Distribution of Different Metals in Coastal Waters of Alexandria, Egypt

Mamdouh S. Masoud^a, Wagdi M. El-Saraf^b, Ahmed M. Abdel Halim^b, Alaa E. Ali^c and Hamad M.I. Hasan^d

^aChemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt ^bNational Institute of Oceanography and Fisheries, Alexandria, Egypt ^cChemistry Department, Faculty of Science, Damanhour University, Egypt ^dFaculty of Science, Omar El-Moktar University, El-Bieda, Libya

Received for publication February 20, 2010 and in revised form March 20, 2010 Accepted March 25, 2010

ABSTRACT: Seasonal variation of some heavy metals (Fe, Mn, Cu, Cd, Pb, Co, Ni, Cr, Sn and Al) are estimated at surface and bottom waters from 10 stations at near-shore, Alexandria coast during 2004. Salinity (16.20-39.10) and pH values (alkaline side) were also measured. The concentrations of heavy metals are at high levels in regions receiving different effluents from wastes of El-Mex region. A comparative study between the different stations was carried out to evaluate the effect of sewage, agricultural and industrial wastes discharged into some regions of Alexandria coast. Different statistical treatments were carried out to calculate the correlation coefficients between metals and the annual average variation.

Key words: Seasonal variation, heavy metals, El-Mex coastal water, surface, bottom.

INTRODUCTION

Alexandria is the second largest city in Egypt and one of the most important industrial centers, comprised 100 large factories and about 260 smaller ones(1), which represents about 40% of the nation's industry. It is also the main summer tourism destination in Egypt for about 4 million citizen and two million summer visitors⁽²⁾. More than 18×10⁶ m³ of untreated sewage and wastewaters are discharged annually from large numbers of outlets into Alexandria coastal area through local-sewerage system⁽³⁾. Chemical pollutants are of major concern in the Mediterranean area and in several marine environments all over the world. A number of these materials can reach the estuaries, coastal areas and open waters of the Mediterranean from land-based sources. Alexandria occupies a narrow stretch along the sea, extending for about 45 km from El-Agami in the west to Abu-Qir in the east between the Mediterranean and Lake Maruit. As a result of this topographic situation, the city of Alexandria appears to be encircled within a belt of degraded aquatic environments, subjected to multiple resource pollution. The present study is carried out to shed some light on the distribution of some metals at coastal water of Alexandria. Different statistical treatments were carried out to calculate the correlation coefficients between metals and the annual average variations.

MATERIALS AND METHODS

Areas of investigation extended along a distance of 40 km from El-Montazah in the east to El-Agami in the west of Alexandria. Ten stations were selected along two horizontal sections parallel to the shore line; five stations along each section to cover five main locations, Figure (1). The first section, stations I, III, V, VII and IX, chosen near the shore at El-Montazah, Gleem, El-Shattbi, El-Mex and El-Agami regions, respectively. The depth ranged from 4-6 m. The second section (stations II, IV, VI, VIII and X) was selected in the off shore at about16-20 m water depth.

Sampling Samples were collected seasonally during February, May, August and November 2004 representing winter, spring, summer and autumn seasons, respectively. The surface and bottom water samples were collected using a Niskin Bottle. Samples were kept in well-cleaned polyethylene bottles were deep-frozen at -20° C. Salinity was determined by measuring the electrical conductivity using an Induction salinometer (BEKMAN model No. RS7C, ...)

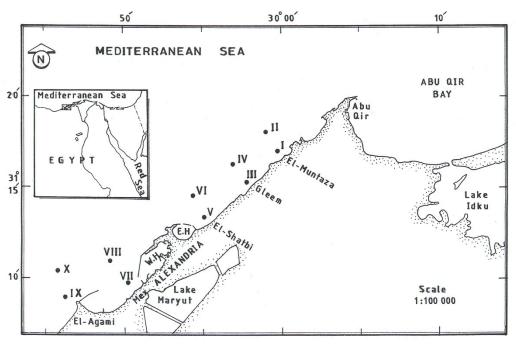


Figure (1): The area of study

to the nearest 0.0001. The salinometer was calibrated using standard sea water of salinity 35‰ at room temperature. The pH of water samples was determined at the time of sampling, using a pocket pH meter (Orien model 201, ...) accurate to 0.01. The instrument was calibrated with buffer solutions pH 4, 7, 10.

Heavy Metals: Iron, manganese, zinc, copper, cadmium, cobalt, lead, nickel, chromium, nickel, aluminum and tin were determined. Water samples were filtrated using membrane filter paper (0.45 μ m). The filtrate represents the dissolved phase which determined according to the method described by the American Public Health Association after digestion using HNO3 and HCl acids. The metals were determined by atomic absorption spectrophotometer (AAS), Perkin-Elmer (Model 2380), were expressed as μ g/l. The data are represented in Tables (1-16).

RESULTS AND DISCUSSION

Salinity: Salinity is affected by several factors such as the rates of renewing, sewage and fresh water inflowing, precipitation, in addition to the physical and climatic conditions. Salinity is the definite property of sea water by which it is distinguished from natural waters⁽⁴⁾ and defined as the total weight of salts in grams in one thousand grams of sea water. In the Mediterranean sea,

salinity is almost higher than 37‰⁽⁵⁾. The salinity of the surface waters of the world is highly variable, depending mainly upon ionic influences of drainage, exchange from the surrounding land, atmospheric sources, equilibrium and exchange with sediments inside the water body. The seasonal variations of water salinity values are given in Table (1) and Figure (2). The data fluctuated in the ranges of 16.20-34.50, 17.50-36.10, 18.90-36.20 and 18.50-37.40‰ in the surface water. For the bottom water, the ranges were 33.00-35.10, 35.20-36.60, 35.90-39.10, and 34.40-38.90% during winter, spring, summer and autumn, respectively. A maximum value was obtained during summer which reached to 39.10‰ in bottom water at station IV. While, a minimum value was given at station VII in the surface water during winter 16.20 ‰, this is probably attributed to the dilution caused by the discharging of El-Umum drain and fresh water of Lake Maruit. In general, the surface water at the near shore stations always showed lower salinity values than those of offshore. However, the salinity values of the bottom water (33.00-39.10‰) were higher than that of the surface water (16.20-37.40‰), probably due to indirect effect of temperature to lead a change in density and viscosity values of water, which in turn, affects the rate of sinking of suspended particles either plankton organisms or clay suspension⁽⁶⁾.

Mamdouh S. Masoud et al.

Stations	Wi	Winter		ring	Sun	nmer	Aut	umn		nual crage	S	D ±
	S	В	S	В	S	В	S	В	S	В	S	В
Ι	32.70	33.00	34.80	35.20	35.00	36.80	34.40	36.50	34.23	35.38	1.05	1.70
II	33.40	34.10	36.00	36.20	35.80	36.90	35.20	36.70	35.10	35.98	1.18	1.28
III	32.90	33.00	36.00	36.10	34.30	37.50	36.10	37.70	37.83	36.08	1.53	2.17
IV	33.00	33.10	36.00	36.10	36.20	39.10	36.80	38.60	35.50	36.73	1.70	2.75
V	33.00	33.40	35.40	35.90	34.60	36.60	35.90	36.80	34.73	35.68	1.27	1.56
VI	33.70	34.00	36.10	36.60	36.00	36.70	36.40	37.80	35.55	36.28	1.24	1.61
VII	16.20	34.16	17.50	36.20	18.90	35.90	18.50	34.40	17.78	35.15	1.20	1.05
VIII	32.20	34.50	35.90	36.20	36.10	38.40	36.30	37.50	35.13	36.65	1.96	1.69
IX	34.40	34.60	34.60	36.10	34.40	35.90	35.20	36.10	34.65	35.68	0.38	0.72
Х	34.50	35.10	35.20	36.20	35.20	36.80	37.40	38.90	33.75	36.75	1.26	1.60
Seasonal Average	31.60	33.89	33.75	36.08	33.65	37.06	34.22	37.10	33.31	36.03	1.16	1.50

Table (1): Seasonal variations of salinity (S%) in Alexandria coast during 2004.

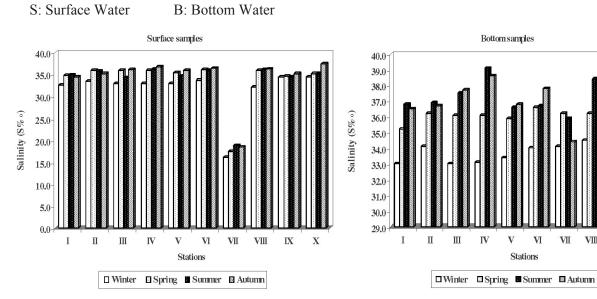


Figure (2): Seasonal variations of salinity in the Alexandria coast during 2004.

Salinity values for the area of study, except for station VII, ranged between 33.00-39.10‰ lower than the normal of open sea water salinity which is 39‰^(7,8). Changing of salinity may affect the variation of pH levels in the aquatic system, where positive correlation between salinity and pH was established (r = 0.461, 0.325, 0.436 and 0.424) during the above mentioned seasons $HCO_{\overline{3}}$.

Hydrogen ion concentration: The pH value is the master control parameter in the aquatic environment for chemical and biological sys-

tems of water. The carbonate cycle composed of CO₂, H₂CO₃, HCO $\overline{3}$ and CO₃^{2–} play a major role in regulating the pH⁽⁹⁾. The importance of alkalinity lies in its role for carbon dioxide chemistry, trace metal speciation and buffer capacity of the sea water^(10,11). The main factors controlling the variation of pH in any aquatic environment are: dissolved oxygen, water temperature, land runoff, decomposition of organic matter, photosynthetic activity, respiration of aquatic organisms and some physio-chemical processes, such as precipitation and oxidation-

VIII

IX

X

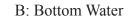
reduction (redox reactions) tacking place in the environment⁽¹¹⁾. The seasonal variations of pH values showed that the data in different stations, Table (2) and Figure (3), in the ranges of 7.65-8.0, 8.19-8.42, 8.20-8.99 and 7.79-8.12 in the surface water, and for the bottom water were, 7.55-7.95, 8.10-8.39, 7.88-8.37 and 7.55-8.0 during winter, spring, summer and autumn seasons, respectively. The slight increase of pH values during spring and summer seasons may be related to the photosynthetic activity which reduce the CO₂ amount in water⁽¹²⁾, and/or may

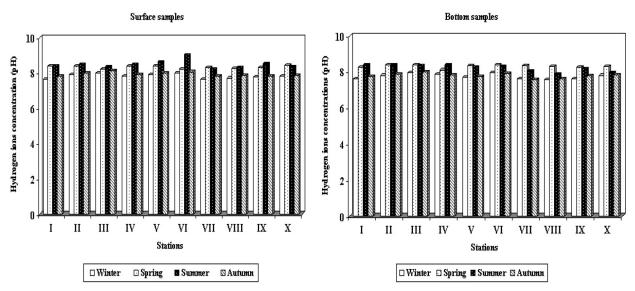
be attributed to the increase in evaporations rates during these seasons. This also is associated with the increase of CO_3 ⁻⁻ contents during spring and summer. However, the elevation of pH is associated with photosynthetic assimilation of dissolved inorganic carbon⁽¹³⁾. The relative decrease of pH values during winter may be related to the high solubility of CO_2 in water, leading to the formation of HCO_3^- , and decrease of both CO_3^{--} contents and pH values⁽¹⁴⁾. The data give a maximum pH 8.99 in the surface water during summer at station VI, while

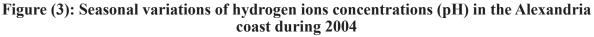
Table (2): Seasonal variations of pH in Alexandria coast during 2004

Stations	Winter		Sp	oring	Sui	nmer	Au	tumn		nual erage	S	D +
	S	В	S	В	S	В	S	В	S	В	S	B
Ι	7.65	7.60	8.37	8.24	8.40	8.36	7.88	7.75	8.06	7.99	0.39	0.37
II	7.90	7.80	8.38	8.39	8.46	8.37	7.98	7.85	8.16	8.10	0.28	0.32
III	8.00	7.95	8.22	8.36	8.35	8.32	8.12	8.00	7.17	8.16	0.15	0.21
IV	7.82	7.85	8.40	8.10	8.45	8.37	7.90	7.81	8.14	8.03	0.33	0.26
V	7.90	7.70	8.36	8.35	8.60	8.24	7.99	7.74	8.21	8.01	0.33	0.34
VI	8.00	7.95	8.19	8.39	8.99	8.30	8.05	7.92	8.31	8.14	0.46	0.24
VII	7.65	7.55	8.30	8.34	8.20	8.05	7.79	7.55	7.99	7.87	0.31	0.39
VIII	7.70	7.57	8.23	8.30	8.30	7.88	7.85	7.62	8.02	7.84	0.29	0.3
IX	7.75	7.62	8.31	8.25	8.50	8.17	7.82	7.77	8.10	7.95	0.37	0.31
Х	7.80	7.80	8.42	8.30	8.33	7.97	7.87	7.83	8.11	7.98	0.32	0.23
Seasonal Average	7.82	7.74	8.32	8.30	8.46	8.20	7.92	7.78	8.13	8.01	0.31	0.29

S: Surface Water







the minimum value of pH reached to 7.55 in the bottom water during winter at station VII. This may due to the effect of brackish water discharged from El-Umum drain. The pH values in the surface water are ranged between 7.65 and 8.99. However, these in the bottom water are fluctuated between 7.55 and 8.39. The data are in harmony with that the decrease in bottom water coincided with the decrease in oxygen content⁽¹⁵⁾. However, the pH of sea water varies with geographical position and depth, ranging from 7.9 to 8.3 in the surface and from 7.5 to 7.9 with depth. In general, the pH values in the present study have all lied on the alkaline side.

Heavy Metals: The list of heavy metals that has been studied were Iron, manganese, zinc, copper, cadmium, cobalt, lead, nickel, chromium, nickel, aluminum and tin.

Iron: Iron is the most abundant metal in the earth's crust. It is an important trace element required for all biological life activities. Iron seafood and fresh water fishes, doesn't constitute a hazard to human consumers. At high concentration the iron II is toxic for most organisms. The results obtained of the iron concentrations are given in Table (3) and Figure (4). The seasonal variations of iron concentrations were in the ranges of 21.30-91.73, 18.30-105.95, 22.35-112.55 and 16.10-90.85 $\mu g/l$ in the surface

water and 38.35-101.65, 28.85-110.12, 33.70-130.14 and $25.33-92.12 \,\mu$ g/l for the bottom water during winter, spring, summer and autumn seasons, respectively. It seemed that, the values of iron have decreased during winter, that may be attributed to the oxidation of Fe⁺² to Fe⁺³ which precipitated as a hydroxide at pH> 7 in presence of higher oxygen concentrations. The slight increase of iron concentrations during spring and autumn may also be attributed to the dissolution of sediments and release of iron to the overlying water⁽¹⁶⁾. The high iron concentrations during summer may be attributed to the high production of organic matter in summer to increase the chance for formation of iron-organo complexes which can pass through a membrane filter of 0.45m leading to the increase the iron content dissolved in water. The maximum values at station VII in the bottom water were 101.65, 110.12, 130.14 and 92.12 µg/l. mainly attributed to the effect of El-Umum drain which receives a direct industrial wastes from chloro-alkali plant, tanneries and slaughter house. Generally, there is a gradual decrease in the dissolved iron content on going far away from the near shore stations. The dissolved iron contents recorded in bottom water $(25.33-130.14\mu g/l)$ are higher than those of the surface water (16.10-112.55µg/l) may be due to:- 1) Sedimentation of the floccules containing iron, 2) the increase in suspended matter

Stations	W	Winter		ring	Sun	nmer	Au	tumn		nual erage	S	D +
	S	В	S	В	S	В	S	В	S	В	S	В
Ι	26.10	39.00	38.40	47.75	38.15	42.16	27.25	32.00	32.48	40.23	6.71	6.57
II	21.30	38.35	18.30	28.85	22.35	33.70	16.10	25.33	19.51	31.56	2.85	5.68
III	41.65	59.17	34.29	40.65	58.61	68.45	46.40	62.11	45.24	57.60	10.21	11.94
IV	38.11	43.92	49.35	62.38	47.80	49.21	38.30	54.18	43.39	52.42	6.02	7.85
V	47.80	60.19	70.44	78.75	73.64	80.07	60.94	61.22	63.21	70.06	11.60	10.82
VI	36.20	44.05	56.12	73.60	62.15	89.20	49.20	54.68	50.93	65.38	11.15	20.04
VII	91.73	101.65	105.95	110.12	112.55	130.14	90.85	92.12	100.27	108.51	10.72	16.19
VIII	74.28	80.12	72.60	74.18	80.02	86.91	80.14	75.92	76.76	79.28	3.89	5.66
IX	45.50	56.16	64.32	60.59	67.15	74.27	53.60	60.94	57.65	62.99	9.98	7.83
Х	35.11	61.23	30.08	51.42	29.80	55.11	37.52	40.90	33.13	52.17	3.18	8.53
Seasonal Average	45.78	58.38	53.99	62.83	59.22	70.92	50.03	55.94	52.25	62.02	3.73	6.59

Table (3): Seasonal variations of iron concentration (µg/l) in Alexandria coast during 2004

S: Surface Water

B: Bottom Water

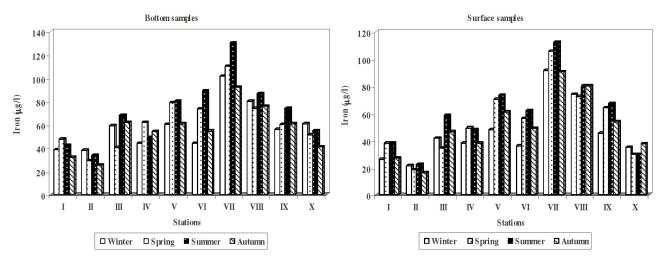


Figure (4): Seasonal variations of iron concentrations (µg/l) in the Alexandria coast during 2004

with adsorbed iron in the bottom water and 3) the release of a certain part of the adsorbed iron from the suspended matter and bottom sediment⁽¹⁷⁾.

Manganese: It is one of the more bio-chemically active transition metals in aquatic environments. The chemistry of manganese is appreciably complicated due to its existence in different oxidation states i.e. (I-VII). The mechanism of oxidation of Mn (II) to Mn (IV) in aquatic systems is a matter of debate(18). Mn (II) is unstable in oxygenated water and easily oxidized to higher forms with the formation of solid MnO₂. The bacterial oxidation leads to the formation of Mn (OH)₃, depending on pH. The seasonal variations of manganese concentrations were in the ranges of 0.20-5.62, 0.19-4.18, ND-4.00 and ND-2.80 µg/l in the surface water during winter, spring, summer and autumn seasons, respectively. For the bottom water, the manganese contents fluctuated between 0.66-7.0, 0.41-5.92, 0.51-4.80 and 0.41-3.71 μ g/l during the above mentioned seasons, respectively, Table (4) and Figure (5). High values recorded during winter, may be due to dissolution of sediment manganese and release to water, and the decrease in uptake by phytoplankton. Meanwhile, the low values and relative decrease in manganese during autumn may be attributed to the removal of manganese from aqueous phase to solid phase during precipitation of Mn as MnO₂ or by adsorption on suspended particles during summer⁽¹⁹⁾. The data gave maximum values at station VII

in the bottom water during the period of the study (7.00, 5.82, 4.80 and 3.71µg/l), mainly attributed to the strong effect of industrial wastes and sewage from El-Umum drain. Non detected (ND) values were recorded in surface water at stations IV, IX and X, far away from El-Umum drain. In general, the concentrations of dissolved manganese in surface water, ND- $5.62\mu g/l$, were lower than that of bottom water $(0.41-7.00 \mu g/l)$, due to sedimentation processes of manganese ion and release of manganese from sediment through anaerobic decomposition of organic matter by bacteria. There is a gradual decrease in manganese content from nearshore to off shore stations. The correlation coefficient matrixes showed a strong significant positive trend between dissolved manganese and iron (r= 0.836, 0.842, 0.779 and 0.781) to indicate their association as oxides and hydroxides in precipitations to the bottom during transpirations and/or depositional reaction. The annual average concentrations of dissolved manganese of station VII (4.15 μ g/l) in surface water is higher than those reported at different Egyptian coastal Mediterranean area, Table (14).

Zinc: The seasonal variations of zinc concentrations were in ranges of 11.25-199.75, 8.30-183.45, 12.15-155.60 and 15.80-208.40µg/l in the surface water during winter, spring, summer and autumn, respectively.

However, for the bottom water, the zinc concentrations varied between 36.70-166.81,

Wi	nter	Spr	ing	Sum	mer	Aut	umn			SE) +
S	В	S	В	S	В	S	В	S	В	S	В
0.81	1.10	0.47	0.76	0.31	0.68	0.53	0.74	0.53	0.82	0.21	0.19
0.50	0.66	0.28	0.14	0.30	0.51	0.29	0.62	0.34	0.55	0.11	0.11
0.25	1.50	0.19	1.25	0.27	1.70	0.48	1.86	0.30	1.58	0.13	0.26
0.20	0.88	1.90	2.18	0.19	1.60	ND	0.93	0.76	1.40	0.98	0.62
1.52	3.71	1.12	2.41	0.72	1.87	0.55	1.15	0.98	2.29	0.43	1.08
2.74	3.08	2.40	2.52	2.10	2.26	1.49	1.78	2.18	2.41	0.53	0.54
5.62	7.00	4.18	5.92	4.00	4.80	2.80	3.71	4.15	5.36	1.16	1.42
2.60	4.91	1.85	3.44	1.26	2.92	2.10	3.30	1.95	3.64	0.56	0.87
1.75	2.43	0.90	1.40	ND	0.90	ND	0.41	1.33	1.29	0.60	0.86
1.02	1.89	0.61	1.21	ND	0.80	0.70	1.15	0.78	1.26	0.22	0.46
1.70	2.72	1.39	2.15	1.14	1.80	1.12	1.57	1.34	2.06	0.27	0.50
Vater		B: 1	Bottom	Water		N	D: Not	Detecte	ed		
	Surface sam	les					1	Bottom sample	s		
Surface samples 600 600 600 600 600 600 600 60											
🗆 Winter 🛛 Spring 🛢 Summer 🖾 Autumn							Winter 🗆 S	pring 🛚 Sum	mer ⊠Autum	n	
	S 0.81 0.50 0.25 0.20 1.52 2.74 5.62 2.60 1.75 1.02 1.70 Vater	0.81 1.10 0.50 0.66 0.25 1.50 0.20 0.88 1.52 3.71 2.74 3.08 5.62 7.00 2.60 4.91 1.75 2.43 1.02 1.89 1.70 2.72 Vater Surface sam	S B S 0.81 1.10 0.47 0.50 0.66 0.28 0.25 1.50 0.19 0.20 0.88 1.90 1.52 3.71 1.12 2.74 3.08 2.40 5.62 7.00 4.18 2.60 4.91 1.85 1.75 2.43 0.90 1.02 1.89 0.61 1.70 2.72 1.39 Vater B: I Surface samples	S B S B 0.81 1.10 0.47 0.76 0.50 0.66 0.28 0.14 0.25 1.50 0.19 1.25 0.20 0.88 1.90 2.18 1.52 3.71 1.12 2.41 2.74 3.08 2.40 2.52 5.62 7.00 4.18 5.92 2.60 4.91 1.85 3.44 1.75 2.43 0.90 1.40 1.02 1.89 0.61 1.21 1.70 2.72 1.39 2.15 Water B: Bottom Surface samples	S B S B S 0.81 1.10 0.47 0.76 0.31 0.50 0.66 0.28 0.14 0.30 0.25 1.50 0.19 1.25 0.27 0.20 0.88 1.90 2.18 0.19 1.52 3.71 1.12 2.41 0.72 2.74 3.08 2.40 2.52 2.10 5.62 7.00 4.18 5.92 4.00 2.60 4.91 1.85 3.44 1.26 1.75 2.43 0.90 1.40 ND 1.02 1.89 0.61 1.21 ND 1.70 2.72 1.39 2.15 1.14	S B S B S B 0.81 1.10 0.47 0.76 0.31 0.68 0.50 0.66 0.28 0.14 0.30 0.51 0.25 1.50 0.19 1.25 0.27 1.70 0.20 0.88 1.90 2.18 0.19 1.60 1.52 3.71 1.12 2.41 0.72 1.87 2.74 3.08 2.40 2.52 2.10 2.26 5.62 7.00 4.18 5.92 4.00 4.80 2.60 4.91 1.85 3.44 1.26 2.92 1.75 2.43 0.90 1.40 ND 0.90 1.02 1.89 0.61 1.21 ND 0.80 1.70 2.72 1.39 2.15 1.14 1.80 Surface samples 7.00 1 1 1 1.00 0.00	S B S B S B S 0.81 1.10 0.47 0.76 0.31 0.68 0.53 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.25 1.50 0.19 1.25 0.27 1.70 0.48 0.20 0.88 1.90 2.18 0.19 1.60 ND 1.52 3.71 1.12 2.41 0.72 1.87 0.55 2.74 3.08 2.40 2.52 2.10 2.26 1.49 5.62 7.00 4.18 5.92 4.00 4.80 2.80 2.60 4.91 1.85 3.44 1.26 2.92 2.10 1.75 2.43 0.90 1.40 ND 0.90 ND 1.02 1.89 0.61 1.21 ND 0.80 0.70 1.70 2.72 1.39 2.15 1.14 1.80 1.12 </td <td>S B S B S B S B S B 0.81 1.10 0.47 0.76 0.31 0.68 0.53 0.74 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.62 0.25 1.50 0.19 1.25 0.27 1.70 0.48 1.86 0.20 0.88 1.90 2.18 0.19 1.60 ND 0.93 1.52 3.71 1.12 2.41 0.72 1.87 0.55 1.15 2.74 3.08 2.40 2.52 2.10 2.26 1.49 1.78 5.62 7.00 4.18 5.92 4.00 4.80 2.80 3.71 2.60 4.91 1.85 3.44 1.26 2.92 2.10 3.30 1.75 2.43 0.90 1.40 ND 0.90 ND 0.41 1.02 1.89 0.61 <t< td=""><td>Winter Spring Summer Autumn Ave S B S B S B S B S 0.81 1.10 0.47 0.76 0.31 0.68 0.53 0.74 0.53 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.62 0.34 0.25 1.50 0.19 1.25 0.27 1.70 0.48 1.86 0.30 0.20 0.88 1.90 2.18 0.19 1.60 ND 0.93 0.76 1.52 3.71 1.12 2.41 0.72 1.87 0.55 1.15 0.98 2.74 3.08 2.40 2.52 2.10 2.26 1.49 1.78 2.18 5.62 7.00 4.18 5.92 4.00 4.80 2.80 3.71 4.15 2.60 4.91 1.85 3.44 1.26 2.92 2.10 3.30 1.9</td><td>S B S D 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.62 0.34 0.55 0.25 1.50 0.19 1.25 0.27 1.70 0.48 1.86 0.30 1.58 0.20 0.88 1.90 2.18 0.19 1.60 ND 0.93 0.76 1.40 1.52 3.71 1.12 2.41 0.72 1.87 0.55 1.15 0.98 2.29 2.60 4.91 1.85 3.44 1.26 2.92 2.10 3.30 1.95 3.64 1.75</td><td>Wilder Spring Summer Autumn Average St S B S B S B S B S B S B S B S B S B S B S B S B S B S B S B S Cold <</td></t<></td>	S B S B S B S B S B 0.81 1.10 0.47 0.76 0.31 0.68 0.53 0.74 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.62 0.25 1.50 0.19 1.25 0.27 1.70 0.48 1.86 0.20 0.88 1.90 2.18 0.19 1.60 ND 0.93 1.52 3.71 1.12 2.41 0.72 1.87 0.55 1.15 2.74 3.08 2.40 2.52 2.10 2.26 1.49 1.78 5.62 7.00 4.18 5.92 4.00 4.80 2.80 3.71 2.60 4.91 1.85 3.44 1.26 2.92 2.10 3.30 1.75 2.43 0.90 1.40 ND 0.90 ND 0.41 1.02 1.89 0.61 <t< td=""><td>Winter Spring Summer Autumn Ave S B S B S B S B S 0.81 1.10 0.47 0.76 0.31 0.68 0.53 0.74 0.53 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.62 0.34 0.25 1.50 0.19 1.25 0.27 1.70 0.48 1.86 0.30 0.20 0.88 1.90 2.18 0.19 1.60 ND 0.93 0.76 1.52 3.71 1.12 2.41 0.72 1.87 0.55 1.15 0.98 2.74 3.08 2.40 2.52 2.10 2.26 1.49 1.78 2.18 5.62 7.00 4.18 5.92 4.00 4.80 2.80 3.71 4.15 2.60 4.91 1.85 3.44 1.26 2.92 2.10 3.30 1.9</td><td>S B S D 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.62 0.34 0.55 0.25 1.50 0.19 1.25 0.27 1.70 0.48 1.86 0.30 1.58 0.20 0.88 1.90 2.18 0.19 1.60 ND 0.93 0.76 1.40 1.52 3.71 1.12 2.41 0.72 1.87 0.55 1.15 0.98 2.29 2.60 4.91 1.85 3.44 1.26 2.92 2.10 3.30 1.95 3.64 1.75</td><td>Wilder Spring Summer Autumn Average St S B S B S B S B S B S B S B S B S B S B S B S B S B S B S B S Cold <</td></t<>	Winter Spring Summer Autumn Ave S B S B S B S B S 0.81 1.10 0.47 0.76 0.31 0.68 0.53 0.74 0.53 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.62 0.34 0.25 1.50 0.19 1.25 0.27 1.70 0.48 1.86 0.30 0.20 0.88 1.90 2.18 0.19 1.60 ND 0.93 0.76 1.52 3.71 1.12 2.41 0.72 1.87 0.55 1.15 0.98 2.74 3.08 2.40 2.52 2.10 2.26 1.49 1.78 2.18 5.62 7.00 4.18 5.92 4.00 4.80 2.80 3.71 4.15 2.60 4.91 1.85 3.44 1.26 2.92 2.10 3.30 1.9	S B S D 0.50 0.66 0.28 0.14 0.30 0.51 0.29 0.62 0.34 0.55 0.25 1.50 0.19 1.25 0.27 1.70 0.48 1.86 0.30 1.58 0.20 0.88 1.90 2.18 0.19 1.60 ND 0.93 0.76 1.40 1.52 3.71 1.12 2.41 0.72 1.87 0.55 1.15 0.98 2.29 2.60 4.91 1.85 3.44 1.26 2.92 2.10 3.30 1.95 3.64 1.75	Wilder Spring Summer Autumn Average St S B S B S B S B S B S B S B S B S B S B S B S B S B S B S B S Cold <

Table (4): Seasonal variations of manganese concentration (μg/l) in Alexandria coast during 2004

Figure (5): Seasonal variations of manganese concentrations (µg/l) in the Alexandria coast during 2004

26.24-151.75, 17.15-132.55 and 40.15-174.30 μ g/l during the above mentioned seasons, respectively, Table (5) and Figure (6). The high values recorded during autumn are attributed to the decrease of the sorption of zinc with the drop in the temperature, and/or due to its contribution from the interstitial water to the overlying water. This may be effective under dynamic conditions such as dredging operations⁽²⁰⁾ and bio-turbation. The relative decrease of zinc contents during spring may be

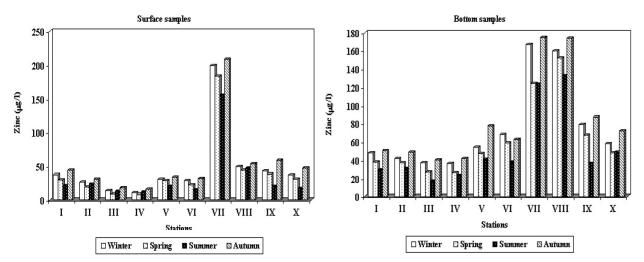
related to the uptake of Zn by phytoplankton and zooplankton. The lower values recorded during summer, may be due to the precipitation at high of temperature and pH. The effect of agricultural waste, sewage and domestic effluents at El-Umum drain increased the zinc concentrations at El-Mex location (station VII) While, a minimum value of 8.30 μ g/l was recorded at Gleem station (IV). In general, the zinc concentrations increased in the bottom water and decreased in surface, except for

Stations	Wi	Winter		ring	Sun	ımer	Aut	umn		nual rage	SI)+
	S	B	S	В	S	В	S	В	S	В	S	B
Ι	37.60	48.23	29.33	38.25	21.20	29.75	44.10	50.25	33.06	41.62	9.95	9.49
II	26.20	41.70	19.70	37.30	23.61	30.82	31.18	49.20	25.17	39.76	4.81	7.72
III	14.31	36.85	9.11	27.38	13.40	17.15	18.25	40.15	13.77	30.38	3.75	10.35
IV	11.25	36.70	8.30	26.24	12.15	22.91	15.80	42.08	11.88	31.98	3.09	8.93
V	30.50	54.22	28.41	47.32	19.82	40.71	34.20	77.60	28.23	54.96	6.10	16.07
VI	29.18	67.90	22.90	59.30	14.95	37.60	31.92	62.95	24.74	56.94	7.25	13.36
VII	199.75	166.81	183.45	123.81	155.60	123.40	208.40	174.30	186.80	147.08	23.23	27.28
VIII	49.30	160.21	44.18	151.75	47.11	132.55	54.00	173.92	48.65	154.61	4.14	17.313
IX	43.26	79.18	38.66	67.40	20.60	36.25	58.67	87.30	40.30	67.53	15.67	22.40
Х	37.00	58.40	31.20	48.15	17.20	48.80	47.35	72.11	33.19	56.87	12.58	11.19
Seasonal Average	47.84	75.02	41.52	62.59	34.56	51.99	54.39	82.99	44.58	68.17	8.49	13.64

Table (5): Seasonal variations of zinc concentration (µg/l) in Alexandria coast during 2004

S: Surface Water

B: Bottom Water





station VII. The lower values in surface water may be attributed to the uptake of Zn by zoo- and phytoplankton and other aquatic organisms. But the higher values in bottom water may be related to zinc release from sediment to the above water layer (3). A significant positive correlation recorded between zinc and copper (r= 0.897, 0.810, 0.910 and 0.832) during winter, spring, summer and autumn, respectively, may be attributed to the biological behaviour. Comparing the results obtained in the present study with the published data, (Table 14), assigned that the concentrations of dissolved zinc at station VII are higher than those of the published data, while the values at other stations are more or less equal to the published data.

Copper: Copper is an essential element for the growth of aquatic organisms. The concentration of copper in presence of phytoplankton has been recorded⁽⁴⁾. It has been suggested that the organic ligands obtained by phytoplankton cells likely to be important for copper complexation in waters affected by dense phytoplankton blooms⁽²¹⁾. The seasonal variations

of copper concentrations of different selected stations were in the ranges of 2.19-10.11, 3.64-9.60, 4.12-11.14 and 2.71-8.49 µg/l in the surface water during winter, spring, summer and autumn, respectively. For the bottom water, the concentrations have fluctuated between 4.10-6.43, 4.82-7.15, 5.39-7.80 and 3.89-6.25 µg/l during the above mentioned seasons, respectively, Table (6) and Figure (7). However, the high contents were recorded during spring and summer seasons, probably due to high evaporation rate with the increase of temperature of water and air during hot seasons, and due to the release of Cu from sediment to overlying water. On the other hand, the minimum values recorded during winter and autumn may be attributed to chelation of copper by aquatic organisms or other artificial compounds deposited on the bottom sediment, and/or due to the adsorption of copper by humic materials and deposited to bottom. The data obtained that the maximum content at station VII in the surface water during winter, spring, summer and autumn: 10.11, 9.60, 11.14 and 8.49µg/l respectively. The industrial and agriculture wastes of El-Umum drain are the main contributors to the copper budget of the El-Mex location (station VII). On the other hand, the minimum value of dissolved Cu recorded at station II reached

2.19µg/l in surface water. In general, the lowest values of Cu concentration were recorded far away from El-Mex pumping. The concentrations of dissolved copper in surface water (2.19-11.14µg/l) are lower than that of bottom water (3.89-7.80 µg/l), due to the release of Cu from sediment to overlying water. The statistical analysis of correlation coefficient of copper with other parameters showed a positive behavior with other heavy metals (Fe, Mn, Zn, Cd, Co, Cr, Ni and Pb), Table (16).

Comparison of values in the present study with those reported for Egyptian coast, Table, (14) suggests that the levels of Cu are in harmony with the reported data.

Cadmium: It exists in the earth's crust with an average concentration of about 0.1 ppm. It comes mainly from copper refining (as a byproduct), lead processing, electro plating, solders, batteries, production of alloys, pigments and sewage sludge⁽²²⁾. Phytoplankton are likely to play a more significant role in scavenging of cadmium than they play in the removal of other metals. The seasonal variations of Cd concentrations were in the ranges of 0.36-3.20, 0.42-4.29, 1.02-6.51 and 0.72-4.12 µg/l in the surface water during winter, spring, summer and autumn, respectively. For the bottom wa-

Stations	Wii	nter	Spi	ring	Sum	mer	Aut	umn		1ual rage	SI) +
	S	В	S	В	S	В	S	В	S	В	S	В
Ι	2.30	4.66	3.91	5.20	4.27	5.81	2.71	3.89	3.30	4.89	0.94	0.82
II	2.19	4.25	3.70	4.82	4.12	5.76	3.05	4.73	3.27	4.89	0.84	0.63
III	4.48	5.91	6.33	7.15	6.14	7.80	5.28	5.74	5.56	6.65	0.85	0.99
IV	3.85	5.28	4.60	6.49	4.37	6.91	2.72	4.41	3.89	5.77	0.84	1.14
V	4.76	5.49	5.07	5.84	6.53	7.35	4.81	6.25	5.29	6.23	0.84	0.81
VI	3.32	4.81	5.44	6.32	5.21	6.48	3.96	5.74	4.48	5.84	1.01	0.76
VII	10.11	6.43	9.60	5.87	1 1.14	6.33	8.49	6.12	9.84	6.19	1.10	0.25
VIII	5.81	5.94	6.20	6.80	6.16	7.26	4.27	5.61	5.61	6.40	0.91	0.76
IX	3.42	4.55	4.14	5.46	5.13	6.41	3.88	5.29	4.14	5.43	0.72	0.76
Х	2.90	4.10	3.64	4.82	4.17	5.39	3.12	5.71	4.46	5.01	0.57	0.71
Seasonal Average	4.31	5.14	5.26	5.88	5.72	6.55	4.23	5.35	4.88	5.73	0.73	0.63

Table (6): Seasonal variations of copper concentration (µg/l) in Alexandria coast during 2004

S: Surface Water B: Bottom Water

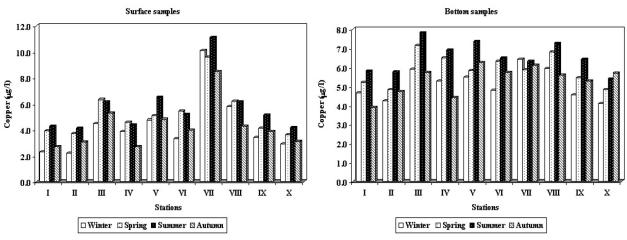


Figure (7): Seasonal variations of copper concentrations (µg/l) in the Alexandria coast during 2004

ter, cadmium contents have fluctuated between 1.20-5.30, 1.73-7.80, 2.00-9.25 and 1.11-5.58µg/l during the above seasons, respectively, Table (7) and Figure (8). The lower values of Cd^{2+} during winter were mainly attributed to its precipitation. The high values of Cd content during summer, are attributed to the dissolution of Cd from sediment to overlying water. But, the relative decrease of Cd contents during spring caused by specific binding of Cd to living phytoplankton⁽²³⁾. In general, the trend in the vertical Cd variations is clearly identified with depth due to the mobilization of Cd from sediment to the above water layer⁽¹⁹⁾. As well as, the uptake of Cd by phytoplankton and zooplankton and other aquatic organisms in surface water leads to decrease of Cd contents in surface water. Comparing the annual average concentrations of Cd deduced in the present study with those of neighboring coastal Mediterranean areas, Table (14), illustrated the high content at station VII, due to the different sewage effluents from El-Umum drain.

Lead: Lead is very important in the aquatic environment because it occurs in large quantities compared to cobalt and chromium. It is used

Table (7): Seasonal variations of cadmium concentration (µg/l) in Alexandria coast during 2004

Stations	Winter		Spi	ring	Sum	mer	Aut	umn		nual rage	SI) +
	S	В	S	В	S	В	S	В	S	В	S	В
Ι	0.88	1.25	1.12	1.73	1.31	2.10	0.90	1.11	1.05	1.55	0.20	0.45
II	0.75	1.90	0.84	1.94	1.10	2.00	1.00	1.28	0.92	1.78	0.16	0.34
III	2.05	3.72	2.10	2.76	2.50	3.71	1.95	2.40	2.15	3.15	0.24	0.67
IV	0.36	1.20	1.37	2.30	1.82	2.95	0.72	1.81	1.07	2.07	0.65	0.74
V	2.92	5.30	3.25	3.78	3.69	4.11	3.91	4.33	3.44	4.38	0.44	0.65
VI	0.92	1.61	0.42	4.50	1.02	4.37	0.96	3.17	0.83	3.14	0.28	1.34
VII	3.20	4.21	4.29	7.80	6.51	9.25	4.12	5.58	4.53	6.17	1.40	2.25
VIII	2.90	4.25	3.16	5.41	3.85	6.04	2.70	4.95	3.15	5.16	0.50	0.75
IX	1.91	3.80	2.51	4.78	2.70	4.65	2.19	3.71	2.33	4.22	0.35	0.53
Х	0.90	1.82	1.92	3.33	1.44	3.71	1.10	2.66	1.34	2.88	0.45	0.83
Seasonal Average	1.68	2.91	2.10	3.83	2.59	4.29	1.96	3.10	2.08	3.53	0.38	0.64

S: Surface Water B: Bottom Water

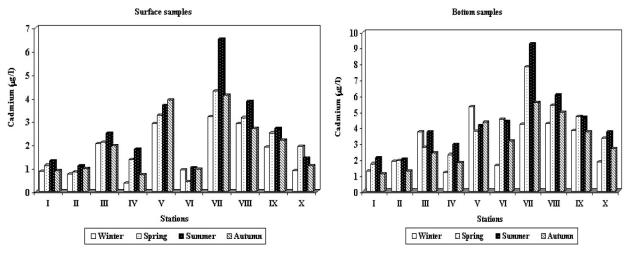


Figure (8): Seasonal variations of cadmium concentrations (µg/l) in the Alexandria coast during 2004

for many industrial purposes such as storage batteries, metal products, pigments and other chemicals. Primary sources of lead include manufacturing process (particularly metals), atmospheric deposition and domestic wastewater. Approximately 96% of all lead emissions originate from anthropogenic sources^(24,25). The results of lead distribution are given in Table (8) and Figure (9). The seasonal variations of lead concentrations gave values in the ranges of 0.21-6.10, ND-5.40, ND-4.22 and 0.40-7.52µg/l in the surface water during winter, spring, summer and autumn, respectively. For the bottom waters the concentrations were fluctuated in the ranges of 0.80-8.25, 0.81-7.35, 0.42-6.60 and $1.20-9.36 \mu g/l$ during the mentioned seasons, respectively. The high values during winter and autumn may be attributed to the decaying of plankton and precipitation of organic matter associated with lead to the sediments(16). However, the decrease of lead concentrations during summer and spring seasons is mainly attributed to the mobilization of lead from the sediment to the above water due to the microbial activities and the degradation of organic matter liberated during hot sea-

Stations	Wi	nter	Spi	ring	Sum	nmer	Aut	umn		nual rage	SE) +
	S	В	S	В	S	В	S	В	S	В	S	В
Ι	2.34	4.11	1.90	3.82	1.87	3.10	2.80	3.64	2.23	3.67	0.44	0.43
II	2.27	3.28	1.81	2.91	1.60	2.98	2.65	3.52	2.08	3.17	0.47	0.28
III	3.40	3.32	2.62	2.84	2.71	3.24	3.30	3.86	3.01	3.32	0.40	0.42
IV	1.31	1.90	1.11	1.70	0.89	1.52	1.81	2.14	1.28	1.82	0.39	0.27
V	2.00	2.95	1.80	2.71	1.81	2.11	2.20	3.48	1.95	2.81	0.19	0.57
VI	0.24	0.80	0.20	0.81	0.41	0.92	0.70	1.51	0.39	1.01	0.23	0.34
VII	6.10	8.25	5.40	7.35	4.22	6.60	7.52	9.36	5.81	7.89	1.38	1.19
VIII	2.20	3.93	2.15	3.40	2.40	3.15	2.50	4.98	2.31	3.87	0.17	0.81
IX	1.36	1.76	1.32	1.46	0.81	1.85	1.74	2.12	1.31	1.80	0.38	0.27
Х	0.21	1.18	ND	0.70	ND	0.42	0.40	1.20	0.31	0.88	0.13	0.38
Seasonal Average	2.14	3.15	2.03	2.77	1.86	2.59	2.56	3.58	2.15	3.02	0.30	0.44

Table (8): Seasonal variations of lead concentration (µg/l) in Alexandria coast during 2004

S: Surface Water

B: Bottom Water

ND: Not Detected

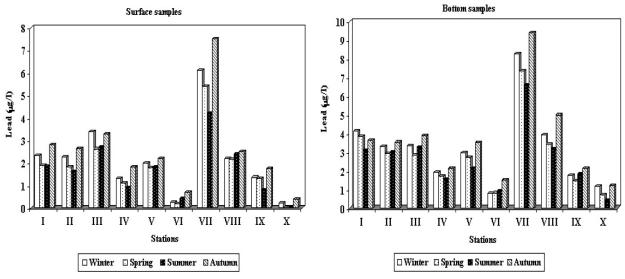


Figure (9): Seasonal variations of lead concentrations (µg/l) in the Alexandria coast during 2004

sons(19). The data show maximum contents at station VII during winter, spring, summer and autumn were 8.25, 7.35, 6.60 and 9.36µg/l, respectively. This is mainly due to the effect of sewage, agricultural and industrial effluents from El-Umum drain. A certain portion of the lead in the air exists as tetra alkyl lead arising from evaporation and incomplete combustion of motor fuels, which acts as an important source in marine and fresh water environments⁽²⁶⁾. Lead is also contributed from industrial effluents and domestic sewage. In general, the concentrations of Pb at offshore stations are lower than those at inshore ones. However, the dissolved lead concentrations in bottom water $(0.42-9.36\mu g/l)$ are higher than that of the surface water (ND-7.52 μ g/l), probably due to the release of Pb from sediment to the above water layer. Comparing the present results with those of the neighboring coastal Mediterranean areas, Table (15), gave that the concentrations at station VII are higher than those of other areas, while the Pb content at other stations are more or less equal to other areas.

Cobalt: It is one of the most biologically important elements in the aquatic environment. It occurs in low concentrations in marine waters. Higher levels of cobalt are probably due to contamination with phytoplankton and other organisms that metabolize vitamin B12(27). Seasonal variations of cobalt concentrations, Table (9) and Figure (10), showed variable concentrations of ranges ND- 1.92, 0.38-2.40,

ND-1.76 and ND-1.93 μ g/l in the surface water and 0.32-2.11, 0.98-2.82, 0.69-2.20 and 0.28-2.32 µg/l for bottom water during winter, spring, summer, autumn seasons, respectively. The relative increase of cobalt content during spring and summer may be attributed to the increase in phytoplankton population during these seasons⁽²⁸⁾. It was suggested that since cobalt belongs to metals that are concentrated in aquatic organisms, biological processes play an important role in enrichment of these metals in sedimentary rocks⁽²⁹⁾. Robenson reported that, the distribution of cobalt in aquatic environments is influenced by assimilation by plankton, adsorption on detritus and suspended matter, chemical precipitation reactions and effluents from ships⁽³⁰⁾. The results show maximum values at station VII in the bottom water during the period of the study: 2.82, 2.20 and 2.32µg/l, due to the effect of El-Umum drain. While, the non detected contents were recorded in the surface water at stations I, II, IX and X. The concentrations of dissolved cobalt in bottom water $(0.28-2.82\mu g/l)$ were higher than that of surface water (ND-2.40 μ g/l), probably due to the release of Co from the sediments. Generally, the regional distribution of dissolved cobalt along Alexandria beach reflected narrow range of variations indicating that it is not influenced by anthropogenic input. Table (15), gave the concentrations of Co at station VII are higher than those recorded in other areas.

Stations	Winter		Spr	ing	Sum	imer	Aut	umn		nual rage	SI) +
	S	В	S	В	S	В	S	В	S	В	S	В
Ι	ND	0.51	0.90	1.81	0.23	1.11	ND	0.91	0.28	1.09	0.43	0.54
II	0.32	0.81	0.64	1.30	ND	1.12	ND	0.70	0.24	0.98	0.31	0.28
III	1.92	2.11	1.35	1.61	1.31	1.24	1.46	1.80	1.51	1.69	0.28	0.36
IV	1.20	1.10	0.70	1.31	0.28	1.90	1.21	1.19	0.85	1.38	0.45	0.36
V	0.84	0.71	0.38	1.27	0.91	1.03	0.67	1.18	0.70	1.05	0.24	0.25
VI	0.41	0.96	1.51	1.96	0.84	1.14	0.62	1.05	0.85	1.28	0.48	0.46
VII	1.80	0.23	2.40	2.82	1.76	2.20	1.93	2.23	1.97	2.14	0.29	0.66
VIII	0.77	1.11	1.20	2.60	1.00	1.25	0.80	1.07	0.94	1.51	0.20	0.73
IX	ND	0.32	0.94	1.39	0.35	0.74	ND	0.55	0.32	0.75	0.44	0.46
Х	ND	0.41	0.71	0.98	0.40	0.69	ND	0.28	0.28	0.59	0.34	0.31
Seasonal Average	0.73	0.93	1.07	1.71	0.71	1.24	0.67	1.11	0.79	1.24	0.19	0.33

Table (9): Seasonal variations of cobalt concentration (µg/l) in Alexandria coast during 2004

S: Surface Water



ND: Not Detected

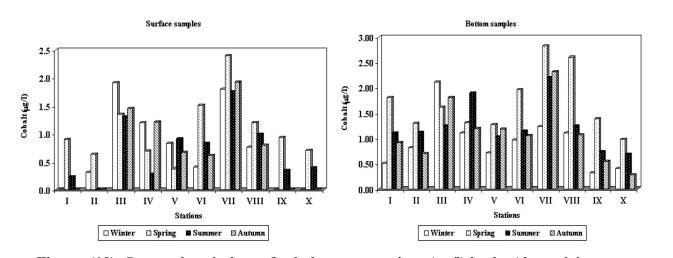


Figure (10): Seasonal variations of cobalt concentrations (µg/l) in the Alexandria coast during 2004

Nickel: About 90% of nickel in aquatic environment occurs as Ni⁺², Ni(OH)₂ and NiS while NiSO₄ constitutes a small ratio. Nickel in water is a very important and biologically active metal. It could result from industrial and urban activities⁽³¹⁾ and may accumulate in many types of fishes and macrophytes. Use of fossil fuel, particularly coal, is widely implicated in the release of nickel to the atmosphere and surface water. The seasonal variations of Ni concentrations, Table (10) and Figure (11), fluctuated in ranges of 0.39-1.85, 0.31-1.76, 0.90-2.03 and 0.58-1.94µg/l in the surface water and 0.72-

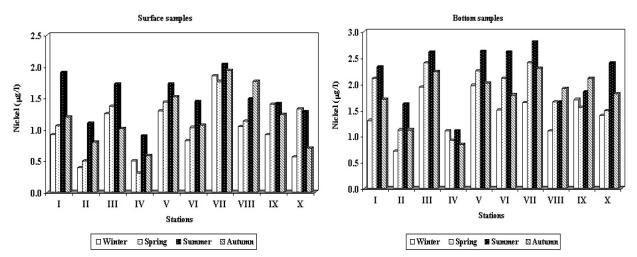
1.97, 0.92-2.40, 1.10-2.80 and 0.84-2.30µg/l for bottom water during winter, spring, summer and autumn seasons, respectively. The concentrations slightly changed among different seasons. The relative increase during summer and spring is probably attributed to contamination of nickel with phytoplankton occurred in large quantities⁽²⁷⁾. The results show maximum contents at station VII during spring, summer and autumn, 2.40, 2.80 and 2.30µg/l, respectively, while the minimum value of 0.31µg/l recorded at station IV in surface water during spring. The concentrations of dissolved nickel

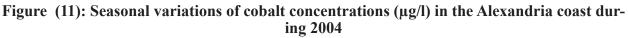
Table (10): Seasonal variation	s of nickel concentration	n (μg/l) in Alexandria c	coast during
2004			

Stations	Winter		Spi	ring	Sum	imer	Aut	umn		nual rage	SI) +
	S	В	S	В	S	В	S	В	S	В	S	В
Ι	0.92	1.30	1.06	2.10	1.91	2.32	1.20	1.71	1.27	1.86	0.44	0.45
II	0.39	0.72	0.50	1.12	1.10	1.62	0.80	1.12	0.70	1.15	0.32	0.37
III	1.25	1.94	1.37	2.40	1.72	2.61	1.01	2.23	1.34	2.30	0.30	0.28
IV	0.50	1.10	0.31	0.92	0.90	1.10	0.58	0.84	0.57	0.99	0.25	0.13
V	1.29	1.97	1.43	2.25	1.72	2.62	1.52	2.01	1.49	2.21	0.18	0.30
VI	0.82	1.50	1.03	2.10	1.44	2.61	1.07	1.79	1.09	2.00	0.26	0.47
VII	1.85	1.64	1.76	2.40	2.03	2.80	1.94	2.30	1.90	2.29	0.12	0.48
VIII	1.05	1.10	1.13	1.65	1.49	1.65	1.77	1.91	1.36	1.58	0.33	0.34
IX	0.92	1.70	1.40	1.55	1.41	1.85	1.24	2.10	1.24	1.80	0.23	0.23
Х	0.56	1.40	1.33	1.49	1.30	2.40	0.70	1.81	0.97	1.78	0.39	0.45
Seasonal Average	0.96	1.44	1.13	1.80	1.50	2.16	1.18	1.78	1.19	1.79	0.23	0.29

S: Surface Water

B: Bottom Water





in bottom water (0.72-2.80µg/l) are higher than that of surface water (0.31-2.03) may be due to release of nickel from sediment. Also, the concentrations of nickel at offshore stations are lower than those of near shore. Total Ni residues in aquatic plants may affect its growth and its effect on fish⁽³²⁾. Ni²⁺ induced changes in the species compositions of benthic algae at concentrations as low as 2µg/l. The chemical behavior of nickel as a strong chelating transition element is obviously clear from its strong correlation with other metals due to its tendency to form organic complexes that are more stable⁽²¹⁾. This evidence is well confirmed in this study from the positive correlation between nickel and other metals, Table (16).

Chromium: It is one of biochemically active transition metal in the aquatic environment. The chemistry of chromium is complicated due to its existence in different oxidation states⁽³³⁾. The seasonal variations of chromium concentrations, Table (11) and Figure (12), gave variable contents in the ranges of 0.40-2.22, 0.32-2.10, 0.62-2.55 and 0.19-2.02µg/l

Stations	Wi	nter	Spi	ring	Sum	mer	Aut	umn		nual rage	SI) +
	S	В	S	В	S	В	S	В	S	В	S	В
Ι	1.21	1.70	1.51	2.00	1.09	1.61	1.11	1.20	1.23	1.63	0.19	0.33
II	1.03	1.81	0.90	1.18	1.42	1.70	0.85	1.60	1.05	1.57	0.26	0.28
III	0.90	1.30	1.04	1.37	1.50	1.82	0.70	1.10	1.04	1.40	0.34	0.30
IV	1.10	1.65	0.72	0.75	1.20	1.41	0.19	0.35	0.80	1.04	0.46	0.60
V	0.72	1.05	0.60	0.91	0.84	1.27	0.58	0.90	0.69	1.03	0.12	0.17
VI	0.41	0.99	0.32	1.14	0.62	1.30	0.41	0.16	0.44	1.15	0.13	0.13
VII	2.22	2.60	2.10	2.30	2.55	2.95	2.02	2.71	2.22	2.64	0.23	0.27
VIII	0.83	1.90	1.15	2.12	1.25	2.10	1.40	2.10	1.28	2.06	0.39	0.10
IX	0.80	1.20	0.92	1.60	0.80	1.60	065	1.35	0.79	1.44	0.11	0.20
Х	0.40	1.11	1.35	1.45	1.21	1.80	0.85	1.32	0.95	1.42	0.42	0.29
Seasonal Average	0.96	1.53	1.06	1.48	1.30	1.76	0.88	1.38	1.05	1.54	0.18	0.16

Table (11): Seasonal variations of chromium concentration (μg/l) in Alexandria coast during 2004

S: Surface Water

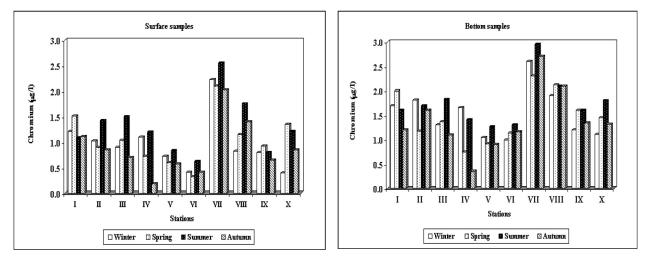


Figure (12): Seasonal variations of chromium concentrations (µg/l) in the Alexandria coast during 2004

in surface water and those for the bottom water were 0.99-2.60, 0.75-2.30, 1.27-2.95 and 0.35-2.71µg/l during winter, spring, summer and autumn seasons, respectively. The results pointed that, the concentrations have slightly changed among different seasons. The relative high content of chromium during summer and spring may be attributed to the high consumption by phytoplankton⁽³³⁾. The higher content in bottom water than surface water is probably due to the release of Cr from sediment to overlying water. It was reported that, the primary

B: Bottom Water

source of chromium includes domestic waste water, manufacturing processes, involving metals and dumping of sewage sludge⁽³⁴⁾. The concentrations of chromium in the offshore waters are lower than that of the nearshore ones. The typical Cr-concentration in seawater is $0.3\mu g/l$, mostly as hexavalent. The trivalent form also exists in water, but it may eventually precipitate or be absorbed⁽³⁴⁾. A positive correlation trend exists with other heavy metals (Fe, Mn, Zn, Cu, Cd, Co, Ni and Pb). A negative correlation was deduced with pH (r= -0.561,

-0.765 and -0.550) during winter, spring and autumn respectively. Generally, the concentrations of dissolved chromium in the studied area (0.19-2.95 μ g/l) is lower than reported in El-Mex Bay water but higher than those of the neighboring coastal Mediterranean Table (15).

Aluminum: It is one of the most abundant elements in the earth's crust. It's forms in solution are mainly dominated by pH. The predominant form of Aluminum below pH= 4 is **A** (H₂O)₆⁺³ , while above pH= 7 [Al(OH)4(H2O2] usually exists. Above pH 8, appreciable amounts of the aluminate ion HAl₂O₄⁻ will present⁽³⁵⁾. The solubility of aluminum as an amphoteric element is also greatly dependent on the pH of the medium and the lowest solubility of aluminum is between pH 5 and $8^{(36)}$. The variations of dissolved aluminum concentrations during summer and autumn of the area under investigation are given in Table (12) and Figure (13). The concentrations at different stations were in the ranges of ND- 2.64 and 0.60-2.78µg/l in the surface water and 1.12-4.79 and 1.76-5.18µg/l for the bottom water during summer and autumn, respectively. The results declared a slight decrease in aluminum content during summer, due to the adsorption of aluminum on diatom frustules under certain conditions the adsorp-

Table (12): Concentrations of aluminum (μg/l) in the Alexandria coastal water during summer and autumn 2004

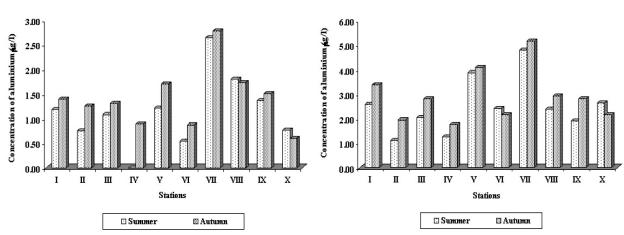
Stations	Sum	mer	Aut	umn	Annual Average		SI) +
Stations	S	В	S	В	S	В	S	В
Ι	1.19	2.60	1.40	3.38	1.30	2.99	0.15	0.55
II	0.75	1.12	1.26	1.95	1.01	1.54	0.36	0.59
III	1.08	2.05	1.31	2.81	1.20	2.43	0.16	0.54
IV	ND	1.26	0.89	1.76	0.89	1.51	0.63	0.35
V	1.21	3.88	1.70	4.09	1.46	3.99	0.35	0.15
VI	0.54	2.42	0.87	2.16	0.71	2.29	0.23	0.18
VII	2.64	4.79	2.78	5.18	2.71	4.99	0.10	0.28
VIII	1.80	2.38	1.73	2.94	1.77	2.66	0.05	0.40
IX	1.37	1.90	1.51	2.81	1.44	2.36	0.10	0.64
Х	0.76	2.64	0.60	2.15	0.68	2.40	0.11	0.35
Seasonal Average	1.26	2.50	1.41	2.92	1.33	2.71	0.19	0.30

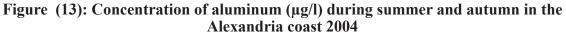
S: Surface Water



ND: Not Detected

Botton





tion of aluminum on diatom frustules may lower their dissolution rates⁽³⁶⁾. The high Al content at station VII may be attributed to the effect of brackish water and industrial effluents from El-Umum drain. A gradual decrease recorded in aluminum concentration with increasing of the distance from the shore line, i.e., near shore stations possess higher aluminum content than offshore ones, this mostly due to the land daring or human activities at near shore stations. The concentrations of dissolved aluminum in surface water (ND-2.78µg/l) are lower than that of bottom water (1.12-5.18µg/l), due to sedimentation processes of aluminum ion and release of Al from sediment.

Tin: Inorganic tin is probably methylated to different forms under various environmental conditions. Sequential mechanisms to yield mono-, di, tri and tetramethyl tin compounds are possible in principle. The organo tin compounds are classified as R4Sn, R3SnX, R2SnX2 and RSnX3. In compounds of industrial importance, R is usually butyl, octyl or phenyl groups and X is chloride, fluoride, oxide, hydroxide or carboxylate substitutions⁽³⁷⁾. The most important of these compounds are the tributyl and tricyclohexyl tin compounds which are used as agricultural and general fungicides, bactericides, antihelminthics, miticides, herbicides, molluscicides, insecticides, rodent repellents and antifoulants in boat paints. The tetrasubstituted organotin compounds (R4Sn) are mainly used as intermediates in the preparation

of other organotin compounds. The occurrence of organotin compounds in aquatic environments are of great concern. Since toxic effects on non-target marine organisms depend on tin substitution, organotin speciation becomes necessary to evaluate the risk associated with the occurrence of this class of compounds⁽³⁸⁾. The tin contents during summer and autumn of the area under investigation in Table (13) and Figure (14), were in the ranges of ND- 4.1 and ND- 3.2 ng/l in the surface water during summer and autumn, respectively. For the bottom water, the concentrations fluctuated between ND-2.4 and ND-1.70ng/l, respectively. The results declared that, no wide variations in tin concentrations during summer and autumn. The slight increase during summer may due to the increase of the boating activities. Tin concentrations in saline and sea waters are approximately 0.01 to 0.3 ng/l with values higher than 1ng/l indicative of pollution⁽³⁸⁾. The increase of tin content at some stations especially during summer may be due to the increase of navigation and boating activities or due to human activities. It was reported that the majority of dissolved tin in river water is transported in the butylated and methylated forms to receiving lakes and coastal seawaters⁽³⁸⁾. The concentrations of dissolved tin in surface water (ND-4.1ng/l) are higher than that of bottom water (ND-2.4 ng/l). The levels of total tin recorded at most stations are considerably of open oceans, which approximate 1 ng/l Tin.

Stations	Sum	imer	Aut	umn	Annual	Average	SI) +
Stations	S	В	S	В	S	В	S	В
Ι	ND	ND	ND	ND	ND	ND	ND	ND
II	3.6	0.2	1.1	0.1	2.35	0.15	1.77	0.07
III	2.2	0.1	1.40	0.2	1.80	0.15	0.57	0.07
IV	1.8	ND	1.70	ND	1.75	0.0	0.07	0.0
V	3.6	2.4	0.90	1.70	2.25	2.05	1.91	0.49
VI	4.1	1.30	3.2	1.66	3.65	1.48	0.64	0.25
VII	2.9	1.0	2.0	0.8	2.45	0.90	0.64	0.14
VIII	ND	ND	ND	ND	ND	ND	ND	ND
IX	ND	ND	ND	ND	ND	ND	ND	ND
X	ND	ND	ND	ND	ND	ND	ND	ND
Seasonal Average	1.82	0.50	1.03	0.45	1.43	0.47	0.56	0.04

Table (13): Concentrations of tin (ng/l) during summer and autumn (2004)

S: Surface Water B: Bottom Water ND: Not Detected

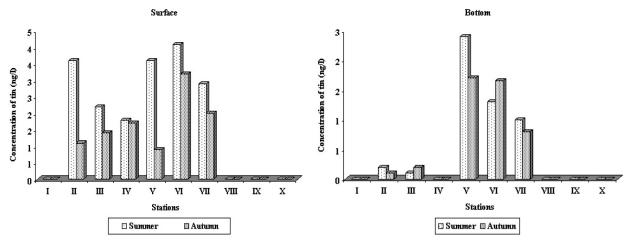


Figure (14): Concentrations of tin (mg/l) during summer and autumn in the Alexandria coast 2004

A 400			Me	etals (µg/l)			Defenences
Area		Fe	Mn	Zn	Cu	Cd	- References
Eastern Harbour		25.7	1.1	140.4	-	2.40	(39)
El-Mex Bay		32.8	1.4	-	-	-	(44)
El-Mex Bay Coastal		-	-	16.1	1.99	0.14	(41)
Mediterranean in front	of Rosetta estuary	26.5	3.50	42.7	9.0	0.79	(42)
El-Montazah	Ι	32.48	0.53	33.06	3.30	1.05	
	II	19.51	0.34	25.17	3.27	0.92	
Gleem	III	45.24	0.30	13.77	5.56	2.15	
	IV	43.39	0.57	11.88	3.89	1.07	
El-Shattbi	V	63.21	0.98	28.23	5.29	3.44	Present
	VI	50.39	2.18	24.74	4.48	0.83	Work
El-Mex Bay	VII	100.27	4.15	186.80	9.84	4.53	
	VIII	76.26	1.96	48.65	5.61	3.15	
El-Agami	IX	57.64	0.66	40.30	4.14	2.33	
	Х	33.13	0.58	33.19	3.89	1.34	

 Table (14): The average values of heavy metals (Fe, Mn, Zn, Cu and Cd) for present study and other Egyptian coastal Mediterranean areas

A			Concentra	tions (µg/l)		Defenerace
Area		Pb	Со	Ni	Cr	- References
Eastern Harbour		0.04-7.80	ND-0.27	0.09-1.43	ND-0.90	(43,44)
Eastern Harbour		-	-	-	ND-2.88	(43)
Abu-Qir Bay		2.6-5.4	-	-	-	(43)
El-Mex Bay		0.17	-	-	0.35-4.38	(40)
El-Mex Bay		0.50	0.17	0.32	0.22	(44)
El-Mex Bay		1.34	-	-	-	(45)
El-Montazah	Ι	2.23	0.28	1.27	1.23	
	II	2.08	0.24	0.70	1.05	
Gleem	III	3.01	1.51	1.34	1.04	
	IV	1.28	0.85	0.57	0.80	Present Study
El-Shattbi	V	1.95	0.70	1.49	0.69	
	VI	0.39	0.85	1.09	0.44	
El-Mex	VII	5.81	1.97	1.90	2.22	
	VIII	2.31	0.94	1.36	1.28	
El-Agami	IX	1.31	0.32	1.24	0.79	
	Х	0.15	0.28	0.97	0.95	

Table (15): Comparison between the concentrations of heavy metals (Pb, Co, Ni and Cr) for present study and other Egyptian coastal Mediterranean areas

Table (16-a): Correlation coefficient matrix of results in surface water during winter (P < 0.05, n=40).

	0.05,	n-40).									
	S%0	pН	Fe	Mn	Zn	Cu	Cd	Со	Cr	Ni	Pb
S%0	1										
рН	0.461	1									
Fe	-0.774	-0.467	1								
Mn	-0.827	-0.410	0.836	1							
Zn	-0.965	-0.561	0.794	0.897	1						
Cu	-0.901	-0.370	0.950	0.833	0.866	1					
Cd	-0.543	-0.253	0.830	0.633	0.574	0.777	1				
СО	-0.579	0.159	0.554	0.286	0.387	0.706	0.476	1			
Cr	-0.889	-0.561	0.574	0.555	0.809	0.719	0.370	0.539	1		
Ni	-0.751	-0.266	0.788	0.716	0.730	0.848	0.861	0.619	0.596	1	
Pb	-0.862	-0.367	0.656	0.556	0.774	0.794	0.620	0.701	0.904	0.782	1

Table (16-b): Correlation coefficient matrix of results in surface water during spring (P < 0.05, n=40)

	0.05,1	u 10)									
	S%0	pН	Fe	Mn	Zn	Cu	Cd	Со	Cr	Ni	Pb
S‰o	1										
pН	0.325	1									
Fe	-0.709	-0.328	1								
Mn	-0.673	-0.292	0.842	1							
Zn	-0.716	-0.094	0.774	0.789	1						
Cu	-0.764	-0.508	0.780	0.792	0.810	1					
Cd	-0.476	-0.090	0.786	0.477	0.703	0.685	1				
Co	-0.680	-0.588	0.616	0.753	0.781	0.875	0.394	1			
Cr	-0.376	0.181	0.333	0.317	0.752	0.496	0.539	0.536	1		
Ni	-0.260	-0.314	0.572	0.275	0.585	0.545	0.711	0.493	0.477	1	
Pb	-0.852	-0.184	0.616	0.527	0.805	0.830	0.697	0.677	0.699	0.452	1

Table (16-c): Correlation coefficient matrix of results in surface water during summer (P < 0.05, n=40).

	S%0	pН	Fe	Mn	Zn	Cu	Cd	СО	Cr	NI	Pb	Al
S%o	1											
рН	0.436	1										
Fe	-0.713	-0.154	1									
Mn	-0.814	-0.024	0.779	1								
Zn	-0.956	-0.477	0.747	0.865	1							
Cu	-0.915	-0.340	0.902	0.860	0.910	1						
Cd	-0.818	-0.491	0.908	0.702	0.855	0.938	1					
Со	-0.688	-0.212	0.850	0.749	0.676	0.885	0.794	1				
Cr	-0.762	-0.765	0.502	0.602	0.844	0.729	0.723	0.594	1			
Ni	-0.593	-0.223	0.587	0.519	0.538	0.659	0.579	0.664	0.356	1		
Pb	-0.736	-0.559	0.668	0.616	0.768	0.820	0.794	0.727	0.820	0.683	1	
Al	-0.763	-0.515	0.765	0.648	0.825	0.825	0.860	0.680	0.691	0.760	0.788	1

	S%0	pН	Fe	Mn	Zn	Cu	Cd	Co	Cr	Ni	Pb	Al
S‰0	1											
рН	0.424	1										
Fe	-0.587	-0.271	1									
Mn	-0.680	-0.250	0.781	1								
Zn	-0.965	-0.547	0.678	0.747	1							
Cu	-0.846	-0.062	0.795	0.722	0.826	1						
Cd	-0.600	-0.167	0.830	0.543	0.635	0.817	1					
Со	-0.583	0.154	0.634	0.531	0.488	0.758	0.503	1				
Cr	-0.785	-0.550	0.586	0.781	0.840	0.668	0.558	0.321	1			
Ni	-0.623	-0.350	0.854	0.752	0.680	0.734	0.853	0.394	0.743	1		
Pb	-0.919	-0.290	0.546	0.591	0.832	0.834	0.630	0.677	0.784	0.641	1	
Al	-0.841	-0.385	0.733	0.634	0.819	0.834	0.842	0.533	0.790	0.882	0.898	1

Table (16-d): Correlation coefficient matrix of results in surface water during autumn (P < 0.05, n= 40)

REFERENCES

- Abd-Alla, M. (1993). Concentration of mercury in fresh, brackish and saline waters in Alexandria region. M.Sc. Thesis, Institute of Graduate Studies and Research, Alexandria University, Egypt.145 pp.
- 3. Abdel-Motai, M.A. (1991). An input/output flux for lead in a coastal bay off Alexandria region. Water Air Soil Pollut. (59): 261-269.
- 4. Riley, J.P. and Skirrow, G. (1995). Chemical Oceanography, Vol. I, II Academic Press, London and New York p. 712 and p. 508.
- 5. Wust, G., 1961: On the vertical circulation of the Mediterranean Sea. J. Geoph. Res., 66, 3261-3271.
- 6. Said, M.A. and El-Deek, M.S. (1990).J. Maritime Res. 15, 34-46.
- Nassim, R.B. (1988). Bull. Inst. Oceanogr. & Fish. 14 (1): 283-292.
- Mahmoud, Th.H. (1985), Phosphorus and nitrogen dynamics in the polluted coastal water of Alexandria, Ph.D. Thesis, Faculty of Science, Alexandria University, Egypt.139 pp.
- Masoud, M.S.; Elewa, A.A. and Abdel-Halim, A.M. (2002). J. Saudi Chem. Soc., 6 (3): 337-398.
- Dyrssen, D. and Wedborg, M. (1974). Equilibrium calculation of the speciation of element in seawater. In: E.D. Coldberg (Editor). The Sea Wiley. Interscience, New York, N.Y., 5: 181-195.

- 11. Saad, M.A. (1979). Arch.Hydrobiologia, 77(4): 411-443.
- Aleem, A.A. and Samaan, A.A. (1969). Productivity of Lake Mariut, Egypt. I. Physical and chemical aspects. Hydrobial, 54, 313-355.
- 13. King, D.H. (1970). The role of carbon in eutrophication J. Water Pollut. 42: 2035-2051.
- Golterman, H.L. (1975). Phisological Limnology, Elsevier Publishing Co. Amsterdam.
- Harry, H.W. (1963). The Chemistry and Fertility of sea waters Combridge Univ. Press, London, 204 p.
- Abdo, M.H. (2002). Environmental studies on Rosetta branch and some chemical applications at the area extends from El-Kanater-Khyria to Kafr El-Zyat City. Ph.D. Thesis, Faculty of Science. Ain Shams University. Cairo, Egypt, 464 pp.
- Brewer, P.G. (1975). Minor elements in seawater In: Chemical Oceanography, 2nd Eds., Vol. 1 (Eds. J.P. Riley and G.S. Skirrow), 415 Academic Press, London.
- Balikungeri, A.; Robin, D. and Goerdi, W. (1985). Toxicol. Envir. Chem., 9, 309.
- Goher, M.A. (1998). Factors affecting the precipitation and dissolution of some chemical elements in River Nile at Damitta Branch. M.Sc. Thesis, Faculty of Science, Menofiya University, Egypt,223pp.

- Wakeman, T. (1976). The Biological Ramifications of Dredging and Disposal Activities. In: Proc. 7th world Conf., on Dredging Env. Effects.
- Mantoura, R.F. (1981). Organometalic Interactions in Natural waters A Review. In Marine Organic Chemistry, Elsevier, Amesterdam, 179.
- 22. UNEP 1996, The state of the Marine and Coastal environment in the Mediterranean region. MAP Technical Reports series 100, UNEP, Athens, Greece.; 142 p.
- Valenta, P.; Duursma, E.K.; Marks, A.G.; Rutzel, H.; Weijden, C.H.; Arnoldus, M.J. and Meurs, C.J. (1977). Desorption of metals from suspended material in the Rhine estuary. Neth. J. Res. 11, 130-145.
- 24. Holleman, J.N. (1968). Water Resources Res., 4, 2.
- 25. El-Nasharty, M.A. (2000). Heavy metals pollution in fresh water and marine Algae, M.Sc., Thesis Institute of Graduate Studies and Research, Alexandria University, Egypt.
- Moore, J.W. and Ramamoorthy, S. (1984). Heavy metals in natural waters. Springer. Verlage. New York, Berlin, Heidelberg, Tokyo.
- 27. Huzinger, O. (1980). The Handbook of Environmental chemistry. The Natural Environment and the Biogeochemical cycles. Springer-Verlage, New York, 1, 258.
- 28. Hamza, W.R. (1985). Phytoplankton production in Lake Manzalah (Egypt), M.Sc. Thesis. Faculty of Science, Alexandria Unviersity.
- 29. Krasuskopf, K.B. (1956). Factors controlling the concentration of thirteen rare metals in seawater. Geochemic. Cosmochim. Acta, 9: 1-32.
- Robenson, D.E. (1970). The distribution of cobalt in oceanic water. Geochemic. Cosmochim. Acta, 34: 513-567.
- Dekov, V.M.; Komy, Z.; Araujo, F.; Van Put, A. and Van Grieken, R. (1997).J. The Science of the Total Environment, 201, 195.
- Amundser, P.A.; Staaldvile, F.J.; Kashulin, N.A.; Popova, O.A. and Reshetnikov, Y.S. (1997).J.The Science of the Total Environment, 201-211.
- Sayed, E.A.M. (2003). Study of some chemical and physical changes of waters and sediments of Lake Edku. M.Sc. Thesis, chemistry Department, Faculty of Science, Alexandria University, Egypt, 217pp.
- 34. Beltagy, A.I. (1973). The geochemistry of some

recent marine sediments from the Gulf of st. Lowerence. Ph.D. Thesis, Mc Gill University, Canada.

- 35. Hem, J.D. and Roberson, C.E. (1967). Form and stability of aluminum hydroxide complexes in dilute solution U.S.G.S. water supply paper 1827-A, 55 pp.
- Willey, J.D. (1975). Reactions which remove dissolved aluminum from seawater.J. Mar. Chem., 3: 227-240.
- 37. Evans, C.J. and Karpal, S.J. (1985). Organometal Chemical Library, 16, 178.
- 38. Mehrem, M.M. (2002). Assessment of the state of pollution by antifouling paints in marine environment of Alexandria coastal region, Ph.D. Thesis, Arab Academy for Science Technology and Marine Transport, Alexandria, Egypt,170pp.
- Emara, H.I.and Shriadah, M.A. (1991). Manganese, Iron, Cobalt, Nickel and Zinc in the Eastern Harbour and El-Mex Bay waters, (Alexandria). Bull. Inst. Oceanogr. & Fish, Egypt,16(3): 99-112.
- 40. Abdel-Halim, A.M. (2004). Chemical equilibria studies of some phosphorus compounds under different conditions, Ph.D. Thesis, Faculty of Science, Alexandria University, Egypt 260 pp.
- Aboul-Dahab, O.M. (1985). Chemical cycle of inorganic pollutants in the ecosystem west of Alexandria between Anfoushi and Agamy, Ph.D. Thesis, Faculty of Science, Alexandria University, Egypt.320 pp.
- 42. El-Khair, E.M. (1993). Chemical studies on the Mediterranean coastal water in front of the Rosetta mouth of the Nile, M.Sc. thesis, Faculty of Science, Alexandria University, Egypt, 250 pp.
- 43. El-Nady, F.E. (1996). Heavy metal pollution problems in the south Eastern Mediterranean waters of Alexandria. The 6th International conference on Environmental protection is A Must, p.364-381.
- 44. Shriadah, M.A. and Emara, H.I. (1991). The distribution of chromium, copper, cadmium and lead in areas of multi-pollution factors of Alexandria. Bull. Inst. Oceanogr. & Fish, Egypt,16 (3): 39-50.
- 45. Abdel-Moneim, M.A. and Shata, M.A. (1993). Study of some heavy metals in Abu-Qir bay under the effect of industrial effluents. Bull of high Inst. of Public Health. XIII (3): 675-695.