NEAR SEASHORE WATERS AND SEDIMENTS HEAVY METALS POLLUTION ALONG THE LIBYAN WESTERN COAST

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ABSTRACT

This study was carried out according to the surveys conducted at four major cities chosen as studied areas along the western Libyan coast Namely Zwara, Tripoli, Khoms and Misurata, to evaluate some heavy metals concentrations in sediments and seawaters. Sediment cores from the sea shore region were studied for the trace element contents. The average concentration of nickel, zinc, cadmium, lead, cobalt and chromium were determined. Lead, cadmium and mercury showed uniform distribution through out the core based on sediment quality guidelines. Results showed that sediments of the western Libyan coast is facing no metal pollution risks. Cadmium was found at the highest concentration ranged between 38.9-54.6 µg/Kg followed by Zn, Ni & Co i.e., 38.3, 35.4 & 22.9 µg/Kg, respectively; whereas, Cd & Cr were the lowest ranging between 2.3- 3.9 µg/Kg. Sweater heavy metals were in the range, unless they vary within limits by time.

***Keywords:*_ Heavy metals, Pollution, Mediterranean, Marine, Sediment, Libya.**

INTRODUCTION

Sediments usually polluted with various kinds of hazardous and toxic substances, including heavy metals. These accumulate in sediments via several pathways, including disposal of liquid effluents, terrestrial runoff and leachate carrying chemicals originating from numerous urban, industrial and agricultural activities, as well as atmospheric deposition. The pollution history of aquatic ecosystem was studied by several researchers such as; (Lopez and Lluch, 2000; Karbassi *et al.,* 2005; Mohamed, 2005). Many researchers have used sediment cores to study the behavior of metals (Bellucci *et al.,* 2003; Bertolotto *et al.,* 2003; Borretzen and Salbu, 2002; Lee and Cundy, 2001; Weis *et al.,* 2001). Currently, because of urbanization and industrial development environmental pollution is a major concern (Alemdaroglu *et al.,* 2003; Heyvaert *et al.,* 2000; Sadiq, 1992). Thus, understanding the transport and distribution of trace metals in estuaries is a goal of environmental chemists (Unnikrishnan and Nair, 2004). One of the most distinguishing features of metals from other toxic pollutants is that, they are not biodegradable. Sediments can incorporate and accumulate many metals added to a body of natural water. The favorable physicochemical conditions of the sediment can remobilize and release the metals to the water column. It has been stated that specific local sources such as discharge from smelters (Cu, Pb & Ni), metal based industries (Zn, Cr & Cd), paint and dye formulators (Cd, Cr, Cu, Pb, Hg, Se & Zn), petroleum refineries (AS & Pb), as well as effluents from chemical manufacturing plants may lead to metal accumulation in sediments (Al-Masri *et al.,* 2002; Bonnevie *et al.,* 1994). In fact, there is a need of controlling both point and non-point discharges and especially pollution prevention by controlling at source discharges of heavy metals from industries (Bakan and Ozkoc, 2007). Geochemical fractions such as Fe, Co, Cr, Cu, Mn, Ni, Pd and Zn were detected in the coastal sediments of central south-west coast of India, in and around Cochin, the second biggest city along the west coast of India (Balachandran *et al.,* 2003). Concentration of dissolved and particulate trace metals and their partitioning ehavior between the dissolved and particulate phases in southern upstream part of the Cochin estuarine system were studied (Unnikrishnan and Nair, 2004). Post depositional remobilization of transition metals in deepsea sediment cores from the Pacific, Atlantic and Indian oceans was reported (Mudholkar *et al.,* 1993). Sedimentation due to erosion is a significant problem leads to the contamination of the water and sediment with heavy metals and other pollutants. In the recent past, there have been increasing interests regarding heavy metal contaminations in the environments, apparently due to their toxicity and perceived persistency within the aquatic systems (Tijani, *et al.,* 2005). There are basically three reservoirs of metals in the aquatic environment: water, sediment and biota (Saha, *et al.,* 2001). The analysis of river sediment is a useful method of studying environmental pollution with heavy metals (Batley, 1989 & Goorzadi, *et al.,* 2009). The occurrence of elevated concentrations of trace metals in sediments found at the bottom of the water column can be a good indicator of man induced pollution rather than natural enrichment of the sediment by geological weathering (Wakida, *et* al., 2008). Seas and oceans became suffering of pollution due to disposal of garbage in it, chemical materials as it is now forming a great concern and danger against human and environment. Libya like other countries was not away from this kind of disturbance in the last four decades. This study was concerned with observing the rate of pollution in Libyan shores by evaluating the heavy metals pollution of marine sediments of the western coast.

MATERIALS AND METHODS

Water samples were collected for 5 sites around each city (*namely, Zwara, Tripoli, Khoms & Misurata*) covering the region of western Libyan coast. Three samples were taken in 2 liters polyethylene containers and then filtered through 0.45 µm membrane filter, which had been previously washed with metal-free water and dried. The extract was digested using 6N HNO_3 near dryness then diluted with de-ionized water to 50 ml. (Standard Methods, 1998). Sediment samples were taken from eastern and western sites only. Samples were collected for 5 months (Jan-May) from the east and west of each location. Samples were collected using clean plastic scoop and stored in polyethylene bags, dried at 105°C for metals analysis. Two grams of the triplicate subsamples from each site were digested with a mixture of nitric acid and perchloric acid at 550°C for 6 hours. Cooled, filtered and made up to 50 ml with distilled water. The concentrations values of Ni, Cd, Co, Pb, Cr and Zn were determined in water and sediments using air-acetylene flame, atomic absorption spectrophotometer: AAS, *Philips, Pye Unicam 9100*, according to Smith *et al*., (1981) and Abaychi & Douabul, (1985).

RESULTS AND DISCUSSION:

Least Significant Differences: LSD intervals results generally revealed that Tripoli sea sediments showing the lowest heavy metals levels; where Zwara location reflecting the highest concentrations, Fig (1). Interactions plots (Fig 1) proved higher levels of the eastern sites than the western once, except in Komes.

Lead (Pb):

The highest value of lead ions concentrations on near sea shore sediment was obtained in the western site of Khoms 54.30 µg/Kg, while the lowest level detected on western Tripoli samples, i.e., 38.9 µg/Kg, Table (1). The highest values of Lead concentration were detected in Zwara and Khoms, i.e., 1.96 µg/L, followed by Tripoli and Misurata, Table (2). In general, the site 300 meters eastern of Komes showed the lowest values (0.98 µg/L). Theses obtained results were much lower than that reported by Rossi & Gamet (2008) of the Mediterranean coastal water and Abdel-khalek (2009) Alexandria coast, and in agreements with the several other authors, such as Cobelo *et al.,* (2004), Pekey *et al.,* (2006) and Guerra *et. al.*, (2007).

Table (1): Heavy Metals Average Concentrations in Sediment:

Location (*City*)	**Site** (*direction*)	**Heavy Metals Concentrations (µg/Kg)**					
		Pb	***Cd***	***Co***	***Ni***	***Cr***	***Zn***
Zwara	*East*	50.90	3.90	22.80	35.40	3.80	26.00
	West	47.10	3.10	22.90	29.20	3.80	19.40
Tripoli	*East*	45.30	3.10	13.20	27.10	2.20	15.20
	West	38.90	3.10	14.40	25.00	2.40	12.80
Khoms	*East*	39.80	2.30	13.20	20.80	2.20	10.40
	West	54.30	2.90	22.80	28.10	3.90	12.50
Misurata	*East*	41.70	3.70	16.20	27.10	2.70	38.30
	West	44.40	3.60	18.00	18.30	3.00	26.70
Sediment threshold values (mg/kg), **Bakan and Ozkoc, (2007)**		***30.20***	***0.68***	***20.00***	***15.90***	***52.30***	***124.60***

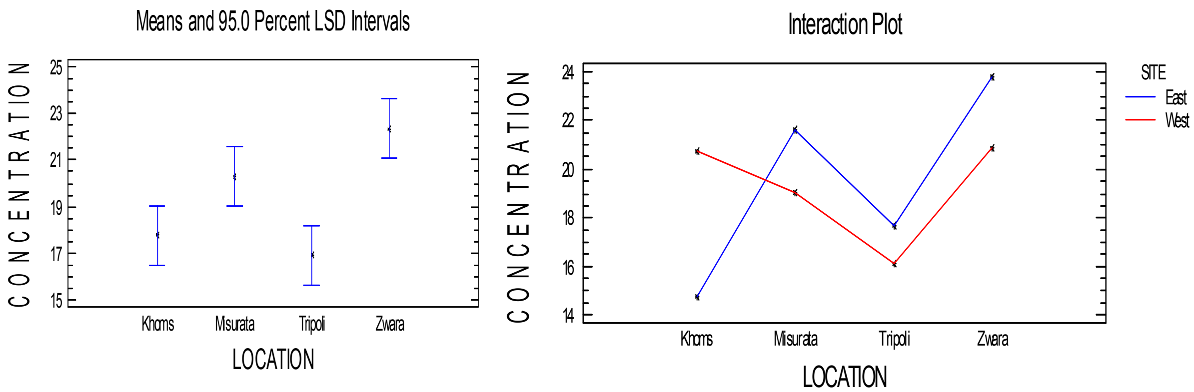


Fig (1): heavy metals concentrations in different locations and sites.

Table (2): Seawater heavy metals levels in the studied cities different sites:

Location (*City*)	**Site** (*distance, direction*)	*Heavy Metals Concentrations (μg/L)* Co	Ni	Cd	Pb	Cr
Zwara	*10W*	1.55	6.63	0.230	2.83	0.195
	300W	1.71	6.48	0.283	2.72	0.195
	500	1.96	6.63	0.554	2.89	0.162
	300E	1.55	6.75	0.334	2.50	0.246
	10E	1.55	7.00	0.334	2.07	0.246
Tripoli	*10W*	1.74	6.00	0.407	2.50	0.260
	300W	1.55	7.00	0.324	2.61	0.195
	500	1.63	7.50	0.502	2.50	0.130
	300E	1.47	6.37	0.334	3.15	0.162
	10E	1.30	6.00	0.209	2.17	0.162
Khoms	*10W*	1.55	6.88	0.599	2.17	0.195
	300W	1.96	7.50	0.470	2.28	0.162
	500	1.39	6.25	0.345	2.39	0.214
	300E	0.98	7.50	0.596	2.17	0.227
	10E	1.63	6.50	0.360	3.15	0.130
Misurata	*10W*	1.79	6.63	0.334	3.26	0.227
	300W	1.55	6.48	0.324	2.50	0.162
	500	1.79	7.13	0.575	2.72	0.124
	300E	1.06	5.00	0.460	2.28	0.214
	10E	1.87	5.50	0.272	3.04	0.130
Seawater threshold values (μg/ L), **UNESCO, (1978)**		***0.05***	***2.00***	***0.11***	***0.03***	***0.20***

Cadmium (Cd):

The maximum value of cadmium ions of marine sediments was observed on the eastern site Zwara, 3.90 μg/Kg , where the lowest level was detected on the eastern part of Khoms site. Seawater cadmium values in general were higher in Komes and the lowest were in Misurata; they were 0.599 μg/L at 10 meters western of Khoms and 0.209 μg/L 300 meters eastern Khoms. These results are lower than the results reported by Rossi & Gamet (2008) Mediterranean coastal water and Abdel-khalek (2009) Alexandria coast. These results were in agreements with the of several authors, such as Lee, *et al.,* (2008), Akan *.et. al* (2009) and Stakeniene *et al.,* (2011).

Cobalt (Co):

The Cobalt ions concentrations in the marine sediments ranges from 2.20 – 3.80 μg/Kg , in all studied sites. Average observed seawater cobalt values in general in Zwara were about 1.664 μg/L, followed by Misurata and Tripoli; where the levels in Khoms around 1.502 μg/L. while the highest value were 1.960 μg/L in Zwara and Khoms and the lowest was 0.98 μg/L at 300 meters western of Khoms. These values were similar to that recorded by Emora, *et al.,* (1995) and Hussain *et al.,* (2010) Saudi Arabian coast line of the aqaba bay and These results were in agreements with the of several authors, such as Guerra *et al.,* (2005); Thilagavathi, *et al.,* (2011); Palanisamy, *et al.,* (2007) and Baolin, *et. al.,* (2011).

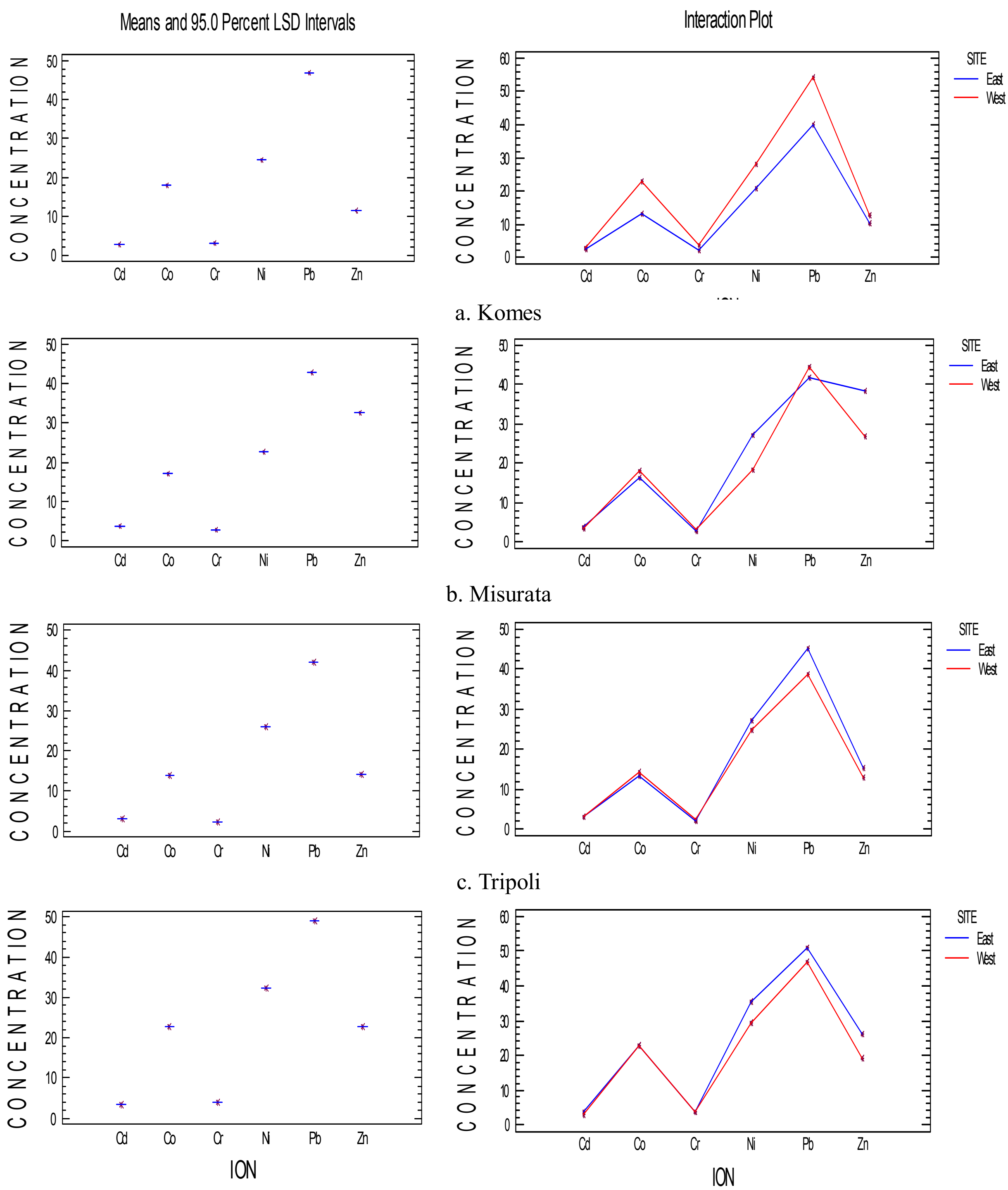
Nickel (Ni):

Nickel concentrations in near sea shore sediment ranges between 20.80 - 35.40 μg/Kg. the highest value of Ni was detected in eastern site of Zwara (35.40 µg/Kg), where the lowest was 20.80 µg/Kg in the west of Misurata. In average point of view, nickel levels showed nearly similar trend in all locations seawater; But it was much higher, i.e., 7.50 µg/L in 2 sites in Khoms and at 500 meters deep Tripoli seawater. Observations of Misurata seawater revealed 5.00 & 5.50 µg/L at 10 & 300 meters eastern the city. Concentrations findings were much higher than that of Emora *et al.,* (1995) eastern harbor of Alexandria Abdel-khalek (2009) Alexandria coast but were in good agreement with that observed by Hussain *et al.,* (2010) Saudi Arabian coast line of the Aqaba bay. These results were in agreements with several authors, such as Cobelo *et al.,* (2004), Oyeyiola *et al.,* (2006) and Cuculic, *et al.,* (2011).

Chromium (Cr):
The highest value of Chromium ions concentrations near sea shore sediment was obtained in the western site of Khoms 3.90 µg/g, while the lowest level detected on eastern site of Tripoli & Khoms samples, i.e., 2.20 µg/g, Table (1). The lowest value detected for chromium was 0.124 µg/L at 500 meter of Misurata deep seawaters, while the highest was at 10 western of Tripoli city. Where in generals, the average concentration of Zwara was the highest (0.209 µg/L) and around 0.171 µg/L in Misurata. Concentrations of Cr ions obtained were much higher than that of the resulted reported by Emora *et al.,* 1995 eastern harbor of Alexandria and Hussain *et al.,* (2010) Saudi Arabian coast line of the aqaba bay but were relatively agreement with those observed by Olufemi *.et al.,* (2011) Ubeji river .These results were in agreements with the several authors, such as El-Rayis *et. al*., (2005) Tankere and Statham (1996) and Hu NingJing *et al*.,(2010).

Zinc (Zn):
The highest value of lead ions concentrations on near sea shore sediment was obtained in the western site of Khoms 54.30 µg/Kg , while the lowest level detected on western Tripoli samples, i.e., 38.9 µg/Kg , Table (1). The lead ions levels were stable on Tripoli and Misurata marine sediments. Fig. (2). Theses obtained results were much lower than that reported by Rossi & Gamet (2008) Mediterranean coastal water and Abdel-khalek (2009) Alexandria coast, and in agreements with the several other authors, such as Cobelo *et al.,* (2004), Pekey *et al.,* (2006) and Guerra *et. al*., (2007).

According to the statistical analysis (*LSD intervals results & Interactions plots*), Komes location revealed higher levels of Pb than Ni, Co, Zn, Cr & Cd, Fig (2). These were more accumulated in the western sites than east, in lower differences between Cr and Cd. According to the statistical analysis, Misurata location revealed higher levels of Pb than Ni, Co, Zn, Cr & Cd. These were more accumulated in the western sites than east, in lower differences between Cr and Cd. According to the statistical analysis, Tripoli location revealed higher levels of Pb than Ni, Co, Zn, Cr & Cd. These were more accumulated in the western sites than east, in lower differences between Cr and Cd. According to the statistical analysis, Zwara location revealed higher levels of Pb than Ni, Co, Zn, Cr & Cd. These were more accumulated in the western sites than east, in lower differences between Cr and Cd, Fig (2).



a. Komes

b. Misurata

c. Tripoli

d. Zwara

Fig (2): Seawater Heavy Metals Levels among the Libyan Western Coast.

In conclusion the highest values of total heavy metals showed during winter and spring seasons 2.943 µg/Kg & 2.848 µg/L. The level of Ni & Co ions records highest values then values of Pb ions 5.522 µg/Kg & 2.318 µg/Kg &1.395 µg/Kg respectively. And other element.

The maximum values of heavy metals detected at Musrata sea water during winter seasons 2.901 µg/Kg which may be attributed to the effluents of industrial wastes discharged. And the lowest values obtained at Tripoli sea water during autumn2.841 µg/L. Highest level of Cd & Co and Cr ions observed during summer seasons at Alkomes sea water 0.467 µg/Kg &3.086 µg/Kg & 0.619 µg/Kg respectively. Where the highest values of Ni & Pb ions showed during spring at Musrata sea water 6.585 µg/Kg &2.568 µg/Kg respectively. The concentration of heavy metals observed in sediment followed this order: Pb< Ni < Zn< Cr< Cd <Co. In conclusion the marine environment in the Libyan coastal sediments is non-polluted zone by the studied heavy metals. It is recommended that point and non-point pollution sources should be managed through several governmental and social authorities and legislations.

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