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Field and Laboratory Studies on Copper and Zinc Concentrations of the Aswan Dam Water Reservoir, Egypt

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Abstract: The present study aimed to deal with the factors affecting the distribution of copper and zinc in Aswan water Reservoir. Result showed that the concentrations of Cu and Zn were higher in eastern side than in the western side during various seasons. The highest levels of Cu and Zn concentrations were recorded during summer and autumn as compared with the lowest concentrations during winter and spring seasons. More than 95% of dissolved copper and 90% of zinc concentrations were removed during the winter and spring seasons when a pH was more than of 8.3. As well as the adsorption of Cu and Zn ions on the surface of fine suspended particles have a unit positive slope at low metal concentrations. While at high levels, reduction of slop of metals removal was obvious. The removal rate of Cu and Zn from reservoir water depend on the initial concentrations of these metals and soluble nutrients as silicate and phosphate. The levels of different physicochemical parameters in the water of Aswan Reservoir water are within the permissible ranges. But these parameters were higher than those previously reported before the transplantation program of grass carp fish in 1995.

Key words: Aswan Reservoir · River Nile · Copper and zinc · Wastewater contamination

INTRODUCTION

Copper and zinc are essential elements for the session of the metabolism cycle of plants and animals at low levels that permit the normal function of some enzymes, while in the high level they become toxic to plants, animals and humans [1].

In Aswan Reservoir, the wastewater contamination due to products from fishing and tourist ships which discharged their wastes in water bodies without any pre-treatment which can cause adverse effects on the water quality. The average concentrations of physical and chemical parameters of Aswan Reservoir water in 1991 before the transplantation program of grass carp fry fish were recorded in Table 1 [2]. A fundamental change occurred in Aswan Reservoir after the recent developments in the transplantation program of grass carp fry fish implemented by the Ministry of Irrigation in the middle of 1990s, This type of fish found huge high amount of food and hydrophytes in this region. The changes in environmental conditions as decreasing in pH value and increasing organic matter content in water cause the mobilization of copper and zinc from sediment to overlying water.

On the other side, the ability of metals to dissolution from sediment to surrounding water depends on pH value and the level of nutrients and organic compounds [3, 4]. In contrast, the kinetic of the metals sorption on the surface of suspended particles and into iron oxides [5, 6] as well as into aluminosilicate depending on pH value [7]. The removal of Cu and Zn ions from water by chelating fiber and on activated carbon obtained from agriculture was conducted by several authors [8, 9].Also; removal of Zn ions from industrial wastewater pants around Cairo was applied [10]. Therefore, the aim of the present work was to throw light on the distribution of copper and zinc as well as physical and chemical parameters in Aswan Dam water Reservoir after the severe drop in the density of aquatic macrophytes associated with the transplantation program of grass carp fish.

MATERIALS AND METHODS

Study Area: The area lies between old Aswan Reservoir and the Aswan High Dam (H.D). It was formed after damming old Aswan Reservoir in 1934. It was built stretching from side of the valley with a total length of 9 km and 2.7 km width. Recently, severe drop in the density

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Table 1: Average values of physicochemical parameters and its seasonal average of Aswan Reservoir water during 1991[2]

Parameters	Winter	Spring	Summer	Autumn	Parameters	Winter	Spring	Summer	Autumn
Temp.^{5} C	17.1	19.7	26.8	23.2	NO_2^- µg l^{-1}	2.77	3.13	1.44	1.83
TDS mgl^{-1}	167	156	169	161	NO_3^- µg l^{-}	35	56	137	123
DO mg l^{-1}	7.33	5.24	3.52	5.4	SiO_3^- mg l^{-1}	3.77	5.29	3.2	4.51
pH	7.67	8.08	7.81	7.73	PO_4^{3-}	58	96	165	99
CO_3 mg l^{-1}	8.7	5.3	3.3	4.7	Ca mg l^{-1}	29.02	28.44	24.0	22.7
HCO_3 mg l^{-1}	126	130	111	113	Mg mg l^{-1}	10.0	10.96	8.6	7.76
TOM mg l^{-1}	7.24	6.44	4.42	5.22	Transperancy	4.2	3.1	3.40	1.90
SO_4^{2-} mg l^{-1}	11.6	14.2	12.1	6.0	TSS	8.5	5.4	12.8	13.2
NH_3 µg l^{-1}	230	190	370	355	Cl mg l^{-1}	6.7	7.61	4.6	5.72
Cu µg l^{-1}	7	13	35	22	Zn µg l^{-1}	1.33	110	126	18

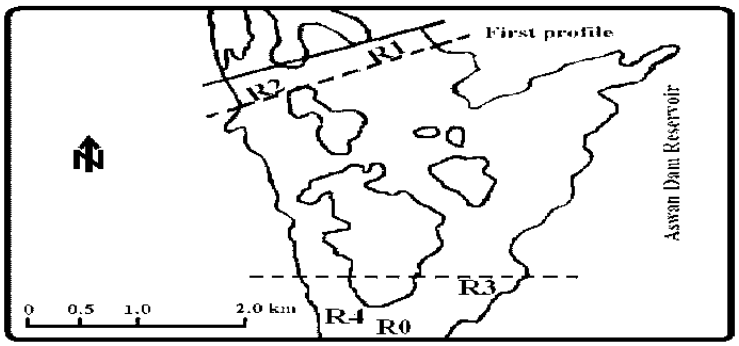

Fig. 1: Map showing sampling sites in Aswan Reservoir Area include sampling sites and include R0 site used in laboratory studies.

of aquatic macrophytes was observed due to the transplantation program of grass carp fish fry implemented by the Ministry of Irrigations in the 1995. In the meantime, the increasing number of tourist boats at this area, represents a major source of water pollution.

The sampling were carried out on quarterly basis from winter to autumn, 2009 and covered two profiles, including 4 sampling stations illustrate in Fig. 1.

The R0 site was not exposed to any polluted sources. It was used in the experimental studies. Water samples were collected from subsurface and near bottom by Van Dorn bottle and preserved in polyethylene bottle.

Methods of Analysis: The temperature in water was measured by thermometer. Electrical conductivity was measured using electrical conductivity meter (Ysi Model33s.c.t). The dissolved oxygen was measured by Winkler's method using azid modification of iodometric method. Carbonate and bicarbonate were directly determined by titration with standard 0.02N H_2SO_4 using phenolphthalein and methyl orange as indicators. The pH value was determined using a portable pH meter calibrated with two different pH buffer solutions (7.0, 9.18). The total organic matter (TOM) as function of COD was determined by dichromate reflex method [11]. Orthophosphate in water was determined using molybdate blue method which is based on the formation of the blue colour as a result of the reduction of phosphomolybdate complex by stannous chloride at=690 nm, while Nitrate was determined by using sodium salicylate method . Nitrite content was determined by using sulfanilic acid and naphthylamine which react with nitrous acid to produce a red colour which is used for the colourmeteric determination at 510 nm. Also, the silicate content was measured by colorimetric molybdosilicate method. While sulphate value in water was measured by turbidmeterically using barium chloride crystal and condition reagent used spectrophotometer at 420 nm [11]. Samples of water were digested by nitric acid. The concentrations of Cu and Zn were determined using Shimadzu Atomic Absorption Spectrophotometer Model AA-6800 and graphite furnace, ASC-6100.The analysis was conducted in the Central Laboratory of NIOF at Alexandria Branch.

Table 2: Frequencies of physicochemical parameters sample was used in laboratory experiments. (A) Physicochemical parameters in water not exposed to any sources of pollution, Ro site (B) Frequencies of sediment taken in same location.

(A)										
Parameters	Temp. C	DO mgl^{-1}	pH	TSS	CO_3^-	HCO_3^1	N O_3	NO_2	PO_4	SiO_3
Levels	21.2	8.4	8.55	7.7	24	132	86	245	35	3.5
(B)										
Parameters	Sand	Silt	Ca	CO_3	TOM	pH	Ca	Na		
Levels	68.2%	24.5%	7.3%	3. 7%	4.2%	7.82	2.91%	0.63 %		

Statistical Analysis: To find general relations between the different parameters correlation coefficient matrix was used between all pair of parameters. Also excel program was used for representation of different obtained data.

Experimental Studied of Aswan Reservoir Water: Physical and chemical properties were investigated in laboratory using water and sediment samples taken from site which was not exposed to any pollutant sources (R0 site) (Table 2).

The first experiment examined the effect of pH value on the Cu and Zn removal from the water. The experiments were carried out on 8 unpolluted samples water from Aswan Reservoir in 500 ml polyethylene bottles. Enriching standard metal separately for each sample 50 $\mu g\ l^{-1}$ was used. Control for the pH values by addition 0.05N Na OH as well as, HCl to produce a series of pH values. The samples were left in the laboratory for two days. The Cu and Zn ions were removed from water system as fine colloid. The precipitate was separated by filtration and the concentrations of Zn and Cu were analyses using AAS.

The second experiment, investigated the adsorption of metal (Cu & Zn) in presence of soluble phosphate. Three liters from water samples were filtrated and transferred into three flat flasks had been scrubbed. Each of them was Enriched with a standard orthophosphate to become 100 $\mu g\ l^{-1}$ and sterilized in a hot plate for 2 hours. Add approximately 50 grams from wetting homogenous sediment to each sample. After that standard metals were added to flasks to become as follows, 25 $\mu g\ l^{-1}$ to flask 1, 50 $\mu g\ l^{-1}$ to flask 2 and 100 $\mu g\ l^{-1}$ to flask3, respectively. Then the final concentration of metals have been determined by AAS after 1, 3, 5,7,9,11,14 days.

The third experiment studied the effect of adsorption of (Cu and Zn) on the surface of natural suspended particles collected from Aswan reservoir. Sorption experiments were performed in 100 ml Teflon [12]. It was used to minimize sorption of metals on vessel. Samples had an initial volume of 100 ml. Add 1.0 ml of prepared suspension electrolyte to each sample. The suspension prepared as follows; the sediment sample was dried and grained, then passed through (0.63 mm) sieve. Ten grams from these fine particle in 1 liter 0.001 M Ca $(NO_3)_2$. Enriching of samples by a standard metals to become the initial concentrations 1, 2, 4, 10, 25, 100, 150, 200,250, 300 $\mu g\ l^{-1}$, respectively. Samples of each Teflon were left for 15 days under continuous shaking at constant pH= 7.8 and laboratory temperature. After adsorption equilibration, the metal containing solids were separated from solution. The particles were re-suspended using equal volume of same electrolyte 0.001M Ca $(NO_3)_2$. Then the concentrations of Cu and Zn were determined as mention in the previous tests.

RESULTS

Laboratory Studies: The percentages of Cu and Zn removal as function of series pH values of Aswan Reservoir water was represented in fig. 2

The highest removal values for Cu and Zn were 94.6 and 92.4% recorded when a pH more than 8.3, respectively.

The rate of Cu and Zn removal adsorbed on the surface of soluble phosphate as function of time are illustrated in figs. 3 and 4.

It can be observed that the removals of zinc and copper ions were highly positively significant with rapid rates during the first seven days from the period of experiment. Then the metal ions were released again with low rates from 7 to 9 days. In the third step the rates of removal of metals return to increase again from 9 to 14 days in different concentrations. Results obtained of third experiment shown in the fig. 5. Result showed that the copper and zinc removal from water have positively proportional with a unit slope at concentration low concentrations. But, the slope was reduced when the metal levels more than 100 $\mu g\ l^{-1}$.

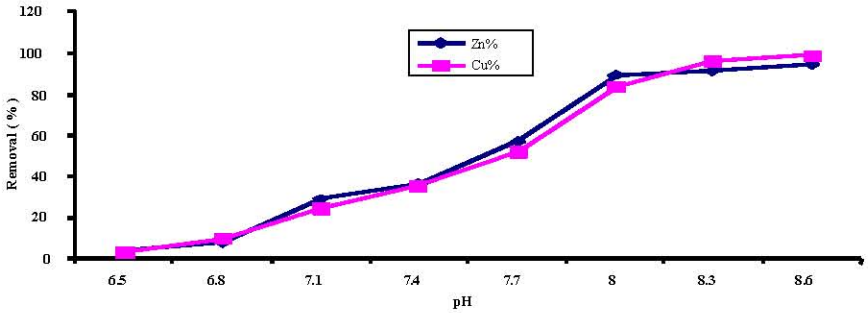

Fig. 2: Percentages of Cu and Zn removal as function of series pH values of Aswan Reservoir wat

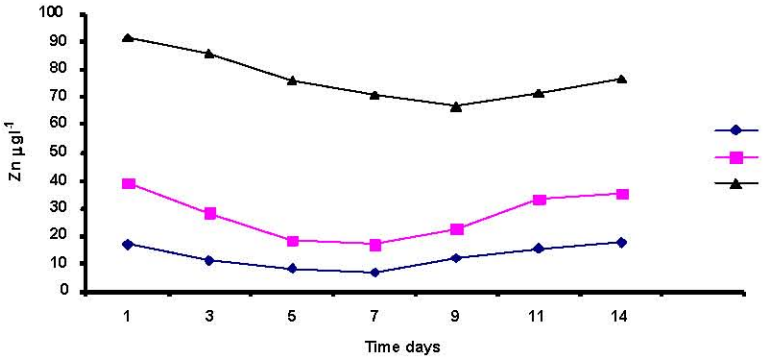

Fig. 3: Zinc removal µg / l in presence of orthophosphate as function of time at three different.

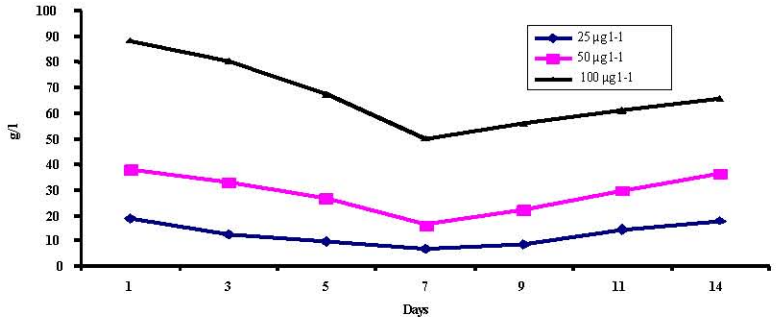

Fig. 4: Copper removal µg / l in presence of orthophosphate as function of time at three different concentrations.

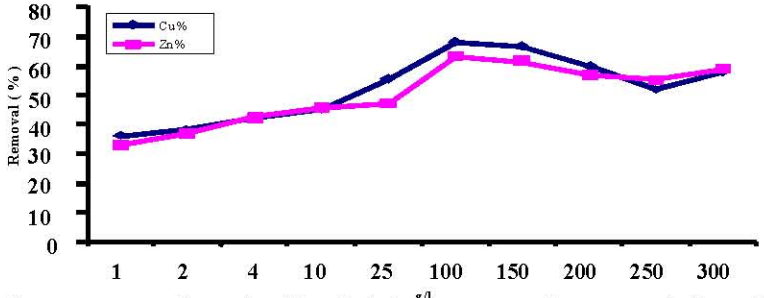

Fig. 5: The removal percentage of metals (Cu, Zn) in presence of suspended particle as function of initial concentrations in Aswan Reservoir water.

Field Studies: The frequencies of various physicochemical parameters during different seasons in the Aswan Reservoir water and its average values are shown in table 3. There was difference in water temperature between surface and bottom water layers during summer with the decrease in dissolved oxygen in bottom water layer. The picture in winter is differed than that at hot period whereas no wide variations were

Table 3: Frequencies and average value of physicochemical parameters and its seasonal average of Aswan Reservoir water during, 2009

	Winter		Spring		Summer		Autumn	
Items	Ranges	Aver.	Ranged	Aver.	Ranges	Aver.	Ranges	Aver.
Temp.^{5} C	17.2-18.4	17.5	21.2-23.4	22.5	25.6-31.3	27.7	23.0- 25.6	24.1
TDS mgl^{-1}	146-161	156.7	142-156	152.5	159-169	162.4	161-173	166.3
DO mg l^{-1}	8.4-10.4	9.3	7.5-8.9	8.2	1.7-4.0	2.4	3.0- 4.8	3.6
pH	8.35-8.83	8.50	8.45-9.05	8.62	7.20-8.40	7.55	7.25-8.15	7.42
CO_3 mg l^{-1}	16-30	20	18-40	24	4-8	6	0.0- 2.0	0.5
HCO_3 mg l^{-1}	126-132	128	128-144	136	110-124	114	136-152	142
TOM mg l^{-1}	8.42-2.98	8.85	8.9-10.4	786	2.44-6.88	4.42	1.56-7.24	3.84
SO_4^{2-} $mg\,l^{-1}$	9.55-15.90	13.2	12.7- 20.25	16.52	3.1-6.85	5.04	8.25-11.55	9.42
NO_2^{-} $mg\,l^{-1}$	75-295	155	53-145	100	330-525	420	55- 105	65
NH_3 µg l^{-1}	205-550	385	90- 480	280	520-745	630	385 -1155	820
NO_3^{-} $mg\,l^{-1}$	550- 880	670	245-480	295	755- 780	1270	780-1145	825
SiO_3^{-} $mg\,l^{-1}$	2.0-3.25	2.8	3.5-5.5	4.5	4.75-7.25	6.10	3.25- 4.75	4.25
PO_4^{3-}	50- 175	125	35-105	65	375-605	420	155- 315	245
Ca mg l^{-1}	26.4-28.8	27.0	28.4-32.6	29.2	22.4-24.8	23.4	20.2 -24.0	22.5
Mg mg l^{-1}	7.2-8.6	7.72	6.38- 8.24	7.88	10.45-14.4	12.15	5.56 -9.6	8.66
CODmgl^{-1}mg	6.24-9.96	8.48	8.24- 12.72	11.24	3.24- 4.48	3.96	3.72 - 7.44	6.24
Trans. M	5.75-7.50	7.10	4.5-5.75	5.20	3.5- 4.25	2.80	2.5- 3.75	3.1
TSS	8.6-11.2	10.1	7.5- 10.2	9.25	17.5-22.4	19.7	16.8-28.4	23.6
Wat. level,MS	106 .0- 107.8	107.02	107.5- 110.2	109.04	110.4-110.8	110.12	110.8-111.5	111.0

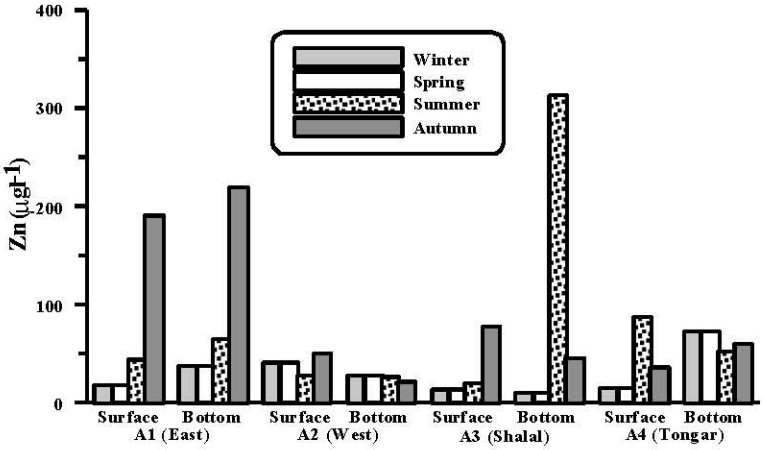

Fig. 6: Distribution of zinc concentrations $\mu g l^{-1}$ in different sites of Aswan Reservoir water

recorded. It can observe that the several physicochemical parameters are differed from results obtained before the transplantation program of grass carp fish fry implement during 1995. The concentrations of pH, sulphate, organic matter and nutrients (nitrate, nitrite and ammonia, orthophosphate) are higher than previous data recorded in 1991, (Table 1). Also the water penetration (Transparency) is higher than those recorded by Toufeek [2].

It can be shown that the lowest Zn and Cu levels were observed during winter and spring while their highest values occurred during summer and autumn, (Figs. 6,7) .

Copper in Aswan Dam water Reservoir ranged between 0.5 and 2.5, ND and 10.8, 1.8 and 31.6, 1.2 and 76.4 with an average values of 1.25, 2.40, 9.7, 15.75 µg l^{-1} during winter , spring , summer and autumn, respectively.

The absolute maximum value was 76.4 µg l^{-1} detected at A3 site during summer as compared with the absolute minimum ND was found during spring. The data showed that the concentrations of Cu were comparatively higher in the eastern sites A1 and A3 than its corresponding values recorded in the western sites A2 and A4 in the various seasons.

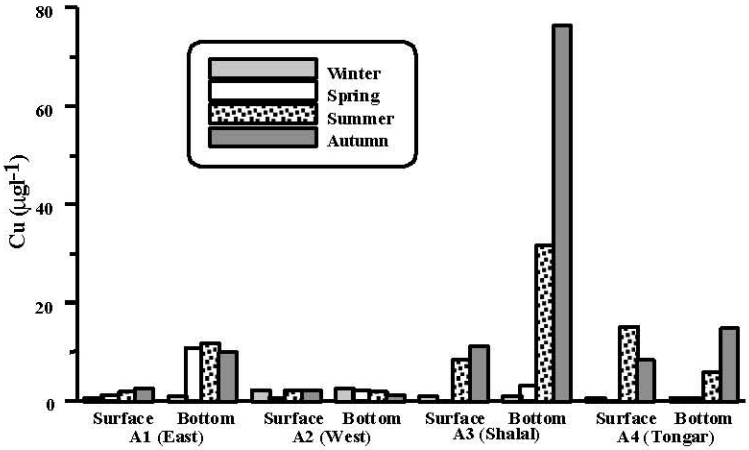

Fig. 7: Distribution of copper concentrations $\mu g l^{-1}$ in different sites of Aswan Reservoir water.

Also, the concentrations of zinc of Aswan Reservoir varied between 9.6 and 50.4, 9.2 and 73.2, 19.2 and 312.6, 20.8 and 218.6 $\mu g l^{-1}$ during winter, spring, summer and autumn, respectively. The highest values were recorded during summer and autumn with a maximum value of 312.6 $\mu g l^{-1}$ occurred at A3 site. As well as the average concentrations of Zn were comparatively high at the eastern site as compared with those found in western one during the studying period.

DISCUSSION

The first experiment, showed three interesting diagram features. First, neutral trip for pH values ranging from 6.5 up to 7.1, whereas the metals were removed in a slow rate. Secondly, when pH ranges between 7.4 and 8.0 moderate rates of metals were removed from the water system. Third trip, at the high pH values above 8.3, whereas the dissolved metals were nearly completely removed from water to bottom sediment. This is probably due to homogeneous precipitation as hydroxyl carbonate metals minerals as $Cu_2(OH)_2CO_3$ & $Zn_2(OH)_2CO_3$. Hence the sorptions of these metals were positively increased with rising of pH values [12, 13]. In the second experiment, the removal of zinc and copper ions were highly positively significant with rapid rates in the first seven days ago from the period of experiment. Hence the concentrations became a minimum values 7.1, 16.1, 50.2 $\mu g\ l^{-1}$ for Cu and 8.5, 17.8, 88.1 $\mu g\ l^{-1}$ for Zn after first seven days. It was observed that the removal percentage of metal ions was higher at low metal levels than its values at high metal concentrations. From 7 to 9 days, the metal ions were released again with low rates. Then the rates of removal of metals return to increase again from 9 to 14 days in different concentrations. This is probably due to the adsorption of metals ions in the surface of orthophosphate and discharged from water to bottom sediment. After that the metal ions can be released again as active ions to overlying water without orthophosphate radical. This is mainly due to the exchangeable reactions as following example.

$$Cu_3(PO_4)_2\downarrow + Ca(NO_3)_2 \dashrightarrow Cu(NO_3)_2\uparrow + Ca_3(PO_4)_2\downarrow$$

In the third experiment, the copper and zinc removed from water have a positive unit slope at concentration low concentrations. But, the slope was reduced when the metal levels reached more than 100 $\mu g\ l^{-1}$. The change of slope of copper and zinc removal probably resulted to saturation of available surface of suspended particles. In general, the removal of metals (Cu, Zn) is mainly due to discharge with fine suspended particles to bottom layer. Regarding field studies, the relative increase in the concentrations of Cu and Zn as well as, sulfate, organic matter and nutrients (nitrate, nitrite and ammonia, orthophosphate), is mainly related to the increasing number fishing and tourist boats at this area, represents a major source of water pollution. As well as, the increasing of water transparency and pH value than previous studies (Table 1). This may probably due to the grass carp fish huge high amount of aquatic hydrophytes. This is led to increasing of water penetration and decreasing of phytoplankton at this region.

Although, the levels of different physicochemical parameters in Aswan Reservoir are lie within the permissible ranges according to World Health Organization (WHO) [14], Egyptian Organization for Standardization (EOS) [15] and United state Environmental Protection Agency (USEPA) [16] , but it was higher than the previous results [2 ,17] before transplantation program of grass carp fish by Ministry of Irrigation since,1995.

The low Cu and Zn concentrations were recorded during winter and spring whereas Cu, Zn ions readily loosed by adsorption on the surface of suspended particles with the increasing of pH value leaving the water with low metal contents during these periods [18-22].

The data showed that copper and zinc are positively correlated with temperature. This result is agreement with several literatures [23-26].This is proved that the Cu and Zn have high levels during hot periods. Also, the positively significance between Cu and NO_2 (r=0.92) indicated that Cu is soluble in water as nitrite form Cu $(NO_2)_2$[27] The negative correlation coefficient relationships between metal ions with silicate carbonate and phosphate mainly were ascribed to the precipitation of these metals as silicate, carbonate and phosphate forms as the following equations:-

$$Me\ Cl_2 + Na_2\ SiO_3 \longrightarrow Me\ SiO_3 \downarrow + 2NaCl$$
$$Me\ (NO_3)_2 + Ca\ CO_3 \longrightarrow Me\ CO_3 \downarrow + Ca(NO_3)_2$$
$$3Me\ Cl_2 + 2\ Na_3\ PO_4 \longrightarrow Me_3\ (PO_4)_2 \downarrow + 6\ NaCl$$

Whereas Me is Zn or Cu....Alc....

The negatively correlation coefficient between orthophosphate with copper(r=-0.639)and zinc (r=-0.662) may probably as result to the adsorption of metal ions on the surface of orthophosphate and discharged to bottom sediment , this type of nutrient easily to return to dissolution to overlying water leaving metal in sediment. This is resulted to exchangeable reactions as the suggested equation:

$$Me_3\ (PO4)_2 \downarrow + Na_2\ SiO_3 \longrightarrow Me\ SiO_3 \uparrow + Na_3\ (PO_4)_2 \uparrow$$

As well as the decrease in Zn and Cu levels observed during winter and spring probably may be due to a reversible relationships between metal values and pH value [5], (r=-0.75 , - 0.73) for Cu and Zn respectively. As well as due to increasing of adsorption metal ions onto organic matter and iron oxides [28].

The correlation coefficient between dissolved oxygen with Cu (r= -0.80) and with Zn (r= -0.83) indicated that these metals are not accumulated at the high oxygen content [29]. While the positive correlation coefficient between sulfate with Cu (r= 0.73) and with Zn (0.69), may due to the formation a soluble compounds in water such as (Cu $(NH_3)_4SO_4$ and Zn $(NH_3)_4\ SO_4$) and due to the oxidation of CuS and ZnS in presence of photosynthetic sulfur bacteria to formation soluble metal sulfate ($CuSO_4.5H_2O$) [30].

It was concluded that copper and zinc levels are higher than values recorded in previous study, but it not exceeded to the permissible limits according to United Nation Environmental Program who reported that the toxicity values of Cu and Zn in water are 1.3, 5.0 mg /l respectively. Data show that concentrations of Cu and Zn were higher in eastern side than those in the western side in various seasons, due to the wastewater contamination flowing from fishing and tourist boats. The relative increase in the concentrations of nitrate, nitrite and ammonia is mainly related to the sewage and domestic wastes from different village located around this region. Although, the levels of different physicochemical parameters in Aswan Reservoir are still bellow the permissible ranges according World Health Organization, but it was higher than the previous results obtained by several authors before transplantation program of grass carp fish by Ministry of Irrigation since, 1995. Results indicated that more than 95% of dissolved copper and 90% of zinc were removed during the winter and spring seasons when a pH more than of 8.3.

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