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Studies of Some Heavy Metals in Water and Sediment in El-Max Fish Farm, Egypt

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Abstract: The present work attempts to establish the distribution of Iron Zinc, Copper, Lead and Cadmium in the water and sediment in El Max fish farm. Metals concentrations in water were varied between 85.5-1240.9; 2.595-23.921; 0.552-25.9; 0.231-18.953 and 0.096-1.902 µg/l for Fe, Zn, Cu, Pb and Cd, respectively. Metals concentrations in sediment ranged from 1193.325 to 4405.0; 86.625 to 331.338; 38.363 to 84.775; 27.240 to 46.463 and 1.260 to 3.325 µg/g dry weights for Fe, Zn, Cu, Pb and Cd respectively. Concentrations of heavy metals in water are compared with many guidelines to predict status of pollution. Effects Range-Low (ERL) and Effects Range-Median; (ERM) are used to reveal adverse biological effect for heavy metals in sediment. Contamination factors and Pollution Load Index are calculated for heavy metals in sediment revealed pollution effect on sediment in some basins. Metal partition coefficients (K_d) are calculated to study the distribution of heavy metals between sediment and water recorded values within the normal range. Data set obtained for Fe, Zn, Cu, Pb and Cd in water are treated using principal component analysis (PCA), which identified three factors responsible for data structure explaining 88.72% of total variance in water. Water quality index (WQI) is calculated for heavy metal in water.

Key words: Heavy Metals · Water Sediment · Pollution · Factor Analysis · El-Max Fish Farm

INTRODUCTION

Aquaculture is considered as one of the most important sources of animal protein production. Countries having over population problems as Egypt have an increase demand for protein production of fishes. So, realize the maximum yield of all useable resources for production food is vital. This is can be realized by increasing the area of cultured fishponds using the facilities of aquaculture methods [1]. Heavy metals are considered as the most important form of pollution of the aquatic environment because of their toxicity and accumulation by marine organisms [2]. Some trace metals are necessary in small amounts for individual metabolic processes, being assimilated by marine organisms. However, their capacity to form complexes with organic substances can result in concentrations up to 1000 times higher than their assimilation and fixation in tissues, becoming toxic to organisms [3]. Recent studies have shown, for instance, that human activities have created ecological pressure on the natural habitat of fish and other marine organism through time. There has been a steady increase in discharge that reaches the aquatic environment from industries [4]. Aquatic systems are very sensitive to heavy metal pollutants and the gradual increase in the levels of such metals in an aquatic environment, mainly due to anthropogenic sources, became a problem of primary concern. Contamination with heavy metals may have devastating effects on the ecological balance of the aquatic environment and the diversity of aquatic organisms becomes limited with the extent of contamination [5]. This is due to their persistence as they are not usually eliminated either by biodegradation or by chemical means in contrast to most organic pollutants. Moreover, the decay of organic materials in aquatic systems together with detritus formed by natural weathering processes provides a rich source of nutrients in both the bottom sediments and overlying water column. Microorganisms are capable of incorporating and accumulating metal species into their living cells from various supply sources. Consequently, small fish become enriched with the accumulated substances [6].

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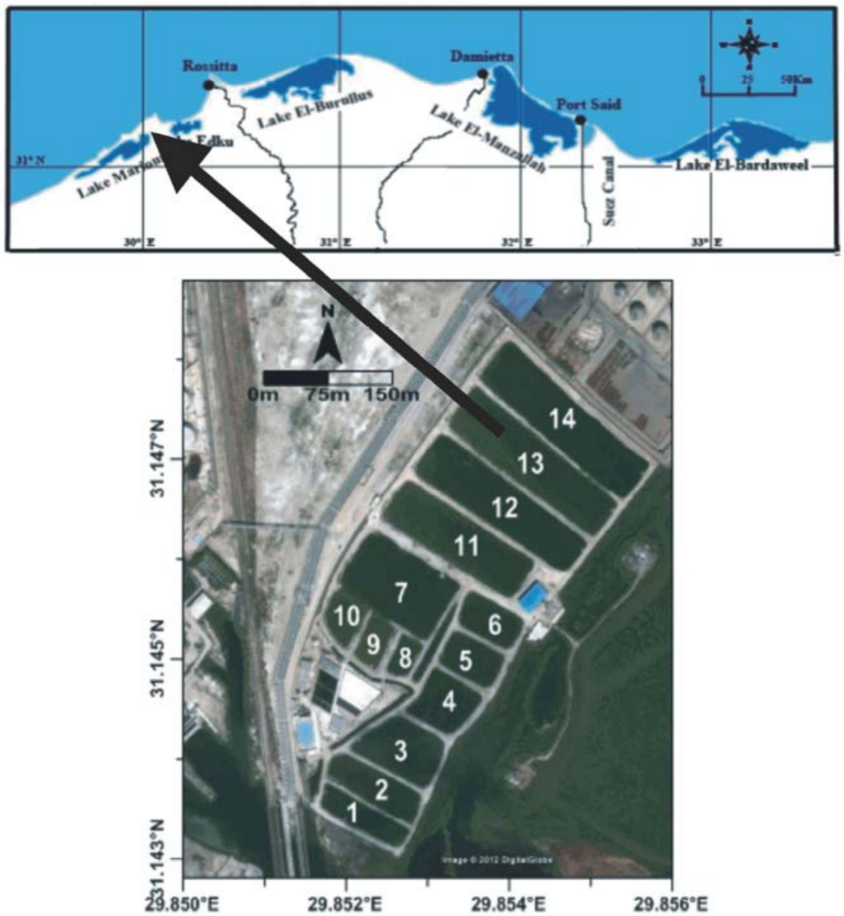

Fig. 1: Map showing the sampling locations of the study area

Study Area: El-Max Fish Farm was established in 1931, at about 15 km. westward of Alexandria City, near Lake Mariout and at about one kilometer south of the Mediterranean Sea Coast. To the north of this farm lies El-Max Pumping Station. It serves to pump out the water from Ummoum drain, which connects the lake to the Mediterranean Sea through a channel of about 800 meters long, so that the level of water in the lake is kept at about 2.8-3.0 meters below sea level. Taking advantage of the difference in level between water in this channel and the low water in basins farm, a line of pipes was constructed to permit the water to flow into the feeding canal, which supplies the fish basins. The total area of this fish farm is about 37 Feddan. This aquatic farm is divided into 14 basins (Figure 1). The water depth of basins is varied from 0.5 to 1.8 m. These aquatic fish farm basins receive the feeding waters coming from El-Nubaria fresh water mixed with the water drained through different waste production such as the irrigation water, industrial products and others, which discharged into Ummoum drain [7]. The present study investigates the distribution of heavy metals in El-Max farm located in Northern Egypt. Five metals (Cd, Cu, Zn, Pb and Fe) were determined in different compartments of the farm (water and sediments).

MATERIALS AND METHODS

Monthly water samples were taken from four basins (7, 12, 13 and 14) during the period (June, July, August and September 2011), beside two water samples from Elmoghazy (Water source channel of the fish farm). All sampling points are shown in Figure 1. The water samples were kept in polyethylene bottles and acidified with Nitric acid. The sample was filtered through membranes filter paper, 0.45 µm pore size (Millipore). The filtrated sample was allowed to pass through a glass column packed with chelating resin"Chelex-100", mesh size (40-60 µm) in ammonium form at a rate of 5 ml/min [8, 9]. The metals on the resin were then eluted with 70 ml of 2N HNO_3 and 10 ml DDW. The eluted and the washing were collected in Teflon cubs and then evaporated on a ceramic hot plate at about 70°C to near dryness.

The residue was re-dissolved in 1ml of 6N HNO_3 and the volume was completed to 25 ml using DDW and then transferred into a plastic vial. The water samples have been analyzed for the following chemical parameters; dissolved oxygen, ammonia, besides pH, temperature and salinity of the water samples as follow; The temperature and the pH values of the water samples measured in the field, immediately after the water sampling using graduating thermometer and portable digital pH meter (Model 201/digital). Water salinity was measured using Salinometer (Bekman, Model RS-10). Dissolved oxygen was determined according to Winkler's method [10]. Ammonia was determined spectrophotometer according to Grasshoff [11].

Sediment samples were collected from the four basins in summer 2011 collected by Van Veen Grab (Figure1). After sampling, the sediments were stored into plastic bags and placed in a cooler at 4°C, transported to the laboratory for analysis. Samples were dried in an oven at 105°C for 3-4 days. Lightly ground in an agate mortar for homogenization and prepared for analyses. A weight (0.5g) of dry sample of sediment was completely digested in Teflon vessels using a mixture of HNO_3, HF and $HClO_4$ (3:2:1) at 70°C [12, 13]. The final solution was diluted to 25ml with double deionized distilled water. pH, salinity, dissolved oxygen, ammonia and temperature of the studied basins (7,12,13and 14) were monitored monthly in aqua cultural period from June to September. AAS/flame mode (Shimadzu AA-6800) was used for measurement of Fe, Zn, Cu, Pb and Cd.

RESULTS AND DISCUSSION

Physical and Chemical Properties of Water: Water temperature exhibited small variations and reflected the interaction with the air temperatures. It is varied between 27.6 ºC in June to 31.4 ºC in August. The pH values were always in the alkaline side with small local changes affected by the seasonal variations. Ammonia fluctuated from 1.0 to 6.5(μ mol l^{-1}) in August and July respectively, with observed decrease of values in August. DO values ranged from 4.7 to 11 mg/l, high values were recorded in July. The recorded ammonia concentrations were lower than that recorded in El Max fish farm in 2005 (1 to 91.36-μ mol l^{-1}) [7], dissolved oxygen concentrations are always low in water sources (Elmoghazy and Elkhandak) their average values are 3.96 and 4.32 mlg1L respectively. [7]. El-Gohary et.al.[8] found that DO values in front of Rosetta branch of River Nile ranged between 3.36-11.61 mg/l with an average of 9.58± 2.37 mg/l. The reported salinity was varied from 3.3 to 4.6 psu. However, Zaghloul *et. al.,* [7] recorded values ranged from 3.87 to 6.79 psu. It is noticed that there is no significance difference in water salinity of other water basins of the fish farm [7].

Dissolved Heavy Metals in Water: Metals concentrations were varied between 85.5-1240.9; 2.595-23.921; 0.552-25.9; 0.231-18.953 and 0.096-1.902 µg/l for Fe, Zn, Cu, Pb and Cd, respectively (Table 1). Fe concentrations in some stations exceed permissible limit according to many guidelines [14-17]. However, Zn, Cu, Pb and Cd recorded values within the permissible limit in most scales. Many authors estimated the concentrations of some heavy metals and concluded that, the different concentrations values of metals in water depend on the seasonal variations and the types of discharges [18, 19]. The concentrations of all dissolved metals tended to decrease with salinity consistent with similar behavior reported in Conwy estuary in England [20] and in El-Max Bay (21). Although it is difficult to differentiate background concentration due to geogenic processes in water, the high variability in the analytical data obtained is indicative of an external source for these elements in water. Comparing the data of this study with many fish farms in El-Fayoum, the heavy metal concentrations in El-Max Fish Farm recorded lower values than that recorded in El-Fayoum farms [22]. The concentrations of heavy metals reveal decreasing in the order: Fe > Zn > Cu >Pb > Cd. Comparing the data of this study with other water sources the results are within the range for many literatures [21-32] Table (2).

Factor Analysis for Heavy Metals in Water: Using factor analysis, linear correlation between metal concentrations in water was determined, which enabled interpretation of correlation of elements in the study area. Elements belonging to a given factor were defined by factor matrix after varimax rotation, with those having strong correlations grouped into factors. The identification of factors is based on dominant influence [34]. The distribution manner of individual association of element in water was determined by principal component method (results are shown in Table (3). Based on eigen values and varimax rotation three factors explained 88.72% of the variability.

Factor 1 exhibit 39.52% of the total variance of 88.72% with high positive loading on Zn (0.963) and Cd (0.940). This factor indicates strong association of Zn and Cd in fish farm water.

Table 1: Concentrations of heavy metals in the water of El-Max fish farm during 2011 (μg/l)

Month	Basin	Fe	Zn	Cu	Pb	Cd	WQI
June	7	282	3.871	9.033	10.4	0.43095	-0.473
	12	85.5	3.6435	18.4	8.63	0.4005	0.038
	13	1152.75	7	9.24	6.452	0.2075	-0.148
	14	166.2	5.2775	15.2	8.065	0.3775	-0.004
July	7	213	5.09	1.903	7.35	0.2125	-0.509
	12	280.9	5.8033	9.386	5.808	0.16898	-0.297
	13	185.98	5.2828	25.9	7.63934	0.2213	0.227
	14	250.6	3.9267	16.4	5.3923	0.1687	-0.176
August	7	919.877	23.921	15.833	18.953	0.903	1.329
	12	915.976	23.285	2.133	6.241	1.902	1.232
	13	766.862	2.595	2.202	0.231	0.123	-0.724
	14	881.473	5.56	5.713	17.093	0.105	0.419
September	7	95.4	5.303	3.34	6.81	0.315	-0.419
	12	801.365	2.619	2.649	3.234	0.096	-0.673
	13	835.568	11.434	2.307	1.617	0.468	-0.129
	14	1240.909	12.169	3.477	0.924	0.561	0.009
	Elmoghazy July	254.5	7.22	11.47	7.885	0.51	
	Elmoghazy Aug	904.575	5.293	0.552	6.703	0.333	
	min	85.5	2.595	0.552	0.231	0.096	
	max	1240.909	23.921	25.9	18.953	1.902	
	mean	568.524	7.739	8.619	9.413	0.417	
Permissible limit	LAW 48/1982	< 1000	< 1000	1000	50	10	
	FAO 1985	2000	5000	200	5000	-	
	USEPA (2000)	1000	1000	1000	50	10	
	CWQGs 2002	300	100	1000	50	5	

LAW 48/1982: Egyptian Law for protection of the River Nile and waterways from pollution, Art. (60): for water quality in River Nile, FAO: Food and Agriculture Organization Guidelines, CWQGs: Canadian Water Quality Guidelines for the protection of aquatic life and USEPA (Environmental Protection Agency)

Table 2: Trace metals (μgL^{-1}) in El Max Fish farm water compared to natural water source

Location	Fe	Zn	Cu	Pb	Cd	Ref.
El Max Fish farm	85.5-1240.9	2.595-23.921	0.552-25.9	0.231-18.953	0.096-1.902	Present study
Fish Farms in Fayoum	1012-2300	43.5-115	26.5-50.1	40-101	3.5-10.6	[22]
Lake Manzala, Egypt		433	84	42	27	[23]
Lake Mariut	2.73-39.53				22	[24]
River Nile	116-1143	5-167	2-470	5-163	1-8	[25]
Nile Delta in Egypt	72	30	29	22	22	[26]
Mediterranean west area (Egypt)		ND-34.07	0.27-72.46	0.04-18.88	0.19-2.40	[27]
El Max Bay	3.36-31.72		1.84-11.71			[28]
Wadi El-Rayan Lakes	465-828	56.0-98.0	59-73	93-129	39-71	[29]
El Max Bay	27.21-70.9	20.79-59.29	3.69-4.90	2.65-6.14	0.66-6.45	[21]
Edku	570	16	11	28	7	[30]
Lake Edku	300-820	8.85-57.55	20-31.5	18.5-95.5	11.25-11.75	[31]
El Max Bay		22	3.8	0.6	0.16	[32]

Table 3: Varimax rotated component matrix for heavy metals in water

1Element	F1	F2	F3
Fe	0.405	**0.735**	0.236
Zn	**0.963**	0.141	0.082
Cu	0.036	-0.917	0.133
Pb	-0.032	0	**0.979**
Cd	**0.94**	0.072	-0.118
Variance	39.52	28.14	21.06
CV (%)	39.52	67.66	88.72

Rotation Method: Varimax with Kaiser Normalization CV: cumulative variance; bold number indicates positive correlation and-ve italic values indicate negative correlation.

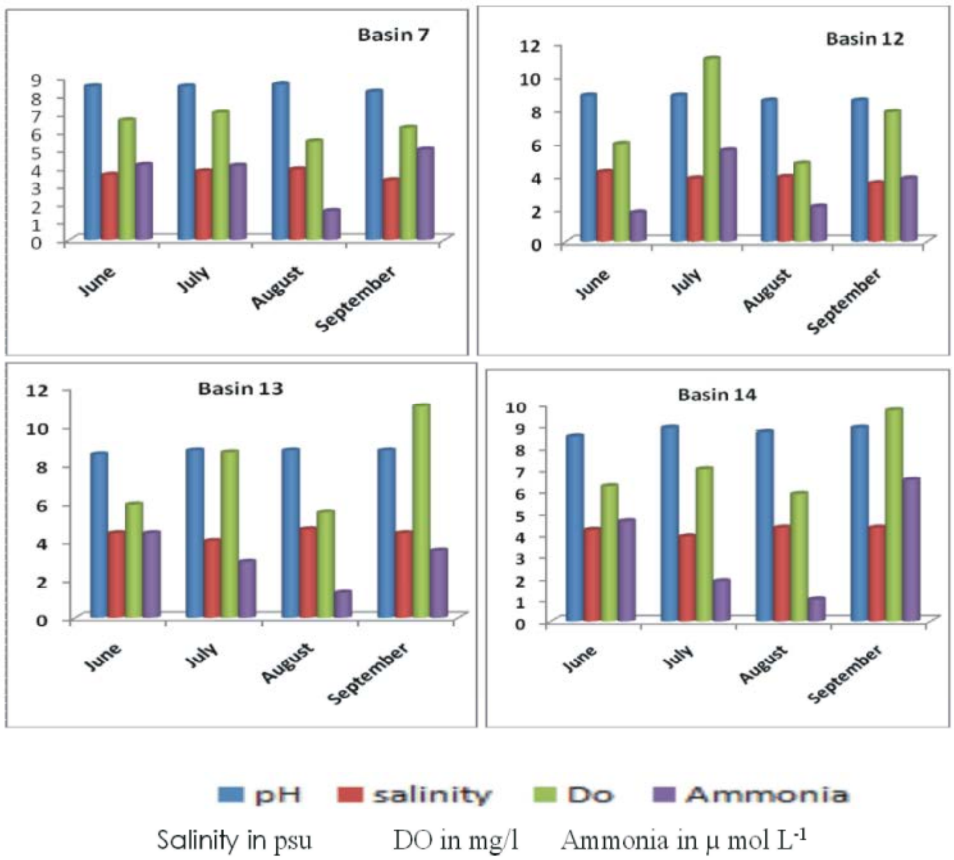

Fig. 2: Monthly and Regional variations of pH, salinity, DO and Ammonia in El-Max fish Farm during the period June-September 2011.

Factor 2 exhibits 28.14% of the total variance with high positive loading to Fe (0.735) and high negative loading on Cu (-0.917). This factor can be attributed to mixed origin of Fe in the area from anthropogenic and geogenic source. The negative loading on Cu indicates that as the Fe concentration increases, Cu level decreases showing the existence of inverse relation.

Factor 3 exhibits 21.06% of the total variance with high positive loading on Pb (0.979). High levels of Pb are mostly restricted to anthropogenic source. Since the aquatic fish farm basins receive the feeding waters coming from El-Nubaria fresh water mixed with the water drained through different waste production such as the irrigation water, industrial products and others which discharged into Ummoum drain.

Water Quality Index (WQI): Water Quality Index (WQI) is calculated according to the following formula: [35]

$$WQI = \sum_{n=1}^{n} (\lambda_n / \sum \lambda) \times PCn$$

For PC Assessment model where n: The number of effective components, λ_n, are the Eigen values of the effective components, $\Sigma\lambda$ sum of the Eigen values and PCn are the n critical principal component scores [36]. According to calculation of water quality index, basins 7 and 12 in August suffer from pollution. The high rate of organic matter decomposition in the summer season is the main reason for the increasing dissolved trace metals concentration in this period due to biodegradation [37].

Heavy Metals in Sediments: The total metal concentrations in sediments are shown in Table (4). Basin 7 exhibited higher concentration for Zn (331.338 mg/kg) and Cd (3.325 mg/kg). Basin13 recorded high concentration of Cu (84.775 mg/kg) and Pb (46.4625 mg/kg).

High concentration of Fe (4405 mg/kg) was recorded in Basin 12.The concentration of heavy metal in the sediment revealed the following order; Fe> Zn> Cu> Pb> Cd. The ERL and ERM delineate concentrations at which adverse biological effects occur

Table 4: Concentrations of metals (µg/g dry weight) in sediments of EL-Max Fish Farm during 2011

Basin	Fe	Zn	Cu	Pb	Cd
7	1622.400	331.338	64.238	38.013	3.325
12	4405.000	241.960	42.730	27.240	1.260
13	1193.325	275.838	84.775	46.463	2.275
14	1735.763	86.625	38.363	29.575	1.538
ERL		150	34	46.7	1.2
ERM		410	270	218	9.6
TLV		200	75	100	1

ERL: Effects Range-Low, ERM: Effects Range-Median;

TLV: Threshold limit value (Long *et al*. 1995; Pekey2004).

Table 5: Concentrations of trace metals (mg/kg dry weight) in El-Max Fish farm sediment compared to surroundings

Location	Fe	Zn	Cu	Pb	Cd	References
El Max Fish farm	1193.325-4405	86.625-331.38	38.363-48.775	27.240-46.463	1.260-33.25	Present Study
Fish Farms in Fayoum	2550-7900	125-315	24.3-50.3	19-34.4	3.3-10.8	[22]
Western Harbour and El-Max Bay	600-26300	17.98-246.27	11.78-377.91	25.94-592	1.33-15.03	[39]
El-Max Bay	512.86-2490.59	51.35-448.34	3.29-47	8.8-88.68	2.54-7.54	[21]
El-Max Bay		80-135	18-64	28-94	1.7-5	[40]
Burullus Lagoon	2551-3816	7.89-754.59	2.67-366.35	4.51-153.07	0.75-24.69	[41]
Western Harbour	8819-36140	58.5-382	39-207	38-1070	0.61-2.44	[42]
Ismailia Canal, Egypt	13900-25432	28.8-74.0	15.0-52.2	13.2-18.8	3.6-9.2	[43]

Table 6: Log values of the partition coefficients (K_D) of heavy metals in El-Max Fish Farm, Egypt

		log K_d				
Basin	Month	Fe	Zn	Cu	Pb	Cd
7	June	3.76	4.93	3.85	3.56	3.89
	July	3.88	4.81	4.53	3.71	4.19
	August	3.25	4.14	3.61	3.30	3.57
	September	4.23	4.80	4.28	3.75	4.02
12	June	4.71	4.82	3.37	3.50	3.50
	July	4.20	4.62	3.66	3.67	3.87
	August	3.68	4.02	4.30	3.64	2.82
	September	3.74	4.97	4.21	3.93	4.12
13	June	3.02	4.60	3.96	3.86	4.04
	July	3.81	4.72	3.51	3.78	4.01
	August	3.19	5.03	4.59	5.30	4.27
	September	3.15	4.38	4.57	4.46	3.69
14	June	4.02	4.22	3.40	3.56	3.61
	July	3.84	4.34	3.37	3.74	3.96
	August	3.29	4.19	3.83	2.71	4.17
	September	3.15	3.85	4.04	4.51	3.44

rarely (<ERL; <10% occurrence), occasionally (between ERL and ERM, 10-50% occurrence) and frequently (>ERM >50% occurrence) [38, 39]. Adverse biological effect occasionally occurs for Zn in basins 7, 12 and 13 but for Cu and Cd in all basins. However, rarely adverse biological effects for Pb occur in all basins. Compared with the literature values reported for the heavy metal content of the sediments, as in (Table 5), the results of previous studies in EL Fayoum fish farm revealed that, Fe recorded in El Max fish farm values lower than that in EL Fayoum fish farm, however, Zn and Cu recorded values nearly in the same range. Pb and Cd recorded in El Max fish farm values higher than that recorded in El Fayoum fish farm [23]. As a literary concept published data given in Table (5) showed that different metal concentration ranges were recorded depending on the nature of the region [22,23,32,40-44]. The partition coefficients of metals, defined as the ratio of the metal concentration in sediment (mg/kg) to content of the dissolved metal concentration in water (mg/l) are shown in Table (6). In natural media, metal contaminants undergo reactions with legends in water and with surface sites on

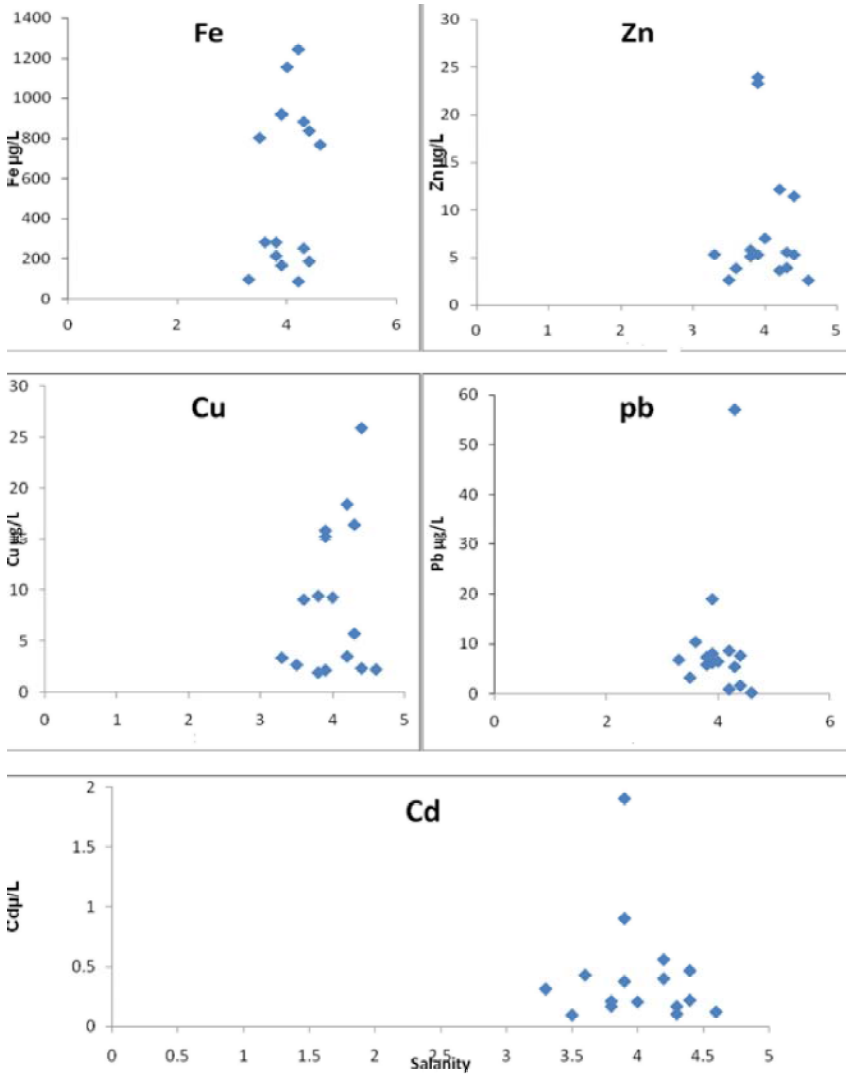

Fig. 3: Concentrations of five trace metals in water as a function of salinity in El-Max fish farm, Egypt

the solid materials with which the water is in contact. Reactions in which the metal is bound to the solid matrix are referred to as sorption reactions and metal that is bound to the solid is said to be sorbed. The metal partition coefficient (K_d; also known as the sorption distribution coefficient) is the ratio of sorbed metal concentration (expressed in mg metal per kg sorbing material) to the dissolved metal concentration (expressed in mg metal per L of solution) at equilibrium. (K_d depends on the nature of the sediment, pH, salinity, geochemical parameters of the water and specific characteristics of each element [45, 46]. The logarithmic values of K_d are shown in Table (6). The log K_d values ranged from 2.71 to 5.30 L/g. Zn exhibited the higher values. Generally, the partition coefficients of examined elements are low and within the range reported for natural water [22, 47].

Evaluation of Sediment Pollution: Contamination factors and Pollution load Index are calculated for heavy metals in sediment Introduced by Hakanson [48]. Individual Contamination Factors are calculated based on the following formula:

$$C_f = M_x / Mb$$

Where, M_x is the concentration of the target metal and Mb is the concentration of the metal in the selected reference background, Cf is defined according to four categories as follows: $C_f < 1$ low contamination factor $1 < C_f < 3$ moderate contamination factor $3 < C_f < 6$ considerable contamination factor $C_f > 6$ very high contamination factor (Table 6).

Table 7: Risk level of different metals based on C_f and PLI

	C_f					
Basin	F_e	Z_n	C_u	P_b	C_d	P_{LI}
7	0.345	3.488	1.428	1.901	3.325	1.61
	low	considerable	moderate	moderate	considerable	polluted
12	0.937	2.547	0.950	1.362	1.260	1.31
	low	moderate	low	moderate	moderate	polluted
13	0.254	2.904	1.884	2.323	2.275	1.49
	low	moderate	moderate	moderate	moderate	polluted
14	0.369	0.912	0.853	1.479	1.538	0.92
	low	low	low	moderate	moderate	unpolluted

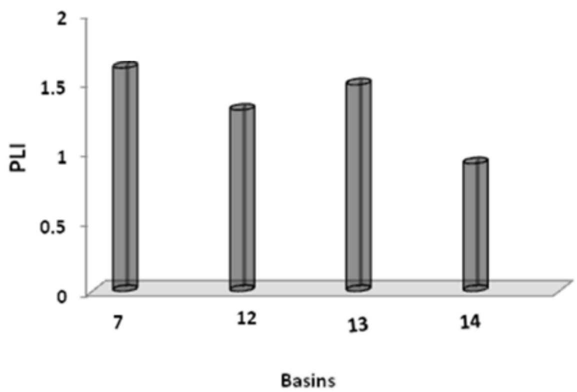

Fig. 4: Pollution load index of (Fe, Zn, Cu, Pb and Cd) in El-Max Fish farm sediment

Pollution Load Index (PLI): Pollution load index (PLI) for each site was evaluated as indicated [49].

$$\text{Pollution load index (PLI)} = (Cf_1 \times Cf_2 \times \ldots\ldots\ldots\ldots Cf_n)^{1/n}$$

Where, n is the number of metals and CF is the contamination factor. The contamination can be calculated from; The PLI value >1 is polluted where as PLI value <1 indicates no pollution [50, 51]. PLI values for heavy metals in sediment are illustrated in Table (7) and Figure (4) revealed pollution effect on sediment in some basins.

CONCLUSION

The case study of heavy metals in water and sediment in El-Max Fish Farm showed that, data set obtained for Fe, Zn, Cu, Pb and Cd in water identified three factors responsible for data structure explaining 88.72% of total variance showing that strong association of Zn and Cd in fish farm water. High levels of Pb are mostly restricted to anthropogenic source, since the aquatic fish farm basins receive feeding waters coming from El-Nubaria. WQI are calculated for heavy metal in water revealed good quality of water however, basins 7 and 12 recorded slightly deviated values from high quality in August due to the high rate of organic matter decomposition in the summer season. Concentrations of heavy metals in water are compared with many guidelines to predict status of pollution. Heavy metal concentrations in sediment revealed adverse biological effect occasionally occurs for Zn in basins 7, 12 and 13 but for Cu and Cd in all basins. However, rarely adverse biological effects for Pb occur in all. Contamination factors and Pollution Load Index are calculated for heavy metals in sediment revealed pollution effect on sediment in some basins. Migration patterns of heavy metals released into the environment can be measured by partition coefficient (K_d). Zn presented the higher distribution. Generally, the partition coefficients of examined elements are low and, within the range reported for natural water.

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