LEACHABLE AND RESIDUAL PB, NI AND CD IN THE SEDIMENTS OF ABU-QIR BAY, ALEXANDRIA, EGYPT

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ABSTRACT

The partitioning of Pb, Ni and Cd between dilute acid leachable and residual (all other modes of association) fractions was studied in the sediments of the Bay of Abu-Qir, west of Alexandria.

Total metal concentrations ranged between 23.7 and 125.9 µg g^{-1} (average 65.5 ± 21.1 µg g^{-1}) for lead, 27.7 to 162.9 µg g^{-1} (average 91.0 ± 35.5 µg g^{-1}) for nickel and 1.58 to 7.20 (average 4.86 ± 1.28 µg g^{-1}) for cadmium, highest concentrations were measured in the vicinity of points recognized as potential sources pollution. Concentrations in the leachable fraction were relatively low and averages for Pb, Ni and Cd were 2.3, 32.0 and 0.10 µg g^{-1} respectively. Taking the leachable fraction as a relative measure of the degree of mobility it appeared that Ni was the most mobile as it had between 26 and 49% of its total concentration present in the leachable form. More than 97% of Pb and Cd are present in forms not available for the dilute acid leaching and are, therefore, less mobile.

Variations of the residual concentrations of Pb and Ni appeared as mostly related to the mud and organic matter content which means that this fraction is tightly held in the crystal lattice and/or present as sulphide and organic complexes. Organic matter and mud contents explain most of the variability of the leachable Pb, which agrees with the high adsorption capacity of the fine fraction. Only the leachable Ni was found to be related to the carbonate content, which explains the relative higher mobility of this element.

INTRODUCTION

Analysis of trace elements in the sediments permits the detection of pollution that may escape water analysis and also promotes information about the critical sites of the aquatic system under consideration (Forstner and Salomons, 1980). Sediments can act as a sink and a possible source of metals for the environment. Some metallic pollutants transported in solution are adsorbed by material in suspension and by fine-grained particles of sediments and

are, therefore, potentially mobile upon contact with seawater (Chester et al., 1986). Therefore, metals in sediments may be classified as lattice-held (residual fraction) which is the part tightly held to the matrix and is hardly released. The non-lattice held is the part of the metal that resides outside the crystal structure and is more or less mobile (Waldichuk, 1985). Pardo et al. (19890) pointed out that the metal present as residual fraction can be taken as guide to show the overall pollution of the system. The greater the percentage of this fraction of metal, the less dangerous pollution effect because this inert phase can not be remobilized easily, at least under normal conditions. On the other hand, the non-lattice-held fraction can be remobilized in the presence of complexing agents or when the environmental conditions, particularly the pH are altered.

The aim of the present investigation was to provide baseline information concerning the distribution of Pb, Ni and Cd in the surface sediments of Abu-Qir Bay. Estimation of the relative mobility of the elements through the determination of the leachable fraction was also intended.

STUDY AREA

Abu-Qir Bay is a shallow (maximum depth 18 m) semi-circular basin, lying at 35 km east of Alexandria city between $30°4'$ and $30°21'$ E and $31°16'$ and $31°30'$ N. It has a shoreline of about 50 km between Abu-Qir peninsula at the west and the Rosetta branch of the River Nile at the east (Fig. 1).

The bay is one of the main fishery basins close to Alexandria; however, it is continuously facing pollution problems. It receives the effluents of many industrial activities (food processing, refineries, fertilizers, paper mill, power station), domestic sewage and agricultural drainage. These wastes are collected and dumped into the bay through El-Tabia Pumping Station (TPS) situated at the southwestern extremity of the bay (Fig. 1). The daily discharge of the combined liquid wastes is estimated to be about 2×10^6 m^3 (Said, 1995). The bay receives also agricultural drainage water from the coastal lake Edku through the narrow channel Al-Maadiya (Fig.1). The annual average of the drainage water discharged into the lake is about 1000×10^6 m^3 (El Sayed et al., 1993). At its northeastern extremity, the bay receives considerable quantities of fresh water from the River Nile (3760×106 m^3 according to the Report of pollution status of Abu-Qir Bay, 1984). This water carries important quantities of suspended sediments and greatly influences the physico-chemical characteristics of the bay water. Several studies have been undertaken in the bay to describe some of its hydrographic and chemical aspects (Dowidar et al., 1976; Abul-Dahab, 1989; El-Tabakh, 1992; Abdelmoneim and Shata, 1993; Said 1995; Hafez, 1999).

MATERIAL AND METHODS

In order to depict the distribution of trace elements in the bay sediments, sampling strategy was designed to insure a denser coverage of the area near the dumping sites (Fig. 1,area A, 13 stations) and a looser sampling network to cover the wrest of the bay area (assigned area B in the text). The exact positions of the sampling stations, determined by a GBS, are given in Fig. (1) and Table 1.

A total of 30 sediment samples were collected using an Ekman grab sampler. Samples, taken from the middle of the grab to avoid contamination from the metallic sides, were kept in plastic bags and transported to the home laboratory. Part of each sample was air dried to determine the proportions of sand, silt and clay using a standard set of sieves. The other part of the sample was oven dried at 40 °C. Representative sub-samples (powdered in agate mortar) were used for the determination of organic carbon (OC), carbonate content and total trace element concentrations. Leachable concentrations were determined using non-powdered samples. OC was measured using the wet oxidation method (Walkly and Black, 1934). Carbonate content was estimated as equivalent to the weight loss resulting from the treatment of the sample with hot 1 M HCl. For the determination of the total concentration of trace elements, appropriate weight of the sample was digested in teflon cups, under reflux, for six hours using 5 ml of concentrated HNO_3, HF and $HClO_4$ (3:3:1 v/v). The leachable fraction was extracted from 1 g sediment by maintaining it in suspension during 12 hours in 25ml of 0.5 M HCl solution. Concentrations of trace elements in the extracts were measured using Atomic Absorption Spectrophtometer. A Perkin Elmer 5000 was used for the flameless analysis while a Varian 1250 was used for flame measurements. The precision of the analysis was tested, by analyzing five replicates of one of the samples, and was found to vary between 5 and 10 % for the ensemble of the elements.

RESULTS AND DISCUSSION

Sediment Characteristics

Major sediment characteristics such as texture, carbonate content and organic carbon concentration are master factors that may control the trace metal concentrations and their mode of association with the sediment (speciation). In general, because of their high specific surface area, fine grained muddy sediments are known to contain high organic carbon and trace element concentrations. Organic matter is also reported to possess high affinity for some trace elements and sediments containing high concentrations of organic matter are generally enriched in trace elements. On the contrary, carbonate rich sediments have low trace element concentrations due to the dilution effect of the carbonate fraction (Basaham and El Sayed, 1998).

Results of the OM, carbonate and mud contents are presented in Table (2). The impact of the different effluents is clearly shown. Area A is characterized by higher OM averaging 2.01 % which is the double of that measured in area B. The highest concentrations are measured at stations 4 and 6, the nearest to the TPS; these stations showed also the highest mud content measured in this area. Values of mud and OM are decreasing eastward but marked a significant increase at station 12 in front of El-Maadiya outlet. The Rosetta branch of the River Nile is also supplying sediments characterized by high organic carbon and mud content. This is clearly shown at stations 26-30 where the average OM reaches 2.48% and the mud content is higher than 95%. Sediments of area A are generally poor in carbonate but it appears that carbonate content increases with increasing depth. This may arise from the presence of unfavorable life conditions for shell building organisms in the very near-shore area due to waste dumping.

Trace Elements

Results of the analysis of Pb, Ni and Cd as leacable, total and residual (the difference between the total and leachable concentrations) are given in Table (3).

Lead

Total Pb concentration in area A varied from 34.3 to 125.9 $\mu g\ g^{-1}$ and averaged 66.3 $\mu g\ g^{-1}$; this average is not very different from that calculated for
area B (64.9 $\mu g\ g^{-1}$). These concentrations are higher than those measured in the sediments of Lake Edku (El Sayed, 1993) and even higher than concentrations measured in some polluted areas (Seng et al., 1987). The highest concentrations in area A were measured at stations 4 and 6 characterized by the highest OM and mud contents. Correlation analysis indicates that more than 80% of the variability of total lead could be explained
by mud and OM fluctuations (Table 4). Concentrations decrease as the distance increases from the TPS but show a noticeable increase in front of Al-Maadiya outlet. In area B, total Pb distribution seems to be controlled by other factors; heavy minerals associated with the Nile sediments may constitute an important host.

Generally, leachable lead seems constituting only a minor fraction of the total lead, which means that most of the lead is found in the residual unavailable form (Table 3). In area A, leachable lead constitutes about 3% of the total element. The highest concentrations are still found at stations 4 and 6 demonstrating the impact of the effluent from the TPS not only on the absolute concentration of Pb but also on its mode of association with the sediment. Both the leachable and the residual Pb are positively correlated with the mud and OM contents (Table 4). In area B, the proportions of the residual and leachable lead are comparable to the values measured in area A (96 and 4% respectively). These results agree with the results of Hafez (1999) who found that exchangeable lead constitutes approximately 1% of its total concentration. The highest value of total lead was measured at station 15 close to the TPS. Despite the relative association of high and low element concentrations in the three detected phases with similarly high and low mud and OM, only leachable lead showed good correlation with the two variables (Table 4).

Nickel

In area A, total Ni concentration averaged 83.4 $\mu g\ g^{-1}$. The highest concentrations were also measured at stations 4 and 6 in the area of waste dumping. Its concentration is apparently correlated with the distribution of mud and OM contents (Table 4). Residual Ni, which constitutes about 74% of the total, is the dominant component, and its distribution follows that of the total concentration. It correlates fairly well with mud and OM. Leachable Ni represents about 26% of the total content, its concentration varied between 5.0 and 70.0 $\mu g\ g^{-1}$. However, its distribution does not follow, as in the case of Pb, the distribution of mud and OM. The rather good correlation with carbonate (Table 4) may explain the elevated concentration of the leachable Ni.

Higher Ni concentrations were measured in area B. Total Ni ranged from 50 to 163 $\mu g\ g^{-1}$ and averaged 163 $\mu g\ g^{-1}$. The highest Ni concentrations were measure at stations that are under the direct impact of Al-Maadiya outlet or the Rosetta Nile branch. Nile sediments carried in suspension are known to supply relatively important quantities of heavy minerals (Frihy et al, 1994) that may represent an important source of sedimentary Ni. The total Ni is

almost equally distributed between the residual and leachable fractions (51 and 49% respectively), only leachable and total Ni distributions appear partially related to the mud fraction as indicated by the correlation coefficients (Table 4).

Cadmium

Cadmium was found in relatively high concentrations in the sediments of the bay (average 4.86 ± 1.28 µg g^{-1}). Comparable values were measured in the sediments of Lake Edku (El Sayed, 1993), which is connected to the bay and is one of its sediment sources. However, slightly lower values (average ≈ 2.50 µg g^{-1}) were measured by Hafez (1999). These high Cd values may find their source in the industrial wastes dumped into the bay and/or the agricultural drainage water in association with the phosphate fertilizers, which are extensively used in the agriculture. Phosphate fertilizers are known to contain high concentrations of Cd (Forstner and Wittman, 1981). Helios-Rybica and Forstner (1986) suggested that Cd might substitute for major cations in the octahedral units of clay minerals.

Comparable total Cd concentrations were found in the two areas, A and B (average 4.74 and 4.96 µg g^{-1} respectively), which may support the idea of non-point source. However, still some high Cd values are measured in the area of the TPS and the Rosetta branch. Residual Cd constitutes the major fraction (98%) of the total in both areas leaving only 2% as leachable Cd. This means that most of the Cd is incorporated in the lattice structures of the forming minerals or associated with insoluble oxides of iron and manganese. Cd did not show any significant correlation with the other sediment components; however it correlates with lead (Table 4).

CONCLUSIONS

Abu-Qir Bay receives water and solid material from three identified sources. The first one is a pumping station (TPS) that dumps water and sediments from industrial and agricultural wastes. The second one is natural and carries mostly drainage water that transits by the adjacent Lake Edku. The third source is the Rosetta branch of the river Nile. These water and sedimentsources have bee shown to influence the sediment nature and to be the vectors for the transport of Pb, Ni and Cd to the bay sediments. The highest concentrations of all the elements were generally found in the areas under the direct impact of these sources in association with high mud and organic matter contents. Analysis of the acid leachable fraction showed that most (> 95%) of Pb and Cd are present in non-labile form i.e. unavailable for any biotic process. Nickel was the most mobile element since its leachable fraction represented between 20 and 48% of the total concentration.

Table 1. Samples locations, mud content (%), organic matter (OM%), carbonate content (CO_3^{2-}) in Area (A) and Area (B) and Abu Qir Bay sediments.

St. No.	Long.	Lat.	Depth (m)	OM (%)	Mud (%)	CO_3^{2-} (%)
			Area (A)			
1	30° 04.4`	31° 18.9`	2	3.04	2.67	17.71 ⊤
2	30° 05.3`	31° 19.1`	5	0.76	0.00 ⁻	9.43
3	30° 05.8`	31° 18.4`	6	0.63	0.13	8.00
4	30° 05.2`	31° 17.1`	3	8.91 ⊤	51.13 ⊤	4.84
5	30° 06.2`	31° 17.8`	6	1.13	1.57	11.71
6	30° 06.2`	31° 16.8`	3	4.28	16.18	6.00
7	30° 06.6`	31° 17.3`	7	1.17	1.96	8.57
8	30° 07.2`	31° 16.6`	4	2.18	5.61	2.29
9	30° 07.2`	31° 17.2`	6	0.88	1.19	5.71
10	30° 08.7`	31° 16.5`	4	0.65	5.38	1.71
11	30° 08.7`	31° 17.1`	6	0.65	0.47	2.57
12	30° 10.4`	31° 16.6`	4	1.21	11.55	1.14 ⁻
13	30° 10.4`	31° 17.1`	6	0.63 ⁻	0.91	1.71
Mean				2.01	7.60	6.26
S.D.				2.26	13.40	4.63
			Area (B)			
14	30° 05.5`	31° 21.1`	5.4	2.61 ⊤	41.46	63.52
15	30° 06.9`	31° 19.6`	5.4	0.90	4.53	21.30
16	30° 09.9`	31° 18.1`	5.4	0.81	24.47	6.42
17	30° 12.8`	31° 19.2`	5.4	0.59	12.90	6.02
18	30° 19.4`	31° 25.6`	5.9	0.23 ⁻	1.52	6.13
19	30° 20.0`	31° 28.6`	5.4	0.29	1.10	8.81
20	30° 19.4`	31° 31.4`	5.9	0.29	7.85	3.89 ⁻
21	30° 09.1`	31° 21.4`	9.0	0.45	0.51	40.64 ⊤
22	30° 10.7`	31° 20.0`	8.1	0.23 ⁻	0.32 ⁻	8.77
23	30° 10.2`	31° 24.8`	18.0	0.41	10.28	6.69
24	30° 12.0`	31° 23.3`	14.8	0.56	21.50	7.34
25	30° 13.5`	31° 22.0`	10.8	0.34	7.11	5.37
26	30° 13.8`	31° 27.0`	16.2	2.30	97.83	7.43
27	30° 14.8`	31° 25.5`	14.4	1.96	98.79	7.29
28	30° 16.4`	31° 24.5`	11.5	2.48	99.53	9.40
29	30° 15.6`	31° 28.8`	12.8	2.25	98.06	8.25
30	30° 17.8`	31° 17.8`	10.8	1.85	99.53 ⊤	10.06
Mean				1.09	36.90	11.78
S.D.				0.91	42.43	10.77
			Abu Qir Bay			
Mean				1.49	24.20	9.39
S.D.				1.72	35.94	9.02
Min.				0.23	0.00	1.14
Max.				8.91	99.53	40.64

Table 2. Concentrations (µg g^{-1}) of leachable (L), residual (R) and total (T) metals in Area (A), Area (B) and Abu Qir Bay sediments.

St. No	Pb			Ni			Cd		
	L	R	T	L	R	T	L	R	T
Area (A)									
1	2.78	70.85	73.63	11.3	67.2	78.5	0.165	5.845	6.010
2	0.96	74.85	75.81	5.4	69.4	74.8	0.059	7.138 ⊤	7.197 ⊤
3	1.43	59.05	60.48	5.0 ⁻	47.9	52.9	0.063	3.853	3.916
4	6.17 ⊤	119.7 ⊤	125.91 ⊤	28.3	119.2 ⊤	147.5 ⊤	0.096	6.455	6.551
5	1.65	58.13	59.78	11.7	65.2	76.9	0.071	5.296	5.367
6	3.09	80.81	83.90	18.3	104.9	123.2	0.251 ⊤	4.988	5.239
7	1.31	58.54	59.85	6.3	86.0	92.3	0.071	5.465	5.536
8	1.61	58.12	59.73	35.8	70.9	106.7	0.173	4.563	4.736
9	1.22	44.18	45.40	10.4	32.2	42.6	0.044 ⁻	3.455	3.499
10	1.31	42.85	44.16	46.3	23.9	70.2	0.074	2.711	2.785
11	0.78 ⁻	33.47 ⁻	34.25 ⁻	15.4	17.9 ⁻	33.3 ⁻	0.071	1.513 ⁻	1.584 ⁻
12	1.52	65.24	66.76	70.4 ⊤	33.9	104.3	0.063	3.539	3.602
13	1.17	71.16	72.33	16.3	64.1	80.4	0.088	5.487	5.575
Mean	1.92	64.38	66.31	21.6	61.8	83.4	0.099	4.639	4.738
S.D.	1.44	21.41	22.66	19.2	30.5	31.9	0.060	1.573	1.586
Area (B)									
14	2.25	67.59	69.84	14.4	67.5	81.9	0.118	5.939	6.057
15	1.59	119.57 ⊤	121.16 ⊤	10.7 ⁻	39.9	50.6 ⁻	0.132	2.924	3.056
16	2.31	52.81	55.12	97.4 ⊤	13.3 ⁻	110.7	0.162	4.754	4.916
17	2.36	54.78	57.14	68.5	56.5	125.0	0.055	4.306	4.361
18	2.14	56.11	58.25	25.6	71.4	97.0	0.052	4.798	4.850
19	1.54	43.88	45.42	19.1	61.7	80.8	0.052	2.856 ⁻	2.908 ⁻
20	1.71	64.61	66.32	30.8	67.4	98.2	0.081	5.731	5.812
21	1.48	56.32	57.8	19.6	40.6	60.2	0.103	4.709	4.812
22	0.61 ⁻	23.09 ⁻	23.70 ⁻			60.1	0.044 ⁻	3.793	3.837
23	2.31	57.78	60.09	46.1	44.0	90.1	0.051	4.396	4.447
24	2.75	54.67	57.42	59.2	41.3	100.5	0.213 ⊤	4.567	4.780
25	3.13	98.63	101.76	45.2	113.8 ⊤	159.0	0.085	6.269	6.354
26	3.08	58.61	61.69	80.6	71.2	151.8	0.155	4.660	4.815
27	3.68	54.82	58.5	66.2	52.6	118.8	0.088	4.985	5.073
28	3.63	69.96	73.59	81.1	32.3	113.4	0.099	6.027	6.126
29	4.73	67.96	72.69	76.9	49.3	126.2	0.074	6.650 ⊤	6.724 ⊤
30	4.73 ⊤	57.53	62.26	76.0	86.9	162.9 ⊤	0.118	5.281	5.399
Mean	2.59	62.28	64.87	51.1	56.9	105.1	0.099	4.861	4.960
S.D.	1.13	20.90	21.14	28.2	23.6	33.6	0.047	1.068	1.071
Abu Qir Bay									
Mean	2.30	63.19	65.49	32.0	59.1	91.0	0.099	4.765	4.864
S.D.	1.27	20.43	21.08	25.8	26.0	35.5	0.051	1.269	1.277
Min.	0.61	23.09	23.70	5.0	13.3	27.7	0.044	1.513	1.584
Max.	6.17	119.74	125.91	81.1	119.2	162.9	0.251	7.138	7.197

Table 3. Percent contribution of leachable fractions to the total concentrations of metals in Area (A), Area (B) and Abu Qir Bay sediments.

St. No.	Pb %	Ni %	Cd %
Area (A)			
1	3.78	14.39	2.75
2	1.27 ¯	7.22	0.82 ¯
3	2.36	9.45	1.61
4	4.90 ⁺	19.19	1.47
5	2.76	15.21	1.32
6	3.68	14.85	4.79 ⁺
7	2.19	6.83 ¯	1.28
8	2.70	33.55	3.65
9	2.69	24.41	1.26
10	2.97	65.95	2.66
11	2.28	46.25	4.48
12	2.28	67.50 ⁺	1.75
13	1.62	20.27	1.58
Mean	2.73	26.54	2.26
S.D.	0.96	20.88	1.30
Area (B)			
14	3.22	17.58	1.95
15	1.31 ¯	26.52	4.32
16	4.19	51.99	3.30
17	4.13	20.31	1.26
18	3.67	16.78 ¯	1.07 ¯
19	3.39	18.92	1.79
20	2.58	17.60	1.39
21	2.56	26.18	2.14
22	2.57		1.15
23	3.84	51.17	1.15
24	4.79	58.91	4.46 ⁺
25	3.08	28.43	1.34
26	4.99	53.10	3.22
27	6.29	55.72	1.73
28	4.93	71.52 ⁺	1.62
29	6.51	60.94	1.10
30	7.60 ⁺	46.65	2.19
Mean	4.10	38.89	2.07
S.D.	1.62	18.94	1.10
Abu Qir Bay			
Mean	3.50	33.36	2.15
S.D.	1.52	20.45	1.17
Min.	1.27	6.83	0.82
Max.	7.60	71.52	4.79

Table 4. Correlation analysis matrix.

Table 4. Correlation analysis matrix.

	Leachable			Residual			Total		
	Pb	**Ni**	**Cd**	**Pb**	**Ni**	**Cd**	**Pb**	**Ni**	**Cd**
Area (A) n = 13									
OM	0.99	ns	ns	0.85	0.76	ns	0.87	0.78	0.44
Mud	0.94	ns	ns	0.81	0.62	ns	0.83	0.78	ns
Carbonate	ns	0.60	ns	ns	ns	ns	ns	ns	0.51
Pb	1	ns	ns	1	0.85	0.75	1	0.83	0.74
Ni		1	ns		1	0.79		1	0.57
Cd			1			1			1
Area (B) n = 17									
OM	0.67	ns	ns	ns	ns	0.49	ns	ns	0.50
Mud	0.84	0.68	ns	ns	ns	0.49	ns	0.60	0.50
Carbonate	ns	ns	ns	ns	ns	ns	ns	0.51	ns
Pb	1	0.71	ns	1	ns	ns	1	ns	ns
Ni		1	ns		1	ns		1	0.55
Cd			1			1			1
Abu Qir Bay n = 30									
OM	0.72	ns	ns	0.55	0.53	ns	0.58	0.43	0.4
Mud	0.75	0.68	ns	ns	ns	ns	ns	0.64	ns
Carbonate	ns	ns	ns	ns	ns	ns	ns	ns	ns
Pb	1	0.51	ns	1	0.55	0.45	1	ns	0.48
Ni		1	ns		1	0.58		1	0.54
Cd			1			1			1

Table 5. The mean concentration of trace metals ($\mu g\ g^{-1}$) in the total and leachable fractions as well as the coefficient of variation (% C/V) in sediments from Area (A) and Area (B).

	Total	% C/V	Leachable	% C/V
Area (A)				
Pb	66.31 ± 22.66	34.2	1.92 ± 1.44	75
Ni	83.4 ± 31.9	38.2	21.6 ± 19.2	88.9
Cd	4.738 ± 1.586	33.5	0.099 ± 0.060	60.6
Area (B)				
Pb	64.87 ± 21.14	32.6	2.59 ± 1.13	43.6
Ni	105.1 ± 33.6	32.0	51.1 ± 28.2	55.2
Cd	4.96 ± 1.071	21.6	0.099 ± 0.047	47.5

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