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Trace metals in marine sediment of Bahrain territorial water

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Table of Content

Table of Content **2**
ABSTRACT **3**
1.0 Introduction **4**
2.0 Methods **6**
2.1 Sample Collection 6
Location **6**
2.2 Sample treatment 7
2.3 Sediment characterization: 8
3.0 Results and Discussion **10**
3.1 Overview 10
3.1.1 Cadmium (Cd) **12**
3.1.2 Chromium (Cr) **13**
3.1.3 Copper (Cu) **14**
3.1.4 Lead (Pb) **15**
3.1.5 Nickel (Ni) **17**
3.1.6 Zinc (Zn) **18**
4.0 Conclusions **22**
5.0 References **23**

ABSTRACT

This report presents trace metals results of an on going Marine-monitoring programs carried out by The General Directorate of Environment & Wildlife Protection.

There have been few studies of trace elements in marine coastal sediment from Bahrain territorial water despite considerable potential for contamination by this class of pollutant.

For the purpose of assessment of marine contamination due to heavy metals, marine coastal sediments were collected from different sites during the period of 2001-2003. These marine coastal sediments were analyzed for 6 trace elements (Cd, Cr, Cu, Ni, Pb, and Zn).

Sediment metal loadings were generally not remarkable, although hot spots were noted. In general, concentrations of trace elements were similar to those of other Bahrain's and were deemed not to be of any toxicological significance. It is worth mentioning that on the basis of characteristics the marine sediments from the studied areas are comparable to those found in unpolluted worldwide areas, and reveal that the effect of anthropogenic enrichment upon concentration of the elements is nominal.

1.0 Introduction

Pollution studies in the Arabian Sea are extremely important. The Gulf comprises a relatively shallow, semi-enclosed sea with very high evaporation rates and poor flushing characteristics (***Sheppard, 1993***). As a result, contaminant inputs undergo more limited dilution and slower dispersion than would occur in open marine systems. The ecosystem is relatively fragile, experiencing elevated temperatures, salinity and UV exposure. Many species function close to physiological limits (Sheppard, 1993), and thus, added stress imposed by pollutants is likely to have severe consequences

Monitoring of sediment contaminants is critical to track regional trends, understand potential toxic impacts to bay resources and make management decisions. The sediments provide both short and long-term memory of contaminant loadings to the bay.

Sediments integrate contaminant concentrations overtime and therefore can alleviate some of these problems. Heavy metals are of concern as contaminants to aquatic systems because of their toxicity at low concentrations. Metal-impacted benthic communities are generally characterized by reduced abundance, lower species diversity, and shifts in community composition from sensitive to tolerant taxa (***Winner et al., 1980; La Point et al., 1984; Clements, 1991).***

Sediments are important carriers of trace metals in the environment and reflect the current quality of the system. Metals can originate from direct discharges or from diffuse pollutants sources like atmospheric deposition ***(De Lacerda et al., 1991)***.

To assess the environmental impact of contaminated sediments, information on total concentrations is not sufficient. Of particular interest is the fraction of the total heavy metal content that may take part in further biological

processes. Therefore, the two important steps in the assessment of heavy metals in sediments according to ***Forstner (1983)***are:

(i) The identification, monitoring and control of pollution sources;

(ii) The estimation of possible effects of polluted sediments.

In order to derive correct results from data on heavy metals content in sediments, two steps are necessary: the evaluation of background levels and the description of geochemical distribution of heavy metals in the sediments of a certain area.

The major sources of coastal pollution in Kingdom of Bahrain are the domestic sewage and industrial effluents, discharged from urban, rural and industrial areas. The effluents are discharged into the marine environment through numerous outfall located along the coast, which affect the heavy metal content in bottom sediments of coastal zones studied. The mineralogical composition of the sediments themselves is a very interesting factor affecting the results of analyses. Until now, on comprehensive study has been carried out on the heavy metal pollution of sediments along the Albanian coast. This paper aims to evaluate the normal levels and the 'hot spots' for coastal areas, through the identification, monitoring and control of pollution sources

2.0 Methods

2.1 Sample Collection

Marine sediment samples were collected in the Bahrain territorial seawater during 2001–2003. In general, all sampling procedures were carried out according to internationally recognized guidelines ***(UNEP, 1991***). All sampling locations are shown in Fig. 1. Exact coordinates for sediment sampling are shown in Table 1.

Table 1

Sampling locations coordinates

Ser #	**Location**	**Latitude**
1	Addur R.O. Plant	N 25 58 240 E 50 37 136
2	Askar	N 26 03 113 E 50 37 918
1	Ras Abu Jarjur R.O.Plant	N 26 04 529 E 50 37 819
4	Alba	N 26 06 137 E 50 37 726
5	Bapco	N 26 06 473 E 50 37 821
6	Sailing club	N 26 07 043 E 50 38 938
7	GPIC	N 26 08 361 E 50 38 938
8	Sitra Power & Desalination Plant	N 26 10 831 E 50 37 799
9	Marine Club	N 26 14 205 E 50 35 955
10	Hidd Power Plant	N 26 13 804 E 50 40 259
11	North Meridien	N 26 19 059 E 50 31 924
12	Jasra	N 26 11 105 E 50 26 528

Surface sediments were collected directly into pre-cleaned Teflon containers using a Van Veen grab. The sediments were transferred to previously prepared aluminum or plastic containers for analysis of organic and inorganic constituents, respectively. All samples were frozen (-18 °C) immediately upon collection and kept frozen for transport to the laboratory. The samples were analyzed for grain size distribution, total organic carbon (TOC), total Kjeldhal Nitrogen (TKN), the following elements: Cd, Cr, Cu, Ni, Pb and Zn

2.2 Sample treatment

All sediment samples were freeze-dried and sieved through a 1 mm clean sieve to remove shell fragments. In some cases where sample size was small, the sieved sediments were ground in an agate mortar. The sieved and/or powdered sediments were then transferred to clean glass bottles and shaken to obtain a fine homogeneous powder. Between 150 and 600 mg of freeze dried sediment material were weighed for digestion. Samples were digested in acid-cleaned Teflon microwave vessels with 5 ml of ultra pure nitric acid and 2 ml ultra pure concentrated hydrofluoric acid. A Milestone MLS Ethios Plus II system was used for samples. Each digestion batch included at least one reagent blank and a representative standard reference material, e.g., MESS-2 or BCSS1 (NRCC, Marine sediment), and generally a sample replicate to check homogeneity and process efficiency. Samples were digested typically for 30–40 min at 200 °C. After allowing at least 1 h for cooling, the vessels were opened and 0.4 g boric acid/gm sediment was added to dissolve the fluoride precipitates. The vessels were then resealed and put back in the microwave digestion system for an additional 20–30 min. Following cooling for at least 1 h, the digested sample was transferred to a graduated plastic test tube with an additional 0.5 ml HF and brought up to volume of 50 ml with Milli-Q water.

Samples were analyzed for metals using a Thermo elemental Atomic Absorption Spectrometer. Results were quantified via an external calibration

curve generated from the responses obtained from multiple dilutions of a multi-element calibration standard that was prepared from single-element standards (Fisher Chemical). Analytical quality control included analysis of a 2% ultra pure nitric acid blank and a drinking water reference material (TMDW1, acquired from High Purity), together with the procedural blank, a reference material of similar matrix, and a sample duplicate from the microwave digestion.

For grain size distribution, total organic carbon (TOC), total Kjeldhal Nitrogen (TKN) and Phosphate the analyses were done according to MOOPAM (1989).

2.3 Sediment characterization:

Sediment contamination is of concern because many aquatic organisms make their home in sediments, in what scientists call the benthos. Benthic animals include insects, worms, shellfish, and fish that feed on the bottom. For example, fish that live in toxic hot spots can build up enough toxins in their flesh that long-term consumption of the fish by humans is not wise. Contaminated sediments can also limit the type of aquatic organisms that can live in them and in the water above them. Contaminants can be chemically or physically bound to the particles in the sediments.

Little is known about the extent and severity of sediment contamination from lax past practices by cities, industry, and agriculture. One question demanding an answer is whether mere detection of a contaminant in sediments is cause for alarm. We also need to know more about how contaminants change while held in sediments.

Many experts suggest that the best strategy for many contaminated sediment sites would be to leave them alone, since remediation can resuspend sediments and also because once in the sediments, many contaminants may stay entombed there.

Grain size and grain size distribution of sediments not only has importance on sediment transport and deposition, but also significantly affects the distribution and concentration of various pollutants. Sediment at Askar showed high content of sand fraction. Low silt fraction at the surface layer in location is an evidence of untouched area as far as dredging and reclamation are concern.

Total Kjeldahl Nitrogen (TKN) values ranged from 1,008.00-1,032.00 $\mu g g^{-1}$, with an average of 1,020.05 $\mu g g^{-1}$.

Total phosphate-P ranged from 200.00-260.00 $\mu g g^{-1}$ with an average of 230.00 $\mu g g^{-1}$. Phosphorous is essential to the growth of organisms and can be the nutrient that limits the primary productivity of a body of water. Under conditions where soluble phosphates are in algae may utilize short supply, phosphates in sediments.

Total Organic Carbon (TOC) ranged from 1.21 % - 1.30 % with an average of 1.26 %, which is consistent with those (.68 % – 1.35 %) reported for the East Coast of Bahrain

3.0 Results and Discussion

3.1 Overview

In this study, 6 elements were determined in the Bahrain territorial Seawater sediments. The range of concentrations for each element is shown in Table 8 on a station basis. It must be stressed that the difference in the trace elements contents in the considered sediments reflects the variation in the overall composition of the sediments.

The concentration of trace metals in the marine life is influenced by several mechanisms. The physical and chemical nature of the marine environment is one of the important factors that determine the level of the elements. Sediment type is another factor. Clay, organic matters and metals oxides as enrichment factor affect trace metal distribution in surface sediment. The sediments grain size at the sampling stations range from coarse to medium sand.

However, in spite of the role of the sediment and the importance of their chemical characterization in monitoring program, the problem related to spatial and temporal variation caused by physical and biological reworking of the bottom deposits made it difficult to obtain representative data. Furthermore, because most heavy metals tend to accumulate in sediments, their presence in the water column is usually the result of recent inputs. Metal concentrations can vary significantly over short distances and as a function of tide. Single measurements at a given site may indicate contamination.

With respect to interpretation of the results, concentrations are compared firstly to the NOAA Marine Sediment Quality Guideline values (Table 3), which designates an Effects Range Low (ERL) and an Effects Range Medium (ERM). In the absence of a NOAA-defined ERL for a substance, the Canadian Interim

Marine Sediment Quality Guideline (ISQG) value has been used. This table also presents the Probable Effects Level (PEL) given by Environment Canada.

Table 3

Sediment Quality Guidelines from NOAA (USA) and Environment Canada

		NOAA		Canada	
Chemical	**Units**	**ERL**	**ERM**	**ISQG**	**PEL**
Cd	µg/g-dry	1.2	9.6	0.7	4.2
Cr	µg/g-dry	81	370	52.3	160
Cu	µg/g-dry	34	270	18.7	108
Pb	µg/g-dry	47	220	30.2	112
Ni	µg/g-dry	21	52		
Zn	µg/g-dry	124	271		

Table-6

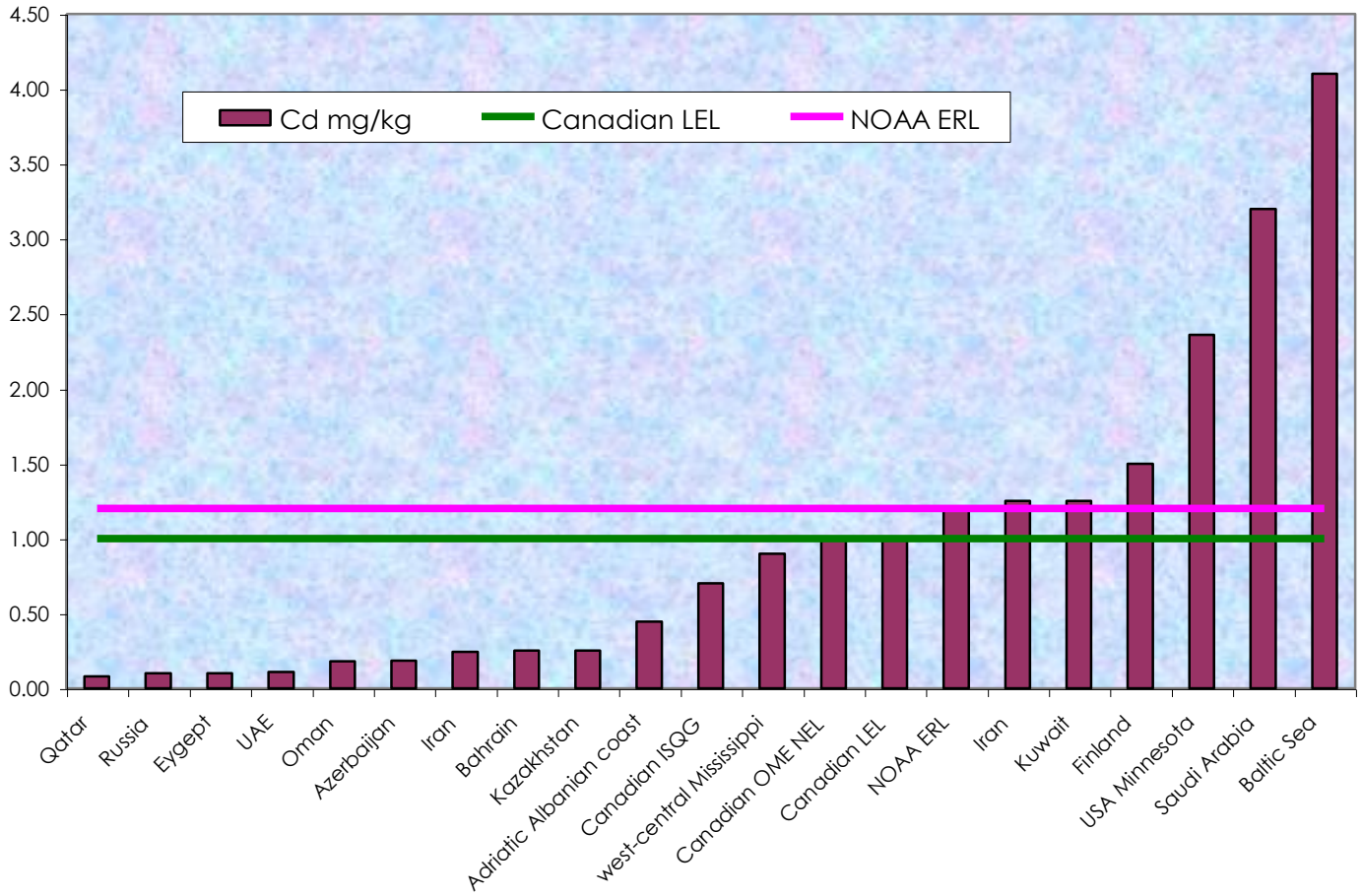
Trace metal levels (μgg^{-1} dry weight, unless otherwise stated) in sediments from Bahrain

Station	**Cd** (ngg^{-1})	**Pb**	**Cr**	**Ni**	**Zn**	**Cu**	**Mn**
Addur	79.31	2.34	22.87	9.06	28.92	59.73	49.61
Askar	136.96	11.20	40.20	6.87	19.07	32.28	41.42
Bapco	326.77	107.73	34.16	15.95	46.55	42.42	
Jasra	249.61	0.56	41.37	11.36	25.95	22.35	23.82
Marina Club	439.55	13.78	22.26	19.03	82.31	61.23	57.44
N. Meredien	213.93	0.92	47.25	13.65	14.02	15.82	45.07
R.O.Plant	168.13	24.96	35.14	10.78	30.95	14.58	
Sitra power plant	394.97	1.34	100.18	18.96	59.00	40.99	
Min	79.31	0.56	22.26	6.87	14.02	14.58	23.82
Max	439.55	107.73	100.18	19.03	82.31	61.23	57.44
Average	251.15	20.35	42.93	13.21	38.35	36.17	43.47

3.1.1 Cadmium (Cd)

Sedimentary rocks; marine phosphates often contain about 15 mg Kg^{-1} (***WHO, 1992***). However, it is about 0.16 mg Kg^{-1} of earth crust. The levels of cadmium in the marine environment can't be linked to a major source. Furthermore, data on sources of cadmium input in the RSA are limited. However, there are no sites in the studied areas with anomalous high levels relative to other locations. The highest concentration of 0.439 mg kg^{-1} was found at Marina Club Resort station, though this concentration never exceeds the NOAA ERL value of 1.2 mg Kg^{-1}.

Figure 2-1
Cadmium in Sediment

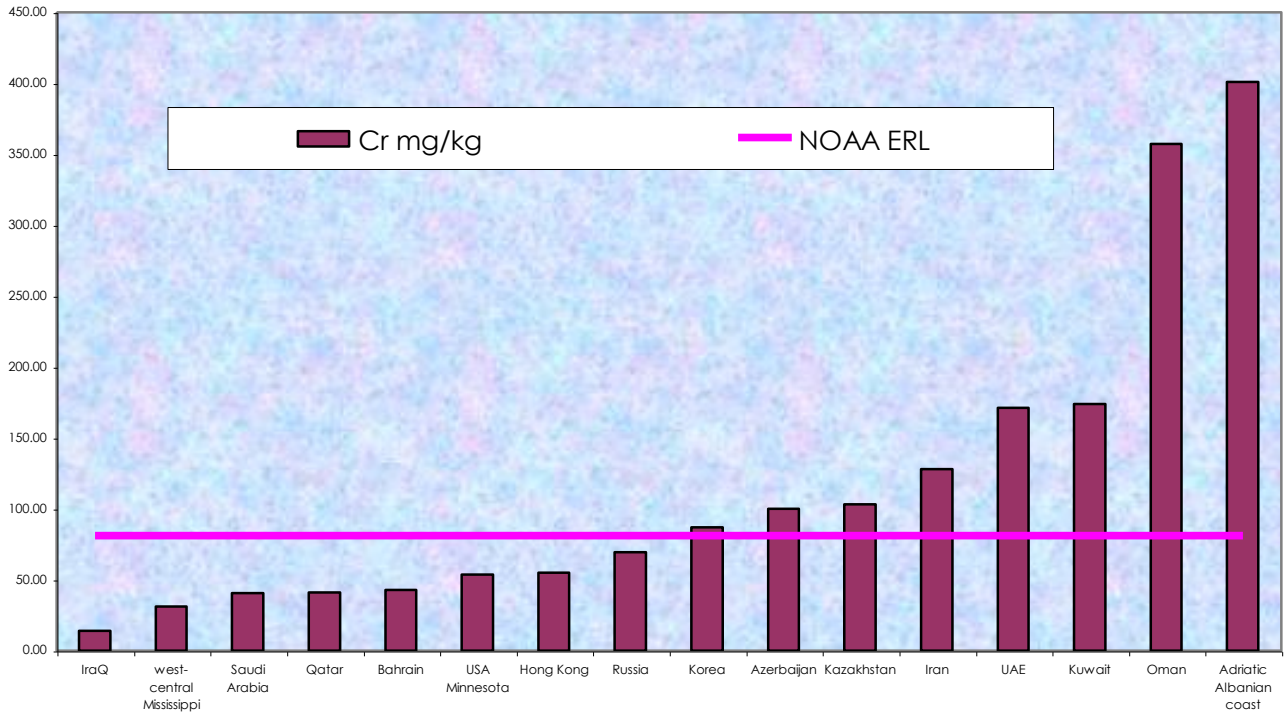


The levels of Cadmium in the marine environment of the region can't be linked to a major source. Furthermore, data on sources of cadmium input are limited. However when more complete data are available from the regional monitoring and lab-based pollution assessment studies have been carried out in all states in ROPME sea area a better understanding of the fate of cadmium will probably be achieved.

3.1.2 Chromium (Cr)

Chromium was detected in all of the sediment samples. The chromium concentrations ranged from 22.26 to 100.18 mg kg^{-1} with a mean of 42.93 mg kg^{-1}.

Figure 2-2
Chromium in Sediment



The highest concentration of 100.18 mg kg^{-1} was found at 1000 m south East of Sitra Power and Desalination Plant outfall which exceeded the NOAA ERL value of 81 mg Kg^{-1}. This elevated value could be attributed to the effect of Balexco effluent used to discharge to the surrounding area. However, all of

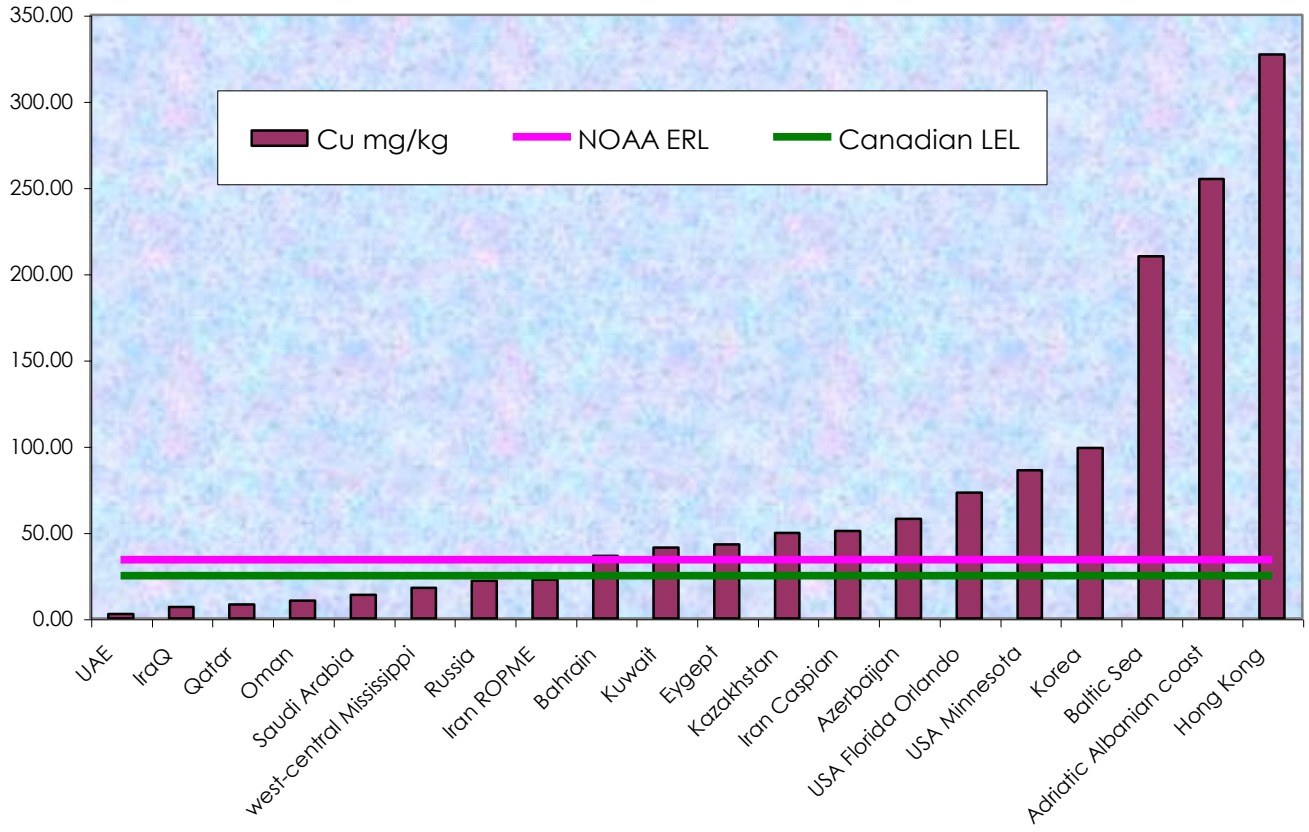
the chromium concentrations other than this value were well below the NOAA ERL of 81 mg Kg^{-1}. In addition, chromium content that is about 125 mg Kg^{-1} in ROPME Sea Area exceeds the NOAA ERL value at every location sampled during the cruise carried out in year 2001. ***SOMER (2004)*** assumed that the high concentrations of chromium stem from its high rate of natural occurrence in the region. It is worth mentioning that the natural content of Chromium in the earth crust is about 122 mg Kg^{-1}.

Compared to the Chromium levels in other parts of the World (Fig- 2.1), the average levels of Chromium in studied area of Bahrain Territorial water sediment is one of the lowest among others.

3.1.3 Copper (Cu)

Copper was detected in all of the sediment samples. The copper concentrations ranged from 14.58 to 61.23 mg kg^{-1} with an average of 35.88 mg kg^{-1}.

Figure 2-3
Copper in Sediment



The highest concentration of 61.23 mg kg^{-1} was found at Marina Club Resort station, this concentration exceeds the NOAA ERL value of 34.0 mg Kg^{-1} However, the level did not exceed the Canadian Level of Tolerance value of 110.00 mg Kg^{-1}.

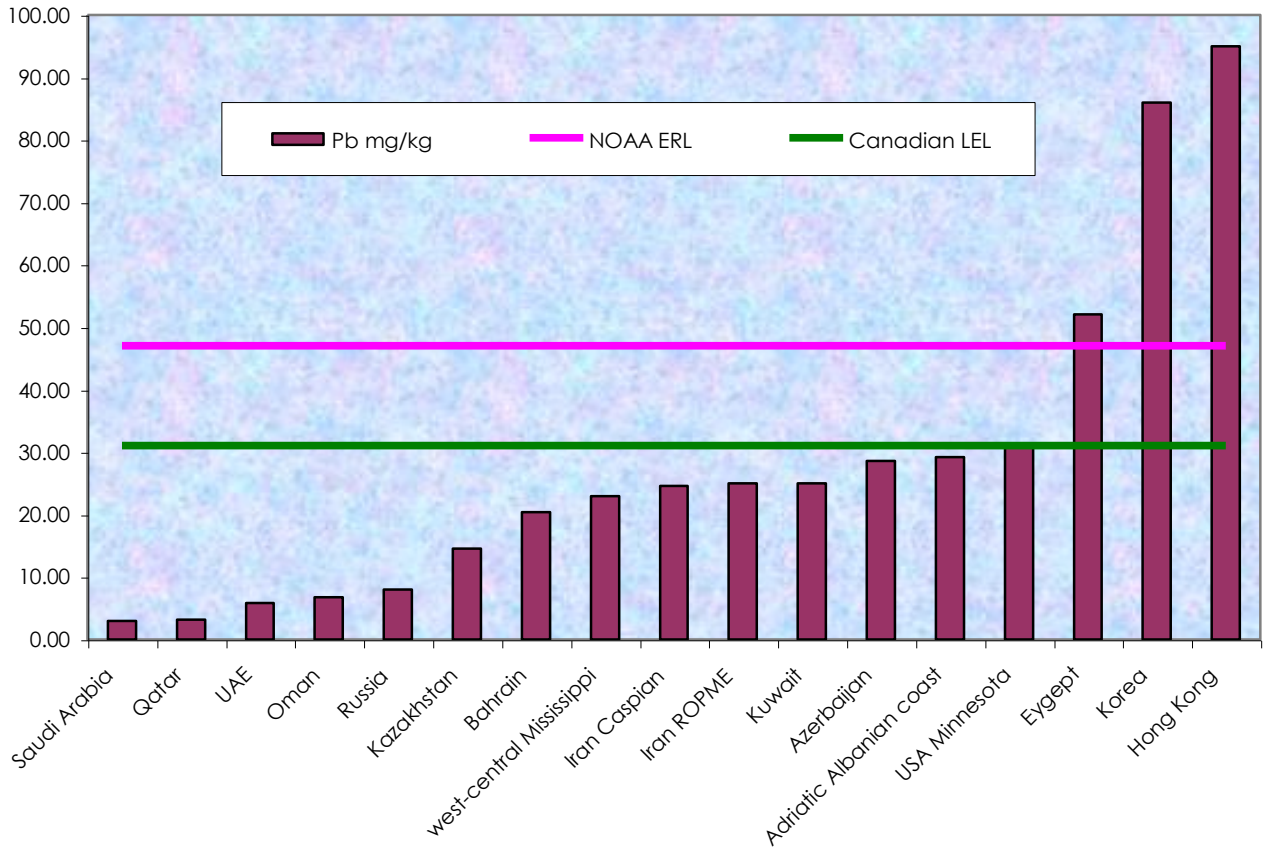
The Concentrations of copper in the sediments, illustrated in Figure 2.3, is quite similar to that shown for chromium. Again, average concentrations are almost equal to NOAA ERL value of 34.0 mg Kg^{-1}. Copper levels in marine sediments range from 2 to 740 mg Kg^{-1} (dry weight). Plants, invertebrates and fish accumulate copper. Higher concentrations of copper have been reported in organisms from copper contaminated sites than in those frown non-contaminated sites. ***WMO (1998)***

3.1.4 Lead (Pb)

Like cadmium, the lead concentrations are not very high for most sites investigated in Bahrain Sea sediment (Figure 2.4)

The average level of lead in studied area of Bahrain Territorial water sediment is about (20.35 mg kg^{-1}), while the maximum concentration (107.73 mg kg^{-1}) is found just east off the BAPCO (Bahrain Petroleum Company) Refinery, almost 1 km away from the effluent discharge, levels exceeded the Canadian Lowest Effect Level value of 31 mg $kg^{-1}$and, NOAA Effect Range Low value of 47 mg $kg^{-1}$and USEPA - Heavily Polluted Category value of 60 mg kg^{-1}. The contamination likely emanates from the industrial and refinery complex around the area situated just shoreward of the sampling site. Relatively high concentrations of lead was also observed nearby at Askar, supporting the hypothesis of a point source of contamination at the BAPCO site for lead (Pb) the effects of which diminish with distance from the source. This spatial decrease is most notable for Pb. Very high metal concentrations in sediments from near this site have been reported since the early 1980s. However, None of the lead Concentrations other than BAPCO and Askar sites exceeded the Canadian LEL of 31.0 mg Kg^{-1}.

Figure 2-4
Lead in Sediment



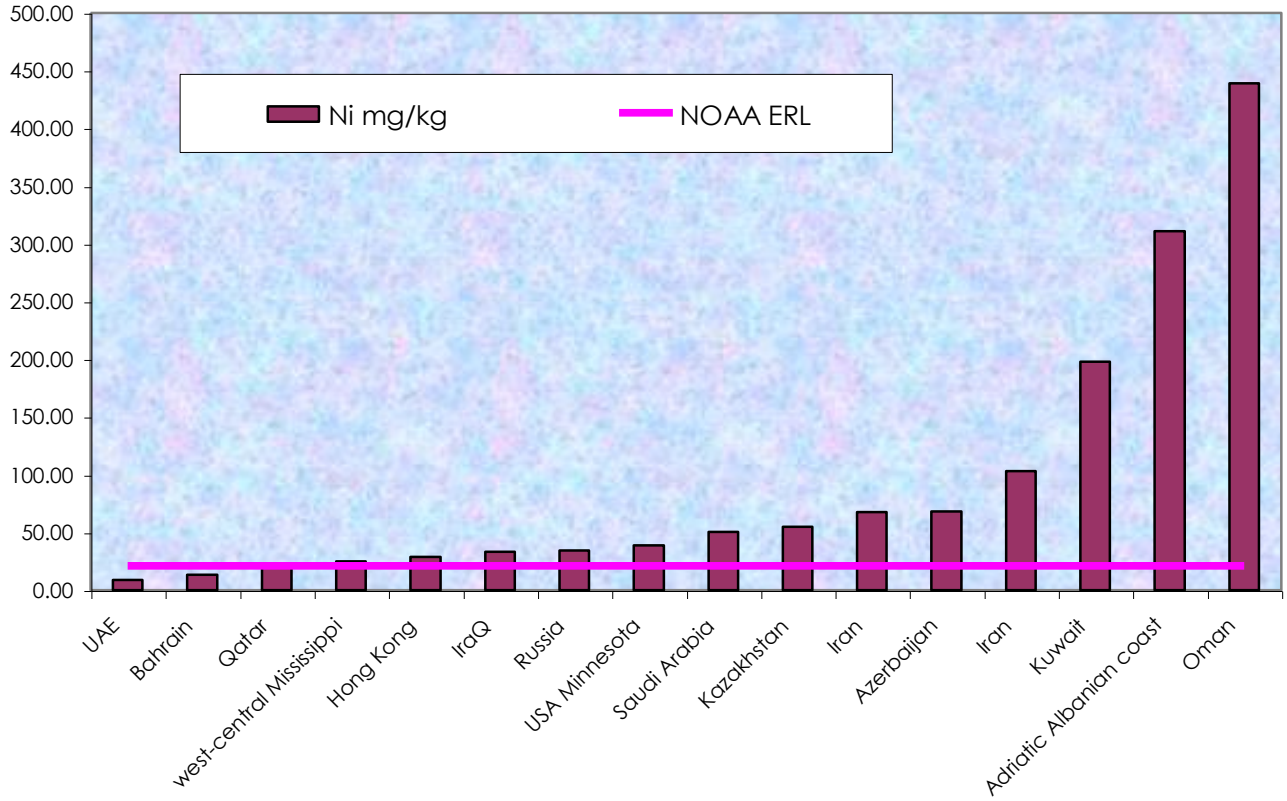
Compared to the lead levels in other parts of the World (Figure- 3-4), the average level of lead (20.35 mg kg^{-1}) in studied area of Bahrain Territorial water sediment is one of the lowest among others.

3.1.5 Nickel (Ni)

Figure 2.5 depicts the nickel average concentration for all sites investigated in the studied area. It is similar to that of cadmium, reflecting the high natural background due to mineralization. Exceptionally, nickel displays low concentrations in sediments throughout Bahrain territorial sea sediment. The NOAA ERL (21 µg g^{-1}) was never exceeded and nickel concentrations were even lower than the NOAA ERM (52 µg g^{-1}) values at several sites. The highest concentrations were found at Marina Club Resort. Nickel levels usually tend to be elevated in areas subject to release of crude oil. However, it should be mentioned that another major source of input of nickel into the marine environment is the corrosion of copper/nickel pipes and fittings used

extensively in this area whereas desalination/power plants and cooling system utilizing water. Despite all these factors, Compared to the nickel levels in other parts of the World (Figure- 2.5), the average level of Nickel in studied area of Bahrain Territorial water sediment is one of the lowest among other, and well below the NOAA ERM of 52.00 mg kg^{-1}.

Figure 2-5
Nickel in Sediment

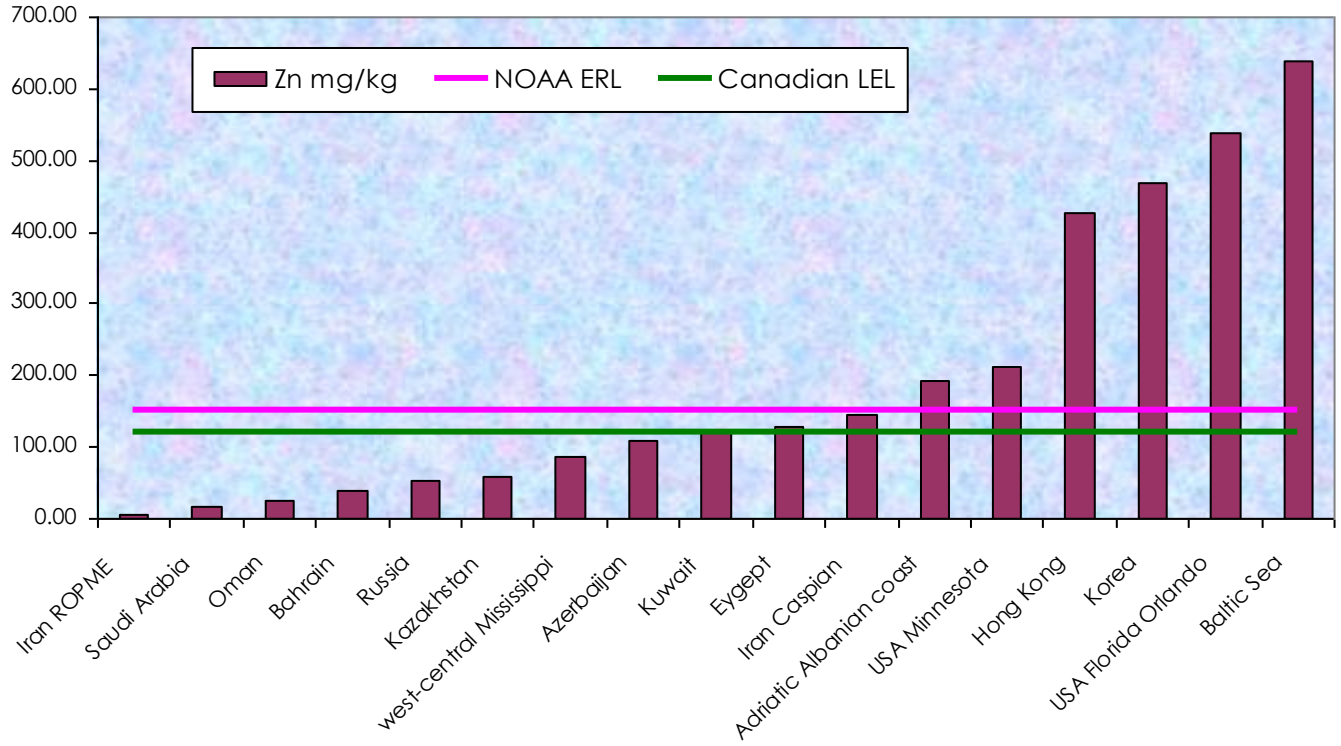


3.1.6 Zinc (Zn)

The distribution of zinc is presented in Figure 2.6. Generally the overall pattern of distribution is like that of lead and copper, again due to the grain size influence. The zinc concentrations ranged from 14.02 to 82.31 mg kg^{-1} with an average of 38.35 mg kg^{-1}. The highest concentration of 82.31 mg kg^{-1} was found at Marina Club Resort station, in which does not exceed the Canadian

LEL value of 120.0 mg Kg^{-1}. However, natural background total zinc concentrations are usually up to 100 mg Kg^{-1} (dry weight) in sediment.

Figure 2-6
Zinc in Sediment



The data suggest that similar levels were earlier reported in Askar area. In the studied area the concentration of elements are comparable to the natural background data of other investigations. And it is worth mentioning that on the basis of the total elements concentrations, the sediments from the studied areas are comparable to those found in unpolluted worldwide areas. Compared to the trace metal levels in other parts of the World (Table- 4), the levels of metals exhibited in this study, other than lead near BAPCO, are fell in the ranges reported previously for these elements in the RSA (***Fowler et al., 1993)***.

Table-6

Trace metal levels (μg/g) in sediments in Bahrain and other areas of the World

Trace metal	Cd mg/kg	Cr mg/kg	Cu mg/kg	Ni mg/kg	Pb mg/kg	V mg/kg	Zn mg/kg	Mn mg/kg	Reference
Azerbaijan	0.19	100.00	57.60	68.00	28.60	136.00	110.00	971.00	De mora et al, 2004
Iran	0.24	128.00	50.90	67.80	24.60	145.00	146.00	1111.00	De mora et al, 2004
Kazakhstan	0.25	103.00	49.50	54.80	14.60	81.20	59.90	630.00	De mora et al, 2004
Russia	0.10	69.30	21.90	34.20	8.03	84.50	52.90	455.00	De mora et al, 2004
USA Florida Orlando			73.00		1025.00		538.00		Baker, M. D., Yousef A. Y., 1991
USA Minnesota	2.36	53.50	86.00	39.00	30.80		212.00	896.00	Minnesota Pollution Control Agency, 2000
Korea		87.00	99.00		86.00		468.00		Kwon, Y and Lee C. 2001
Egypt	0.10		43.00		52.00		128.00		Egyptian Environmental Affairs Agency (1999)
Baltic Sea	4.10		210.00				640.00		Baltic Marine Environment Protection Commission, 1987
Finland	1.50								Baltic Marine Environment Protection Commission, 1987
Adriatic Albanian coast	0.45	401.00	255.00	311.00	29.20		193.00	6149.0	Celo,V and Et al, 1999
Portugal	0.16 – 0.38		22 - 46					101 - 246	Caetano, M and et al, 2002
Hong Kong		55.00	327.00	29.00	95.00		428.00	383.00	Tanner, P.A., Leong, L.S., 1997
West-central Mississippi	0.90	31.23	17.93	24.95	22.90		85.38	316.80	Mississippi Department of Environmental Quality, 1996
Bahrain	0.25	42.93	36.17	13.21	20.35		38.35	69.25	This study
Kuwait	1.25*	174.00	41.00	198.00	25*	120.00	119.00	845.00	* Anderline et al., 1986, Basaham A S. and Al Lihaibi, S S, 1993
Iran RSA	1.25		22.50	103.0	25.00	40.00	5.50	450.00	Anderline et al., 1986
Oman	0.18	357.0	10.40	439.0	6.79	48.00	26.30	310.00	Fowler et al., 1993
Qatar	0.08	40.80	8.02	20.80	3.16	32.10			De mora et al, 2005
UAE	0.11	171.00	2.62	8.60	5.88	35.50			De mora et al, 2005
Saudi Arabia	3.20	54.00	15.00	61.00	3.05	33.00	25.00	179.00	Basaham A S. and Al Lihaibi, S S, 1993
Mt.Mitchell ROPME Sea Area	.060-0.400		0.2-18	2.3-89	0.2-64	2.6-41.5	4.2-410.3	17-405	Al Abdali et al, 1996
Umitika-Maru ROPME Sea Area	0.06-0.40		2.3-142.0	1.9-109.2	1.0-64.3	1.4-99.9	4.2-410.3	8.9-517.0	Al-Majid et al, 1998

4.0 Conclusions

Overall, local source strengths and the propensity of fine-grained material to accumulate influence the distribution of contaminants in sediments of the studied area. The Bahrain territorial Sea is a shallow water environment with quite coarse sediments. They tend to often have high carbonate content.

So far, there is not yet an inventory of significant marine areas in the region of RSA where nutrients input are causing or likely to cause pollution directly or indirectly. However, it should be noted that the levels of nutrients are in many cases lower than in other areas, but in low energy and shallow bays and intertidal areas, the intensive heat of the summer months reduces the oxygen content for the point where relatively low levels of nutrients are enough to produce anoxic conditions.

As no quality standards for trace metal for Bahrain marine Sediment, an overview of critical levels of toxic was made based on compared firstly to the NOAA Marine Sediment Quality Guideline values, which designates an Effects Range Low (ERL) and an Effects Range Medium (ERM). In the absence of a NOAA-defined ERL for a substance, the Canadian Interim Marine Sediment Quality Guideline (ISQG) value has been used. A comparison between these assessment levels shows that all the measured trace metals remained within the specified limits.

It is worth mentioning that on the basis of the total elements concentrations, the sediments from the studied areas are comparable to those found in unpolluted worldwide areas, and reveal that the effect of anthropogenic enrichment upon concentration of the elements is nominal.

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