Heavy metals contaminant evaluation in sediments of Khour-e-Musa creeks, northwest of Persian Gulf

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Abstract: Surface sediments contamination to heavy metals was evaluated in eight creeks of Mahshahr coastal waters (north-west of the Persian Gulf) from October. 2005 to November 2006. Sediments were collected seasonally by Peterson grab and the concentrations of heavy metals were measured using voltammetry and polarography methods. The range and the mean concentrations obtained in mg/kg were 15.03-35.16 (27.01) for Cu, 65.57-171.41 (102.67) for Ni, 4.63-20.06 (13.22) for Co, 0.093-0.78 (0.22) for Hg, 65.07-379 (113.70) for Zn, 0.27-1.00 (0.56) for Cd and 7.09-29.72 (14.66) for Pb. The background values for different heavy metals were calculated and the contamination factor for each metal and the degree of contamination for each creek were determined as well. Measured concentrations were compared with international standards. According to the contamination factor (C_f), the concentration of some elements such as Hg, Zn, and Ni were at risk level; according to the degree of contamination (C_d), all of the studied creeks could be classified as moderately polluted except for Ghannam that showed a considerable degree of contamination.

Keywords: Heavy metals, Bottom sediment, Contamination factor, Khour-e-Musa creeks, Khouzestan

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Introduction

Marine sediments can be sensitive indicators for monitoring contaminants in aquatic environments (Pekey *et al.*, 2004). Renewable resources and an uncontaminated marine environment play a pivotal role in regional prosperity and sustainable development. The Persian Gulf marine environment is becoming increasingly important in fulfilling social, economic, development and strategic objectives of the region (Price *et al.*, 1994). Coastal uses and other human activities have inevitably impinged on the Persian Gulf environment, the extent and magnitude of which vary geographically.

Heavy metals such as cadmium, mercury, lead, copper and zinc are regarded as serious pollutants of aquatic ecosystems because of their environmental persistence, toxicity and ability to be incorporated into food chains (Kishe & Mahchiwa, 2003).

The major environmental pressures in the Persian Gulf, including Khuzestan coastal waters, are shipping and transport, residential and commercial expansion, industrial development, particularly oil and petrochemical industries, mining, power plants, fishing, recreation and agriculture, which are considered as the major threats to this highly potential area that entails important habitats for many commercial aquatic organisms and their life cycles (Sheppard *et al.*, 1992; Price, 1993).

Several studies have been conducted on heavy metals concentration in water and sediment of Khouzestan coastal waters and central part of the Persian Gulf (Mazaherinejad, 1996; Morrovvaty, 1997; Sabzalizadeh & Nilsaz, 1999; Karbassi, 2001; Ebrahimi *et al.*, 2008). Determination of four trace element concentrations (cadmium, nickel, lead and vanadium) in fish, surficial sediments and water has also been carried out from the northern part of the Persian Gulf from Strait of Hormouz to vicinity of the Khour-e-Musa (Pourang *et al.*, 2005). The aim of the present study is to investigate on sediment heavy metals (Zn, Cu, Co, Hg, Ni, Cd and Pb) concentration as sediment quality and to evaluate the sediment contamination level of Mahshahr creeks.

Materials and methods

Numerous creeks are located in Mahshahr (Khuzestan coastal waters) in the northern Persian Gulf (longitude 49° to 49° 20' and latitude 30°15' to 30° 32'). The sampling sites in the eight creeks are depicted in Fig. 1.

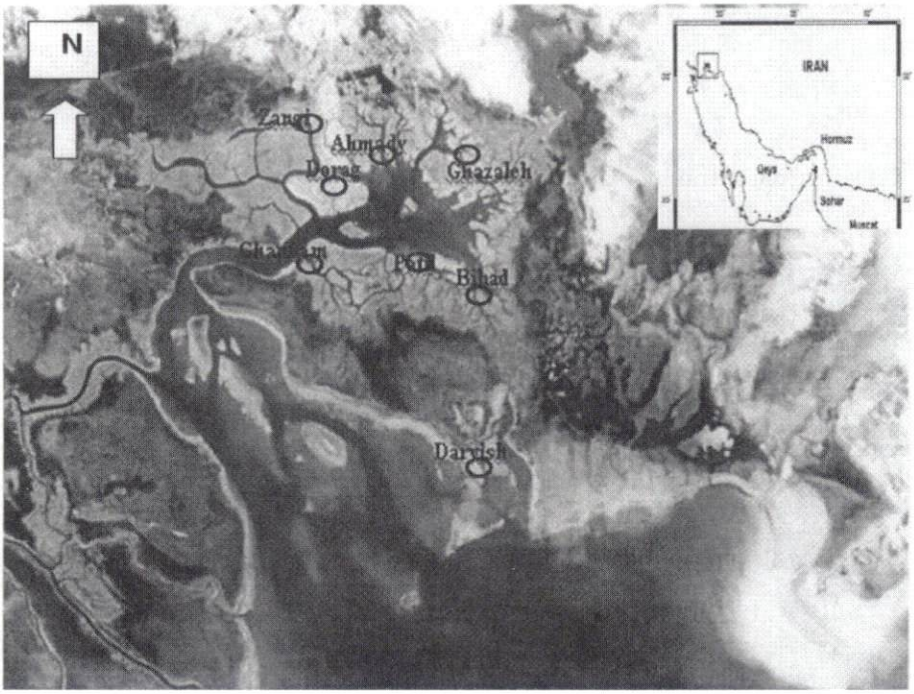

Figure 1: Location of studied area in Mahshahr creeks (Khour-e-Musa, Northwest of the Persian Gulf)

Seasonal sampling with three replicates from each site were carried out over a one year study from September, 2005 to October, 2006. Surface sediment samples were collected by Peterson grab sampler at 8 creeks (Ahmady, Ghazaleh, Doragh, Patil, Darvish, Zangy, Bihad, Ghannam). After drying in oven, the samples were divided into two portions. The first portion was used for grain size analysis by sieving method (Holme & Mcintyre, 1984) and the second portion was used for chemical analysis. The dried homogenized sediment samples were sieved through 50µm screen and kept in clean plastic containers ready for analysis. Powdered samples less than 50µm were used for heavy metal analysis: 1g of sample was digested with Aqua regia (HNO3:HCl) and HF (Loring & Rantala, 1992).

The samples were analyzed separately by using a voltammetry (for Hg) and polarography (for other metals) methods* (Methrom 797) and Standard addition were used for calibration technique. Quality control samples were prepared as standard values and the percentage recovery for standard samples ranged from 97.5 to 103 % (Table 1).

Table 1: Concentration of different metals (µg/lit or ppb) in standard materials (from Merck standards)

Metal	Zn	Cu	Ni	Co	Pb	Hg	Cd
Found	149.01± 1.6	51.24± 0.7	102.98± 0.15	49.55± 0.85	51.5± 0.4	9.71± 0.7	9.82± 0.18
Certified	150	50	100	50	50	10	10

The results of trace metals concentrations were determined on a dry weight basis in mg/kg (or ppm). Total organic matter of the investigated sediments was determined by physical method (Holme & Mcintyre, 1984).

To evaluate the levels of sediment contamination, two techniques were used,

1) Contamination factor (C_f) for each metal and degree of contamination (C_d) for each creek were calculated. Hakanson (1980) introduced the term contamination factor C_f to describe the contamination of a given toxic substance in a basin:

$C_f = C_e / C_{pi}$

Where C_e =concentration of the element in sediment samples, and C_{pi} = pre industrial reference value (natural reference) for the element.

The degree of contamination, C_d, is defined as the sum of all contamination factors for various heavy metals.

$C_d = \sum^7 C_f$

* Anodic Stripping Voltammetry (ASV) and Adsorptive Stripping Voltammetry (ADSV), a hanging mercury drop electrode (HMDE) is used in the differential pulse mode.

With this approach, we have contamination factors for 7 heavy metals (Cu, Hg, Pb, Ni, Cd, Co and Zn) in surface sediments and the degree of contamination in different creeks were calculated by using the raw elements data (C_e) and the background concentration (C_{pi}) values in mg/kg: Cu=17, Hg=0.05, Pb=25, Zn=43, Ni =70, Cd =2.18, and Co =24.

The background value or pre-industrial reference for different elements was defined as the mean value plus one standard deviation (Hakanson, 1980; Aksu *et al.*, 1997). In the present study, sediment heavy metal concentrations from previous studies conducted in the area were used (Morrovvaty, 1997; Omidy, 1998; Sabzalizadeh & Nilsaz, 1999). Due to the unavailability of enough data and lack of old data in this area, the calculated background values could not be used as pre-industrial values. Since these values are considered as crude reference values, we have also equalized this sum (x + sd). The following terminology was used in this pollution Index to get a uniform way of describing the contamination factor (Hakanson, 1980; Aksu *et al.*, 1997; Nasr *et al.*, 2006):

$C_f < 1$ = Low contamination factor (indicating low sediment contamination of the substance in question);

$1 \leq C_f < 3$ = Moderate contamination factor;

$3 \leq C_f < 6$ = Considerable contamination factor;

$C_f \geq 6$ = very high contamination factor.

The following terminology has been used for the degree of contamination of each creek in the present study (Hakanson, 1980; Aksu *et al.*, 1997):

$C_d < 7$= Low degree of contamination;

$7 \leq C_d < 14$ = Moderate degree of contamination;

$14 \leq C_d < 28$= Considerable degree of contamination;

$C_d \geq 28$ = very high degree of contamination indicating serious anthropogenic pollution.

2) Using of the global baseline values and sediment quality guidelines (Table 2):
Sediment quality values are a useful tool for evaluating the potential for contaminations within sediments to induce biological effects. Here, metal concentrations from different creeks were compared with NOAA (National Oceanic and Atmospheric Administra-

creeks were compared with NOAA (National Oceanic and Atmospheric Administration) and ISQGs (Interim Sediment Quality Guidelines) sediment quality guidelines (Long *et al.*, 1995; Buchman, 1999; CCME, 1999).

SPSS, Excel and Primer softwares were used for data analyzing and Two way ANOVAS.

Table 2: Sediment quality guidelines and definitions from NOAA (USA) and environment Canada guidelines for the studied heavy metals (mg/kg/dry sediment)

	ERL[1]	ERM[2]	ISQG (TEL[3])	PEL[4]
Cd	1.2	9.6	0.7	4.2
Cu	34	270	18.7	1.8
Pb	47	220	30.2	112
Hg	0.2	0.7	0.1	0.7
Ni	21	52	15.9	42.8
Zn	150	410	124	271

1-ERL= Effects Range Low

2-ERM = Effects Range Medium

3- TEL = Threshold Effect Level (Maximum concentration at which no effect are observed)

4- PEL = Probable Effect Level (Lower limit of the range of concentrations at which adverse effects are always observed).

Results

Some general characteristics of the sediments are shown in Table 3. The minimum and the maximum silt/ clay materials were found in Patil (52.12%) and Ghazaleh (96.88%), respectively. The range of the total organic matter in the sediments was (7.75-13.95)(%dry weight) and tends to be higher in Bihad, Zangy and Ghazaleh sediments.

Table 3:General characteristics of sediments sampled in Mahshshr creeks (2005-2006)

	Bihad	Patil	Doragh	Zangy	Ghazalleh	Ghannam	Ahmady	Darvish
Depth (m)	5-31	5-31	7.5-20	7-20	9.5-16	13-21	4-15	7-16
TOM (%)	13.95	7.8	8.43	13.54	13.51	8.05	11.75	7.75
Fines<63μm (%)	78.16	52.12	75.85	82.37	96.88	72.71	83.37	70.47

The range and average concentrations measured in mg/kg were: 15.03-35.16 (27.01) for Cu, 65.57-171.41 (102.67) for Ni, 4.63-20.06 (13.22) for Co, 0.093-0.78 (0.22) for Hg, 65.07-379 (113.70) for Zn, 0.27-1.00(0.56) for Cd and 7.09-29.72 (14.66) for Pb (Table 4).

According to Fig. 2 and also Table 4, the highest mean values of Zn (179.8), Cu (30.28), Hg (0.31) and Ni (121) mg/kg were recorded in the Ghannam creek. For Cd, Zangy and Ghannam showed higher mean values with 0.72 and 0.69mg/kg, respectively, and the higher Pb concentration was observed in Doragh and Zangy with 17.4 and 17.3 mg/kg, respectively. The highest mean value of Co (16.5) mg/kg was recorded in Darvish creek. The results of two way ANOVAs showed no significant differences between creeks for each of the measured metals except for Co and Ni ($P<0.05$).

There was seasonal variation in mean values of different metals (Fig. 3). The results of two way ANOVAs showed significant differences among seasons for each metal ($P<0.05$), except for Cd that no seasonal significant difference was observed.

Based on sediment quality guidelines, the nickel concentrations were higher than ERM in most of creeks and Hg values were higher than ERL in Ghannam, Ahmady, Patil, Ghazaleh and Zangy. Zn values were higher than ERL in Ghannam and were higher than ISQG in Doragh. Other heavy metals were observed under standard levels (Fig. 4).

Table 4: The mean, maximum and minimum concentration of heavy metals (mg/kg) in the sediment of Mahshahr creeks, 2005-2006

	Cu	Ni	Co	Hg	Pb	Zn	Cd
Ahmady	**29.54** (30.33-28.92)	**104.485** (115.8-105.93)	**15.615** (20.06-15.79)	**0.27** (0.56-0.095)	**13.22** (19.49-9.84)	**87.68** (107.54-69.67)	**0.505** (0.61-0.340)
Patil	**25.8** (27.8-21.58)	**96.145** (110.47-86.04)	**12.505** (17.38-8.65)	**0.187** (0.3-0.16)	**12.057** (15.07-8.59)	**96.975** (144.96-70.38)	**0.52** (0.61-0.42)
Ghazaleh	**28.93** (34.53-19.43)	**78.47** (87.98-65.57)	**8.847** (13.37-4.63)	**0.2075** (0.34-0.13)	**12.705** (15.25-10.01)	**100.753** (128.3-84.48)	**0.52** (0.67-0.41)
Darvish	**27.225** (33.51-19.29)	**119.50** (171.41-107.91)	**16.51** (19.77-13.33)	**0.1942** (0.23-0.171)	**15.672** (25.39-7.09)	**99.0975** (121.74-79.6)	**0.483** (0.54-0.39)
Doragh	**26.77** (29.37-23.05)	**102.578** (134.17-67.5)	**13.99** (18.79-9.83)	**0.155** (0.19-0.13)	**17.367** (29.72-8.14)	**138.31** (253.09-82.69)	**0.598** (0.95-0.4)
Zangy	**23.245** (32.54-15.03)	**106.358** (148.43-77.96)	**13.025** (16.27-11.11)	**0.2175** (0.41-0.11)	**17.295** (29.45-8.35)	**106.975** (200.34-65.07)	**0.72** (1-0.47)
Ghannam	**30.275** (35.16-24.19)	**120.885** (130.13-126.64)	**14.672** (16.37-13.4)	**0.3075** (0.78-0.11)	**16.597** (22.41-13.31)	**179.815** (379-105.19)	**0.685** (0.79-0.52)
Bihad	**24.355** (30.2-16.78)	**92.95** (112.2-80.43)	**10.587** (14.11-7.67)	**0.145** (0.18-0.13)	**12.37** (17.74-8.78)	**100.03** (141.75-76.43)	**0.443** (0.66-0.27)

*** Maximum values were shown as marked value.**

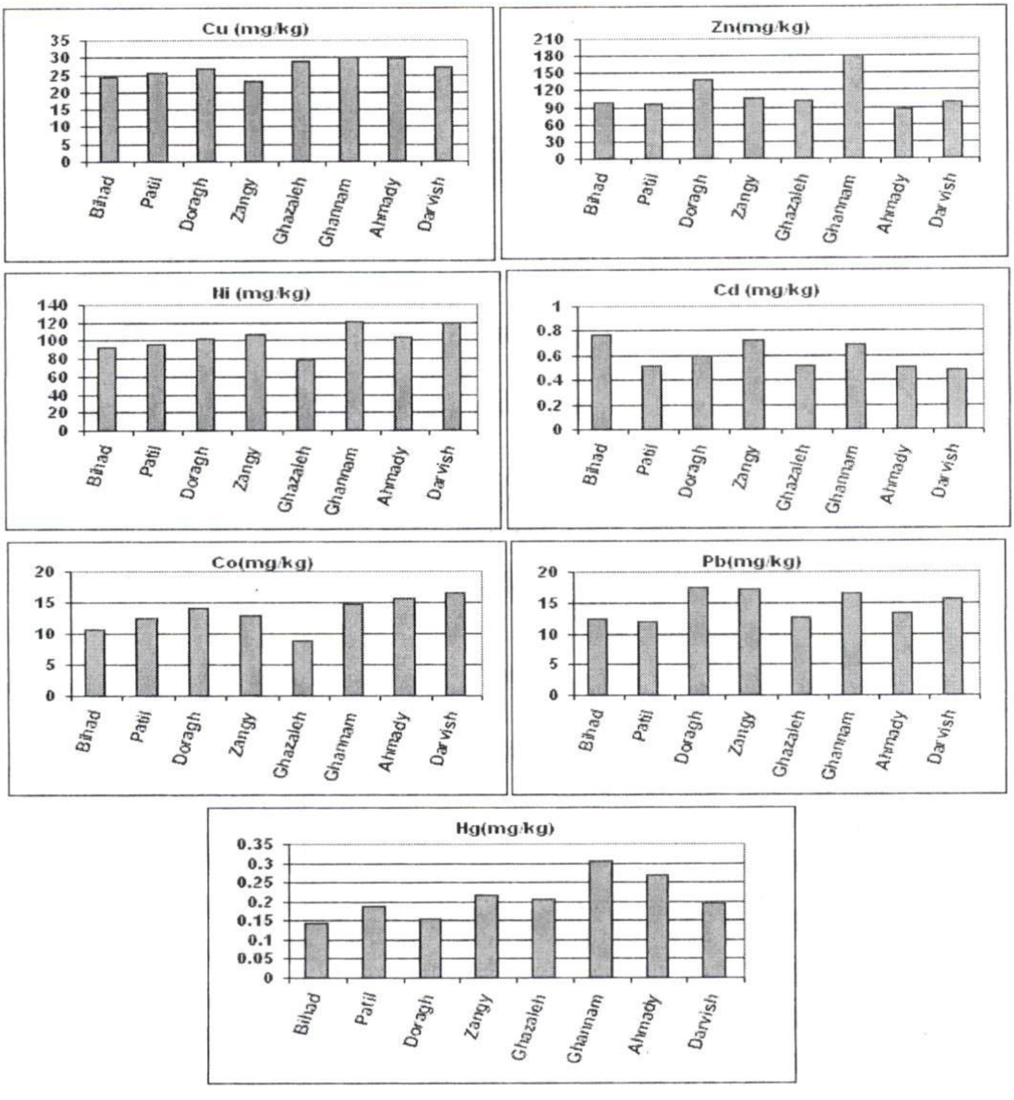

Figure 2: Mean values for seven measured heavy metals (mg/kg dry sediment) in surface sediments of different creeks of Mahshahr waters (2005-2006)

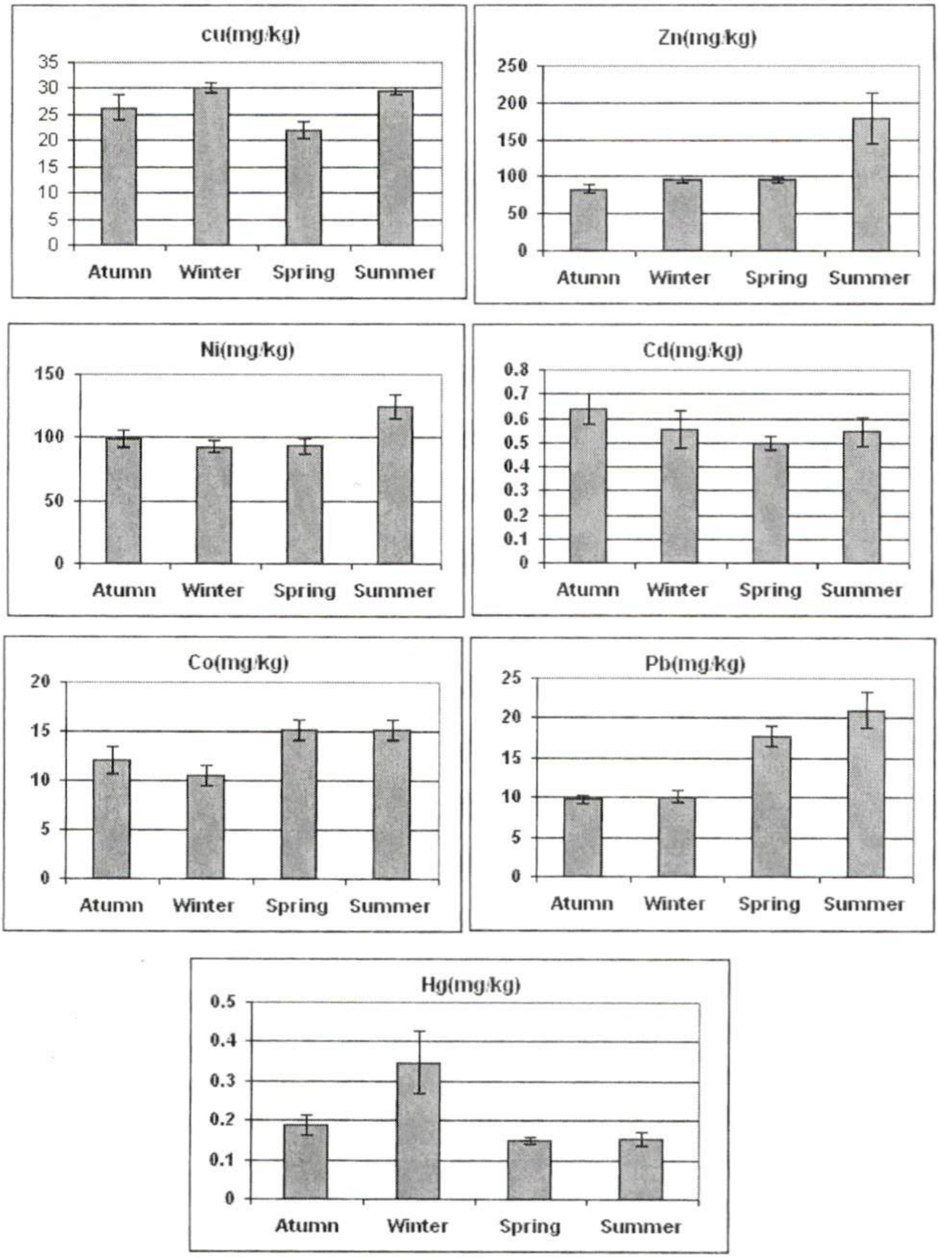

Figure 3: Seasonal variations in mean values of sediment heavy metals in Mahshahr creeks (2005-2006)

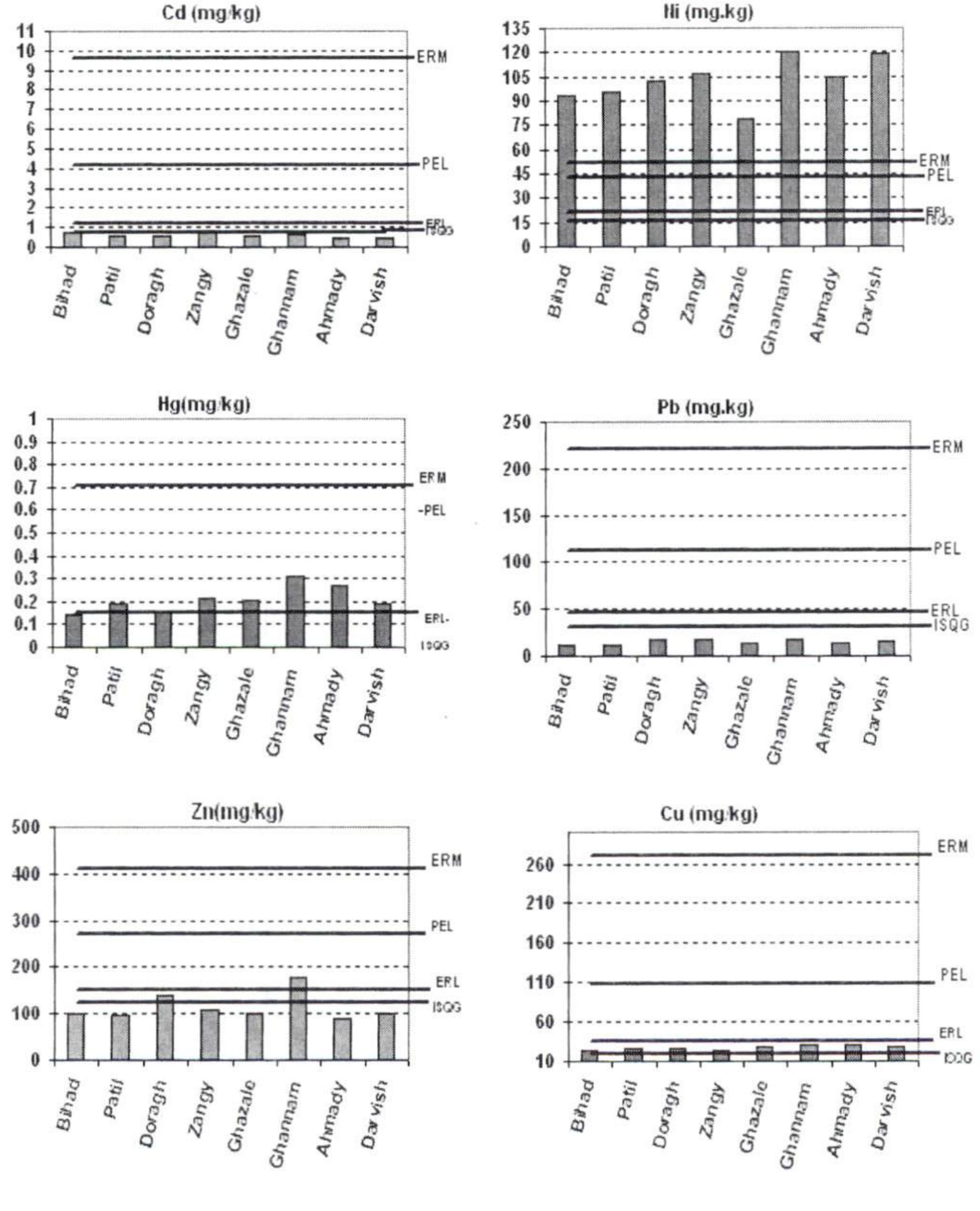

Figure 4: Heavy metals concentrations (mean values) in different creeks: ERL=Effects Range Low, ERM=Effects Range Medium, PEL=Probable Effect Level, and ISQG= Interim Sediment Quality Guidelines.

The values of contamination factor for each metal were shown in Table 5. The maximum values for Zn (4.18), Hg (6.159), Ni (1.73) and Cu (1.78) were obtained in Ghannam creek. Heavy metals background values from different studied area and present study are shown in Table 6.

In general, the contamination factors of heavy metals in the present study are ordered as following: Hg > Zn > Cu ≥ Ni > Pb ≥ Co >Cd

According to the degree of contamination (C_d), the studied creeks are ordered as follow:

Ghannam > Ahmady ≥ Zangy > Doragh ≥ Darvish > Ghazaleh >Patil >Bihad

Most creeks are classified as having a moderate degree of contamination except for Ghannam that showed considerable contamination (Table 7).

Clustering similarity, based on C_f indicated 3 groups of heavy metals with different levels of contamination (Fig. 5-A) and based on mean values of heavy metals it showed that Ghannam was largely separated from others (Fig. 5-B).

Data obtained from present study was compared with global guidelines and other studies in the Persian Gulf sediments (Table 8).

Table 5: Contamination factor (C_f) and contamination degree (C_d) of sediment heavy metals in Mahshahr creeks (2005-2006)

Creeks	Hg	Pb	Zn	Ni	Cu	Co	Cd	$C_d=\Sigma C^i_f$
Ahmady	5.42	0.53	2.04	1.49	1.74	0.64	0.23	12.09
Patil	3.75	0.48	2.20	1.37	1.52	0.58	0.23	10.14
Ghazaleh	4.15	0.51	2.30	1.12	1.70	0.37	0.23	10.42
Darvish	3.89	0.63	2.31	1.71	1.60	0.69	0.22	11.05
Doragh	3.10	0.70	3.22	1.32	1.57	0.58	0.27	10.35
Zangy	4.35	0.69	2.49	1.52	1.37	0.54	0.33	11.41
Ghannam	6.15	0.66	4.18	1.73	1.78	0.61	0.31	16.22
Bihad	2.90	0.49	2.33	1.33	1.43	0.44	0.20	8.74

*** Maximum values were shown as marked value**

Table 6: Background values from different studied area and present study (mg/kg)

Studied area	Hg	Pb	Zn	Ni	Cu	Co	Cd	Reference
Indian Estuarine	-	20	-	68	45	19	0.3	Turekian & Wedepohl,1961
Aden Gulf Yemen	-	20	70	38	20	13	-	Nasr *et al*, 2006
Izmir Bay Turkey	0.05	8.5	65	-	17	-	0.03	Aksu *et al*,1997
Central part of Persian Gulf		4.5	69	86	33	15	2.7	Karbassi, 2001
Mahshahr creeks	0.05*	25	43	70	17	24	2.18	Present study

*For mercury background value in pristine marine sediment was used (Sadiq, 1992).

Table 7: Risk level of different metals (based on C_f) and pollution degree (Based on C_d), in Mahshahr creeks (2005-2006)

	Hg	Zn	Ni	Cu	Pb, Co ,Cd	Pollution degree
Ghannam	$C_f>6$ Very high	$3\leq C_f<6$ Considerable	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$C_f<1$ Unpolluted	Considerable degree
Ahmady	$3\leq C_f<6$ Considerable	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$C_f<1$ Unpolluted	Moderate degree
Zangy	$3\leq C_f<6$ Considerable	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$C_f<1$ Unpolluted	Moderate degree
Doragh	$3\leq C_f<6$ Considerable	$3\leq C_f<6$ Considerable	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$C_f<1$ Unpolluted	Moderate degree
Darvish	$3\leq C_f<6$ Considerable	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$C_f<1$ Unpolluted	Moderate degree
Ghazaleh	$3\leq C_f<6$ Considerable	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$C_f<1$ Unpolluted	Moderate degree
Patil	$3\leq C_f<6$ Considerable	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$C_f<1$ Unpolluted	Moderate degree
Bihad	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$1\leq C_f<3$ Moderate	$C_f<1$ Unpolluted	Moderate degree

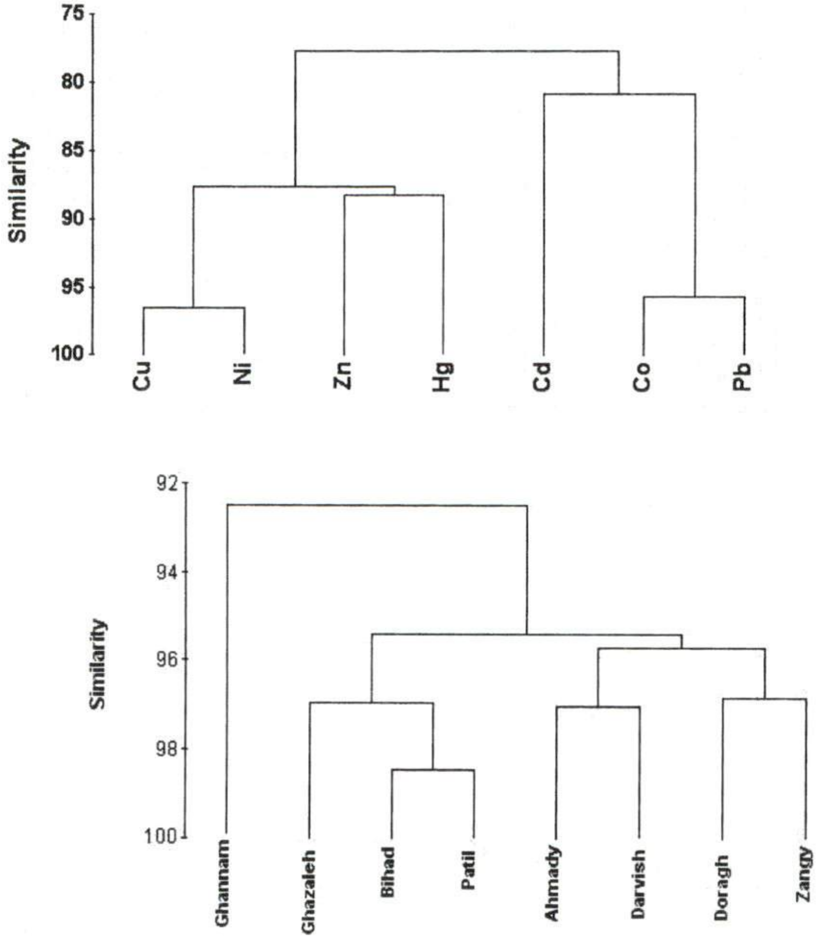

Figure 5: The dendrograms for similarity cluster analysis, A: based on contamination factor of different heavy metals and B: based on mean values of sediment heavy metals in studied creeks, in Mahshahr area.

Table 8: Mean or range of heavy metal concentrations in marine sediments (mg/kg dry weight)

Geographical area and global standards	Ni	Cu	Zn	Pb	Cd	Co	Hg	Reference
Mahshahr creeks, Northern Persian Gulf	102.7	27.01	113.7	14.66	0.56	13.22	0.22	Present study
Mahshahr creeks, Northern Persian Gulf	29.81	4.95	25.53	13.15	1.9	19.81	---	Sabzalizadeh & Nilsaz, 1999
Khour-e-Musa, Northern Persian Gulf	52-82	15-25	77-478	44-58	---	21-26	---	Mazaherinejad, 1996
Persian Gulf, northern coastal waters	64.9	---	---	90.5	2.9	---	---	Nikoyan *et al.*, 2005
Persian Gulf, Central part	133	38	95	39	4	27	---	Karbassi, 2001
ROPME Sea Area-2001	55-104	10-33	50-2200	4.2-17.5	0.1-0.7	---	0.012-0.125	ROPME, 2004
ROPME Sea Area Guideline	70-80	---	---	15-30	1.2-2	---	---	ROPME, 1999
ISQG (Canadian interim marine sediment quality)	15.9	18.7	124	30.2	0.7	---	0.13	CCME, 1999
Global baseline values	52	33	95	19	0.3	14	---	Bowen,1979

Discussion

Grain size analysis of the sediments showed that the studied area was covered with fine materials, which had higher silt/clay content at most creeks (Table 3). Only the samples from Patil creek showed about 50% fine material and the other creeks showed higher than 70 percent silt/clay material. Fine material, with a larger surface to volume (or weight) ratio, has a greater potential to scavenge both inorganic and organic pollutants from the water column. In general terms, fine mud/silt/clay sediments with high organic content retain more contaminants than relatively coarse sandy sediment (De Mora & Sheikholeslami, 2002).

In previous studies in Khour-e-Musa area, except for Cd and Co, the mean values of Ni, Zn, Cu and Pb were reported several times less than present study (Sabzalizadeh & Nilsaz, 1999; Mazaherinezhad, 1996). Pourang and his colleagues (2005), found that concentrations of three elements (Pb, Cd and Ni) in northern part of Persian Gulf were considerably higher than global baseline values, RSA (ROPME Sea Area) and the ERL

(Effects Range Low) guidelines, and also the concentration of Ni exceeded the ERM (Effects Range Medium) Guideline. In the present study, Hg concentration was more than ERL level in some of creeks (Fig. 4).

No significant differences in metals concentrations were observed and more than 90% similarity index were obtained in different creeks (Fig. 5-B), which could be due to closeness and same nature of water dynamic in this area.

Ghannam Creek that demonstrated serious contamination is a smaller creek, while Bihad, Patil and Ghazaleh are vaster creeks with more branches and directly connected to open sea.

Such significant variations in sediment metals concentrations in such a short period are generally unusual. However considering the dynamic nature of this marine environment in terms of pollution sources and water circulation, some temporal (seasonal) variations in metal content may be real (Algan *et al.*, 1999). Due to high tidal circulation and water mixing, high sedimentation rate, and high re-suspension of surface sediments, such variations can be expected.

It is difficult to make an overall assessment of the degree of metal concentration in estuarine and marine sediments (Rubio *et al,* 2000). This is a consequence of variations in analytical procedures between studies and the presence of an unknown natural background in the sediments (Nasr *et al*, 2006).

Overall, it could be concluded that some metals such as Hg, Zn, Ni and Cu were much higher than the background values and were found to be at risk level, while earlier studies showed moderate to considerable contamination level for sediment heavy metals. Longer term monitoring of sediment and also a biological survey particularly of the benthic community (species composition, abundance, diversity and biomass) would be necessary to better assess the variations in metals content of the sediments in these creeks.

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