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Distribution and speciation of Fe, Mn, Zn, Cu, Pb and P in surface sediments of Lake Mariut, Egypt

by

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Abstract

Lake Mariut is suffering from pollution as it receives industrial effluents and a mix of sewage from different drains, often lacking treatment systems. Sequential extraction procedures were applied for the speciation of heavy metals (Fe, Mn, Zn, Cu and Pb) and P in the lake sediment to evaluate their potential bioavailability. Total concentrations of metals had low values compared with the sediment quality guidelines. The chemical speciation data for Mn and Zn indicate a potential pollution level since the non-residual fractions contain up to 77.6 and 64.9% (respectively) of the total metal content. However, Fe, Cu and Pb are mostly linked to the inert fraction. Risk assessment of metals was carried out using the mobility factor, the contamination factor, the risk assessment code and the enrichment factor. All the analytical approaches indicated the accumulation of pollutants exceeding the adsorptive capacity of Lake Mariut sediments. The organic phosphorus fractions dominated in the sediment accounting for 51.4%, while the most abundant form of inorganic phosphorus was Ca-bound phosphorus. The rank order of P fractions was HCl-P > NaOH-P > BD-P > NH_4Cl-P > Res-P. The decrease both in the dissolved oxygen level in the lake water and the Fe:P ratio in the lake sediment resulted in the high contribution of the phosphorus fractions to the overlying water.

Key words: heavy metals, chemical speciation, risk assessment, phosphorus, sediment, Lake Mariut

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Introduction

The erection of the Aswan Dam, accompanied by an increase in the population size and consequently in human activities, constitutes the main cause of pollution in the Coastal Delta lakes (Abdel-Satar & Goher 2009). Since the 1960s, Lake Mariut is suffering from pollution as it receives industrial effluents and a mix of sewage from different drains, often lacking treatment systems (Khalil et al. 2013). Thus, the eutrophication and dispersion of heavy metals are the major problems in Lake Mariut (Saad 1980). Sediments serve as a sink of metals that could be released into the overlying water from natural and anthropogenic processes such as bioturbation and dredging, resulting in potential adverse health effects (Nowrouzi & Pourkhabbaz 2014). Heavy metals are toxic to aquatic life (Huu et al. 2010; Yahaya et al. 2012; Ogunfowokan et al. 2013), often show high enrichment factors and a slow removal rate, hence they are considered to be the most serious inorganic pollutants (Moore et al. 2015). Accumulation of metals from the overlying water in the sediment depends on a number of environmental factors such as pH, ionic strength, anthropogenic input, concentration and the type of inorganic and organic ligands, as well as the surface area available for adsorption (Moore et al. 2015).

Lake Mariut is suffering severe ecological degradation due to social development, because the lake serves as a collection basin for industrial wastewater in addition to the agricultural drainage and municipal sewage. Lake sediments become enriched with various elements (Ag, As, Sb, Cr, Hg, Ni, Pb, Cd, Zn and Cu), which were found to be at levels comparable to the ranges recommended by the U.S. Environmental Protection Agency (EPA) that may have a possible effect on the bottom fauna and other organisms, including fish (El-Rayis 2005). The concentration of Se and B reached 4.92 and 2.65 μg g^{-1} (respectively) in the lake sediment with a high value of the enrichment factor (more than 1.5) (Khalil et al. 2013).

To assess the emission potential of pollutants, chemical extraction is used to study the distribution of pollutants among the geochemical phases that contain carbonates, oxides/hydroxides, sulfide and organic substances as major components (Rauret 1998). Distribution of heavy metals in different geochemical phases in sediment is the main parameter used to assess the bioavailability of metals where their mobility depends not only on their total concentration, but also on their chemical form (Yuan et al. 2004).

Phosphorus is one of the most important limiting nutrients for the growth of phytoplankton and terrestrial ecosystems (Hudson-Edwards et al. 2014). The phosphorus cycle is characterized by the accumulation of inorganic phosphorus, degradation of organic phosphorus, and interaction of phosphate with metal oxides in the sediment (Wang et al. 2013). The phosphorus content in surface lake sediments depends on the sediment composition, the sedimentation rate, the physicochemical conditions and the extent of digenetic processes (Anshumali & Ramanathan 2007).

Eutrophication of Lake Mariut has been a serious problem in the recent decades, because the lake becomes enriched with organic matter and nutrients originated from autochthonous and allochthonous sources (Saad 2003). To assess the risk of eutrophication in a lake system, it is necessary to know not only the content of total phosphorus in the sediments but also the content of different phosphorus fractions (Abdel-Satar & Goher 2009). The bioavailability of phosphorus in sediments depends on the original existing chemical forms (Fytianos & Kotzakioti 2005; Anshumali & Ramanathan 2007; Wang et al. 2013).

Several procedures for phosphorus extraction from sediments have been proposed to suit studies of different sediment mineral phases. These sequential extraction schemes made possible to classify the various forms of P distributed in sediments, such as labile-P, reductant-P, metal bound-P, occluded-P and organic-P (Pettersson et al. 1988; Zhou et al. 2001; Ribeiro et al. 2008). Regarding the potential P-bioavailability, the extracted fractions may be classified as water soluble-P, easily desorbable-P, algal available-P or ecologically important-P (Pettersson et al. 1988; Zhou et al. 2001). Inorganic phosphorus in sediments is found in combination with amorphous and crystalline forms of Fe, Mg, Al, and Ca (Malecki et al. 2007). Loosely adsorbed phosphorus, iron-bound phosphorus, and aluminum-bound phosphorus are easily desorbed from sediments and released into the overlying water under specific conditions. One of the important indicators affecting the phosphorus mobility and bioavailability is the iron-bound phosphorus fraction, which has a close relation with the nutrient status of water (Zhu et al. 2006).

Our attention in this study was focused on phosphorus and chemical forms of heavy metals to show the effect of untreated sewage and industrial wastes on their distribution in Lake Mariut sediment. Thus, the distribution, speciation, and ecological risk of Fe, Mn, Zn, Cu, Pb and P were determined to estimate the potential bioavailability of these elements.

Materials and methods

Site description

Lake Mariut is a shallow brackish water body with no direct connection to the sea. The lake is located at the longitude of 29°56'E and 29°51'E and the latitude of 31°10'30"N and 31°3'30"N (Fig. 1). The feeding waters of the lake are agricultural waters from El-Umoum Drain, sewage and industrial wastewater from El-Qalaa Drain and fresh water from the Nubaria Canal. The lake is heavily polluted by industrial wastes, in addition to raw and treated sewage from point and nonpoint sources such as agricultural runoff containing fertilizers and pesticides through these drains (Donia 2016). The lake is divided into four basins (Fig. 1): the Main Basin (14.77 km^2), the Aquaculture Basin (9.44 km^2), the West Basin (11.59 km^2) and the South Basin (33.77 km^2). The four basins are interconnected with each other by several breaches in the dikes of El-Umoum Drain and the Nubaria Canal. The central portions of the Main Basin receive most of their water from El-Qalaa Drain, in addition to water from El-Umoum Drain via several fractures in its embankment. Lake Mariut surface is maintained at 2.8 m below mean sea level by pumping water from the lake (West Basin) to the sea through El-Max Pumping Station (Khalil et al. 2013). Properties of the water in Lake Mariut are presented in Table 1.

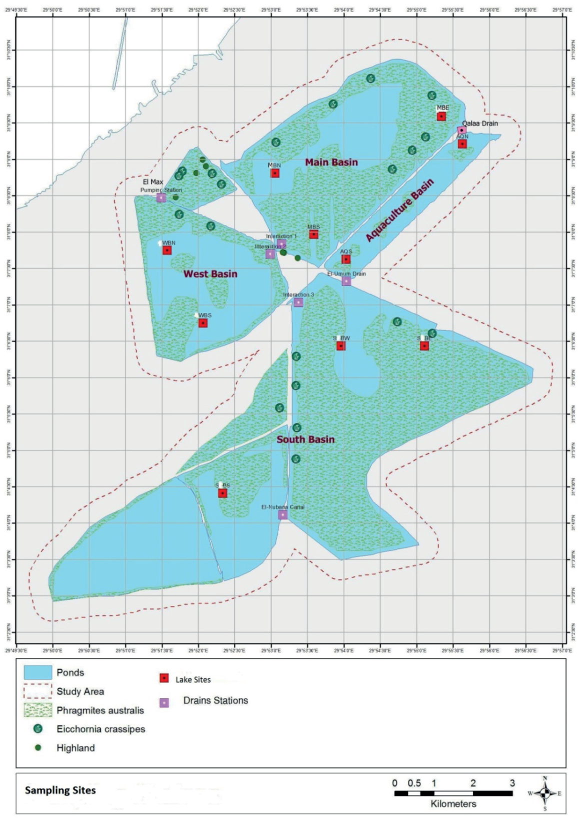

Figure 1

Map of sediment sampling sites at Lake Mariut

Sediment sampling

Table 1

Physical and chemical characteristics* of Lake Mariut water

Variable	Units	Value
Surface area	km^2	62
Water depth	m	50-150
Altitude		-2.8
Natural trophic status		Hypertrophic
Transparency	cm	20-60
Salinity	PSU	2.8-4.0
Dissolved oxygen (DO)	mg l^{-1}	0.0-12.0
pH		7.0-8.6

* Cited from El-Shabrawy and Goher (2011)

Ten sampling sites in Lake Mariut were selected for sediment collection from the top 20 cm layer using an Eckman Dredge device during winter 2013 (Fig. 1). The sites were distributed as follows: 2 sites in the Aquaculture Basin (AQ), 3 sites in the Main Basin (MB), 2 sites in the West Basin (WB) and 3 sites in the South Basin (SB). Samples were air-dried and passed through a 2-mm sieve to remove plant fragments and stones. The sieved samples were powdered and analyzed for P, Fe, Mn, Zn, Cu and Pb fractions, in addition to the total metal concentration. The summary of sieve test results as well as the content of organic matter (OM) and carbonates for Lake Mariut sediment samples are presented in Table 2.

Sequential extraction of heavy metals

Extraction of 1 gm of each sediment sample was made through sequential steps (Tessier et al. 1979; Abdel-Satar & Goher 2015) as shown in Table 3. For the determination of Fe, Mn, Zn, Cu and Pb in the total content of metals and fractions, an atomic absorption spectrometer GBC (model SavantAA AAS) with a graphite furnace GF 5000 was used.

Risk assessment of heavy metals

Mobility factor determination

The mobility factors (f) were calculated based on the "total metal/residual metal" ratio. This concept was applied to differentiate between natural values and those of anthropogenic origin (Lesmes 1996; Abdel-Satar & Goher 2015).

Table 2

Results of grain size* and the level of organic matter and carbonate for Lake Mariut sediment

Site Name	Site code	Gravel (%)	Sand (%)	Mud (%)	Type	OM** (%)	Carbonate** (%)
Aquaculture Basin (south)	AQS	0.00	43.70	56.30	Sandy mud	18.00	41.2
Aquaculture Basin (north)	AQN	0.05	71.71	28.24	Gravelly muddy sand	10.53	31.4
West Basin (south)	WBS	1.02	49.8	49.18	Gravelly muddy sand	10.11	49.0
West Basin (north)	WBN	2.36	67.88	29.76	Gravelly muddy sand	13.94	50.2
Main Basin (east)	MBE	0.11	72.88	27.01	Gravelly muddy sand	17.86	29.6
Main Basin (south)	MBS	0.00	72.55	27.45	Muddy sand	14.01	34.3
Main Basin (north)	MBN	0.00	65.76	34.24	Muddy sand	13.08	37.0
South Basin (south)	SBS	2.69	64.07	33.24	Gravelly muddy sand	6.26	24.7
South Basin (west)	SBW	3.05	80.51	16.44	Gravelly muddy sand	7.52	39.2
South Basin (east)	SBE	3.96	71.45	24.59	Gravelly muddy sand	5.72	25.0

* Personal communication with Dr. Hassan Farahat (NIOF)

** Unpublished data

Table 3

Sequential extraction scheme for heavy metals

Extraction step	Reactive/concentration/pH	Solid phase
1	1 M $MgCl_2$ (pH = 7)	Exchangeable fraction (F1)
2	1 M CH_3COONa, CH_3COOH (pH = 5)	Carbonate bound fraction (F2)
3	0.04 M $NH_2OH.HCl$, CH_3COOH (pH = 2, 96±3°C)	Fe/Mn oxides bound fraction (F3)
4	H_2O_2 (HNO_3 pH = 2, 85 ±2°C), 3M CH_3COONH_4	Organic matter and sulfide bound fraction (F4)
5	HNO_3:$HClO_4$ (4:1) (150°C)	Residual fraction (F5)

Contamination factor determination

The individual contamination factors (ICFs) for each sampling site were computed by dividing the sum of the four fractions (i.e. exchangeable, carbonate-bound, reducible, and oxidizable-organic forms) by the residual. Furthermore, the global contamination factor (GCF) was calculated by summing the ICFs for metals obtained for each site (Moore et al. 2015). The ICF and GCF are expressed for each site as follows:

$$ICF_{metal} = \frac{C_{non-residual}}{C_{residual}}$$

$$GCF = \sum_{i=1}^{n} CF_i$$

Enrichment factor determination

The metal enrichment factor was computed as follows to assess the level of contamination with heavy metals in Lake Mariut sediments:

$$EF = \frac{\left(\frac{M}{Fe}\right)_{sample}}{\left(\frac{M}{Fe}\right)_{background}}$$

Iron was used as a conservative tracer to differentiate natural from anthropogenic components. $(M/Fe)_{sample}$ is the ratio of metal and Fe concentration in the sample in the examined environment and $(M/Fe)_{background}$ is the ratio of metal and Fe concentration of the background (Yahaya et al. 2012). The background concentrations of Fe, Mn, Zn, Cu and Pb in the average shale obtained from Turekian and Wedepohl (1961) were used. Five contamination categories were recognized on the basis of the enrichment factors: EF < 2 (depletion to minimal enrichment), EF = 2 to 5 (moderate enrichment), EF = 5 to 20 (significant enrichment), EF = 20 to 40 (very high enrichment), EF > 40 (extremely high enrichment) (Yahaya et al. 2012).

Risk assessment code (RAC)

RAC is used to measure the hazard of specific metals based on the percentage of exchangeable and bound to carbonate metal fractions in the sediment. Five categories were recognized on the basis of RAC:

RAC < 1 (no risk),

RAC = 1 to 10 (low risk),

RAC = 11 to 30 (significant enrichment),

RAC = 31 to 50 (high risk),

RAC > 50 (very high risk) (Perin et al. 1985)

Phosphorus analysis

Sediment P fractions were characterized using a modification of the sequential fractionation procedure (Paludan & Jensen 1995). Phosphorus fractions were identified by this procedure based on the extractant. To estimate loosely sorbed P (Lsor-P), the sediment sample was shaken in 1 M NH_4Cl. Bicarbonate dithionite (BD) was used to extract P adsorbed to oxidized Fe and Mn (Fe-P) in the remaining soil pellets. To estimate P associated with clay and Al oxides (Al-P), remaining soil pellets were shaken with 0.1 M NaOH. The extracts were acidified to pH 1 and filtered to isolate P associated with humic acids (HA-P). To extract Ca-bound P (Ca-P), remaining soil pellets were shaken with 1 M HCl. In each step, soil residues were washed twice by the extractant and then by deionized water, where P was analyzed in the combined three extracts. Refractory organic P (Res-P) was estimated as P remaining in each soil pellet following the HCl-P extraction. Pellets were dried and subsamples were combusted at 550°C in a muffle furnace, and Res-P was extracted with 1 M HCl in a block digester. The inorganic P (Inorg-P) content of each extract was colorimetrically determined as orthophosphate by the procedure of Murphy and Riley (1962). Lsor-P, Fe-P, and Al-P extracts were subsequently digested, and organic P (Org-P) content in these extracts was calculated as a difference between Inorg-P concentrations of digested and non-digested extracts. For Res-P and HA-P extracts, all P was considered to be Org-P, but for Ca-P extracts, all P was considered to be Inorg-P. Total P was calculated by summing the content of Inorg-P and Org-P.

Risk assessment of phosphorus release

The pollution phosphorus index was calculated as follows (Wang et al. 2013):

$$S_i = \frac{C_i}{C_s}$$

where S_i is the pollution index, C_i is the phosphorus concentration of sample i (μg g^{-1}), and C_s is the phosphorus standard value (μg g^{-1}). Wang et al. (2013) considered 600 μg g^{-1} as the phosphorus standard value which causes the minimum ecological risk. When S_i is more than 1, the phosphorus concentration exceeds the standard.

Statistical analysis

The precision of phosphorus and heavy metal analysis was controlled by using triplicate samples for each analysis. The obtained data were recorded as the average with relative standard deviations less than 5%, which was considered as a satisfactory precision. The correlation coefficients between the studied variables in the sediment samples were calculated. Also all sediment sampling data for P and metals were tested for significant differences between different sites by means of one-way ANOVA.

Results and discussion

Heavy metals analysis

The distribution trends of the total heavy metals are shown in Table 4. Iron has the highest mean concentration at all sampling sites and was followed by Mn. The total metal (TM) concentrations at the investigated sites varied in a narrow range of values (Table 4).

Although the lake is exposed to different pollution sources (agricultural, sewage and industrial effluents), the total Zn, Cu and Pb concentrations in Mariut sediments were mostly below the guidelines cited by the Canadian Council of Ministers of the Environment (CCME 2001) for the protection of aquatic life (Tables 4, 5). The prevalence of sand fractions in Lake Mariut sediment may be responsible for the decrease in the total concentration of metals (Table 2), where the greater the size of the sediment fraction, the smaller the amount of metals bound to this fraction due to the reduction in specific surface area of the larger fractions (Ong et al. 2013).

Significant positive correlations at $P < 0.05$ between each of the total Zn, Cu and Pb

Table 4

Distribution of heavy metals in Lake Mariut sediment

Metal	Site	F1		F2		F3		F4		F5		TM	Recovery
		µg g^{-1}	%	µg g^{-1}	%	µg g^{-1}	%	µg g^{-1}	%	µg g^{-1}	%	µg g^{-1}	%
Fe	AQS	6.4	0.7	12.2	1.4	273.4	31.4	187.0	21.5	390.7	44.9	911	95.5
	AQN	6.4	0.7	12.2	1.4	298.2	32.9	200.2	22.1	388.8	42.9	898	100.9
	WBS	6.4	0.7	12.2	1.4	248.5	28.7	211.2	24.4	388.8	44.8	901	96.2
	WBN	6.4	0.8	16.1	1.9	248.5	29.5	191.0	22.7	381.1	45.2	851	99.1
	MBE	6.4	0.7	16.1	1.9	271.3	31.4	187.5	21.7	383.3	44.3	912	94.8
	MBS	6.9	0.8	16.1	1.9	271.3	31.7	174.3	20.4	387.4	45.3	909	94.2
	MBN	6.9	0.8	16.1	1.8	301.3	34.0	174.3	19.7	387.4	43.7	920	96.3
	SBS	6.4	0.7	20.2	2.3	278.2	31.9	187.0	21.5	379.3	43.5	911	95.6
	SBW	6.4	0.8	12.2	1.5	242.5	29.0	191.0	22.8	384.4	46.0	860	97.3
	SBE	9.0	1.1	12.2	1.5	242.6	28.9	191.0	22.8	384.4	45.8	858	97.8
Mn	AQS	19.31	7.77	64.00	25.76	62.62	25.21	56.84	22.88	45.65	18.38	260.3	95.5
	AQN	10.44	5.01	66.12	31.74	70.91	34.03	16.70	8.01	44.18	21.20	227.4	91.6
	WBS	17.84	7.45	69.03	28.83	71.53	29.87	16.75	7.00	64.27	26.84	248.8	96.2
	WBN	25.94	11.15	66.85	28.73	67.77	29.12	16.93	7.27	55.22	23.73	254.4	91.5
	MBE	15.13	7.55	59.93	29.91	60.21	30.05	21.22	10.59	43.89	21.90	222.4	90.1
	MBS	37.24	14.10	72.13	27.30	71.87	27.20	22.91	8.67	60.08	22.74	259.2	101.9
	MBN	25.74	9.82	70.31	26.83	68.25	26.04	43.68	16.67	54.08	20.64	255.8	102.4
	SBS	16.28	6.74	67.82	28.07	72.42	29.97	23.39	9.68	61.75	25.55	248.7	97.2
	SBW	10.12	4.13	65.33	26.67	67.30	27.48	47.36	19.34	54.83	22.39	248.0	98.8
	SBE	10.12	3.92	66.55	25.79	68.23	26.44	60.54	23.46	52.65	20.40	250.0	103.2
Zn	AQS	3.91	4.33	16.97	18.80	29.37	32.54	10.39	11.51	29.63	32.82	87.55	103.1
	AQN	4.17	5.58	10.72	14.33	28.49	38.09	5.11	6.83	26.31	35.17	80.03	93.5
	WBS	4.04	5.90	9.90	14.46	22.53	32.91	5.07	7.40	26.92	39.32	76.73	89.2
	WBN	5.67	5.63	27.47	27.26	31.11	30.88	5.08	5.04	31.42	31.19	99.45	101.3
	MBE	8.98	8.26	30.19	27.78	31.85	29.31	5.19	4.77	32.45	29.86	111.60	97.4
	MBS	5.35	7.10	15.38	20.38	23.94	31.73	5.09	6.75	25.68	34.04	83.08	90.8
	MBN	5.03	5.58	20.33	22.54	27.40	30.38	7.87	8.73	29.58	32.78	95.23	94.7
	SBS	4.36	7.86	2.57	4.64	19.78	35.65	5.28	9.52	23.49	42.34	62.45	88.8
	SBW	4.36	5.90	11.50	15.57	24.15	32.69	5.59	7.57	28.27	38.27	84.63	87.3
	SBE	5.61	6.31	15.86	17.82	29.14	32.74	7.20	8.09	31.18	35.04	86.78	102.6
Cu	AQS	1.39	4.51	3.16	10.27	3.62	11.79	3.52	11.46	19.05	61.97	28.30	108.6
	AQN	0.41	1.92	2.74	12.92	3.31	15.64	2.59	12.22	12.14	57.30	24.73	85.7
	WBS	0.73	1.96	3.31	8.93	3.48	9.39	2.70	7.28	26.86	72.45	43.05	86.1
	WBN	1.40	2.33	4.60	7.66	3.90	6.49	2.82	4.70	47.33	78.83	58.13	103.3
	MBE	1.18	1.55	7.02	9.27	4.22	5.57	4.43	5.84	58.88	77.77	73.05	103.6
	MBS	0.74	1.97	5.69	15.20	3.80	10.15	2.85	7.62	24.34	65.06	43.85	85.3
	MBN	0.63	1.78	6.49	18.46	3.72	10.59	2.64	7.52	21.66	61.64	40.00	87.9
	SBS	0.45	2.24	2.40	11.91	3.78	18.77	2.64	13.14	10.85	53.94	22.50	89.4
	SBW	0.28	1.37	2.75	13.65	3.07	15.25	2.97	14.76	11.07	54.97	21.70	92.8
	SBE	0.87	4.19	2.61	12.55	3.49	16.82	2.94	14.17	10.85	52.28	22.53	92.1
Pb	AQS	1.51	9.90	5.48	35.83	2.29	15.00	1.84	12.03	4.16	27.24	18.02	84.9
	AQN	1.51	6.06	5.09	20.36	1.84	7.36	1.64	6.58	14.90	59.64	23.82	104.9
	WBS	1.00	6.56	1.78	11.70	1.58	10.41	2.03	13.41	8.79	57.93	16.02	94.7
	WBN	2.16	6.68	1.91	5.89	1.71	5.27	2.16	6.68	24.45	75.48	31.82	101.8
	MBE	1.78	5.27	1.97	5.85	2.36	7.00	2.29	6.81	25.29	75.07	39.26	85.8
	MBS	1.97	8.63	6.71	29.39	2.30	10.05	1.84	8.05	10.02	43.88	26.04	87.7
	MBN	2.10	11.60	2.36	13.03	1.90	10.52	1.78	9.81	9.96	55.04	20.42	88.6
	SBS	1.78	10.78	5.02	30.49	2.03	12.33	2.10	12.76	5.54	33.64	18.22	90.4
	SBW	2.03	11.97	1.78	10.44	1.84	10.82	2.03	11.97	9.31	54.79	19.80	85.8
	SBE	1.71	12.72	2.30	17.11	2.23	16.59	2.03	15.15	5.16	38.43	15.78	85.0

Table 5

Canadian Sediment Quality Guidelines (μg g^{-1}) for the protection of aquatic life (CCME, 2001)

	Freshwater		Marine	
	TEL	PEL	TEL	PEL
Zn	123	315	124	271
Cu	35.7	197	18.7	108
Pb	35	91.3	30.2	112

TEL = Threshold effect level; PEL = Probable effect level (CCME, 2001)

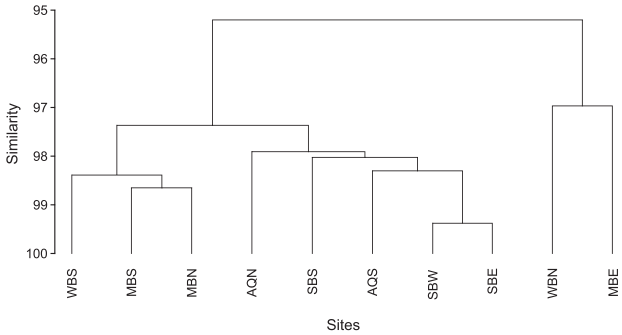

Figure 2

Cluster diagram indicating connection of the sites

concentrations and OM content (r = 0.68, 0.67 and 0.61, respectively, n = 10) were often related to the complexation and adsorption of metals by OM, indicating that the interaction between metals and OM is an important process for the fixation and removal of metals in Lake Mariut sediment (Kljaković-Gašpić et al. 2009). With respect to the role of carbonate content in the dispersion of metals, no trend was observed between the carbonate content and the concentrations of all the studied metals in the lake sediment.

The result of the speciation analysis of the metals is presented in Table 4. The summation of the five fractions is consistent with the total metal concentrations. High percentage recoveries were recorded for metals (84.9-104.9%), which proved that the sample preparation method and the analytical procedure described in this study were satisfactory (Table 4). The recovery of the sequential extraction procedure was computed as follows (Abdel-Satar & Goher 2015):

$$Recovery = \frac{F1+F2+F3+F4+F5}{TM}\times 100$$

Cluster analysis can be used as an important tool for analyzing heavy metal data to understand the relationship between sampling sites. The cluster diagram shows two clusters (Fig. 2). The first cluster A is formed by WBN and MBE sites with the similarity index of 96.7%, while the cluster B has two subclusters containing the remaining sites with similarity indices ranging from 97.9 to 99.5%. These two clusters are accounted for by the prevalence of different environmental conditions (Rita et al. 2012).

The correlation coefficient matrix summarizes the strength of linear relationships between each pair of variables. Cu-Zn, Cu-Pb and Pb-Zn pairs are significantly positively correlated at $P < 0.05$ with each other (r = 0.75, 0.85 and 0.73, respectively; n = 10), which may suggest common pollution sources or similar mechanisms of transport and accumulation within the sediments (Ong et al. 2013). Furthermore, no significant differences ($P > 0.05$) in the concentrations of metal fractions were observed at the ten sites in Lake Mariut, despite the differences in sediment environment.

The potential environmental risk of trace elements in sediments is associated with both their total content and their speciation. The amount of metals coming from the anthropogenic input, the prevailing chemistry of the sediment-water interface and the species of metals represent serious factors to be considered when accounting for the levels of metals in a fraction (Ogunfowokan et al. 2013). Fe, Cu and Pb in Lake Mariut sediment were present mainly in the residual phase, which implies that these elements were strongly linked to the inert fraction of the sediments. The order of abundance of the Fe fractions was as follows: residual (45%) > Fe-Mn oxides (31%) > organic fraction (22%) > carbonate (1.7%) > exchangeable (0.8%). Residual phases of metals are generally much less toxic to organisms in the aquatic environment (Ogunfowokan et al. 2013; Moore et al. 2015; Abdel-Satar & Goher 2015). The residual fraction was the dominant Cu host in all analyzed samples and this phase carried approximately 63% of the total Cu concentration.

Like Fe and Cu, the average percentage of Pb in Lake Mariut sediments was bound mainly to the residual fraction (52.1%) and the fraction of carbonates (18.0%), and in a smaller amount – to hydrated oxides of iron and manganese (10.5%), organic matter (10.3%) and the exchangeable form (9.0%). Metals bound to different fractions will behave differently in the sedimentary environment, and thus will have different potentials for remobilization and uptake by biota (Fytianos & Lourantou 2004).

The high percentage of Zn in the non-residual fractions (≈65%) may be indicative of high cation exchange capacity of the sediment samples (Ogunfowokan et al. 2013). Zn is mainly associated with the reducible phase (F3 = 32.7%) due to the strong binding of Zn with hydrous Fe-Mn oxides forming stable complexes (Moore et al. 2015). The low content of Zn in the residual fraction was likely due to the low association or retention ability of the mineral's crystal structure, such as with detrital silicates and resistant sulfides (Ogunfowokan et al. 2013).

Like Zn, sediment Mn was found abundantly in the first three fractions (F1+F2+F3 > 64%), which means that Lake Mariut has a Mn potential risk. The increases in exchangeable Mn species mostly resulted from anthropogenic activities (Akcay et al. 2003). Moreover, Mn was rather poorly absorbed from organic matter (F4 = 13.4%), so the bioavailability of Mn in organic matter of sediments was low (Ogunfowokan et al. 2013). The predominance of Mn in non-residual fractions of the samples from Lake Mariut was similar to that obtained from the East China Sea (≈85.5%) (Yuan et al. 2004) and Daya Bay (≈69.7%) (Gao et al. 2010).

A relatively low percentage of metals was bound to organic matter (average = 21.9%, 13.4%, 7.6%, 9.9% and 10.3% for Fe, Mn, Zn, Cu and Pb, respectively) in the sediments of Lake Mariut reflecting either a low percentage of organic matter itself or low retention capacity of organic matter (Abdel-Satar & Goher 2015). On the whole, organic matter and sulfides are important factors that control the bioavailability of heavy metals, but the low percentage of heavy metals in the oxidizable fraction suggested that organic matter is not the main factor affecting the behavior of metals in the sediment of Lake Mariut (Moore et al. 2015).

Risk assessment of metals

Mobility factor

The mobility factors of Cu and Pb (Table 6) exhibited low values (close to 2) in the studied lake. However, the mobility factor of Mn was high (close to 5). The order of mobility of the metals in the studied lake was: Mn > Zn > Fe > Pb > Cu. Site AQS showed higher mobility factors for Mn and Pb compared to the other sites, reflecting high levels of heavy metal inputs from El-Umoum Drain.

Contamination factor

The highest individual contamination factor (ICF) for Mn and Zn (Fig. 3) reflects the risk of contamination of the lake water by metals. The order of average individual contamination factors at the sediment sampling sites was as follow: Mn (3.52) > Zn (1.88) > Fe (1.24) > Pb (1.12) > Cu (0.60).

Table 6

Mobility factors of different metals in Lake Mariut sediment

Site	*ƒ Fe*	*ƒ Mn*	*ƒ Zn*	*ƒ Cu*	*ƒPb*
AQS	2.23	5.44	3.05	1.61	3.67
AQN	2.33	4.72	2.84	1.75	1.68
WBS	2.23	3.73	2.54	1.38	1.73
WBN	2.21	4.21	3.21	1.27	1.32
MBE	2.26	4.57	3.35	1.29	1.33
MBS	2.21	4.40	2.94	1.54	2.28
MBN	2.29	4.85	3.05	1.62	1.82
SBS	2.30	3.91	2.36	1.85	2.97
SBW	2.18	4.47	2.61	1.82	1.83
SBE	2.18	4.90	2.85	1.91	2.60

The global contamination factor (GCF), analyzed based on ICF values, indicated that site AQS (in front of El-Umum Drain) and site SBE were highly affected by metal pollutants (Fig. 4). Metals tend to accumulate in sediments and contamination from each source tends to be localized in a hotspot near the input point and then dispersed regionally in lower percentage (Moore et al. 2015). Subsequently, the obtained results revealed that the AQS site, followed by the SBE site, represents a potential risk to aquatic biota with respect to heavy metals. Generally, the Coastal Delta lakes suffered from anthropogenic heavy metals. Masoud et al. (2011) recorded very high global contamination factors (31.3-59.0) for Lake Burullus, and the individual contamination factors recorded the order of Cd > Cu > Zn > Mn > Pb > Fe.

Enrichment factor

The computed metal enrichment factors in the sediments of Lake Mariut are shown in Table 7. It appears that Lake Mariut sediments were significantly enriched with Mn and very highly enriched with Zn and Cu. The difference in EF values was highly affected by the magnitude of input for each metal in the sediments and/or the removal rate of each metal from the sediments (Yahaya et al. 2012). The EF values between 0.5 and 1.5 suggested that the metal comes entirely from crustal materials or natural processes, whereas the EF values higher than 1.5 indicated that sources were mostly anthropogenic (Nowrouzi & Pourkhabbaz 2014). In fact, all the studied heavy metals show the maximum EF values greater than 5,

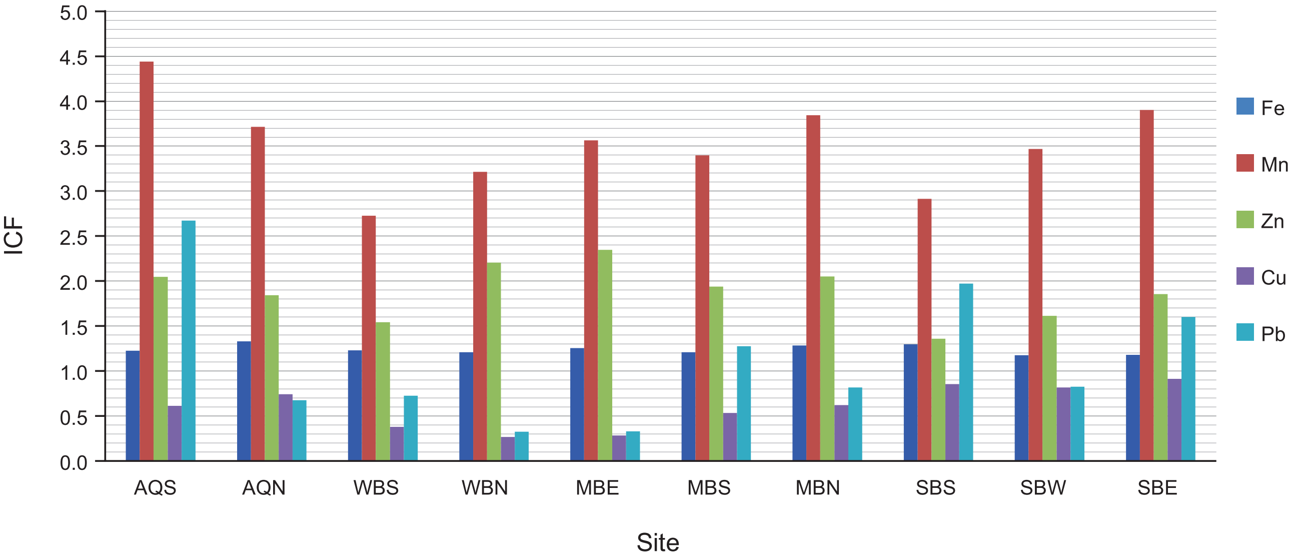

Figure 3

Bar diagrams indicating ICF at surficial sediments of Lake Mariut

indicating a risk of heavy metals in sediment samples. However, Khalil et al. (2013) showed that the EF values in Lake Mariut surface sediments were below 1.5 for Co, Bi, Na, K and Ca suggesting lithogenic origin, while EF for Se showed the highest degree of enrichment (> 1.5), reflecting the human activity. Also for the Coastal Delta lakes (Manzalah, Burullus, Edku), the overall average EF of Cd, Fe and Ni was close to 1.5 (EF < 1.5), while EF of Pb, Cu, Mn, Zn and Cr was above 1.5 (Gu el al. 2013).

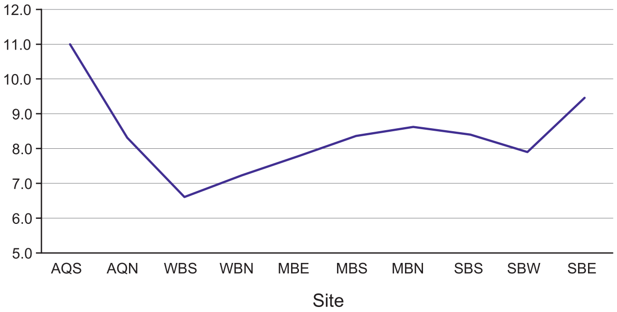

Figure 4

Trend of GCF at surficial sediments of Lake Mariut

Table 7

Metal enrichment factors with respect to the background level in surface Mariut sediments

	Rang	*SD*	*Mean*
Mn	12.0-14.7	0.84	13.7
Zn	34.3-61.2	7.72	48.6
Cu	27.4-89.0	21.51	46.9
Pb	44.5-107.6	21.25	64.2

Risk assessment code (RAC)

The percentage of exchangeable and carbonate fractions of Mn ranged from 30 to 41% of the total Mn content, resulting in high risk according to RAC (Table 4). Medium RAC values were found for Cu carbonate and exchangeable fractions of 10-20%. Also RAC indicated medium to high risk for Zn and Pb (11-46%).

Phosphorus analysis

Phosphorus released from the sediments is the most important factor determining the P content in the overlying water (Abdel-Satar & Goher 2009). Such release may affect the water quality and may result in continuing eutrophication of the aquatic system (Aydin et al. 2009). The current results show that the West Basin in Lake Mariut, which collects water from different basins and discharges it into the sea, and the Main Basin that receives effluents from El-Umoum and El-Qalaa Drains (924 µg g^{-1}) recorded high average total P concentrations (1074 µg g^{-1}), while the South Basin showed the lowest values (693 µg g^{-1}). This suggests that different sediments had different P content due to their different drainage basins and pollution sources, where phosphorus gets into the marine environment from diffuse sources (particularly agriculture) and point sources (treated and untreated sewage effluents) showing significant differences (Aydin et al. 2009).

The sediment of Lake Mariut showed the decrease in Inorg-P percentage (48.6%) (Fig. 5) compared to other Coastal Delta lakes such as Manzalah that contains more than 55% of phosphorus originating

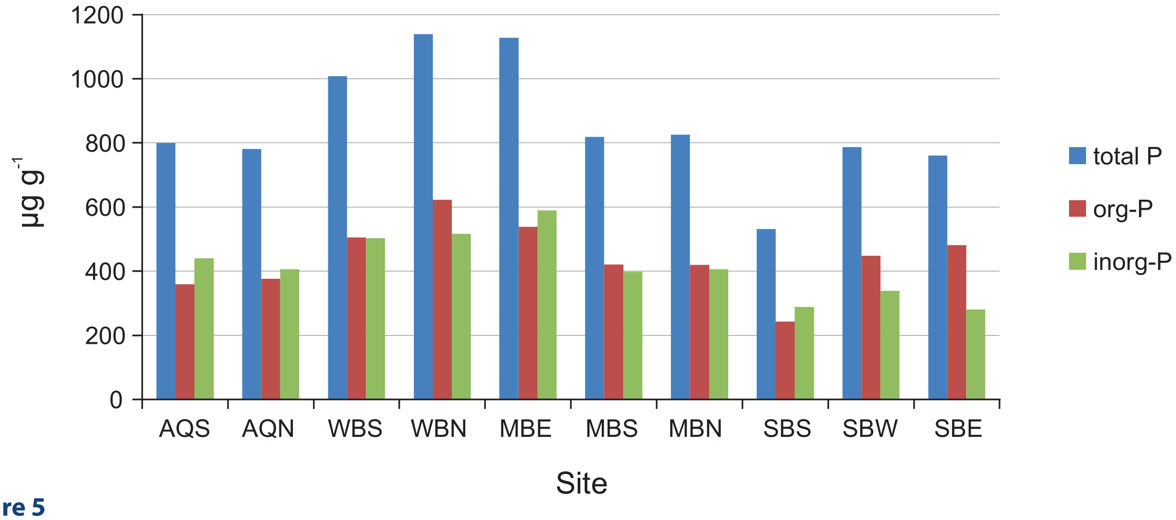

Figure 5

Total P and relative contribution of each organic and inorganic P fraction in Lake Mariut sediment

from the inorganic form (Abdel-Satar & Goher 2009). This is consistent with the richness of phytoplankton in Lake Manzalah compared to Lake Mariut (Khairy et al. 2015), where dissolved inorganic phosphate is the major form absorbed by aquatic primary producers (aquatic macrophytes and phytoplankton) (Abdel-Satar & Sayed 2010).

NH_4Cl-P, BD-P, NaOH-P, HCl-P and Res-P content in the surface sediments of Lake Mariut are presented in Fig. 6. Phosphorus fractions showed different distribution patterns, where HCl-P contributed the highest fraction to the total sedimentary P. The HCl-P fraction was deemed as a relatively stable fraction of Inorg-P in the sediments and consists mainly of apatite P (natural and detritus), including P bound to carbonates (Abdel-Satar & Sayed 2010). The relative abundance of phosphorus forms followed the order:

HCl-P (31.6%) > NaOH-P (28.6%) > BD-P (21.1%) > NH_4Cl-P (12.7%) > Res-P (6.5%)

where the South Basin recorded the highest NH_4Cl-P percentage (17.7%) and the lowest Res-P percentage (4.0%). No significant differences ($P > 0.05$) in the content of the sediment P fraction were observed between the studied sites. The distribution of HCl-P,

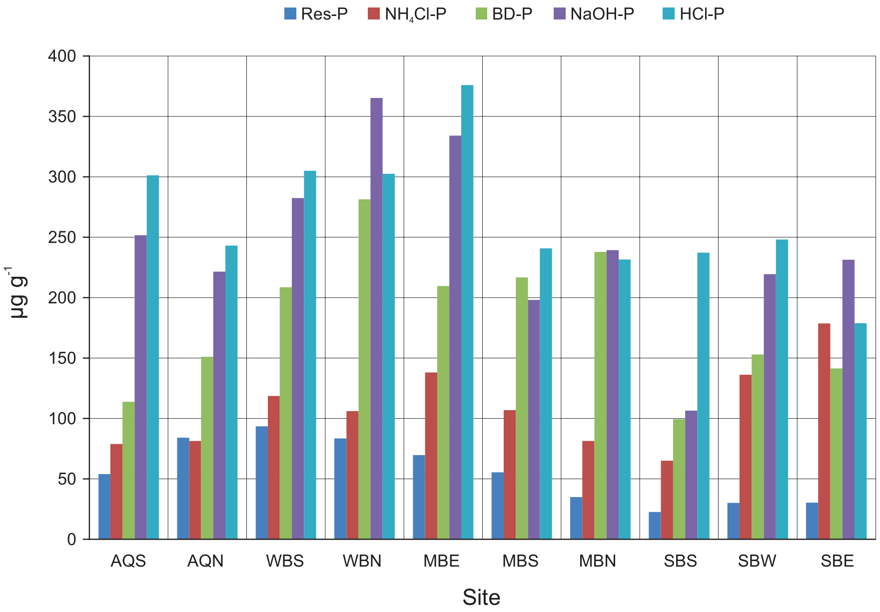

Figure 6

Phosphorus fractions concentration in Lake Mariut sediments

NaOH-P, BD-P, NH_4Cl-P in the studied lake was similar to the rank observed in lakes Volvi and Koronia, Greece (Fytianos & Kotzakioti 2005), and totally different from those observed in Egypt for lakes Manzalah (Abdel-Satar & Goher 2009), Qarun and Wadi El-Rayan (Abdel-Satar & Sayed 2010).

NaOH-P is exchangeable, including P bound to metal oxides (mainly Fe and Al), and is an indicator of algal-available P (Abdel-Satar & Goher 2009). This fraction recorded a relatively high percentage of total sedimentary P (28.6%). It can be released for the growth of phytoplankton when anoxic conditions prevail at the water-sediment interface (Abdel-Satar & Sayed 2010). It is likely that the depletion of DO occurred in the water of the studied lake (Table 1), which resulted in the high contribution of NaOH-P to the overlying water. Compared to the other Coastal Delta lakes such as Lake Manzalah, NaOH-P dominated (48.4%) in the total sedimentary P. The significant positive correlation (r = 0.96, n = 10) between the total amounts of P released from Mariut sediments and those in the NaOH fraction indicated that NaOH-P was the main fraction that can release P easily.

The contribution of redox-sensitive P (BD-P) that includes P bound to Fe/Mn hydroxides to the total P was relatively low in comparison to HCl-P and NaOH-P in the studied lake. This result may be associated with the increase in organic matter, which inhibits the formation of BD-P by competitive bonding with Fe (Zhang et al. 2013). Also the organic matter mineralization resulted in pH changes, thus further affecting the P release (Wang et al. 2008). An increase in the pollution of lakes results in a significant decrease in DO and an increase in pH of the overlying water, which leads to a significant increase in the release of NaOH-P and/or BD-P from the sediments (Zhang et al. 2013). The Fe:P ratio is an indicator of P release from the sediments in shallow lakes, and it may be possible to control the internal P loading by keeping the surface sediment oxidized if the weight-based Fe:P ratio exceeds 15 (Zhang et al. 2013). The Fe:P ratio of Lake Mariut sediment was much lower than 15 (0.48-1.15), indicating that Fe cannot regulate the P release and the contribution of NaOH-P and BD-P to the P content in the overlying- water was high.

NH_4Cl-P content in the sediments was the lowest among the phosphorus fractions, accounting for approximately 13% of the total P. It might be released from calcium carbonate associated P or from decaying cells of bacterial biomass in deposited phytodetrital aggregates (Wang et al. 2013).

The Org-P fraction dominates in sedimentary P (average = 51.4%; Fig. 5). It is one of the phosphorus fractions, which is generally retained in sediment during mineralization (Topcu & Pulatsü 2008). The surface sediment from Lake Mariut contained 17.3% of Org-P as exchangeable P, in addition to 73.92 μg g^{-1} of humic substances-bound P (average 16.6% of total Org-P). There is a significant positive correlation (r = 0.75, n = 10) between P in the humic fraction with both total P and Org-P.

Ca-P substantially contributed to the supply of Inorg-P in sediments of Lake Mariut (68.8%; Fig. 7). The average of Ca-P and Al-P accounted for 31.6% and 10.3% of the total P, respectively. Available-P and Fe-P were the lowest in the phosphorus fractions, which varied between 10.49 to 56.29 μg g^{-1}, and less than 4% in the total P content. Generally, available-P, Fe-P, Al-P

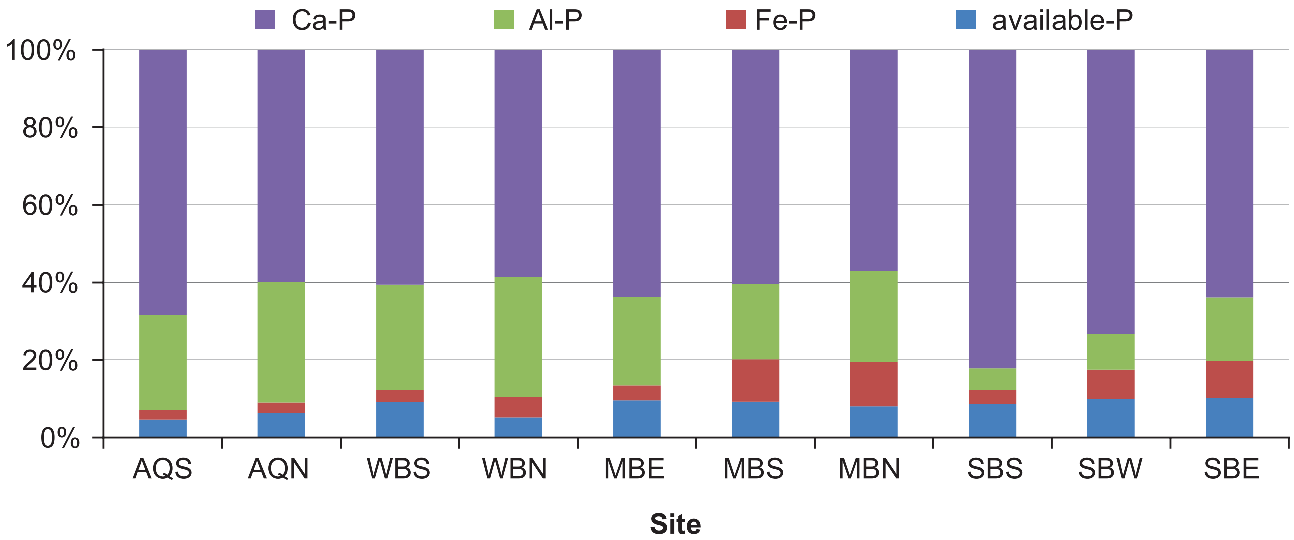

Figure 7

Relative contribution of each Inorg-P fraction to the sum of total inorganic phosphorus in Lake Mariut sediment

Table 8

Correlations between different phosphorus fractions in sediments

	Lsor-P	*Fe-P*	*Al-P*	*Ca-P*	*Org -P*	*Inorg -P*	*Total-P*
Available-P	1.00						
Fe-P	0.21	1.00					
Al-P	0.30	-0.05	1.00				
Ca-P	0.57	-0.26	0.67*	1.00			
Org -P	0.47	0.31	0.62	0.42	1.00		
Inorg -P	0.60	-0.02	0.89**	0.91**	0.63	1.00	
Total P	0.59	0.17	0.83**	0.73*	0.91**	0.90**	1.00

Correlation is significant at * $P < 0.05$, ** $P < 0.01$; n = 10

and part of Org-P are easily desorbed from the lake sediments and released into the overlying water. These are referred to as the bioavailable fraction of P in the lake sediment (Wang et al. 2013).

The correlation between various phosphorus fractions is presented in Table 8. Highly positive significant correlation between total P content and Inorg-P, Org-P and Al-P content ($P < 0.01$) was determined. As one of the inorganic phosphorus fractions, Al-P and Ca-P content was also closely related to Inorg-P content ($P < 0.01$).

Risk of phosphorus release into sediments

Pollution P indices at Lake Mariut sampling sites were higher than 1, except site SBS (0.88), while the maximum value was recorded at site WBN (1.90), indicating that Lake Mariut sediments were at a potential phosphorus risk, especially in the West Basin.

Conclusions

Concentrations of heavy metals in sediment depend not only on agricultural, industrial and municipal waste inputs but also on the geochemical composition of the studied lake. Although the recorded total Zn, Cu and Pb concentrations in Mariut sediments were mostly below the sediment quality guidelines for the protection of aquatic life, the lake is likely to be at a potential risk. The results of the heavy metal fractionation scheme in Mariut sediment revealed that Fe, Cu and Pb were present mainly in the residual phase (inert fraction). The dominance of Zn and Mn in non-residual phases poses a relatively high ecological threat resulting from the anthropogenic impact.

The comprehensive assessment of the potential pollution risk of heavy metals by using the global contamination factor showed that site AQS (in front of El-Umum Drain) was impacted by metal pollutants, while site SBE was characterized by the highest individual contamination factors recorded for Mn and Zn. Also all the studied metals had the maximum EF values greater than 5, indicating the study lake is threatened by heavy metals coming from anthropogenic sources. The chemical composition of P in sediments and its bioavailability are important factors for predicting the future internal P loading in lake ecosystems. The West Basin in Lake Mariut, which collects water from different basins and discharges it into the sea, and the Main Basin that receives effluents from El-Umoum and El-Qalaa Drains were characterized by high average total P concentrations (1074 µg g^{-1}). Lake Mariut sediment contained inorganic and organic-P forms (on average 48.6% and 51.4%, respectively). The rank order of P fractions in the lake sediment was HCl-P > NaOH-P > BD-P > NH_4Cl-P > Res-P, where Ca-P substantially contributed to the supply of Inorg-P (68.8%). The contribution of phosphorus fractions to the overlying water was high as a result of the decrease in both the DO level in the lake water and the Fe:P ratio in the lake sediment.

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