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Geochemical Assessment of Heavy Metals Pollution and Ecological Risk in the Nile Delta Coastal Sediments, Egypt

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Abstract: A geochemical assessment of the heavy metals was carried out in the coastal sediments of the Nile Delta. The objective of the assessment was to evaluate the spatial distribution pattern of heavy metals and their ecological risks in the sediments of surf, breaker and offshore zones. Twenty nine samples were collected from six transects at different depths and distances from the shoreline. The assessment revealed that the average concentrations of Al, Cu, Fe, Mn, Pb and V were lower than the world average values, whereas the average concentrations of Cd, Co, Cr, Mo, Ni, Zn and U were higher than the world average. Very high degree of contamination with Mo and Cd was detected at the breaker and surf zones of the eastern transect of El-Burullus with values averaging 83.16 and 70.26, respectively which is attributed to the very high contamination factors of Mo and Cd. Pollution load index values showed that the transects of the western part of El-Burullus and Rosetta are generally more contaminated than the eastern part. Very high risk index and elevated potential ecological risk factors were detected and attributed to Cd contamination at the offshore zone of the western transects of Rosetta and El-Burullus. The grain size and heavy metals distribution was controlled by beach erosion and accretion, depositional energy, source of sediments and human activities.

Keywords: Heavy metals, Nile Delta coastal sediments, contamination indices, Pollution Load Index, Risk index

Introduction

Pollution of the natural environment by heavy metals is a worldwide problem due to their persistence, bioaccumulation problems and most of them have toxic effects on living organisms, when they exceed a certain concentration (Ghrefat and Yusuf, 2006; Nouri et al., 2006; Robin et al., 2012). Worldwide, concentrations of heavy metals in aquatic ecosystems have increased considerably due to the inputs of industrial waste, sewage runoff and agriculture discharges (Prica et al., 2008 and Yang et al., 2012). The study of the distribution of heavy metals in coastal sediments is very important from the point view of environmental pollution because sediment concentrates metals, and represents an appropriate medium to monitor contamination (Sarkar et al., 2004).

Heavy metals are introduced to the marine environment via natural erosion and by domestic and industrial activities as anthropogenic pollutants (Veerasingam et al., 2012). Much of this input is ultimately carried to the sea through rivers and wind that accumulates in the estuarine zone and continental shelf, which are important sinks for suspended matter and associated land-derived contaminants (Leong and Tanner, 1997; Özşeker and Erjiz 2011; Dassenakis et al., 2003). Heavy metals concentration and distribution are affected by sedimentological and mineralogical characteristics, sediment transport mechanisms and anthropogenic discharges (Nobi et al., 2010; Gopinath, et al., 2010). Moreover, adsorption, biological-uptake and accumulation are three mechanisms that cause an important variation of heavy metals concentration in sediments (Nobi et al., 2010; Hart, 1982).

Environmental quality indices are a powerful tool for anticipating environmental and human risk due to heavy metal accumulation in bottom sediments. Different metal assessment indices applied to marine environment have been recently developed (Caeiro et al., 2005; Spencer and MacLeod, 2002).

The present work aims to assess major and trace elements spatial distribution patterns and its ecological risks in the Nile Delta coastal sediments. The data obtained will be used along with previous data to assess any change in metals background levels due to coastal processes such as erosion and accretion or anthropogenic activities and to provide a scientific basis for environmental risk assessment and public health management.

Materials and Methods

Study Area

The area under investigation is the Nile Delta coastal region which is a part from the Mediterranean coast of Egypt (Figure 1). It covers area about 280 km^2 of coastal sediments bounded by latitudes 31º28/- 31º35/N and longitudes 30º21/ - 31º50/E. Generally, the Nile Delta coast is highly active and affected by River Nile discharge. Coastal erosion has been observed and induced on the Rosetta and Damietta Promontories after construction of the Aswan High Dam in 1964 due to elimination of fluvial sediments (Frihy and Khafagy, 1991). Many artificial coastal protection structures such as sea walls, detached breakwaters and groins have been established at the Nile Delta coast to control the erosion process.

Badr and Lotfy (1999) addressed the erosion and accretion problems in Nile Delta coastal area. They studied dispersion and rate of sediment movement using fluorescent sand tracers at Rosetta, Burullus and Damietta Promontories. There is a net eastwards littoral sand transport in the surf zone attesting severe erosion at the tips of these promontories.

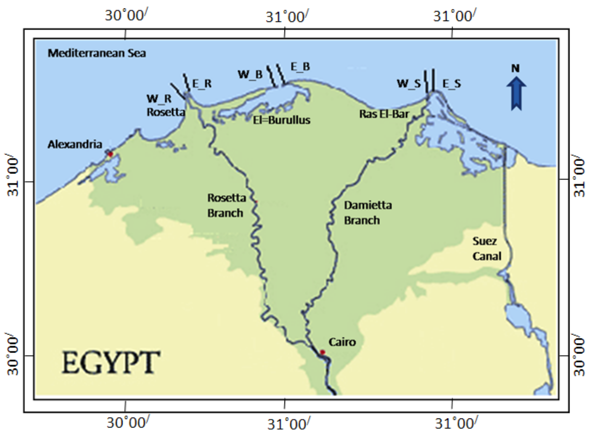

Fig. 1. Sampling profiles in Nile Delta coastal area. W_R = west of Rosetta, E_R = East of Rosetta, W_B = West of El-Burullus, E_B = East of El-Burullus, W_S = West of Ras El-Bar, E_S = East of Ras El-Bar.

El-Gamal (2014) differentiate the 6 transects under investigation according to erosion and accretion conditions as four categories. The first transect is under erosion condition such as W_R, and the second is transect under accretion condition such as E_B. The third is the transect start as erosion (100 – 200 m distance) and end as accretion (400 – 500 m) sites such as E_R and E_S and the fourth is start as accretion and end as erosion sites such as W_B and W_S.

The areas selected experience intensive human activities such as fishing, shipping, some industrial plants, etc (FAO, 1994) and impacted by several possible sources of pollution including agricultural, industrial, organic compounds and domestic discharge (Badr and Tayel, 2001; Taha et al, 2004; Kaiser et al., 2012). Badr and Tayel (2001) introduced nine years data of heavy metals in sediments samples collected during May 1999 from the study area at Rosetta and El-Burullus. The data of Cu, Zn, Fe and Mn will be useful for comparison with the same heavy metals measured in this work.

Sampling and sample preparation

In order to study the behavior of heavy metals, 29 surface sediment samples were collected using Van Veen grab sampler at the end of May 2008 from six coastal transects running perpendicular to the shoreline. The samples were collected with variable depths at distances 100, 200, 300, 400, 500 and 600 m from fixed points at the beach (Fig. 1). The coastal transects include east and west Damietta Promontory (E_S and W_S), east and west El-Burullus Outlet (E_B and W_R) and east and west Rosetta Promontory (E_R and W_R) (Fig. 1).

Samples were taken from the central part of the grab sampler to avoid contamination from the metallic sampler. The samples were packed in polythene bags and frozen at -4°C immediately until further analysis. The samples were washed to remove salts, oven dried and sieved using mechanical shaker to determine grain sizes. For heavy metal measurements, samples were weighed, dried for 48 h in an oven at 70ºC and screened through 2.0 mm sieve. A 0.5 g dried sediment sample was digested with acids mixture (HNO_3/$HClO_4$/HF) 3:2:1 in a previously cleaned and dry Teflon beaker and evaporated to near dryness at 80°C. These procedures were carried out in compliance with Al-Trabulsy et al. (2013).

Metal concentrations (Al, Fe, Cd, Cu, Co, Cr, Mo, Ni, Pb, Zn, V, U and Mn) were measured using Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES, Perkin-Elmer, Optima 2100 DV). Suitable chemical standards (Merck, Germany) were used to calibrate the instrument. Precision and accuracy of the metals were checked by the marine sediment standard reference material from National Institute of Standards and Technology, USA. The analytical precision expressed as coefficients of variance was <10% for all the metals, based on replicate analysis (FAO, 2015).

Theoretical calculations

The anthropogenic contribution or natural enrichment of the selected heavy metals in marine sediments can be estimated from the metal enrichment relative to a background level. In order to quantifying metal enrichment in surface sediments, comparison was executed between the metal content of each sample was compared to the average upper continental crust. These background values respectively introduced by Hu and Gao (2008) for Co, Cu, Mo, Ni, V, Zn and U, by Taylor & McLennan (1995) for Al, Fe and Mn, by Hökanson (1980) for Cd and Cr and by McLennan (2001) for Pb. Multiple indices were used to assess the heavy metals enrichment, contamination and possible ecological risks (see Table 1).

Statistical analysis

Multivariate statistical analyses including Pearson correlation analysis, Factor Analysis (FA), and Cluster Analysis (CA) were conducted using the statistical software Statgraphics plus 4 to identify the association of metals and geochemical parameters. A correlation matrix was used to understand the relationship among the metals. R-mode factor analysis was applied to transform the correlation matrix, with an aim of explaining the relationships between different factors. Hierarchical Cluster Analysis (HCA) was performed on the normalized data set by means of Ward′s method**.**

Table 1. Indices applied to assess the heavy metals contamination and ecological risks.

Name	Equation	Equation Number
Anthropogenic Contamination Factor (CF)	$CF = \frac{Cm}{Bm}$	1
Degree of Contamination (Cdeg)	$C\deg = \sum \left(\frac{Cm}{Bm}\right) i$	2
Enrichment factor (EF)	$EF = \frac{(Cm/CFe)_{Sample}}{(Bm/BFe)_{crustalaverage}}$	3
Element contamination index (ECI)	$ECI = \left(\frac{Cm - Bm}{Bm}\right)$	4
Overall metal contamination index (MCI)	$MCI = \sum \left(\frac{Cm - Bm}{Bm}\right) i$	5
Geo-accumulation Index (Igeo)	$I_{geo} = log_2 \frac{Cm}{2.5\ Bm}$	6
Pollution load index (PLI)	$PLI = (CF_1 x CF_2 x CF_3 \ldots \ldots .. CF_n)^1$	7
Risk factor (Er)	$Er^i = Tr^i x Cm^i$	8
Potential ecological risk index (RI)	$RI = \sum_{i=1}^{6} Er^i$	9

Where:
Cm = the measured metal concentration in sediment; Bm = the background concentration value of metal (m); letter "i" represents the respective metal; CFe = the measured Fe concentration in sediment; BFe = the background concentration value of Fe; Tr = the toxic-response factor for a given substance.
References of Equations: 1= (Aikpokpo-dion et al., 2010), 2,8,9 =(Hökanson, 1980), 3 = (Kersten and Smedes, 2002), 4,5 = (Meybeck et al., 2004), 6 = (Abrahim and Parker, 2008), 7 = (Tomlinson et al., 1980)

Results and discussions

The Nile Delta coastal area was divided into three zones according to the depth. In this work we recognize surf zone covers depths less than 2 m followed by breaker zone includes depths between 2 and 4 m and the offshore zone covers all depths greater than 4 m.

Grain size analysis

As shown in Figure 2, the mean grain size of the sediments collected from the eroded sites at the eastern and western parts of Rosetta was find sand at variable depths from -4.6 m to maximum -7.1 m. While at Damietta promontory, the eastern and western sites were characterized mainly by fine sand at distances 100-300 m and very fine sand at distances 400-500. Some irregularities have been recognized at El-Burullus outlet sites. The very fine sand appear starting from distance 300 m and extended to 500 m except at the eastern site which has fine sand at the 500 m distance due to the nature of this location.

Concentrations of heavy metals

The average concentrations of heavy metals and their descriptive statistics of the three zones (surf, breaker and offshore) in the six coastal transects are shown in Table 2(a,b) and Figures 3 and 4.

According to the sampling depths and due to erosion at these places, sediments collected from east and west Rosetta are belong to offshore zone and those from east Ras El-Bar transect cover breaker and offshore zones. Comparison between the measured average values of the elements under investigation with the world average concentrations (Cox, 1989; James and Lord, 1992; He et al., 2005) as referred to Al-Trabulsy et al., (2013) and the other referenced data was carried out.

The average concentrations of heavy metals in the surf zones were relatively higher than their counterparts in the breaker and offshore zones except for Cu, Cd and Pb. This may indicated to the source of the relatively higher values of heavy metals was the discharging of the different kinds of wastes (industrial, agricultural and domestic) to the coastal area. On the other hand, the lowest average concentrations of heavy metals were detected from the sediments of breaker zone. The average concentrations of Al, Cu, Fe, Mn, Pb and V of the three zones were lower than the world average values. On the other hand, the average concentrations of Cd, Co, Cr, Mo, Ni, Zn and U of the present study were higher than the world average values. Excluding the Al, Fe, Mn and U), the concentration of other metals arranged in the order of Ni>Zn>Cr>V This high content could be explained as due to geological formation of the parent rocks from which they were derived (Al-Trabulsy et al., 2013; Veiga et al., 2006; Dragovic et al., 2008) and industrial pollution discharged into this coastal area (EIMP/EEAA, 2012).

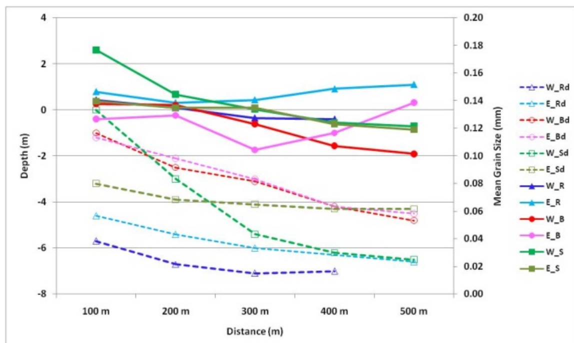

Fig. 2. Mean grain size (doted lines in mm) with depth (solid lines in m) of the sediments under investigation.

Copper (Cu), Zn, Fe and Mn average concentrations in the present study were compared with results of Badr and Tayel (2001). The comparison of Cu measurements revealed that the values obtained during this work are lower than the historical ones except at W_B surf zone.

Comparison of the results with reference data obtained from the same sites during 1999 has been carried out. The results of Cu measured in sediment samples collected from W_R, E_R, W_B surf, W_B offshore, E_B surf and E_B offshore were 18.24, 4.55, 11.95, 16.61, 11.06 and 16.10 mg kg^{-1} measured in this work were lower than the values obtained during 1999 at the majority of the same sites as 29.04, 27.61, 5.67, 26.55, 30.43 and 20.38 mg kg^{-1}, respectively. The value of Cu in W_B surf is looking as higher than the previous measurement during 1999.

The comparison of Zn values revealed that the results obtained during this work are lower than the 1999 data except at W_B surf zone as recognized in Cu data. The Zn values measured in this work were 68.22, 23.18, 46.34, 57.84, 58.78 and 77.30 mg kg^{-1} compared with 287.36, 312.76, 13.95, 81.62, 96.81 and 76.1 mg kg^{-1} measured during 1999 for samples collected from W_R, E_R, W_B surf, W_B offshore, E_B surf and E_B offshore, respectively.

The investigation of Mn values obtained during this work with the comparison with 1999 data revealed that the new values are lower than the historical ones. The Mn measured values were 0.67, 0.22, 0.46, 0.55, 0.49 and 0.51 g kg^{-1} compared with 6.26, 5.01, 1.37, 7.37, 11.1 and 6.7 g kg^{-1} measured during 1999 for samples collected from W_R, E_R, W_B surf, W_B offshore, E_B surf and E_B offshore, respectively.

Finally, reverse behavior was observed with significant increase of Fe measured values than the 1999 data. The Fe data were 38.01, 13.44, 32.48, 38.00, 30.27, and 34.04 g kg^{-1} measured in this work compared with 4.79, 5.08, 1.94, 5.27, 5.31 and 5.13 g kg^{-1} measured during 1999 for samples collected from W_R, E_R, W_B surf, W_B offshore, E_B surf and E_B offshore, respectively.

Table 2a. Average values of heavy elements concentrations in surface sediments of surf, breaker and offshore zones of the Nile Delta coastal area collected during 2008.

	Al	Cd	Co	Cr	Cu	Fe	Mn
	(g kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(g kg^{-1})	(g kg^{-1})
W_R offshore	19.28	14.82	34.50	143.63	18.24	38.01	0.67
E_R offshore	10.46	1.31	12.71	49.68	4.55	13.44	0.22
W_B Surf	23.62	3.51	29.26	122.63	11.95	32.48	0.46
W_B Breaker	17.79	2.52	22.31	93.82	8.85	25.13	0.34
W_B offshore	26.28	10.31	34.50	126.65	16.61	38.00	0.55
E_B Surf	21.93	3.17	25.11	151.94	11.06	30.27	0.49

E_B Breaker	26.61	4.00	32.42	177.73	14.91	37.12	0.55
E_B offshore	24.59	3.57	29.58	104.64	16.10	34.03	0.51
W_S Surf	16.55	2.91	20.88	108.84	7.43	24.90	0.69
W_S Breaker	15.29	1.54	13.41	46.26	4.52	16.18	0.28
W_S offshore	21.00	4.01	30.25	133.37	11.24	35.21	0.63
E_S Breaker	6.00	0.85	8.99	42.38	2.81	8.94	0.17
E_S offshore	6.72	0.69	8.27	27.07	2.39	8.39	0.14
Average (Present Study)	18.16	4.09	23.24	102.20	10.05	26.31	0.44
Range (Present Study)	6.00-26.61	0.69-14.82	8.27-34.50	27.07-177.73	2.39-18.24	8.39-38.01	0.14-0.69
*World Average	80.4	0.06	10.4	20.2	20	50.2	1.1
Alexandria, Egypt[1]					29.42	2.3	0.19
Red Sea, Saudi[2]	37.9	0.07	3.03	295.6	7.39	15.6	0.38
Medit. France[3]					8.4	13.4	0.34
Medit. Italy[3]				21.8	18.7	6.1	
El-Gamil, Egypt[4]		2			4.2	1.928	0.20
Rosetta, Egypt[5]					29.04	4.79	6.26
El-Burullus, Egypt[5]					5.67	1.94	1.37

*Cox (1989), James and Lord (1992), and He et al. (2005). 1= (Nasr et al., 1990), 2= (Al-Trabulsy et al., 2013), 3=(Rigollet et al., 2004), 4=(Kaiser et al., 2012), 5=(Badr and Tayel, 2001)

Table 2b. Average values of heavy elements concentrations in surface sediments of surf, breaker and offshore zones of the Nile Delta coastal area collected during 2008.

	Mo	Ni	Pb	V	Zn	U
	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(mg kg^{-1})	(g kg^{-1})
W_R offshore	8.34	94.81	4.32	108.15	68.22	0.43
E_R offshore	1.15	23.64	0.99	46.39	23.18	0.29
W_B Surf	5.43	60.97	1.70	104.17	46.34	0.35
W_B Breaker	4.89	53.15	2.43	77.45	30.68	0.25
W_B offshore	6.12	67.62	4.81	128.57	57.84	0.41
E_B Surf	28.93	409.34	1.83	105.55	58.78	0.30
E_B Breaker	39.24	179.79	5.36	124.16	57.60	0.39
E_B offshore	6.24	65.93	3.29	111.68	77.30	0.35
W_S Surf	4.90	50.16	2.71	89.07	203.43	0.36
W_S Breaker	2.65	32.88	2.74	43.84	33.36	0.14
W_S offshore	3.08	49.83	3.32	105.18	55.20	0.37
E_S Breaker	0.71	17.12	0.00	35.22	10.80	0.31

E_S offshore	1.40	16.77	0.00	23.95	45.65	0.29
Average (Present Study)	8.70	86.31	2.58	84.87	59.11	0.32
Range (Present Study)	0.71-39.24	16.77-409.34	0.00-5.36	23.95-128.57	10.80-203.4	0.14-0.43
*World Average	1-5	40	10.15	190	10.3	0.003
Alexandria, Egypt[1]					74.56	
Red Sea, Saudi[2]	1.28	8.25	9.51	23.8	36.5	
Medit. France[3]		12.7	6.1		61.6	
Medit. Italy[3]		8.9	13.8		36.1	
El-Gamil, Egypt[4]			18.4		34.6	
Rosetta, Egypt[5]					287.36	
El-Burullus, Egypt[5]					13.95	

*Cox (1989), James and Lord (1992), and He et al. (2005). 1= (Nasr et al., 1990), 2= (Al-Trabulsy et al., 2013), 3=(Rigollet et al., 2004), 4=(Kaiser et al., 2012), 5=(Badr and Tayel, 2001)

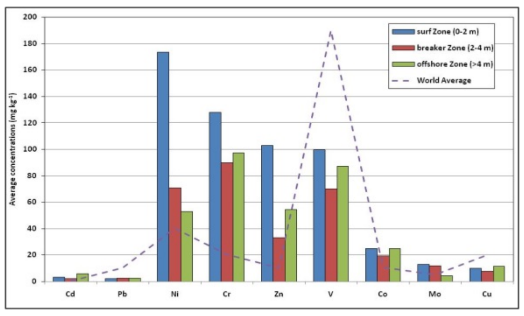

Fig. 3.Average concentration values of Cd, Pb, Ni, Cr, Zn, V, Co, Mo and Cu (mg kg^{-1}) in surf, breaker and offshore zones of the Nile Delta coastal profiles during 2008.

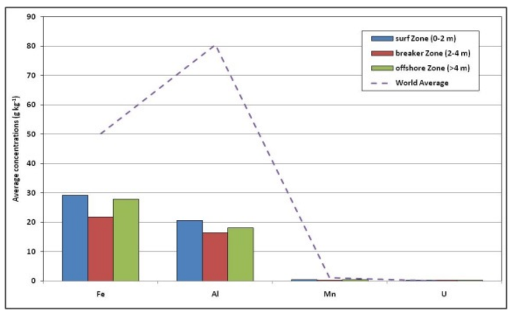

Fig. 4.Average concentration values of Fe, Al, Mn, and U (g kg^{-1}) in surf, breaker and offshore zones of the Nile Delta coastal profiles during 2008.

Environmental implications

In order to have complete picture of the distribution of heavy metals in the Nile Delta coastal sediments, different indicators have been calculated. To study heavy metal retention in bottom sediments, the contamination factor, and degree of contamination of elements, metal pollution index and risk assessment code in Nile Delta coastal area samples were calculated.

1 Contamination Factor (CF) and degree of Contamination (Cdeg):

The contamination factor (Cf) is used to evaluate the degree of contamination of the sediment. Its estimation is based on the current content of the respective metal to its content from average crustal composition (background values) (Aikpokpodion et al., 2010). According to Hökanson (1980) the CF was classified into four groups starting with $Cf \geq 6$ which refers to very high contamination factor. The other three categories are refer to considerable ($3 \leq Cf < 6$), and moderate ($1 \leq Cf < 3$) as listed in Table 3. The low contamination factor (CF < 1) category has the rest of the heavy elements under investigation.

Very high and considerable contamination factors were obtained for Mo and Cd at the three zones of Eastern and western El-Burullus and the western area of Rosetta and Ras El-Bar and for Ni at the eastern profile of El-Burullus as listed in Table 3. While the majority of lower values of contamination factors for the metals under investigation were found at breaker zone and offshore zone of the eastern part of Ras El-Bar, at offshore zone of the western part of Ras El-Bar and at the offshore zone of the eastern part of Rosetta.

The assessment of sediments contamination was carried out using the CF as single-metal index and as the integrated form of CF is the degree of contamination (C_{deg}) based on four classification categories recognized by Hökanson (1980). It started with $C_{deg} < 8$ implied low degree of contamination as integration of 8 elements. In this work we used $C_{deg} < 12$ as starting value to recognize the low degree of contamination class for the 12 elements under investigation. The four categories of C_{deg} were listed in Table 3.

The degree of contamination (C_{deg}) for the selected heavy metals reaches very high with values of 83.16 and 70.26 at the breaker zone and surf zone of the eastern profile of El-Burullus. So it can be concluded that the inshore area (breaker and surf zones) of the eastern part of El-Burullus, as a whole, is characterized by a very high contamination (Table 3).

Table (3) Ranking order of sediment contamination of the investigated Nile Delta coastal zones according to C_{deg} value and the sequence of the very high, considerable and moderate contamination factor (Cf). * E = East, W = West, R = Rosetta, B = El-Burullus and S = Ras El-Bar.

Degree of contamination (C_{deg})	Contamination factor (CF)				
	Zone	C_{deg}	Very high $Cf \geq 6$	Conside-rable $3 \leq Cf < 6$	Moderate $1 \leq Cf < 3$
Very High	E_B Breaker Zone	83.16	Mo	Ni > Cd	Co > Cr > V > Fe
$C_{deg} \geq 48$	E_B Surf Zone	70.26	Mo > Ni	Cd	Cr > Co
Considerable	W_R Offshore Zone	39.79	Cd > Mo		Ni > Co > Cr > Mn > Fe > V
$24 \leq C_{deg} < 48$	W_B Offshore Zone	30.65	Cd > Mo		Co > Ni > Cr > V > Fe
Moderate	E_B Offshore Zone	23.02	Mo	Cd	Co > Ni > Cr > V > Zn
	W_B Surf Zone	21.18	Mo	Cd	Co > Ni > Cr
	W_S Surf Zone	18.49	Mo		Cu > Zn > Ni > Co > Cr > Mn
$12 \leq C_{deg} < 24$	W_S Offshore Zone	18.04		Mo > Cd	Co > Cr > Ni > Mn > Fe
	W_B Breaker Zone	17.44	Mo		Cd > Ni > Co > Cr
Low	W_S Breaker Zone	10.18		Mo	Cd
	E_R Offshore Zone	6.85			Mo > Cd
$C_{deg} < 12$	E_S Offshore Zone	5.23			Mo
	E_S Breaker Zone	4.65			Mo

2. Enrichment factor (EF)

Enrichment factor can be used to evaluate the metal enrichment in a comprehensive way relative to a certain background. This method normalizes the measured heavy metal concentration with respect to a reference metal such as Fe or Al (Ravichandran et al., 1995).

Fe and Al usually have relatively high natural concentrations and are therefore not expected to be substantially enriched from anthropogenic sources in coastal sediments (Niencheski et al., 1994). Currently, Fe is the most frequently used geochemical normalize in the coastal sediments under investigation as refer to Kersten and Smedes, (2002). The enrichment value can be classified into seven categories according to the value of the enrichment factor as suggested by Acevedo-Figueroa et al., (2006). The scale of EF was listed in Table (4).

The results of the enrichment factor (EF) of the metals under investigation are presented in Table 4. Result showed that, the only heavy metal found as extremely severe enrichment with EF ≥50 is Mo measured at the breaker and surf zones of the eastern part of El-Burullus. Severe enrichment was monitored for Ni and Cd at surf zone of the eastern profile of El-Burullus and at the offshore zone of the western part of Rosetta. As indicated by their respective enrichment factor (EF) values, the enrichment of heavy metals in Nile Delta coastal sediments decreases in the order Mo >Ni > Cd > Zn > Cr > V > Co > Mn > Cu > Al > Pb.

3 Element contamination index (ECI) and overall metal contamination index (MCI):

ECI and its integrated form MCI are expression of single metal contamination within a sample or combined metal contamination for a sample relative to the background values of the respective metal. According to Meybeck et al., (2004), MCI was designed to describe general trace elements contamination on a scale from 0 to 100, with MCI of < 5 implies very low contamination; 25-50 high contamination; 50-100 means very high contamination and > 100 implies extremely high contamination.

Table (4) The Enrichment factors (EF) of the Mo, Ni and Cd as relatively higher heavy metals in Nile Delta coastal zones during 2008, the other heavy metals under investigation were recognized as minor or no enrichment. *

	Mo	Ni	Cd
W_R offshore Zone	Severe	Minor	Severe
E_R offshore Zone	Moderate	Minor	Moderate
W_B Surf Zone	Moderately severe	Minor	Moderate
W_B breaker Zone	Severe	Minor	Moderate
W_B offshore Zone	Moderately severe	Minor	Moderately severe
E_B Surf Zone	Extremely severe	Severe	Moderate
E_B breaker Zone	Extremely severe	Moderat e	Moderate
E_B offshore Zone	Severe	Minor	Moderate
W_S Surf Zone	Severe	Minor	Moderate
W_S breaker Zone	Moderately severe	Minor	Moderate
W_S offshore Zone	Moderately severe	Minor	Moderate
E_S breaker Zone	Moderate	Minor	Moderate
E_S offshore Zone	Moderately severe	Minor	Minor

Extremely severe (EF ≥ 50), very severe (25 ≤ EF < 50), severe (10 ≤ EF < 25), moderately severe (5 ≤ EF < 10), moderate (3 ≤ EF < 5), minor (1 ≤ EF < 3) and Not (EF < 1) scale according to Acevedo-Figueroa et al., (2006).

According to Meybeck et al., (2004) classification of MCI, the studied sediments ranged from very low contamination to extremely high contamination. Result of MCI showed that, the sediments at 300 m distance from the eastern profile of El-Burullus are the relatively higher contamination site of the entire studied area.

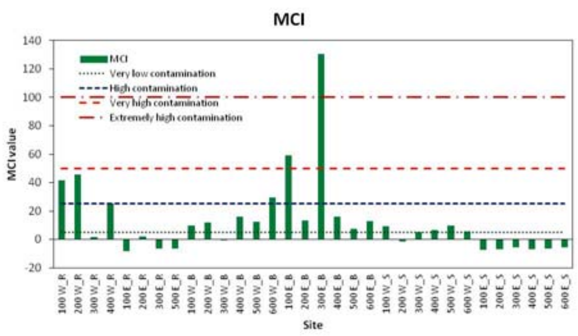

Fig. 5. Overall metal contamination index (MCI) for the sites under investigation.

4. Geo-accumulation Index (Igeo)

The geo-accumulation index (Igeo), originally defined by Muller (1979) is a quantitative measures of the metal pollution in aquatic sediments (Ranjan et al., 2008). Igeo was designed to describe general trace elements contamination on a scale from 0 to 5, with Igeo = 0 implies practically uncontaminated and Igeo = 5 or more to extremely contaminated.

Data of Igeo revealed that the heavily and extremely contamination was found due to Mo at the eastern profile of El-Burullus as shown in Figure 6. Moderate contamination to heavy metal by Cd was recorded at western profile of Rosetta and El-Burullus. The Igeo factors are in general comparable to results reported for EF sand CFs.

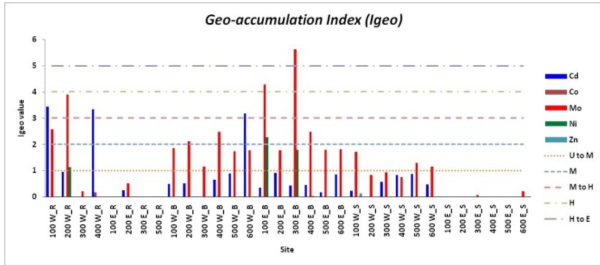

Fig. 6. Geo-accumulation index (Igeo) for the sites under investigation. Al, Cu, Fe, Mn, Pb and V are PU at all sites under investigations. U to M = uncontaminated to moderately contaminated, M = Moderately contaminated, M to H = Moderately to heavily contaminated, H = Heavily contaminated and H to E = Heavily to extremely contaminated.

5. Pollution load index (PLI):

The Pollution load index (PLI) is used to determine the synthetic pollution effect at different locations by the metals. Values of PLI = 1 indicate heavy metal loads close to background, and values above 1 indicate progressive pollution (Tomlinson et al., 1980).

The results of PLI for the entire transects (profiles) at the eastern part of Ras El-Bar and Rosetta were determined as less than 1 (Figure 7), so these profiles could be classified as “unpolluted” with respect to the heavy metals examined in this study. These two profiles have the same coastal process behavior as started as erosion sites and ended with accretion sites as described by El-Gamal (2014). PLI values showed that the profiles of the western part of El-Burullus and Rosetta are more contaminated than the eastern part except at distance 300 m. Also, the eastern profile of El-Burullus observed as contaminated sites except at distance 500 m. The eastern sites of Ras El-Bar profile characterized by low values of pollution load index but the profile contains erosion sites at 100-300 m and accretion sites at 400-600 m. The higher concentrations of

PLI in the Nile Delta coast may be attributed to the erosion condition such as W_R at distances 100-200 m and W_B at distance 400-600 m. On the other hand, the lower concentrations of PLI may be attributed to the accretion condition such as W_S at distance 200 m, E_R at 300 m and W_B at 300 m as shown in Figure 7. Environmental pollution is reflected in the high concentrations of heavy metals in sediments in highly industrialzed and populated areas. As Badr and Tayel, (2001) mentioned that most of these sediments are enriched with metals from municipal, industrial wastes and surface run off. Untreated domestic sewage and industrial effluents which are seen directly dumped into the coast can be considered as possibly sources of the estimated PLI values.

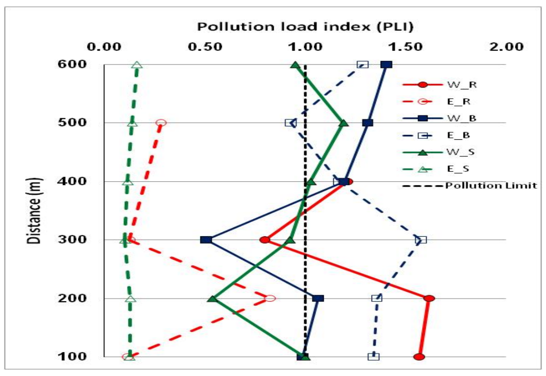

Fig.7. Pollution load index calculation for all the sites under investigation.

6. Risk factor (Er) and Potential ecological risk index (RI)

The potential ecological risk index method (Hökanson, 1980) was applied to assess the degrees of heavy metal contaminations. The risk factor was categorized into five categories as listed in Table (5) started with Eri < 40 which used to describe the low potential ecological risk factor. Risk index lower than 150 was recognized as low ecological risk for the sediments under investigation according to Hökanson (1980) classification. RI was recognized into four categories as listed in Table (5).

The potential ecological risk index method provides a quantitative evaluation on the potential ecological risk for a given contaminant (Hökanson, 1980). This method not only takes the pollution degrees of heavy metals into account, but also indicates the biological hazard degrees. Therefore, this evaluation method is a relatively stable, fast, simple and standard method (Ren, et al., 2012).

Table 5 summarizes the potential ecological risk factors (Er^i) and risk indices (RI) for each site, and the entire zone, based on the mean concentration of Cd, Ni, Cu, Cr, Pb and Zn metals concentrations in profile sediments. Cd is the only metal of the six metals under test recognized as very high potential ecological risk factor with very high risk index at offshore zone of the western profile of Rosetta (RI = 467.17) and El-Burullus (RI = 327.26). The potential ecological risk at offshore zone of the western profile of Rosetta and El-Burullus in the order of Er (Cd) >Er (Ni) > Er (Cu) > Er (Cr) >Er (Pb) > Er (Zn) have been obtained, which showed that Cd was the most important factor leading to risk. This in agreement with the finding of Jiang et al., (2014) that Cd is the leading metal to risk and Zn is the lowest one. Also, Cd is recognized as considerable potential ecological risk factor with considerable risk index at the three zones of the eastern profile of El-Burullus, surf zone and offshore zone of the western part of Ras

El-Bar and at surf zone of the western part of El-Burullus.

Table 6 summarizes the higher and lower polluted sites with the source metals of the higher pollution. It is evident from the results that based on all the 6 methods, Mo, Ni and Cd exhibit the higher significant source of pollution in the area under investigation. The higher pollution sites were found at the eastern part of El-Burullus and the western part of Rosetta. On the other hand, the lower pollution sites were found at the eastern part of Ras El-Bar and the eastern part of Rosetta.

Statistical analysis

Cluster analysis has been carried out for the metals under investigation. This procedure as created 1 cluster from the 13 variables supplied. The clusters are groups of variables with similar characteristics. Similar groups were joined together such as Co and Fe, Cr and V, Cd and U, and Mo and Ni. Using Ward's Method, Squared Euclidean revealed that Mo and Ni are clustered in one cluster with highest distance as shown in Figure 8. These two metals are observed as the most polluted metals in the Nile Delta coastal area.

Analysis of variance (ANOVA) as multivariate test was undertaken for the 13 metals under investigation. The F-ratio is a ratio of the between-group estimate to the within-group estimate. Since the P-value of the F-test is less than 0.05, there is a statistically significant difference between the mean data from one level of metal to another at the 95.0% confidence level. To determine which means are significantly different from which others, Multiple Range Tests was carried out. Homogenous groups are identified using columns of X's at the 95.0% confidence level. Within each column, the levels containing X's form a group of means within which there are no statistically significant differences. The method currently being used to discriminate among the means is Fisher's least significant difference (LSD) procedure. This test revealed that statistically, the Al and Fe as one more dominant metals category have significant difference among the other metals under investigation. The enrichment of heavy metals in Nile Delta coastal sediments decreases in the order Mo >Ni > Cd > Zn > Cr > V > Co > Mn > Cu > Al > Pb.

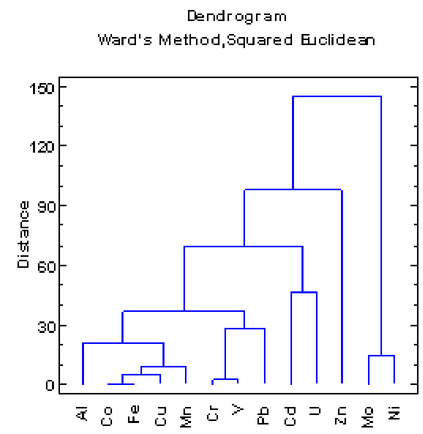

Fig. 8. Cluster analysis for all parameters under investigation.

Table (5). The potential ecological risk factors (Er^i values) and risk indices (RI values) of the profiles of the Nile Delta coastal zones during 2008. * W = West, E = East, R = Rosetta, B = El-Burullus, S = Ras El-Bar.

				Potential ecological risk factor (Er^i)			
Risk index (RI)		Zone*	RI	Very high $Er^i \geq 320$	High $320 > Er^i \geq 160$	Considerable $160 > Er^i \geq 80$	Moderate $80 > Er^i \geq 40$	Low $Er^i < 40$
	Very High RI ≥ 200	W_R Offshore Zone	467.2	Cd				Ni > Cu > Cr > Pb > Zn
		W_B Offshore Zone	327.3	Cd				Ni > Cu > Cr > Pb > Zn
	Considerable 100 ≤ RI < 200	E_B Surf Zone	162.0			Cd	Ni	Cr > Cu > Zn > Pb
		E_B Breaker Zone	155.5			Cd		Ni > Cr > Cu > Pb > Zn
		W_S Offshore Zone	134.5			Cd		Ni > Cr > Cu > Pb > Zn
		E_B Offshore Zone	124.0			Cd		Ni > Cu > Cr > Zn > Pb
		W_B Surf Zone	120.2			Cd		Ni > Cr > Cu > Zn > Pb
		W_S Surf Zone	102.1			Cd		Ni > Zn > Cr > Cu > Pb
	Moderate 50 ≤ RI < 100	W_B Breaker Zone	88.1				Cd	Ni > Cr > Cu > Pb > Zn
		W_S Breaker Zone	54.1				Cd	Ni > Cr > Cu > Pb > Zn
	Low RI < 50	E_R Offshore Zone	45.4					Cd> Ni > Cr > Cu > Zn > Pb
		E_S Breaker Zone	29.7					Cd> Ni > Cr > Cu > Zn > Pb
		E_S Offshore Zone	24.8					Cd > Ni > Zn > Cr > Cu > Pb

Table (6). Summary of the pollution evaluation tests showing the most three high and less polluted sites and the higher ranked sources of metals of the Nile Delta coastal zones during 2008.

Evaluation method	Higher pollution sites	Higher Pollution source	Lower pollution sites
Anthropogenic Contamination Factor (CF) and degree of Contamination (Cdeg)	E_B Breaker Zone > E_B Surf Zone > W_R Offshore Zone	Mo > Ni > Cd	E_S Breaker Zone < E_S Offshore Zone < E_R Offshore Zone
Enrichment factor (EF)	E_B Breaker Zone > E_B Surf Zone > W_R Offshore Zone	Mo > Ni > Cd	E_S Breaker Zone < E_R Offshore Zone < W_S Offshore Zone
Element contamination index	E_B 300 > E_B 100 >	Integrated	E_R 100 < E_S 100 <

(ECI) and overall metal contamination index (MCI)	W_R 200		E_S 200
Geo-accumulation Index (Igeo)	E_B 300 > E_B 100 > W_R 200	Mo > Cd > Ni	E_R 100, E_R 300, E_S 100, E_S 200, E_S 400 and E_S 500
Pollution load index (PLI)	W_R 200 >E_B 300 > W_R 100	Integrated	E_S 300 < E_S 400 < E_R 100
Risk factor (Er) and Potential ecological risk index (RI)	W_R Offshore Zone > W_B Offshore Zone > E_B Surf Zone	*Cd > Ni > Cu	E_S Offshore Zone < E_S Breaker Zone < E_R Offshore Zone

Tested for Cd, Ni, Cu, Cr, Pb and Zn

Summary and Conclusion

- The study of heavy metals in the surface sediments of the Nile Delta coastal area using different indicators and indices revealed that the average concentrations of Al, Cu, Fe, Mn, Pb and V were lower than the world average values and Cd, Co, Cr, Mo, Ni, Zn and U were higher than the world average values.

- The surf zones have average values of heavy metals higher than the other zones under investigation.

- Very high and considerable contamination factors were obtained for Mo and Cd at the three zones of Eastern and Western El-Burullus and the western area of Rosetta and Ras El-Bar and for Ni at the eastern profile of El-Burullus.

- The degree of contamination (Cdeg) for the selected heavy metals reaches very high with values of 83.16 and 70.26 at the breaker zone and surf zone of the eastern profile of El-Burullus.

- Result of metal contamination index (MCI) showed that, the sediments at 300 m distance from the eastern profile of El-Burullus were the relatively higher contamination site of the entire studied area.

- Data of geoaccumulation index (Igeo) revealed that the heavily and extremely contamination was found due to Mo at the eastern profile of El-Burullus. Moderate contamination with Cd was recorded at western profile of Rosetta and El-Burullus.

- Pollution load index (PLI) values showed that the profiles of the western part of El-Burullus and Rosetta are more contaminated than the eastern part except at distance 300 m. Also, the eastern profile of El-Burullus observed as contaminated sites except at distance 500 m. The distribution of PLI is related to the erosion and accretion pattern of the area under investigation.

- Cd is the only metal of the six metals under test recognized as very high potential ecological risk factor with very high risk index at offshore zone of the western profile of Rosetta and El-Burullus.

- The potential ecological risk at offshore zone of the western profile of Rosetta and El-Burullus in the order of Er (Cd) > Er (Ni) > Er (Cu) > Er (Cr) > Er (Pb) > Er (Zn) have been obtained, which showed that Cd was the most important factor leading to risk.

- Cluster analysis shows similar groups joined together such as Co - Fe, Cr - V, Cd - U, and Mo - Ni.

- ANOVA indicated that there is a statistically significant difference between the mean data from one level of metal to another at the 95.0% confidence level.

- Fisher's least significant difference (LSD) procedure revealed that the more dominant metals Al and Fe are the only metals that have significant difference between each other and with the other metals under investigation.

Therefore, we concluded that the El-Burullus and Rosetta coastal area need more environmental efforts for their rehabilitation especially at Edku and El-Burullus Lakes which are the main sources of their outlet profiles. Concerned the potential ecological risk values, Cd appeared as the most critical heavy metal in the area under investigation and the second element is the Ni. We recommend more environmental work to trace the sources of the heavy metals considered as higher than the background to stop this increasing and continue the monitoring program to check the levels of the heavy metals in the Egyptian coasts.

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التقييم الجيوكيميائي للتلوث من المعادن الثقيلة والمخاطر البيئية في الرواسب الساحلية لدلتا النيل، مصر

أيمن الجمل و إبراهيم صالح

المستخلص تم اجراء تقييم جيوكيميائي للمعادن الثقيلة في الرواسب الساحلية في دلتا نهر النيل. وكان الهدف من التقييم تقدير ودراسة نمط التوزيع المكاني للمعادن الثقيلة والمخاطر البيئية في رواسب المنطقة الساحلية المقسمة الى ثلاثة أجزاء هى منطقة السيرف المتاخمة لخط الشاطئ حتى عمق 2 متر ومنطقة تكسر الأمواج والمنطقة البحرية التى تليها. وقد جمعت تسعة وعشرون عينة من ستة مقاطع عرضية في أعماق مختلفة و من مسافات مختلفة من خط الشاطئ . كشف التقييم أن متوسط تركيزات الألومنيوم ، النحاس ، الحديد ، المنجنيز والرصاص والفاناديوم كانت أقل من المتوسط العالمي ، في حين أن متوسط تركيزات الكادميوم ، الكوبالت، الكروم ، الموليبدينوم ، النيكل، الزنك و اليورانيوم كانت أعلى من المتوسط العالمي . تم الكشف عن درجة عالية من التلوث نتيجة من عنصرى الموليبدينوم و الكادميوم في مناطق تكسر الأمواج و منطقة السيوف فى القطاع الشرقي من بوغاز البرلس وكان متوسط درجة التلوث تقابل 83.16 و 70.26 ،على التتابع وهو ما يرجع إلى درجة تلوث عالية من الموليبدينوم والكادميوم . وأظهرت نتائج دراسة قيم مؤشر حمل التلوث أن المقاطع العرضية للجزء الغربي من بوغاز البرلس ورشيد عادة ما تكون أكثر تلوثا من الجزء الشرقي . وأيضا تم الكشف عن مخاطر بيئية محتملة ترجع إلى التلوث بعنصر الكادميوم في المنطقة البحرية من المقاطع العرضية الغربية من رشيد و بوغاز البرلس . ومن العوامل المؤثرة على توزيع حجم الحبيبات والمعادن الثقيلة وجود ظاهرتى النحر والترسيب للمنطقة الساحلية و توزيع الطاقة الترسيبية، ومصادر الرواسب المختلفة و الأنشطة البشرية