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Trace Metal Behavior in Mediterranean-Climate Coastal Bay: El-mex Bay, Egypt and its Coastal Environment

Maha Ahmed Mohamed Abdallah

National Institute of Oceanography and Fisheries, Alexandria, Egypt

Abstract: The distribution of heavy metals in El-Mex Bay located in Northern Egypt was studied. Eight metals (Cd, Cr, Co, Cu, Zn, Pb, Mn and Fe) were determined in water, Suspended Particulate Matter (SPM) and sediments. The Bay presents higher metal concentrations in aqueous Cd, Co and Pb are above the chronic freshwater quality criteria for aquatic life. Most of the dissolved trace metals displayed a negative association with salinity, indicating Omoum Drain as a source of inputs for them. In the Bay water, Fe, Mn and Zn are the most abundant elements in suspended particulate matter whereas Co the less abundant. El-Mex Bay exhibited relatively lower concentrations of all the examined metals in sediments, comparing with other regions in the world. The distribution coefficient, *Kd*, of Zn, Cd, Mn and Cu decreased with SPM, consistent with the so-called ''particle concentration effect''. Significant inter-relationships existed between the concentrations of certain metals in SPM, suggesting similar sources for and/or similar geochemical processes controlling such metals.

Key words: Trace metals · distribution coefficients · suspended matter · sediments · water

INTRODUCTION

El-Mex Bay is a part of Alexandria coast on the Mediterranean Sea, it is adjacent to Alexandria City center that is populated with about six million inhabitants, in addition it consider as one of the main fishing sources in Egypt. The contaminants are introduced through waterway and through several landbased sources into the Bay.

El-Mex Bay having several industrial plants situated close to the coast and directly discharges its effluents into it. In addition this Bay is an estuarine zone of huge agricultural drain (Omoum Drain), which crosses areas of intensive agriculture and a county with rapidly growing population density and industrial activities, its discharge rate about 2547.7×10^6 m^3/year [1]. As a result, large amounts of nutrients, organic compounds, heavy metals and Suspended Particulate Matter (SPM) were supplied to the bay.

Besides aquatic inputs, El-Mex Bay is also exposed to atmospheric pollution from the same activities that cause aquatic pollution. Identification and quantification of trace metal sources to the bay, as well as the fate of those trace metals in that ecosystem, are important environmental scientific issues. Earlier studies on the bay tackled some of these aspects, but most of them focussed only on metals in sediments, including their speciation, distribution and mobility [1-3], As a result, a general picture of the metal sources, their distribution in and between the various compartments of the bay and their bioavailability are not, or only to a limited extent, available.

The present study investigates the distribution of heavy metals in El-Mex Bay, Northern Egypt. For this purpose the concentrations of eight metals (Cd, Cr, Co, Cu, Pb, Zn, Mn and Fe) were determined in different compartments of the bay (water, suspended particulate matter and sediments). Distribution coefficients of metals between water and particulate phases were calculated and discussed.

MATERIALS AND METHODS

Sampling

Surface water: Surface water samples were taken at 8 stations covering El-Mex Bay during three sampling campaigns, organized in February 2007 and September 2007. All sampling points are shown in Fig. 1. Sampling details for each expedition are as follows: two stations [4, 7] in the western part; (6) in the middle part; (1) Omoum

Corresponding Author: Dr. Maha Ahmed Mohamed Abdallah, National Institute of Oceanography & Fisheries, Alexandria, Egypt

Fig. 1: Map of El-Mex Bay showing the main sampling stations

Drain mouth; [5, 8] at the entrance of Alexandria Western harbour and [2, 3] in the southern part at the front of chloroalkali plant and petroleum refinery respectively. Water samples were collected by opening and closing pre-cleaned bottles approximately 20 cm below the water surface and stored in the bottles in individual polythene bags in cool boxes filled with ice packs.

Sediment: Surficial sediment samples were carried out in May 2007 and collected by Van Veen Grab from eight stations (Fig.1). After sampling, sediments were stored into plastic bags and placed in a cooler at 4°C, then transported to the laboratory for analysis. Samples were dried in an oven at 50°C for 3-4 days. Lightly ground in an agate mortar for homogenization, sieved to pass <63 µm [4] and prepared for analysis.

Analysis: After transportation to the laboratory water samples were filtered through 0.45-µm membrane filter for separation of Suspended Particulate Matter (SPM). Filtered samples (dissolved phase), were acidified using nitric acid and trace metals were preconcentrated and measured using Atomic Absorption Spectrophotometry, the procedures adopted followed [5, 6] for dissolved phase of water. Filters loaded with SPM were dried in a ventilated oven at 45°C for 2 days, re-weighed and digested with a mixture of HNO_3/HCl (4/1 v/v) at 60°C in an oven for 12 h, after cooling digestions were diluted to 30 ml with Milli-Q water.

The powdered and dried sediments were digested in a mixture of HF-$HClO_4$-HNO_3 [7] and brought into solution in 0.5M HCl (12 ml) using Milli Q water. Samples were analyzed on a flame AAS (Varian Techtron-Model 1250). Blanks were included in each batch of analysis. Calibration standards were regularly performed to evaluate the accuracy of the analytical method. The accuracy of the analytical procedure was checked using a triplicate analysis of certified reference material (BCSS-1) from the National Research Council of Canada.

RESULTS AND DISCUSSION

Dissolved trace metals: Dissolved trace metals in El-Mex Bay ranged from 0.66 to 6.45, from 1.48 to 7.06, from 7.37 to 20.46, from 3.69 to 4.90, from 2.65 to 26.14 and from 20.79 to 59.29 µg/L, respectively, for Cd, Cr, Co, Cu, Pb and Zn (Table 1). In comparison with other natural water system (Table 2), dissolved trace metal concentrations in El-Mex Bay are at low and safe for Cu and Zn [8-10]. On the other hand, Cd, Cr, Co and Pb represent high level comparing with that at other sites includes other sites on Egyptian Mediterranean coast and in the natural water. The salinity profiles of eight dissolved trace metals are shown in Fig. 2. It is clear that

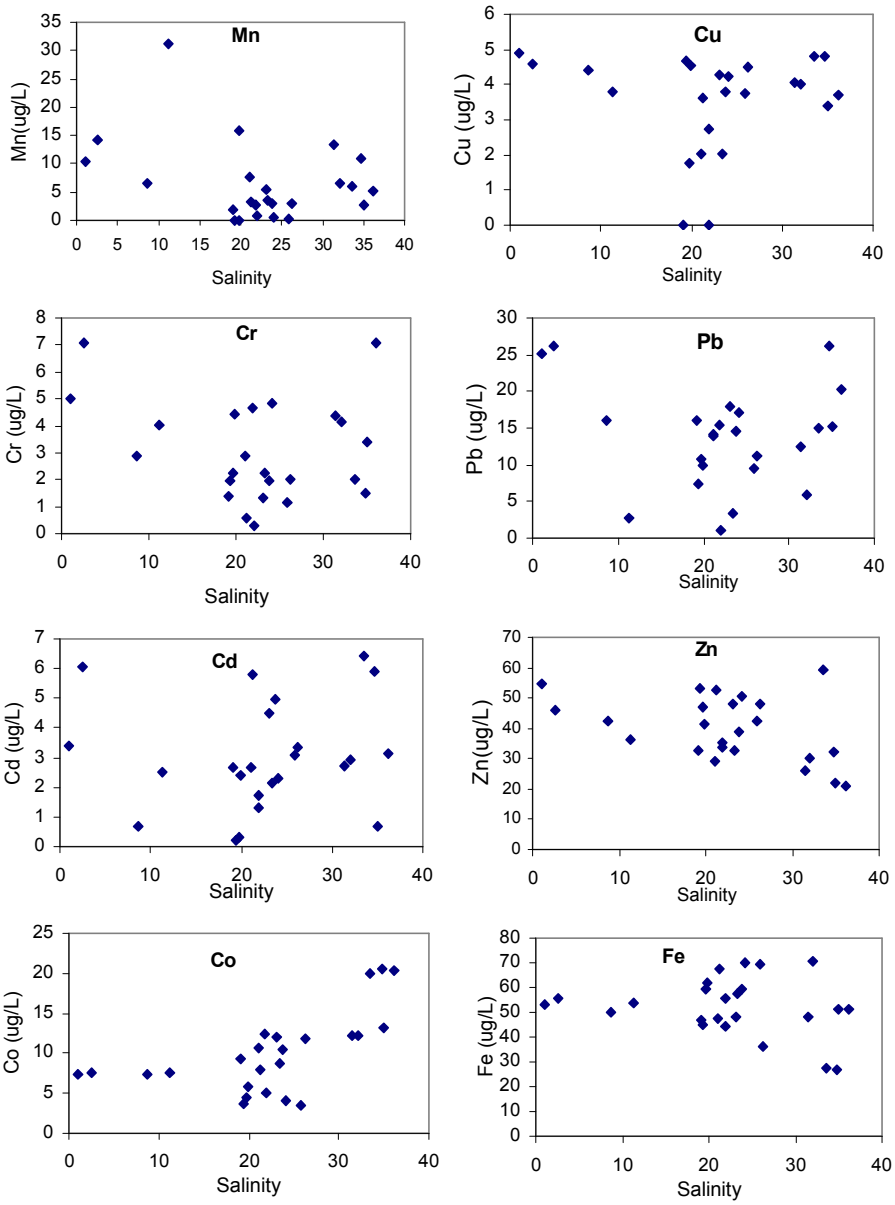

Fig. 2: The concentrations of eight trace metals in water as a function of salinity in El-Mex Bay

the trace metals did not show strong monthly variations. Different metals displayed different salinity relationships. Concentrations of all dissolved metals, with the exception of Cd and Co and in particular Mn, Zn and Fe tended to decrease with salinity, consistent with similar behaviour reported in Conwy estuary in England [11].

In general, dissolved Cr, Co, Pb and Cu concentrations in the bay were relatively homogeneously distributed. The concentrations of Zn and Cd were more variable. The western, eastern and southern parts are more contaminated than the middle and off Omoum drain mouth because the inflow from both Western Harbour (eastern part) and Dekhaila Harbour (western part) in addition the industrial outfalls in the southern part affected El-Mex Bay water. The order of magnitude of dissolved metals ranked as Zn>Pb>Co>Cu>Cr>Cd.

Metals in Suspended Particulate Matter (SPM): Altogether eight metals including Cd, Cr, Co, Cu, Pb, Zn, Mn and Fe were determined in suspended particulate matter (SPM). The means, median and standard deviations of total concentrations for each metal are listed in Table 1.

Table 1: Descriptive statistics on dissolved and particulate metal concentrations in El-Mex Bay

Elements	Range	Mean	Median	±SD
	Dissolved form (mg/L)			
Cd	0.66-6.45	3.12	2.8	2.1
Cr	1.48-7.06	3.68	3.7	1.7
Co	7.37-20.46	14.15	12.7	5.5
Cu	3.69-4.90	4.29	4.3	0.46
Pb	2.65-26.14	14.19	15.1	7.5
Zn	20.79-59.29	33.58	31.1	12.7
Mn	2.7-31.28	10.32	6.5	9.1
Fe	27.21-70.91	47.58	50.8	14.3
	particulate form (mg/g)			
Cd	N.D-6.71	2.52	2.17	2.3
Cr	0.48-4.66	2.51	2.39	1.9
Co	N.D-0.41	0.13	0.13	0.1
Cu	0.18-14.16	7.00	7.74	4.6
Pb	N.D-14.48	2.22	0.24	5.0
Zn	5.40-37.99	21.49	26.43	12.5
Mn	5.40-46.58	24.24	25.20	15.8
Fe	125.84-947.24	539.69	510.72	282.7
	Sediments (mg/g)			
Cd	2.54 -7.54	4.97	5.10	1.7
Cr	12.2 -102.7	38.65	19.70	34.7
Co	1.37 -10.3	6.41	6.41	2.9
Cu	3.29 -47.38	17.53	9.45	16.3
Pb	8.80 -88.63	48.64	57.17	25.3
Zn	51.35 -448.34	222.71	238.42	134.6
Mn	159.31 -361.98	250.85	238.51	66.3
Fe	512.86 -2490.59	1683.05	1755.02	801.8

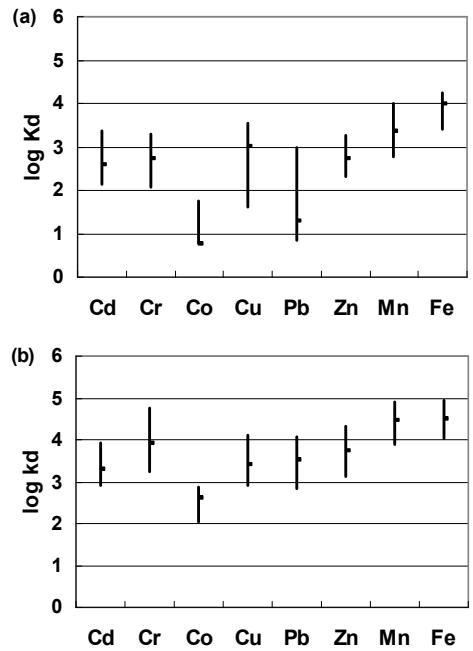

Fig. 3: Distribution Coefficient (log kd) of metals in El-Mex Bay (a) ratio of the metal concentration in SPM (ug/kg) to dissolved metal concentration (ug/L); (b) ratio of metal concentration in sediments (ug/kg) to dissolved metal concentration (ug/L)

Table 2: Average concentrations of dissolved trace metals (mg/L) in El-Mex Bay and at other regions

Study area	Cd	Cr	Co	Cu	Pb	Zn
Darwin Harbour[a]	0.006	-	0.025	0.281	0.008	0.132
Scheldt estuary[b]	0.09	-	-	1.37	0.087	4.50
Balaton lake[c]	0.002	-	0.066	0.49	0.14	0.73
Eastern Harbour[d]	N.D-2.5	N.D-2.88	0.3-5.16	0.6-12.2	0.4-18.8	1.0-39.8
Abu Qir Bay[e]	N.D-4.3	N.D-4.82	0.5-38.5	0.3-4.17	2.64-54.0	0.4 -117
Metals in Natural waters[f]	<1	-	<1	10-100	<10	<5000
El-Mex Bay[g]	0.66-6.45	1.48-7.06	7.37-20.46	3.69-4.90	2.65-26.14	20.79-59.29

[a]Munksgaard and Parry (2001)10 [b]Turner *et al*. (1998)18 [c]Nguyen *et al*. (2005)15 [d]El-Nady (1996)19 [e]El-Nady (1996)19 [f]Galvin (1996)8 [g]This study

Table 3: Spearman correlation coefficients for inter relationship (r2) between the total concentrations of particulate trace metals and SPM concentration

	Cd	Cr	Co	Cu	Pb	Zn	Mn	Fe	SPM
Cd	1.00								
Cr	0.79*	1.00							
Co	0.71*	0.52	1.00						
Cu	-0.21	-0.16	-0.09	1.00					
Pb	-0.33	-0.03	-0.21	0.17	1.00				
Zn	0.94*	0.84*	0.74*	-0.07	-0.37	1.00			
Mn	0.78*	0.75*	0.68	-0.38	-0.29	0.75	1.00		
Fe	0.77*	0.56	0.84*	0.27	-0.26	0.86*	0.47	1.00	
SPM	-0.55	-0.64	-0.31	-0.19	-0.45	-0.58	-0.28	-0.53	1.00

*Significant at $p<0.01$ (n = 24)

Table 4: Average concentrations of trace metals (mg/g) in El-Mex Bay sediments and at other regions

Study area	Cd	Cr	Co	Cu	Pb	Zn	Mn	Fe
Cochin estuary, India[a]	14.94	-	-	53.15	71.28	1266	-	61800
Jurujuba sound, Brazil[b]	-	-	-	51.0	61.0	158.0	-	13000
Tolo harbour, Hong Kong[c]	-	-	-	84.0	144.0	270.0	-	-
Izmit Bay, Turkey[d]	4.9	74.3	-	67.6	102.0	930.0	-	-
Koahsiung Harbour, Taiwan[e]	0.1-6.8	0.2-900	-	5-946	9.5-470	52-1369	-	-
Eastern Harbour, Egypt[f]	3.8	-	32.29	14.09	-	64.49	95.08	582.67
Mean crust[g]	0.11	100	-	50	14	75	41000	9500
El-Mex Bay, Egypt[h]	4.97	38.65	6.41	17.53	48.64	222.71	250.85	1683.05

[a]Balachandran *et al.* (2005)20, [b]Baptista Neto *et al.* (2000)21, [c]Owen and Sandhu, (2000)22, [d]Pekey (2006)23, [e]Chen *et al.* (2004)24, [f]Abdallah and Abdallah (2007)25, [g]Bowen, (1979)15, [h]This study

Significant relationships between SPM and each of Fe, Cr, Zn and Cd were obtained (Table 3). Such distribution profiles could be due to the fact that suspended particles are constantly interacting with trace metals and hence depending on the kinetics and reversibility of such reactions, the concentrations of metals in SPM may not change significantly during a limited period of time [11].

The concentrations of metals in SPM fluctuated throughout the bay. Fe, Co, Co, Zn, Cu and Cd tended to show trend of decreased concentrations seaward. A similar behavior of Zn, Mn and Fe in suspended particles has also been reported in Conwy estuary [11] suggesting mixing of river-borne material of high metal content with marine or re-worked estuarine sediment of lower metal content.

Many previous studies [e.g. 12] have identified sediment concentration as a very important parameter in trace metal partitioning in estuaries. It is important to assess to what extent the concentration of SPM can affect trace metal levels in SPM. All eight metals showed an inverse relationship with SPM concentration, although the most significant relationship was found for Cd, Cr, Zn and Fe (Table 3). The results are consistent with the findings by [13]. Similar inverse relationships have also been reported in many laboratory-based studies [12]. Such a trend may be explained by the fact that when SPM concentrations are low, the particles tend to be of fine particle size and be enriched in trace metals [13].

As trace metal concentrations in both SPM and water have been determined, this provided a good opportunity to study the equilibrium distribution of metals. Calculating the distribution coefficients (*K*d) of metals that defined as the ratio of the metal concentration in particulate matter (µg/kg) to the dissolved metal concentration (µg/L) have been calculated performed this. *K*d depends on the nature of suspended solids or sediments, geochemical parameters of the water and specific characteristics of each element [14,15]. The logarithmic values of *K*d are shown in Fig. 3a. The log *K*d values ranged from 2.89 to 5.69 L/kg. Fe, Cr and Mn exhibited the higher values. The ranking of log *K*d values in El-Mex Bay is Fe >Cr >Mn > Zn> Co> Pb ~ Cd> Cu and lower association with particulate matter was observed for Cu in El-Mex Bay.

Metals in sediments: The total metal concentrations in sediments are shown in Table 1. Station 5 exhibited higher concentrations of nearly all the examined metals. The concentrations of metals in sediments from the Bay followed the order: Fe >Mn > Zn >Pb >Cu >Cr > Co > Cd. The distribution coefficients of metals, defined as the ratio of the metal concentration in sediment (µg/kg) to the dissolved metal concentration (µg/L) are shown in Fig. 3b. The values of log *K*d ranged from 2.05 to 4.71 L/kg. The ranking of log *K*d values were found in the Bay; Fe, Mn and Cr presented the higher distribution coefficients whereas, Co the lower (Fe~Mn>Cr>Cu~Pb >Zn >Cd > Co in El-Mex Bay). Generally, the distribution coefficients of examined elements are low and, within the range reported for natural water [16].

Most metals occurred at higher concentrations in sediments than in SPM. Co and Pb were found at 22-49-fold, Mn, Zn and Cr at 10-15-fold and Cd, Cu and Fe at 2-3-fold higher concentrations in sediments. However, similar concentrations in sediments were The concentrations of heavy metals in sediments from El-Mex Bay were compared with other results concerning sediments from various marine environments presenting various levels of contamination. Values were compared results with the background concentrations of elements [15] as shown in Table 4. The following observations were made: (1) when compared with the elemental background compositions, surface sediments were observed to be not contaminated with Cr, Cu and Mn, however, other

elements, Cd, Pb, Fe and Zn, with greater anthropogenic inputs, were observed to be enriched in the Bay sediment samples and (2) most of the element concentrations were lower than other areas reported in the literature (Table 4).

Inter-element relationships: As some trace metals may originate from similar sources and have similar reactivates towards biological and non-biological particles, it is probable that some of them may have their particulate-bound concentrations closely related to each other. As shown in Table 3, a significant relationship was found between total Cd and both of Cr and Mn in SPM ($r^2 = 0.79$ and 0.79 respectively) and between Fe and Cd ($r^2 = 0.77$). More significant correlations existed between Cd and Zn ($r^2 = 0.94$) and between Zn and Cr ($r^2 = 0.84$) and between Fe and Co ($r^2 = 0.84$) and between Fe and Zn ($r^2 = 0.86$). Some other significant relationships were also shown in Table 3. Similar correlations were also found between various metals in SPM in the Scheldt estuary [17] and in Conwy estuary [11].

The concentrations of heavy metals in sediments from other regions are shown in Table 4. The concentrations of Cd, Cr, Cu, Co, Pb, Zn and Fe in El-Mex Bay sediments are relatively lower than the other regions, on the other hand the concentrations of Cd, Cu, Zn, Mn and Fe in the sediments are higher than that recorded in the Eastern Harbour.

Most metals occurred at higher concentrations in sediments than in SPM. Pb and Co were found at 22-49-fold, Mn, Zn and Cr at 10-15-fold and Cd, Cu and Fe at 2-3-fold higher concentrations in sediments.

CONCLUSIONS

Eight heavy metals (Cd, Cr, Cu, Fe, Mn, Co, Pb and Zn) were determined in water, suspended particulate matter and sediments of El-Mex Bay located in Northern Egypt. The Bay exhibited higher concentrations in water, above the natural water quality criteria, for Cd, Co and Pb. El-Mex Bay exhibited relatively lower concentrations of all the examined metals in sediments, comparing with other regions in the world. Zn, Fe and Mn are the most abundant metals in suspended particulate matter and in sediments, while Zn, Fe, Pb and Cr are the most abundant metals in water.

The distribution coefficient, *Kd*, of Zn, Cd, Mn and Cu decreased with SPM, consistent with the so-called ‘‘particle concentration effect’’. This phenomenon can probably be explained by the mixing of suspended particles of different size and character, presence of colloidal particles in solution and potential desorption of metals from SPM in the presence of salts. The concentration of SPM decreased with increase in salinity, indicating a dominant supply of particulate matter from river inputs. Particulate metals associated with SPM decreased with increasing SPM concentrations; due probably to the higher levels of trace metals in fine-sized particles at low SPM concentrations than those on coarse particles at high SPM concentrations.

Significant inter-relationships existed between the concentrations of certain metals in SPM, such as between Zn and both of Cd and Cr and between Fe and Co suggesting similar sources for and/or similar geochemical processes controlling such metals.

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