Journal of the Persian Gulf
(Marine Science)/Vol. 9/No. 34/ December 2018/6/65-70

Issue of Second International Conference on Oceanography for West Asia (RCOWA) 2020

Geochemical and Environmental Survey of Elements in the Superficial deposits of Caspian Sea sediments: Application of Geoaccumulation Index, Enrichment, and Contamination Factors for Assessing Elemental Contaminations

Pouya Besharati[1], Shahrzad Parsinezhad[2*], Pedram Masoud Zamani[3], Sajad Azizi[4]

[1] *Msc. In Geochemistry, Faculty of Earthscience, Kharazmi University, Tehran- 15719-14911*
[2] *Msc. In Economical Geology, Faculty of Earthscience, Azad University, Lahijan*
[3] *General manager of marine geology office, PhD in sedimentology of Wuerzburg university of Germany, 1473733471*
[4] *Msc. In Organic Chemistry, Payam e Nour University, Wastewater treatment process analysis expert, 41446-73755*

Abstract

Many elements such as Arsenic (As), Cadmium (Cd), Copper (Cu), Chromium (Cr), Lead (Pb), Zinc (Zn), and others are major environmental problems due to their toxic nature, nonbiodegradability and accumulative behaviors. There are anthropogenic or geogenic sources that accumulate or rotate elements in sediments. Sediments served as excellent indicator of metal pollution in coastal environments as larg inputs (>90 %) of heavy metals ultimately find their way to the estuarine zone and on the continental shelf. Twenty one samples of superficial deposits were collected from the 3- 47 meter depths during the summer of 2019 using a grab sampler. In the present investigation, bulk concentration of elements in sediments measured and assessed. The degree of Contamination Factor (CF), Enrichment Factor (EF), and Geo- accumulation Index (I_{Geo}) was evaluated. Cluster analysis and dendrogram in other assesses guide our to some anthropogenic or geogenic sources in studied area.

Keywords: Caspian Sea, Assessment, Geochemistry, Sediment

1. Introduction

In many aquatic systems, deposition of contaminants, including heavy metals, can lead to elevated sediment concentrations that have the potential to cause toxicity to aquatic biota (Yang and Rose 2003; Heyvart et al., 2000). Elements specially heavy metals are toxic and causes serious problems to environmens as they are long persistent and not easily oxidized, degraded, removed, or converted to less harmful components through biological or chemical processes (Sharifuzzaman and et al., 2016). The studied area is located in southern part of Caspian Sea, at Langaroud geological map (scale: 1: 100000) of Guilan province. The geographic coordinates are 50ْ, 00′, 00″ - 50ْ, 30′, 00″ E and 37ْ, 00′, 00″ - 37ْ, 30′, 00″ N (Fig. 1).

* Corresponding Author name: Shahrzad Parsinezhad
E-mail address: shparsinezhad@gmail.com

2. Materials and Methods

Twenty one samples of superficial deposits were collected from the 3- 47 meter depths during the summer of 2019 using a grab sampler (Fig 1). The samples were oven- dried at 80 (̊c) for 1 day and sieved through a 2-mm sieve to remove large materials and stored in closed plastic bags and send to lab. All samples were analysed via ICP- MS and XRF in laboratory of the Geological Survey of Iran. All statistical methods were applied to process the analytical data in terms of its distribution and correlation among the studied parameters. To calculate the statistical parameters and identify the relationship among elements in sediments and assessment of the their possible sources, Pearson‹s correlation coefficient analysis and dendrogram of cluster analysis for elements were perfomed via SPSS and Excell software in present study.

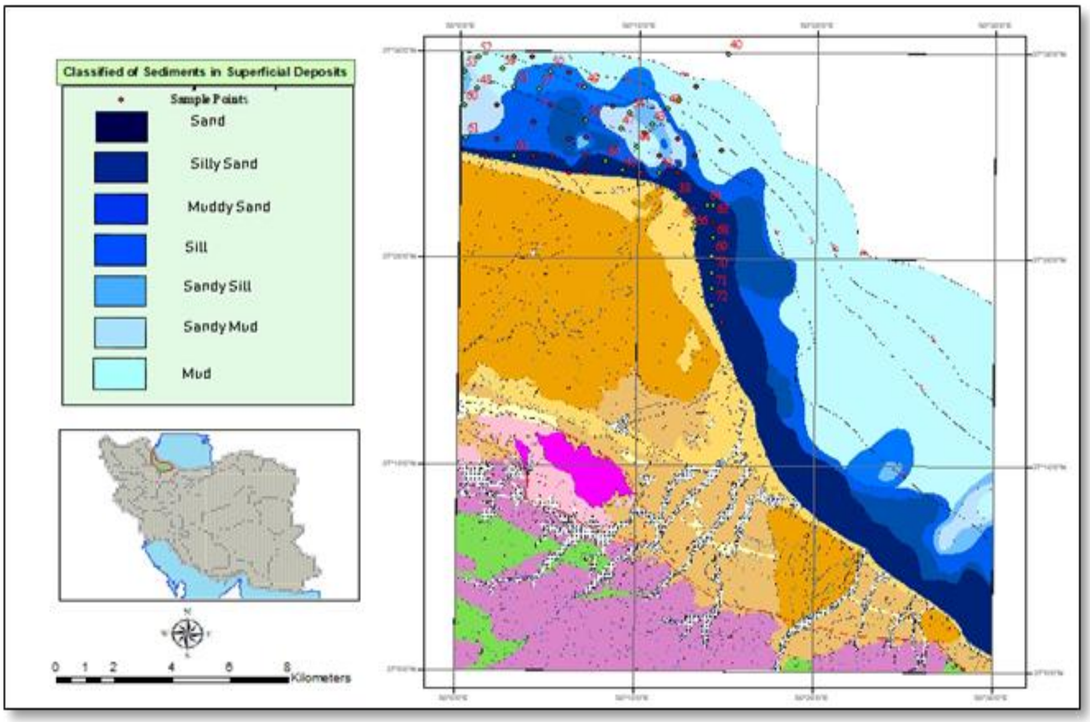

Fig. 1: Modified map of the study area showing sampling sites on the type of sediments distributions map in superficial deposits of Caspian Sea (Karimkhani and et al., 2016)

3. Discussion

The results of comparisons between bulk element̒s concentrations and their mean elemental abundences of Earth̒s crust indicate the elements arranged according to their abundences in superficial deposits of Caspian Sea as follows: Al> Ca> Fe> Mg> Ti> Na> K> S> Mn (Fig. 2). As naturally occurring constituents of the Earth,s crust, the concentrations of heavy metals in marine sediments are usually expected to be in low range (ppm). In this cases the concentrations of major elements and heavy metals (e.g., As, Cd, Cu, Cr, Zn, Pb, and etc) have been increased by some times higher compared to concentrations recorded in mean elemental abundences of Earth‹s crust (Bowen, 1979).

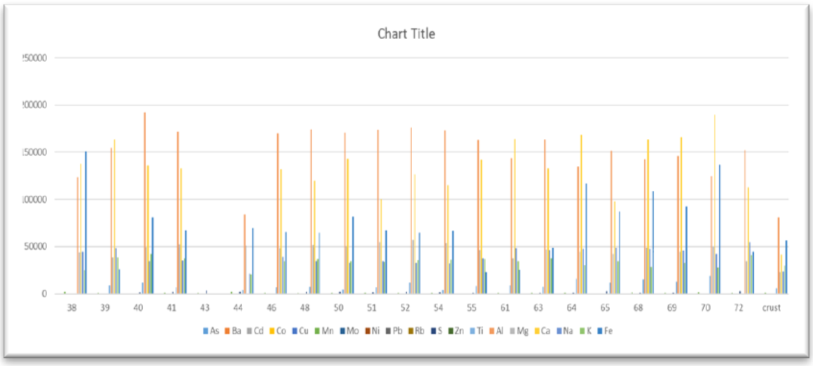

Fig. 2: Concentration of elements in Caspian sea sediments in compared with crustal abundance (Bowen 1979)

3.1. Assessment of pollution

Enrichment Factor (E.F) is commonly used to distinguish metals originating from anthropogenic and geogenic sources. To determine E.F values (Eq.1), iron (Fe) is commonly selected as normalizing element because it is a Quasi- Conservative Tracer of the natural metal- bearing phases in fluvial and coastal sediments (Schiff and Weisberg 1999; Turner and Millward, 2000). According to this, we can calculate E.F by sample element (X) to Fe concentration ratio divided by the background element/ Fe concentration ratio as:

$$\mathrm{EF} = \frac{\left(\frac{X}{Fe}\right)sample}{\left(\frac{X}{Fe}\right)background} \quad (1)$$

The average crustal abundance data used to background elements values because regional values havn't been suggested. Calculations of the Enrichment Factor (EF) according to the degree of Taylor (1964) classification, shows most of elements studied have minor enrichments, Ca, Cd, Mo, and S has moderate enrichments just in one sampling station (Fig 3).

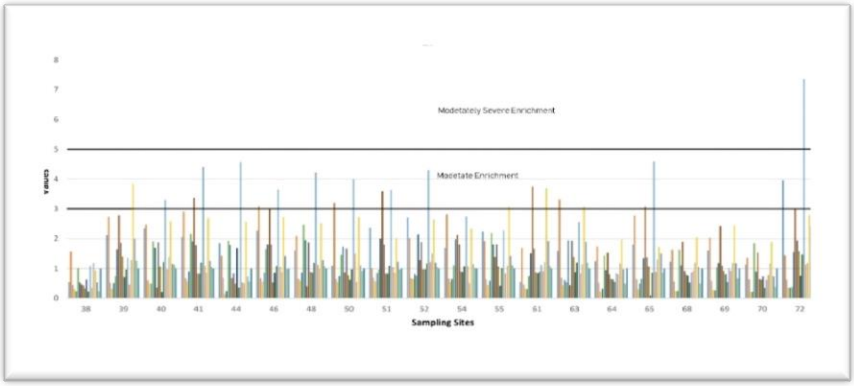

Fig. 3: E.F values and degree of pollutions in Caspian Sea sediments (After Taylor (1964)

In the present investigation, the degree of sediment‘s contamination was evaluated using a Contamination Factor (CF) that we can calculate C.F by metal concentration in sediment (Cn) divided to background value of metal (Cb) (Eq.2) as:

$$CF= \frac{C\ n}{C\ \ b} \tag{2}$$

According to the degree of Hakanson (1980) and Pazi(2011) classifications, the values of CF identify most of elements studied have low and moderate contaminations. Also Pb, Cr, Cd, As, Zn, Ti, Ca, Fe, S, and Mo are considerable, and Ca, Cd, As, and S have high contamination in several sampling stations (Fig 4).

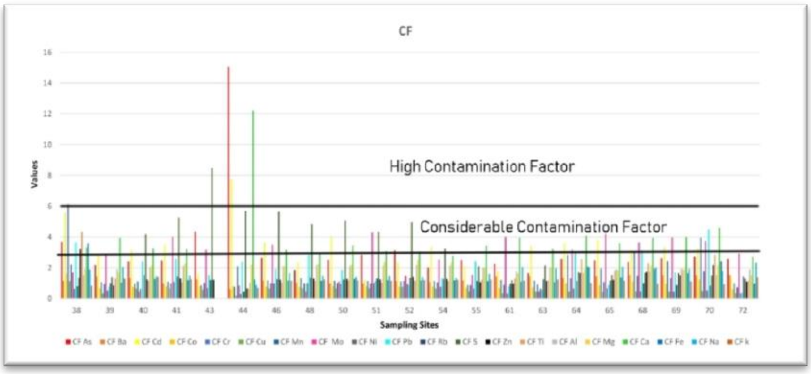

Fig. 4: C.F values and degree of pollution in Caspian Sea sediments (Hakanson, 1980; Pazi , 2011)

Geo- accumulation index (i_{geo}), which was introduced by Müller (1979), can be used to determine the degree of elements pollution in sediment. The formula to calculate I_{geo} value is expressed (Eq. 3) as:

$$I\ geo = \log 2\left(\frac{Cn}{1.5\ \text{Bn}}\right) \tag{3}$$

Where metal concentration in sediment is Cn and Bn is the geochemical background concentration of metal. Müller (1979), as well as others have used the concentration of elements in shale and the average crustal abundences data as a substitute for select background elemental values, while regional background haven't been suggested (Christophoridis, 2009; Rubio, 2000; Hu, 2013). The Geo-accumulation Index (Igeo) indicates all elements studied are unpolluted and unpolluted to moderately polluted for 1 and 2 classes according to the Müller (1979) classification (Fig. 5).

Bivariate correlation (Pearson, two- tailed) matrices between the studied elements were conducted to investigate potential sources of them and are shown in figure 6. Various degree of correlations were found some significant correlations, both positive and negative in study area showed. According to correlation coefficients indicate and interpretation of relationship intensity of Pearson correlation (adapted of Morton and et al., 1996; Zou and et al., 2003):

A: Al- K, Rb- K, and Rb- Al show strongly positive correlation and identify same sources for them.

B: Mn- K show strongly negative correlation and its indicate different sources for them.

C: there are moderately positive correlation between Ca- Na, Pb- Fe, Ni- Al, Ni- Mg, Mn- Fe, Cu-Ni, Co- Cu, Cd-Fe, Cd-Cu, Cd-Co, Ba- Na, and As- S. therefore we can propose same sources for them.

According to the dendrogram of elements, they contents in two major clusters, "A" and "B" (Fig 7). Ca and Al were clustered in "A" . Na, K, and Mg formed clustered and Fe joins to them as "B1". Finally, As, Mo, Cd, Co, Pb, Cu, Ni, Rb, Zn, Ba, Mn, S, and Ti formed "B2" that grouped to "B1" and make major cluster "B".

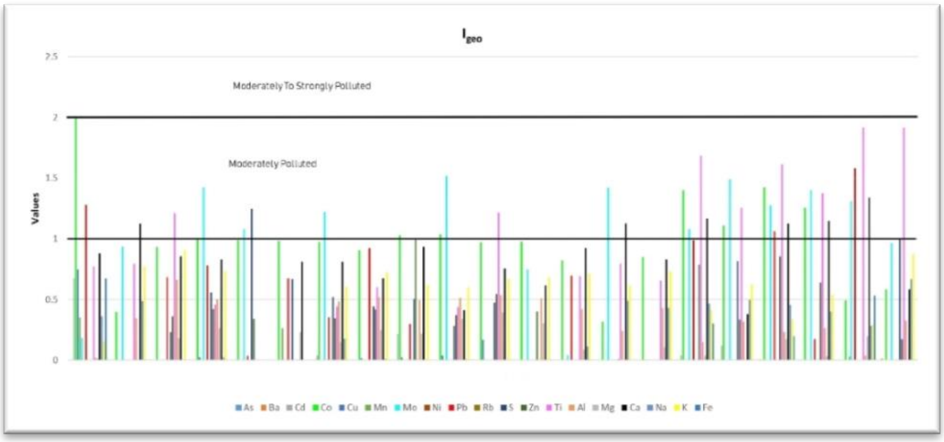

Fig. 5: I geo values and degree of pollution in Caspian Sea sediments (After Muller 1981)

	As	Ba	Cd	Co	Cu	Mn	Mo	Ni	Pb	Rb	S	Zn	Ti	Al	Mg	Ca	Na	K	Fe
As	1																		
Ba	0.278	1																	
Cd	-.472*	0.000	1																
Co	-0.270	-0.115	.837**	1															
Cu	-0.283	-.496*	.583**	.670**	1														
Mn	-0.229	0.025	0.016	-0.001	0.184	1													
Mo	0.203	0.034	0.015	0.045	-0.168	-0.004	1												
Ni	-0.058	-.687**	0.362	0.418	.759**	-0.127	-0.093	1											
Pb	-0.184	0.030	0.331	0.059	0.315	.547*	-0.064	0.104	1										
Rb	0.359	-0.269	0.107	0.262	0.317	-.689**	-0.068	.542*	-0.331	1									
S	.577**	0.110	-.499*	-0.210	-0.151	-0.269	-0.130	0.077	-0.345	0.355	1								
Zn	0.280	-0.162	-0.037	0.296	-0.038	-0.398	0.075	0.247	-0.284	.498*	0.303	1							
Ti	0.201	0.410	0.102	-0.161	-0.263	-0.037	0.306	-0.178	0.334	-0.084	-0.266	0.154	1						
Al	0.231	-0.423	0.182	0.280	0.376	-.724**	-0.104	.593**	-0.356	.913**	0.180	.478*	-0.032	1					
Mg	0.136	-0.377	-0.035	-0.026	0.426	0.187	-0.253	.617**	0.292	0.179	0.169	0.252	0.134	0.272	1				
Ca	-0.188	0.300	.542*	0.271	0.176	-0.104	0.309	0.010	0.229	0.174	-.598**	0.030	.513*	0.270	-0.241	1			
Na	-0.023	.591**	0.302	0.282	-0.206	-0.184	.453*	-0.386	-0.204	0.043	-0.296	-0.088	0.190	-0.056	-.798**	.575**	1		
K	0.339	-0.054	-0.016	0.053	0.007	-.853**	-0.092	0.213	-.583**	.855**	0.310	0.314	-0.119	.852**	-0.152	0.230	0.201	1	
Fe	-0.155	0.226	.583**	0.354	0.440	.590**	0.116	0.106	.721**	-0.296	-0.255	-0.138	0.310	-0.388	0.214	0.182	0.036	-.611**	1

* correlation is significant at the 0.05 level (p=0.05)(2-tailed)

** correlation is significant at the 0.01 level (p=0.01)(2-tailed)

Fig. 6: Correlation coefficients between the elements of superficial deposits in Caspian Sea sediments

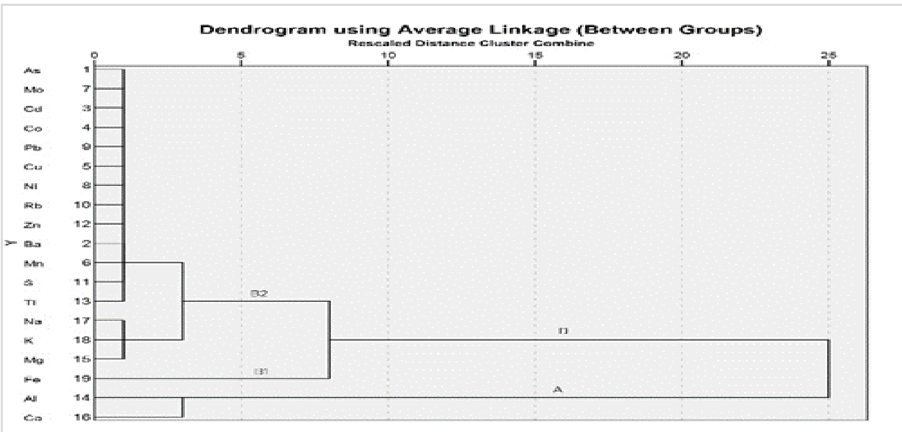

Fig. 7: Denrogram of cluster analysis for elements of superficial deposits in Caspian Sea sediments

4. Results and originating

Pay attention to geochemical affinity, behavior of each clusters and geological setting specially distribution of suitable lithogeochemical media for their elements, we propose several sources for clusters. Its clear that both types of geogenic and anthropogenic origins exist, but what is very important in transporting elements to continental shelf and superficial deposits of Capian Sea, seems to be the specific role of streams and rivers such as Dehka or Heshmat Roud and Sefid Roud.

There are probably both acidic and basic rocks. Gabbroes and basalts as the sources of the Cu, Cr, Ni, Fe, Mg, Co, and rhyolites, ignembrites, acidic tuffs also metamorphosed sediments (slates and phyllites) as the origins of the As, Cd, Mo, Pb. Lahijan granite and its accompanying metamorphic rocks can be a significant geogenic sources. Emamzade Hashem ophiolithes can be other source too. However strongly seems to be a hybrid geogenic sources as elemental origin in studied area. It should be considered that the function of streams causes dissolution and leaching the elements due to weathering of rocks, specially hidden ophiolites units, metal- bearing clay minerals, organic matter containing metals, sulfide compounds of elements that left over from lagoons dried and oxidize in oxidative conditions. They will obviously transmit elements from humanity, industrial, and agricultural activities to Caspian Sea.

References

Aires, F., Miolane, L., Prigent, C., Pham, B., Fluet-Chouinard, E., Lehner, B., & Papa, F. (2017).

Al- Edresy M., O Wasel S., Al- Hagibi A., echological risk assessment of heavy metals in coastal sediments between Al- haymah and Al- mokha, south red sea, yemen, 2019, international journal of hydrology.

Hakanson L., ecological risk index for aquatic pollution control, a sedimentological approach, 1980, water Res 14: 975- 1001

Müller, G., the heavy metal pollution of the sediments of Neckars and its tributary: a stocktaking, 1981, scientific Research.

Sharifuzzaman S.M., Rahman H., Ashekuzzaman S.M., Islam M., Chowdhury R., Hossain M., heavy metals accumulation in coastal sediments, 2016, Springer Japan.

Zou, correlation and simple linear regression 1, 2003, department of Radilogy, Harvard medical School.