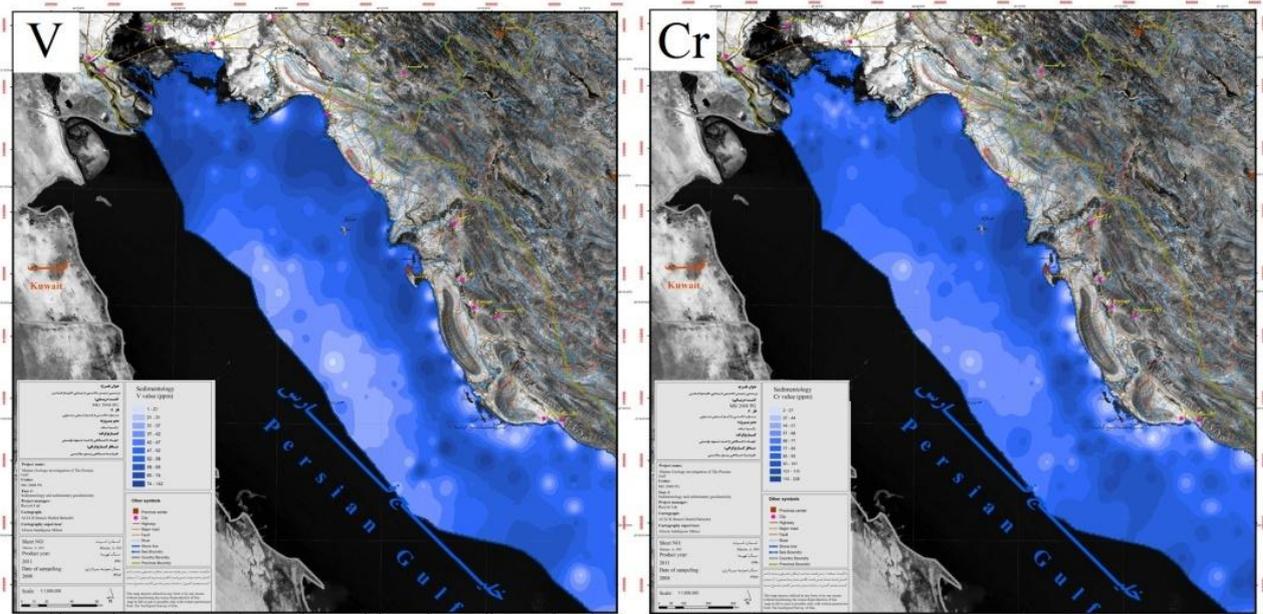


Figure 2) Dispersion of V and Cr in north- west of Persian Gulf.

3.3.3– Vanadium

Because of oily source of Nickel and vanadium, their concentration in petroleum varied strongly. For example the vanadium concentration varied from 0.2 to 1180 ppm (Crans *et al.*, 1998). About vanadium contamination should be added that cadmium concentration in petroleum product including petrochemicals is high and on the other hand many of petroleum products transport to all over world by ship and

permeation of those products is another cause of cadmium contamination in study area. Also oil exploration is the other increaser vanadium concentration factors in this place. As shown in Figure 3 vanadium dispersion trend is accorded with the nickel dispersion trend in study area sediments and the highest quantity of vanadium in this place is 110 ppm. This value is lower than shale average (130 ppm) for these elements (Turkianand Wedephol, 1964) but mentioned

factors may have affect on vanadium enrichment in north- west Persian Gulf.

3.3.4– Chromium

Average of chromium concentration in soil in United State is 37 ppm (ATSDR, 2008) and in Canada is 43 ppm (Cary, 1982). Average chromium concentration in shale sediments is 90 ppm (Turkian and Wedephol, 1964). Based on the Table 1 Chromium concentration in bed sediments of study area is 80 ppm that is higher than mentioned values and the highest quantity of chromium is 136 ppm closed to coast. The most important industrial source of chromium is metallurgy, tannery, chromium extraction, welding, steel production and pigments. And the most important source of chromium entry to seawater in world scale is domestic wastewater with abundant of 32% of all chromium of the oceans (Barceloux, 1999). According to Figure 3 dispersion of this element is very similar to nickel and vanadium dispersion trends that show chromium accumulated in area with clay beds. Also accumulation of this elements closed to coast shows the role of lands in providing chromium and its similar elements.

4–Conclusions

According to the correlation coefficient and factor analysis data, elements in the studied area have by their origin divided into three classes. First group include elements with clastic source that originate from outside of sedimentation basin including Al, Fe, Cr, Cu, Mn, Ni, Ti and V. second group include As and Mo that have not clastic source and maybe originate from industrial and agricultural activities from outside of sedimentation basin and these activity can affect As and Mo enrichment in studied area. Third group elements are Ca and Sr that have biogenic source in the basin. As value increase by distancing from coast and when depth become increase. These matter shows the biogenic origin of As. But other elements value decrease by depth increasing and accumulate in

coast vicinity that shows those elements originate from out of basin.

The elements by their relationship with grain size divided into two groups. First group are elements that enriched by clay and silt grain including V, Al, As, Cd, Mo, Mn, Cr, Cu, Fe, Ni, Ti. But the second group elements are Ca and Sr that enriched with gravel and sand grain.

This relationship shows the biogenesis source of calcium and strontium.

Temperature and salinity are two important factors for elements bioavailability. These two are most effective factors on the existence of coastic waters and also can affect acute toxicity of many heavy metals (Yalcin, 2009). The correlation coefficient between elements concentration and physical parameter of water including salinity and water temperature shows that cadmium and strontium have a direct relationship with salinity and if salinity increase (or decrease) the cadmium and strontium concentration also increase (or decrease).

As Larsen *et al.* (1983) say The Ni average concentration in surficial sediments of Penobscot Gulf in United States of America is 26.6 ppm and its concentration in Casco Bay in Mexico Gulf bed sediments is 17.6 ppm. Base on this research the Ni average concentration in bed sediments of north-west part of Persian Gulf is 64 ppm and its Maximum is 123 ppm that in comparison with mentioned points and Shale Average show Ni pollution in study area.

The Cd concentration in ROPME sea area varies from 0.1 to 0.7 $\mu\text{g/g}$ in dry sediment (ROPME, 2003). Base on this research the Cd average concentration in bed sediments of north-west part of Persian Gulf is 0.19 ppm. The low concentration of Cd in sediments could be caused by its high solubility in water (Warren, 1998).

The standard of Cr abundance in marine sediments is 35 mg/Kg (Obhodas and Valkovic, 2010). This element average concentration in

studied samples is 80 ppm that is higher than its standard. So these elements high concentration in marine sediments could be source of marine environmental pollutions and these elements import into the human body through the food chain.

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