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Trace Metals and Major Elements in Sediments of the Northern Persian Gulf

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Abstract

The concentrations of sixteen elements and organic carbon were determined in 78 marine sediment samples collected from the Iranian coastal waters of the Persian Gulf. Nine transects perpendicular to the coastline were sampled. Sixteen elements, including As, Ba, Cd, Co, Cu, Mn, Ni, Pb, Zn (trace metals) and Ca, Fe, Mg, Na, P, S, Si (major metals), were determined by Inductively Coupled Plasma Mass Spectrometry (ICP MS) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES), respectively. In this study, the element concentrations in sediments have not exceeded the sediment quality guidelines and pose no environmental concerns with the exception of Ni, which is over than ERM. The spearman correlation matrix demonstrated that all elements except for arsenic, cadmium, barium and silicon, were significantly ($P<0.01$) correlated with iron. The Relative Contaminated Factor (RCF) for elements which had ISQG values and Enrichment Factors (EF) using Fe demonstrated that there was no metal enrichment by natural or anthropogenic sources except for Ni. High EF level for Ni demonstrated that nickel level in sediments of the Persian Gulf could have originated from anthropogenic sources.

Keywords: *Persian Gulf, Sediment, Trace metals, Major elements, ICPMS, AES.*

1. Introduction

Protecting sediment as habitat for many benthic and epi-benthic organisms is important, because polluted sediments potentially accumulate in tissues of aquatic organisms. Sediment is an indicator for investigating of trace metal pollution; therefore, analysis of trace metals is an important part of environmental pollution studies (Soylak et al., 2002).

Arsenic is released into the environment through natural and anthropogenic sources (US EPA, 2006). The World Health Organization (WHO), the Environmental Protection Agency (EPA) and several studies (Wilson, 2005) have shown that inorganic arsenic can increase the risk of lung, skin, bladder, liver, kidney and prostate cancer in humans (WHO, 2004). Cadmium, with reported carcinogenic effects in humans (Goering et al. 1994), is one of the most toxic elements after mercury (Krajnc 1987). Cobalt shows toxicity in aquatic environment, but is not toxic for human except at very high inhalation levels, which has respiratory effects on lung, liver and kidneys (ATSDR, 1992). Copper is an essential micronutrient and can readily be accumulated by aquatic organisms, but is not biomagnified in aquatic

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ecosystems (Jaagumagi, 1990). Lead is carcinogenic to human. Children absorb lead much more efficiently than adults (4 to 5 times more), which affects their IQ (WHO 2004; Galvin, 1996). Manganese occurs naturally in many food sources (Galvin 1996). Nickel is not generally very toxic, but high ingestion of it can cause renal problems and skin allergies by contact (WHO, 1990 and 1991). Zinc is also an essential micronutrient (WHO, 2001).

The main objectives of this study were to evaluate trace metals and major elements in sediment from northern part of the Persian Gulf and to assess relationship between the elemental contents and organic carbon. In this study, sixteen trace metals and major elements in sediments throughout the northern areas of the Persian Gulf are sampled, analyzed and compared at once.

2. Sampling

2.1. Sampling Area

The Persian Gulf is a relatively shallow, semi enclosed body of water, with average depth of 35 meters. The western part of the Persian Gulf is very shallow, with extensive intertidal areas that are less than 5 m deep and up to 5 km long, while the deepest parts are located along the Iranian coasts, near the Strait of Hormuz, with a depth of about 100 m. The bottom topography of the Persian Gulf is mostly flat and featureless, dominated by soft sediments. The dominant water circulation pattern in the Persian Gulf is counter-clockwise and driven by density gradients. Water of normal oceanic salinity from the Indian Ocean enters the Persian Gulf through the surface waters of the Strait of Hormuz, moves northwards along the Iranian coast, turns southward along the western coast and exits along the bottom of the Strait as dense hyper saline water. This process, which takes between 3 to 5 years, plays an important role in salinity and likewise pollutant distributions of the Persian Gulf (Kardovani, 1995).

2.2. Pollution in the Persian Gulf

Besides pollution through riverine inputs from adjacent countries (Iran, Iraq, Kuwait, Saudi Arabia, United Arab Emirate and the Emirates of Bahrain, Qatar and Oman), the Persian Gulf has been exposed to various additional contaminants as a consequence of marine transports, marine accidents and wars in recent years. Industrial areas situated around the main ports on the coast are the main potential pollution sources. The largest ports on the Iranian coast are Bandar-e-Abbas, which is located in the Strait of Hormuz near Larak Island followed by Bushehr located in the north-east, near Farsi Island (Agah et al., 2008).

3. Materials and methods

3.1. Sample Collection and Pretreatment

The selected 27 stations in 9 transects represented both industrial and non-industrial regions in the Iranian coastal waters. 78 sediment samples were collected in January 2004 using an Ekman Grab (Hydro Bios) and stored frozen in PE bottles. Nine transects perpendicular to the coast were sampled in the Northern part of the Persian Gulf, belonged to the Hormozgan and Bushehr provinces. Three stations were fixed in each transect. At each station, three replicate grabs were taken and analyzed individually. The sampling stations are indicated in Figure 1.

The geographical locations and water hydrology of sampling sites are reported in Table 1.

Prior to analysis, sediment samples were lyophilized (Leybold Heraus Lyophilizer), then passed through a 1mm PE sieve to remove large particles and grounded in a mechanical mortar (Fritsch Pulverisette) to have fine homogenized sediment.

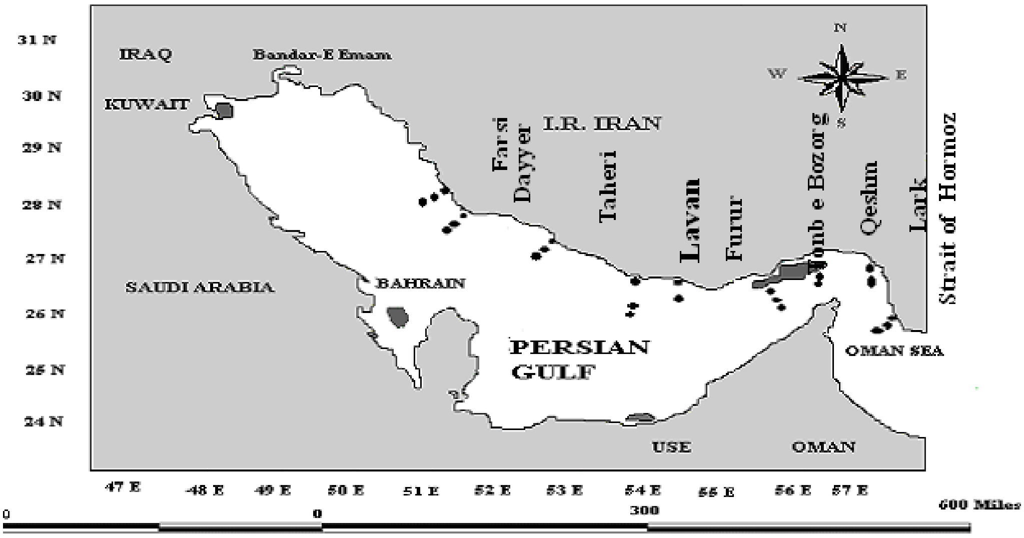

Fig. 1: The location of the sampling sites in the Persian Gulf

Table 1. Geographical locations and water hydrology of sampling sites.

Provinces	Transects	Station No	Industrial/ Rural	Latitude	Longitude	Water depth (Cm)	*Temperature (°C)*
Hormozgan	Strait of Hormoz	01	Industrial	26 ° 08'.60''	57 ° 08'.90 ''	1339	25
		02		26 ° 01'.80 ''	57 ° 01'.40 ''	9373	26
		03		25 ° 55'.00''	56 ° 54'.10 ''	9912	27
	Lark Island	04	Local fishing village	26 ° 47'.30 ''	56 ° 56'.20 ''	1881	25
		05		26 ° 37'.30''	56 ° 54'.10 ''	5940	26
		06		26 ° 27'.40 ''	56 ° 52'.30 ''	6865	26
	Qeshm Island	07	Industrial	26 ° 55'.10 ''	56 ° 16'.90 ''	1771	25
		08		26 ° 45'.20 ''	56 ° 15'.40 ''	5149	25
		09		26 ° 35'.40 ''	56 ° 13'.60 ''	8284	27
	Tonb-e Bozorg	10	Local fishing village	26 ° 25'.60 ''	55 ° 28'.30 ''	1943	25
		11		26 ° 16'.00 ''	55 ° 24'.90 ''	6767	27
		12		26 ° 06'.60 ''	55 ° 20'.70 ''	7100	28
	Farur Island	13	Non-residential area	26 ° 26'.60 ''	54 ° 35'.40 ''	1836	25
		14		26 ° 16'.40 ''	54 ° 33'.60 ''	6069	22
	Lavan Island	16	Petrochemical industries	26 ° 46'.70 ''	53 ° 27'.00 ''	2396	22
		17		26 ° 32'.90 ''	53 ° 20'.50 ''	8800	25
		18		26 ° 18'.90 ''	53 ° 14'.20 ''	8488	27
Bushehr	Taheri port	19	Industrial	27 ° 28'.10''	52 ° 34'.90 ''	2230	23
		20		27 ° 18'.20''	52 ° 23'.00 ''	7989	25
		21		27 ° 07'. 50''	52 ° 11'.30 ''	7170	27
	Dayyer Port	22	Semi industrial +Port	27 ° 48'.70''	51 ° 56'.40 ''	1578	22
		23		27 ° 38'.90''	51 ° 53'.70 ''	1940	24
		24		27 ° 30'.80''	51 ° 48'.40 ''	3411	22
	Farsi Island	25	Nonresidential area- Near ships passage	28 ° 15'.20''	51 ° 10'.20 ''	1851	24
		26		28 ° 09'.60''	50 ° 57'.40 ''	5016	26
		27		28 ° 03'.80 ''	50 ° 45'.50 ''	6237	25

3.2. Analytical Procedures

All Teflon and glassware used for extraction and analyses were cleaned thoroughly with laboratory detergent (Extran 2%), soaked overnight in nitric acid solution 5% and finally they were rinsed with deionized (Milli-Q) water. All the reagents employed were of analytical grade.

To mineralize the sediment samples, 0.5 gr lyophilized and homogenized sediment was weighted in Teflon vessels and digested with nitric acid (65%, Suprapur) and hydrochloric acid (4:1, v: v) over night in normal oven at 70±5 °C (Agah et al., 2008). Trace metals (Co, Ni, Cu, Zn, As, Cd, Pb) and major elements (Ba, Ca, Fe, Mg, Mn, Na, P, S and Si) analysis were performed by Inductively Coupled Plasma Mass Spectrometry (ICP-MS) using a VG-Elemental model PQ2 instrument (Thermo-Finnigan) and Inductively Coupled Plasma Atomic Emission Spectrometry (ICP-AES) using a Thermo Spec/win (IRIS, Thermo Optek), respectively. The details of the analysis are described in (Agah et al., 2008).

Organic carbon in lyophilized and homogenized sediment was determined by element analyzer (Carbo Erba NA1500) (Agah et al., 2008). Organic matter was determined as ignition loss at 450 °C.

The precision and accuracy of the applied analytical method was estimated on Certified Reference Materials (CRM), IAEA 405, trace elements and methyl mercury in estuarine sediment-International Atomic Energy Agency. Quality control included the use of procedural blanks and certified reference materials in each digestion batch and also triplicates analysis. Our results obtained on the CRM (Table 2), compared well with the certified values, except for Fe and Mn with almost 90 % recoveries. For Ba, Ca, Na, P, S and Si, there were no certified values.

Table 2. Trace elements in estuarine sediment reference material IAEA 405 in mg kg^{-1} (n=6).

Element	Certified values	Our results	Element	Certified values	Our results
As	22.9-24.3	23.1-24.9	Mg	11400-13200	11520-12390
Cd	0.68-0.78	0.75-0.84	Mn	484-506	430-450
Co	13.0-14.4	13.0-14.8	Ni	31.1-33.9	31.4-33.3
Cu	46.5-48.9	48.0-53.7	Pb	72.6-77.0	70.7-76.2
Fe	36700-38100	30400-32500	Zn	272-286	266.8-286.9

The detection limits were set as three times the standard deviation of the procedural blanks are 2, 6, 13, 163, 26, 2, 3, ng. g^{-1} for Co, Ni, Cu, Zn, As, Cd, Pb, and are 2, 33, 4, 4, 0.1, 4, 4, 6 and 2 in µg. kg^{-1} for Ba, Ca, Fe, Mg, Mn, Na, P, S and Si.

3.3. Statistical Method

Statistical analysis of the data including correlation and regression calculations, were carried out by using SPSS V13. Spearman correlations were calculated between element concentrations. In order to classify and reduce the variables to detect the relationships between them without losing much information, Principal Component Analysis (PCA) was performed. Prior to PCA a Kolmogorov-Smirnov test was accomplished to analyze the normality of data distribution. In addition, one way ANOVA and factor analyses were used to assess significant differences between the mean element levels in different sampling stations. A P-value equal or lower than 5 % indicates that significant relationship between the corresponding variables exists.

4. Results and discussion

Average concentrations of trace metals and major elements in the surface sediments expressed on a dry-weight are summarized in Tables 3 and 4.

In our study, the detected concentrations of the metals (triplicate measurements) were higher than the corresponding detection limits.

The ranges and median values of the trace metals were: **As**: 4-21 (7); **Ba**: 9-36 (17); **Cd**: 0.1-0.3 (0.2); **Co**: 3-22 (14); **Cu**: 5-33 (20); **Mn**: 53-566 (357); **Ni**: 20- 192 (111); **Pb**: 3-10 (7) and **Zn**: 4-79 (37) **µg g^{-1} d.w**. The ranges of major elements were **Ca**: 78-349 (192); **Fe**: 2-24 (15); **Mg**: 16-33 (26); **Na**: 7-21 (14); **P**: 0.6-4 (2); **S**: 2-12 (5); and **Si**: 0.1-1.2 (0.2) mg g^{-1} d.w. This leads to the following ranking: Ca>Mg>Fe>Na>S>P>Mn>Si>Ni>Zn>Cu>Ba>Co> As, Pb>Cd

Table 3. The mean levels of trace metals (µg g^{-1} d.w) in sediments of the Persian Gulf.

Transects	Depth (m)	Co	Ni	Cu	Zn	As	Cd	Pb	Ba	Mn	OC %	OM %
Strait of Hormoz	13	20±1	150±9	26±1	64±8	5±0.1	0.16±0.04	10±0.2	10±1	566±65	0.6±0.1	6
	93	19±1	160±8	28±2	69±5	4±0.4	0.18±0.03	8±0.1	9±1	390±5	1.1±0.1	11
	99	15±0.2	134±1	27±0.1	51±1	4±0.3	0.33±0.04	6±0.1	12±1	308±5	1.8±0.02	11
Larak Island	19	22±2	184±4	27±2	61±1	6±0.2	0.13±0.01	9±0.1	14±1	556±3	0.4±0.1	4
	59	22±1	192±15	33±2	79±2	4±0.2	0.18±0.01	9±0.1	9±1	422±10	1.1±0.1	13
	69	16±0.2	137±1	24±0.4	54±2	5±0.2	0.16±0.01	7±0.1	10±1	343±23	1.1±0.01	11
Qeshm Island	18	5±0.4	38±1	7±0.3	15±1	21±1	0.22±0.01	6±0.2	20±4	263±24	1.1±0.6	4
	51	10±0.4	65±3	11±0.4	24±1	8±0.2	0.20±0.01	7±0.2	16±3	348±24	0.7±0.05	4
	83	10±0.4	81±5	18±1	32±1	4±0.2	0.14±0.04	5±0.3	36±3	297±34	1.5±0.1	9
Tonb-e Bozorg	19	16±0.8	130±6	20±1	48±4	7±0.6	0.16±0.01	8±0.3	22±1	492±63	0.7±0.04	8
	68	10±0.2	70±3	15±0.7	26±1	6±0.4	0.14±0.01	5±0.2	19±1	222±21	1.7±0.1	8
	71	7±0.2	36±1	8±0.4	11±1	11±1	0.13±0.01	5±0.2	17±2	143±9	1.3±0.3	5
Farur Island	18	16±0.5	138±5	22±1	52±4	6±0.2	0.18±0.01	7±0.0	12±1	416±53	0.8±0.1	13
	61	14±0.5	117±5	24±1	43±2	8±0.0	0.19±0.01	6±0.2	21±1	391±4	1.1±0.2	11
Lavan Island	24	3±0.1	20±1	5±0.2	4±0.3	5±0.7	0.12±0.01	3±0.0	12±1	53±6	1.2±0.7	8
	88	15±0.5	96±3	23±0.8	34±3	7±0.2	0.19±0.01	7±0.1	16±1	309±22	1.3±0.05	10
	85	19±1	144±10	33±2.6	55±6	6±0.4	0.25±0.02	7±0.5	17±5	369±0	1.3±0.3	13
Taheri port	22	6±0.2	42±1	7±0.1	17±2	10±0.8	0.14±0.01	4±0.3	12±4	127±12	1.7±0.5	6
	80	14±1	104±7	22±1	35±1	9±0.6	0.19±0.01	6±0.1	15±2	372±30	1.8	11
	72	11±0.8	79±7	18±1	33±1	5±0.2	0.15±0.01	5±0.2	18±2	303±5	2.1±0.3	9
Dayyer Port	16	11±0.7	92±5	16±0.8	33±3	10±0.7	0.19±0.01	6±0.1	20±1	331±21	1.1±0.01	7
	19	9±0.4	75±3	10±0.1	26±1	7±0.4	0.18±0.01	5±0.2	25±2	369±4	1.4±0.2	4
	34	14±2	118±17	18±2	39±6	10±2	0.19±0.01	8±0.1	23±4	431±22	1.2±0.3	10
Farsi Island	18	15±0.4	129±4	21±0.2	48±4	9±0.6	0.206±0.011	8±0.3	20±3	365±2	0.8±0.02	11
	50	18±1.0	146±6	25±1	66±4	5±0.2	0.,19±0.01	8±0.2	17±1	370±26	1.3±0.2	12
	62	12±0.6	83±5	17±1	32±3	7±0.8	0.19±0.01	7±0.4	17±1	294±22	1.4	8

Table 4. Mean levels of major elements (mg g^{-1} d.w) in sediments of the Persian Gulf.

Transects	Depth (m)	Ca	Fe	Mg	Na	P	S	Si
Strait of Hormoz	13	88±9	24±3	28±3.8	8±0.3	4.2±0.1	6.7±0.3	0.2±0.04
	93	108±0.0	23±0.3	28±1.2	15±1	2.7±0.4	6.7±1.0	0.2±0.00
	99	176±2	17±0.3	26±0.3	15±2	1.8±0.1	5.9±0.9	0.2±0.01
Larak Island	19	78±1	21±0.3	23±0.7	7±0.3	2.2±0.3	5.9±1.2	0.2±0.02
	59	97±2	24±0.5	31±0.2	17±1	4.4±0.6	12±1.7	0.4±0.01
	69	18±11	18±0.6	26±0.7	15±1	2.2±0.1	5.7±0.2	0.3±0.04
Qeshm Island	18	275±31	13±1.8	18±1	8±0.2	2.7±0.4	3.1±0.5	0.1±0.01
	51	192±4	11±0.5	21±2	7±1	1.6±0.1	3.2±0.3	0.2±0.01
	83	244±15	12±1	22±1	16±2	1.3±0.1	5.4±0.5	0.2±0.02
Tonb-e Bozorg	19	150±14	20±4	32±5.0	11±0.2	1.8±0.1	5.0±0.04	0.3±0.02
	68	255±13	10±1	22±0.7	15±1	1.1±0.1	4.9±0.3	0.7±0.08
	71	315±4	6±0.3	16±0.7	13±0.0	0.8±0.01	5.2±0.01	0.3±0.03
Farur Island	18	160±12	20±4	33±4.1	15±1	2.1±0.2	5.2±0.3	1.1±0.06
	61	192±8	17±0.0	30±0.1	21±2	1.7±0.05	6.9±0.3	0.1±0.01
Lavan Island	24	349±16	2±0.2	16±0.7	11±1	0.6±0.05	2.7±0.2	0.1±0.02
	88	232±12	13±1	24±1	16±1	1.0±0.03	4.9±0.3	0.9±0.1
	85	173±7	16±0.0	27±2	19±1	1.6±0.2	6.7±0.2	1.1±0.1
Taheri port	22	303±4	7±0.6	23±2	10±1	2.1±0.3	4.3±0.3	0.5±0.02
	80	206±6	15±1	27±2	17±1	1.4±0.7	5.9±0.3	0.2±0.01
	72	242±6	11±0.4	21±2	16±2	1.2±0.1	4.4±0.5	0.1±0.02
Dayyer Port	16	206±9	13±1	26±2	11±1	1.3±0.1	3.7±0.3	0.2±0.02
	19	194±2	10±0.2	20±0.5	7±0.5	0.9±0.1	2.0±0.2	0.1±0.00
	34	171±5	18±0.7	29±1	11±1	1.3±0.1	5.2±0.4	0.3±0.04
Farsi Island	18	163±3	18±0.4	27±2	13±0.5	1.3±0.1	7.4±0.9	0.2±0.01
	50	156±7	19±1.0	30±1	17±1	1.4±0.2	6.4±1.1	0.2±0.03
	62	218±5	13±0.7	22±0.7	12±1	1±0.05	4.0±0.04	0.3±0.01

Organic Carbon values were referred from earlier studies (Agah et al., 2008). In order to detect the accumulation pattern of elements in sediment, the metal concentrations were plotted versus stations in Figure 2. The patterns of Co, Cu, Ni, Zn, Fe, Mg, Na, S and P variation in sediments were similar and comparable.

4.1. Eco Toxicological Sense of Heavy Metals Contamination

In order to detect the pollution level in sediments of the Persian Gulf and detect the protection of benthic organisms, the concentrations of elements detected in this study were compared with NOAA Marine Sediment Quality Guideline (ERL♣ and ERM♠) and the Canadian Interim Marine Sediment Quality Guideline (TELs and PELs, Royal, 2003; Table 5). The Threshold Effect Level, TEL, was the level below which adverse effects rarely occurred and the probable effect level, PEL, was the level above which adverse effects frequently occurred.

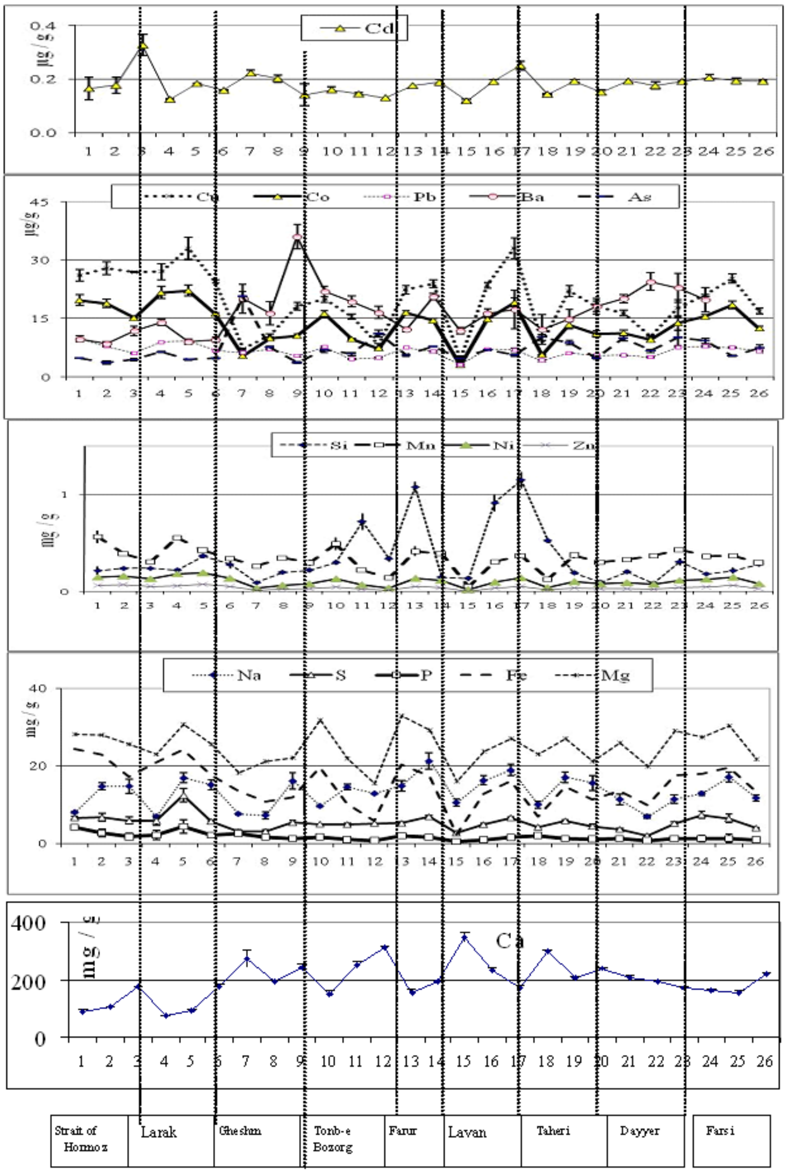

Fig. 2: Plots of element concentrations were versus stations

♣ ERL: Effects Range Low;
♠ ERM: Effects Range Medium

Table 5. Comparison between the averages detected level of elements in µg g^{-1} d.w (For Fe g. kg^{-1} d.w) with the NOAA and ISQGs Marine Sediment Quality Guideline values.

Elements	Average of our results	ERL	ERM	ISQG/TEL*	PEL	RCF	Average shale	EF
As	7	8.2	70	7.24	41.6	0.97	30	0.7
Cd	0.2	1.2	9.6	0.7	4.2	0.28	0.3	2.1
Cu	20	34	270	*18.7 Non polluted<25 Moderate polluted 25-50 Heavily polluted > 50	108	1.07	45	1.4
Pb	7	47	220	*30.2 Non polluted<40 Moderate polluted 40-60 Heavily polluted > 60	112	0.23	20	1.1
Zn	37	-	-	*124 Non polluted<90 Moderate polluted 90-200 Heavily polluted > 200	271	0.3	95	1.2
Ni	111	21	52	Non polluted<20 Moderate polluted 20-50 Heavily polluted > 50	-	5.6	68	5.1
Mn	357	460	1100			0.78	900	1.2
Fe	15 1.5%			LEL:20 SEL:40		0.75	46.7	

RCF: Relative Contamination Factor; EF: Enrichment Factor; ERL: Effects Range Low; ERM: Effects Range Medium;TEL: Threshold Effect Level; PEL: Probable Effect Level; SQG: Sediment Quality Guidelines; LEL: Lowest Effect Level; SEL: Severe Effect Level

According to Ontario Provincial Sediment Quality Guidelines (Persaud et al., 1993), Lowest Effect Level (LEL) and Severe Effect Level (SEL) for Fe were 20 and 40 mg g^{-1} d.w, respectively.

In this study, the element concentrations in sediments did not exceed the sediment quality guidelines and posed no environmental concerns with the exception of Ni (over than ERM). However the concentration of As in all the sediments were lower than PEL, but about 30 % of them were higher than TEL, which belonged to the coastal parts of Qeshm, Taheri, Dayyer, Farsi and deeper parts of Tonb-e Bozorg, Farur and Dayyer port.

Relatively higher Cu levels in some stations might be originated from cupriferous ores inland (ROPME. 1999). Relatively higher barium levels were detected at Qeshm, Tonb-e Bozorg, Dayyer and deeper parts of Farur, which might reflect drilling mud. However, barium was not an element of concern with respect to environmental toxicity. We found that cadmium, zinc and lead concentrations in the Persian Gulf sediments appeared to be lower than TELs, therefore at present no environmental concern is associated with pollution regarding these elements.

The concentrations of nickel in all sediments were higher than Severe Effect Level (SEL), except for coastal areas of Qeshm and Lavan and deeper parts of Tonb-e Bozorg. Nickel has a high natural background in this mineral-rich region. A part of high level of Ni in the sediments could be the result of natural mineralization of ophiolite rocks (De Mora et al., 2004).

Concentrations of cobalt in this study were lower than freshwater sediments (20 mg kg^{-1}; Canadian Technical Report. 2004). Toxicological values were unavailable for magnesium and manganese (US EPA. 2008). Comparisons were made with literature data for the elements lacking toxicological guidelines. Calcium, magnesium, manganese, iron, copper, cobalt, chromium and zinc are nutrient and are unlikely to present ecological problems in the areas where they were elevated (US EPA, 2008).

Comparing the element levels in nine transects demonstrated that relatively elevated concentrations of some elements occurred in similar areas: relatively higher concentrations of Co, Ni, Mn, Fe, P and S were detected at the Strait of Hormoz and Larak; Ba, Mn at Qeshm and the Srait of Hormoz; Mg, Si, Na at Farur, Tonb-e Bozorg and Lavan. Maximum detected levels of Mg, Na and Si were observed in Farur Island and calcium in Lavan and Tonb-e Bozorg. In this comparison, elevated levels did not indicate whether there were potential toxicological concerns associated with these levels.

4.2. Statistical Analysis between Levels of Heavy Metals

Spearman correlation matrix between all the trace metals and major elements as well as organic carbon and corresponding water depths were calculated (Table 6). In addition, a Principle Factor Analysis was also performed on all these variables. In agreement with Rubio et al. (2000), in this study all elements, except arsenic and sodium did not show any significant correlation with increasing distance from the shoreline.

There are significant inter-elemental correlations (e.g., Co-Ni, Co-Cu, Co-Zn, Co-Fe, Ni-Zn, Ni-Cu, Zn-Fe ($r>0.90$, $P<0.01$)). Inverse correlations between As, Ca, Ba with almost all other elements was observed. The correlation matrix demonstrated a strong and significant correlation between sulfur and almost all other metals ($P=0.05$- 0.01; $r=0.8$-0.3); under some conditions trace metal-sulfides might also act as a metal source. The statistical analysis revealed that the high degree of correlation and significant regression relations among the metals indicated the identical behavior of metals during their transport in the Persian Gulf.

Four principal components or groups of elements were extracted from the element concentrations in the sediments, explaining 78 % of the total variation. Factor 1 (expressing 48 % of total variance) includes Co, Ni, Cu, Zn, As, Mn, Ca, Fe, Pb, P, S and Mg; factor 2 (explaining 17 % of total variance) includes depth, and Na; factor 3 (Ba) and factor 4 (Cd) explaining 7 and 6 % of total variance, respectively.

From the Principal Component Analysis, Spearman correlation matrix and the loading plot (Fig. 3), it appeared that a positive strong significant correlation existed between Co, Ni, Cu, Zn, Mn, Fe, Pb, P, S and Mg, which were clustered in the first component. Arsenic and calcium have negative correlation with other elements in the first component. This component included potential bioavailable elements such as Cu, Co, Fe, P, Mn, Mg and Zn, accompanied with toxic element (Pb) and element with low toxicity (Ni). The results revealed that the presence of these metals in the same groups might reflect a similar behavior or suggest common bio-originated sources.

Table 6. The Spearman Correlation Matrix between element levels in the sediment from the Persian Gulf.

Elements	Depth	Co	Ni	Cu	Zn	As	Cd	Pb	Ba	Mn	Ca	Fe	Mg	Na	P	S	SI	OC
Depth	1.00																	
Co	.04	1.00																
Ni	0.02	0.98**	1.00															
Cu	0.30	0.94**	0.93**	1.00														
Zn	0.06	0.97**	0.99**	0.94**	1.00													
As	-0.37*	-0.43*	-0.45*	-0.53**	-0.48**	1.00												
Cd	0.06	0.20	0.21	0.24	0.23	0.23	1.00											
Pb	-0.21	0.84**	0.82**	0.69**	0.80**	-0.16	0.28	1.00										
Ba	-0.18	-0.39*	-0.37*	-0.42*	-0.37*	0.42*	0.12	-0.26	1.00									
Mn	-0.26	0.78**	0.80 **	0.66**	0.77**	-0.15	0.15	0.82**	-0.07	1.00								
Ca	0.19	-0.91**	-0.93 **	-0.79**	-0.91**	0.32	-0.21	-0.90**	0.26	-0.91**	1.00							
Fe	-0.19	0.91**	0.93**	0.80**	0.92**	-0.30	0.23	0.89**	-0.30	0.84**	-0.93**	1.00						
Mg	-0.12	0.76**	0.79**	0.68**	0.80**	-0.18	0.27	0.68**	-0.11	0.77**	-0.77**	0.83**	1.00					
Na	0.62**	0.33	0.31	0.51**	0.38*	-0.31	0.23	0.01	-0.07	0.04	-0.05	0.17	0.41*	1.00				
P	-0.16	0.57**	0.61**	0.55**	0.61**	-0.21	0.13	0.58**	-0.47**	0.52**	-0.61**	0.71**	0.50**	-0.02	1.00			
S	0.23	0.78**	0.79**	0.83**	0.81**	-0.34*	0.17	0.60**	-0.31	0.56**	-0.67**	0.74**	0.68**	0.55**	0.49**	1.00		
SI	0.30	0.33	0.28	0.29	0.23	-0.06	-0.09	0.15	-0.26	0.04	-0.13	0.1	0.30	0.27	0.12	0.21	1.00	
OC	0.72**	-0.12	-0.13	0.10	-0.08	-0.15	0.20	-0.38*	0.07	-0.39*	0.38*	-0.28	-0.07	0.70**	-0.34*	0.22	0.25	1.00

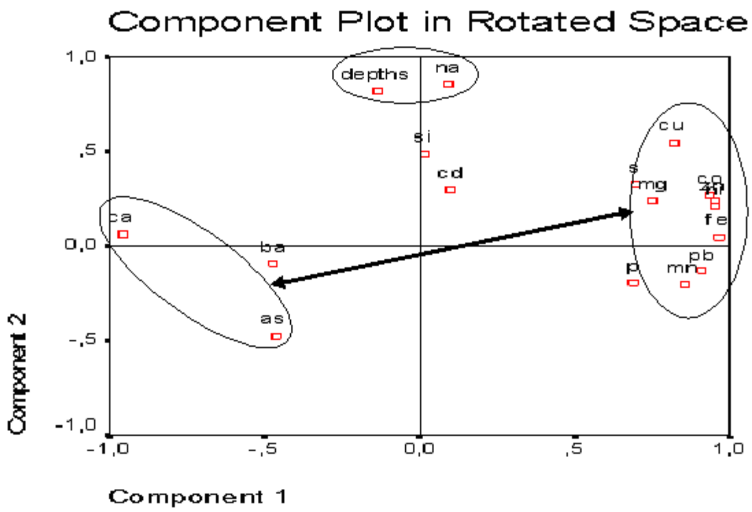

Fig. 3: PCA loading plot of the 16 elements in sediment from the Persian Gulf Factor Loading (>0.5) (Varimax normalized).

4.3. Assessment of Heavy Metal Pollution by Normalization Process and Relative Contamination Factors (RCFs)

According to literatures, iron oxides and hydroxides play an important role in the sorption of metals in marine environment (Sadiq, 1992). All elements except for arsenic, cadmium, barium and silicon, were significantly (P<0.01) correlated to iron (Table 6), however association between Fe-P and Fe-S were less strong than other metals. In agreement with investigation of (Alma et al., 1998), the sorption affinity of iron oxides for metals might be responsible for strong associations between Fe and metals in sediment in this study.

Several authors have successfully used iron to normalize heavy metals contaminants (Covelli and Fontolan 1997; Zhang 2007). Some of the associations with Fe are shown in Figure 4.

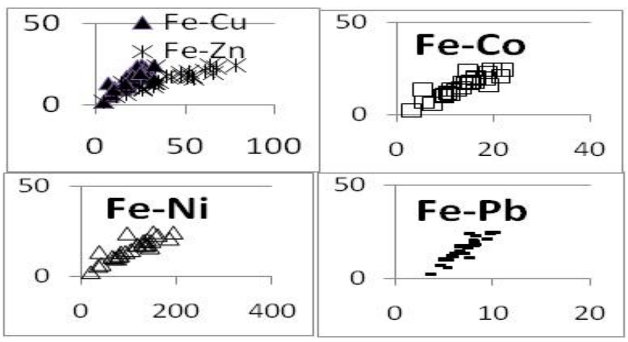

Fig. 4: Associations of some elements with Fe.

4.4. Comparison with Literature Data

In Table 7, concentrations of different elements obtained in this study are compared with the literature data from several other geographical sites.

Very little information is available on extent of trace metals pollution in the Persian Gulf. In an investigation Karbasi et al. (2005) and Karbassi et al. (2005) reported concentration of some elements in the surface sediment collected from the North-western parts of the Persian Gulf, which were comparable with the results of this study. An important observation was that, in general, concentration of almost all elements in this study except Pb and Cd, were higher than the quantities obtained from other investigations (Al-Arfaj and Alam, 1992; Shriadah, 1997; ROPME, 1999) in sediment of the Southern part of the Persian Gulf. This fact showed that finer particles in Northern part of the Persian Gulf could adsorb more trace metals and being deposited in the Iranian coasts than relatively coarse sandy sediment in the Southern part.

The concentration of Cd and Pb in sediments of the Persian Gulf were comparable with those in the Caspian Sea (De Mora and Sheikholeslami, 2002), but lower than that from Hong Kong, Lake Balaton Hungary (Nguyen et al., 2005), Scheldt Estuarine Nederland (Zwolsman et al., 1996) and Izmir bay Turkey (Kucuksezgin, 2001).

Table 7. Trace metal concentrations in various sediments in the marine environments.

Areas	Elements (μg.g^{-1} d.w.)	References
Persian Gulf- Iran	As: 7; Ba: 17; Cd: 0.2; Co: 14; Cu: 20; Mn: 357; Ni: 111; Pb: 7; Zn: 37; Fe: 15000; Mg: 26000; OC %: 1.2	Our results
Persian Gulf North-west	Cu: 22; Pb: 44; Zn: 63; Ni: 109; Mn: 459	(Karbassi, et al., 2005)
Persian Gulf Kuwait Emirate	Pb: 122; Cu: 18; Ni: 59; Mn: 214; Zn: 32.5; Cd: 4; Fe : 11000 Cd: 5; Co: 10 ; Cu: 7; Mn: 84; Ni: 36; Pb: 28; Zn: 11; OC %: 0.63	ROPME., 1999 Shriadah, 1999
Southern part	Ba: 6-28, Cd: 1-7, Co: 1-7, Cu: 3-8, Mn: 39-150, Ni: 3-39, Pb: 8-36, Zn: 2-20	Al-Arfaj, and Alam, 1992
Caspian Sea Northern parts Southern parts	 Cd: 0.02-0.3; Pb: 0.7-15; Ni: 2-68 Cd: 0.1-0.2; Pb: 11-25; Ni: 29-68	De Mora & Sheikholeslami. 2002
Hong Kong	Cd: 1; Cu: 1995; Ni: 37; Pb: 151; Zn: 197	Wong, 2000
Lake Balaton Hungary	Cu: 0.7-36; Mn: 160-760; Co: 1.7-17; Ni: 4.4-55; Zn: 13-250; Cd: 0.1-0.7; Pb: 2-160	Nguyen, et al., 2005
Scheldt Estuarine, Nederland	Ni: 3-220; Cu: 1-2600; Zn: 9-1500; Cd: 0.1-20; Pb: 4-455	Zwolsman, et al., 1996
Izmir bay Turkey	Mn: 128-390 ; Ni : 13-146; Cu: 4-79; Zn: 22-311; Cd: 0.1-0.8; Pb : 7-103	Kucuksezgin, 2001

The concentration of Ni in our study was comparable with that in Scheldt Estuarine (Zwolsman, et al., 1996), but was higher than Caspian Sea (De Mora and Sheikholeslami, 2002), Hong Kong (Wong et al., 2000), Lake Balaton Hungary (Nguyen et al., 2005) and Izmir bay Turkey (Kucuksezgin, 2001). Cobalt level in the sediments were comparable with that in Lake Balaton Hungary (Nguyen et al. 2005), while Zn value was much lower than that in Hong Kong (Wong et al., 2000), Lake Balaton Hungary (Nguyen et al., 2005), Izmir bay Turkey (Kucuksezgin, 2001) and Scheldt Estuarine (Zwolsman et al., 1996). Mn concentration in our study was almost comparable with literature.

In order to distinguish pollution source(s) in the Persian Gulf Relative Contamination Factors (RCF) and Enrichment Factors (EF) were calculated. For the elements that had corresponding ISQG, Relative Contamination Factors was calculated to quantify the degree of metal enrichment in sediments.

A RCF was calculated as the ratio between the average metal level in sediment and the relevant ISQG value (Table 5). RCF was classified into four groups in (Pekey et al., 2004), when RCF<1, there was no metal enrichment by natural or anthropogenic inputs; 1≤RCF<3 for a particular metal meant that the sediment was moderately contaminated by the element; 3≤RCF<6 means that there was considerable contamination; and if RCF>6, then there was very high contamination for that metal. In this study, the RCFs for elements which had ISQG values demonstrated that there was no metal enrichment by natural or anthropogenic sources except for Ni, which was in the higher range of considerable contamination (Table 5).

Enrichments Factors (EF) using Fe was calculated in table 5.

$$EF = (Cs\_C_{Fe})_{sample}/(Cs\_C_{Fe})_{shale}$$

While (Cs_CFe)sample were the average element level and Fe concentrations in our study, respectively and (Cs_CFe) shale were the average element level and Fe concentrations in shale, respectively. EF was used as an index to evaluate anthropogenic influences of heavy metals in sediments. When 0.5≤ EF≤1.5, it suggested that the trace metals might have originated entirely from crustal materials or natural weathering processes. When EF>1.5, it suggested that a significant portion of trace metals were provided by other sources (Zhang et al., 2007). High EF level for Ni demonstrated that nickel level in sediments of the Persian Gulf could have originated from anthropogenic sources.

5- Conclusions

Our results revealed that the element concentrations in sediments of the Northern part of the Persian Gulf did not exceed the sediment quality guidelines and posed no environmental concerns with the exception of Ni, which was greater than ERM.

Oil mining and recent regional wars in the Persian Gulf have released millions of oil barrels to the sea, which consisted of detectable trace metals (Leonov and Pishchal'nik, 2005). Seawater desalination plants in the Persian Gulf with capacity of millions cubic meters freshwater per day is other heavy metal pollution source in the area. In addition to pollutants, patterns of sediment contamination were affected by hydrological factors (specifically sedimentation patterns), and by the physical and chemical characteristics of the sediments. Fine-grained sediments with high surface area-to-volume ratios and/or high organic carbon contents, for example, acted as good absorbents for many pollutants.

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