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Metals pollution assessment in water and sediment of El-Sharkawia Canal, River Nile, Egypt

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Summary: El-Sharkawiacanal is an irrigation canal located at El-Qualubiagovernorate and receiving water directly from River Nile. 40 water and 36 sediment samples were collected to covering the canal. Nine heavy metals; Fe, Mn, Zn, Cu, Ni, Co, Cr, Pb and Cd were assessed in water and sediment samples. The concentration levels of the measured metals in water samples were found to be Fe; 125.80-1478.47, Mn; 1.80-119.00, Zn; 1.60-40.40, Cu; 0.60-4.12, Ni; 1.75-20.20, Co; 0.80-13.60, Cr; 5.20-25.20, Pb; 3.40-32.60 and Cd; ND-1.21 µg/l. On the other hand,in the sediment samples they varied in the ranges; 11.20-30.64 mg/g, 152.02-677.11, 50.20-248.53, 20.90-111.11, 23.40-128.22, 0.30-27.00, 11.70-90.60, 6.00-102.10and ND-0.88 µg/g for Fe, Mn, Zn, Cu, Ni, Co, Cr, Pb and Cd,respectively. The concentrations of Zn, Cu, Co, Cr and Cd in water were within the permissible limits, but that of Fe, Mn, Ni and Pb were higher than the permissible limits.For sediment, the most metals were within the permissible limits except for Ni and Cu. The geo-accumulation index (Igeo) suggested "unpolluted to moderate pollution" for all studied metals (Igeo<1)and there is no spatial significant difference for most of the measured metals according to ANOVA.

Introduction

El-Sharkawiacanal is an irrigation freshwater canal originates from the River Nile at Shoubra El-Kheima region, 12 km upstream the bifurcation of the Nile at El-Qanater El-Khairia (Shebin El-Qanater General Administration of Irrigation). It passes through El-Qualubia governorate to about 30.00 km with average 2.00-4.00 m depth.(1)The total surface area is about 142,000 feddans with 5.00-20.00 m width (Qalyub General Administration of Irrigation). It is one of the main sources of irrigation and drinking water in El-Qualubia governorate, in addition, it is considered as an important source for fishing in the surrounding area. Its direct irrigation reins is 1208 feddans, but the total irrigation reins is 162,700 feddans (Benha General Administration of Irrigation). The average water flow is 232 m^3/sec, with an average discharge of 3.3 million m^3/day (39.19 m^3/sec) directly to the canal.(2)

The environmental pollution by heavy metals comes from anthropogenic sources such as smelters, mining, power stations and the application of pesticides containing metal, fertilizer and sewage sludge and the irresponsible disposal of wastes by various industries. They can become mobile in soils depending on soil pH and their speciation.(3)Heavy metals are regarded as serious pollutants for aquatic ecosystem because of their environmental persistence and toxicity effects on living organisms.(4)In the aquatic environment, the trace elements are partitioned among various environmental components (water, suspended solids, sediments and biota).(5)Heavy metals are of high ecological significance since they are non-biodegradable and are not removed from water as a result of self-purification. Once they are discharged into water bodies, they are adsorbed on sediment particles, accumulate in reservoirs and enter the food chain.(6)The elevation of metal levels in a reservoir is shown mainly by an increase in their concentrations in the bottom sediments.The heavy metals are widespread pollutants of great environmental concern as they are non-degradable, toxic and persistent with serious ecological ramifications on aquatic ecology.(7,8) Since sediments play a very important role in the physico-chemical and ecological dynamics, any change in toxic concentrations of heavy metal residues on the sediments will affect the natural aquatic life support systems. In natural aquatic systems, the geochemical processes responsible for the exchange of metals at the water-sediment interface are adsorption and precipitation.(9) Thetrace elements of the River Nile sediment increased significantly ($P < 0.05$) from Aswan towards Damietta and Rosetta branches. Such increase proves the presence of large quantities of organic and inorganic pollutants in Rosetta and Damietta water. This was expected due to the fact that the water of such branches receives high concentrations of organic and inorganic pollutants from industrial, domestic as well as diffuse agricultural wastes water in the Ismailia canal and other branches of the River Nile.(10,11,12)

The aim of the present study is to determine the spatial and temporal distribution of some heavy metals (Fe, Mn, Zn, Cu, Ni, Co, Cr, Pb and Cd) in water and sediment of El-Sharkawia canal to assess the environmental status of the canal.

Experimental

El-Sharkawia Canal is considered as an important source for drinking water in El-Qualubia governorate. So many drinking water plants are constructed on its banks, as shows in Table (1).

Table (1): Drinking Water Plantsintake from El-Sharkawiacanal.

Water Plants	Intake m^3/day*	Uptake m^3/day*
Shoubra El-Kheima water plant	460,000	400,000
KafrTaha water plant	10,000	8,200
KafrShebin water plant	10,000	7,000
Shebin El-Qanater (1) water plant	10,000	7000
Shebin El-Qanater (2) water plant	4,800	2,000
Kafr El-Shubak water plant	2,400	1,800
El-Gaafrahwater plant	10,000	8,600

*Data collected from Shoubra El-Kheima and Benha water plants (personal communication).

Sampling locations

Ten subsurface water and sediment samples were selected along El-Sharkawiacanal to covering all area under investigation. Details of the sampling locations with their longitude and latitude are represented in Fig. (1) &Table (2) respectively.

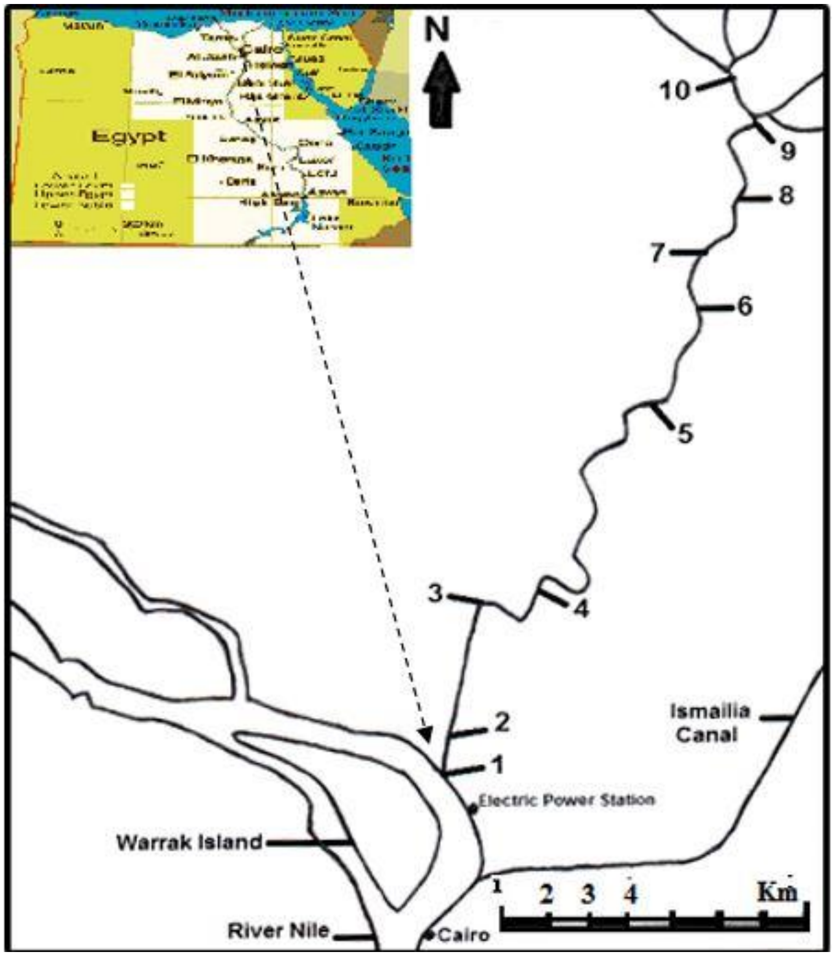

Fig. (1).Map of El-Sharkawia Canal illustrating the sampling stations.

Table (2).Latitude and longitude of sampling locations.

Stations	Features of Stations	Latitude	Longitude
1	After Shoubra El-Kheima Electric Power Station	30° 07′ 35.50″	31° 14′ 06.50″
2	Manti bridge (about 100 m downstream Shoubra El-Kheima water purification plant)	30° 08′ 12.30″	31° 14′ 11.40″
3	Omar bridge	30° 10′ 19.00″	31° 14′ 41.00″
4	KomIshfin water plant (at KomIshfin bridge)	30° 10′ 34.00″	31° 15′ 38.00″
5	Al-Hazzaniyyah bridge	30° 13′ 42.70″	31° 17′ 30.90″

6	Sindewah water plant	30^{o} $15^{\backslash}$ $15.00^{\backslash\backslash}$	31^{o} $18^{\backslash}$ $16.90^{\backslash\backslash}$
7	KafrTaha water plant	30^{o} $16^{\backslash}$ $06.80^{\backslash\backslash}$	31^{o} $18^{\backslash}$ $13.30^{\backslash\backslash}$
8	KafrShebin water plant (at Al-Murayj bridge)	30^{o} $17^{\backslash}$ $01.20^{\backslash\backslash}$	31^{o} $18^{\backslash}$ $48.30^{\backslash\backslash}$
9	Shebin El-Qanater (1) water plant	30^{o} $18^{\backslash}$ $28.40^{\backslash\backslash}$	31^{o} $19^{\backslash}$ $06.80^{\backslash\backslash}$
10	Shebin El-Qanater (2) water plant	30^{o} $19^{\backslash}$ $06.80^{\backslash\backslash}$	31^{o} $18^{\backslash}$ $51.60^{\backslash\backslash}$

Water analysis

Water samples were collected by a polyvinyl chloride Van Dorn plastic bottle (2L) and kept in icebox on the spot, then preserved immediately after collection by acidifying with concentrated nitric acid to ($pH<2$); by using 5 ml HNO_3 for 1 liter water sample. Heavy metals were extracted from water samples using nitric acid digestion method according to American Public Health Association (APHA, 1998).(12)

Sediment analysis

The sediment samples were collected superficially seasonally using Ekman Dredge, washed with deionized water, oven dried at 105^{o}Cand finally grinded in an agate mortar, then stored in polyethylene bags. The sediment samples were digested according to Kouadiol and Trefry, (1987).(13) Total metals (Fe, Mn, Zn, Cu, Ni, Cr, Co, Pb and Cd) in water and sediment samples were measured using GBC (Australia) atomic absorption reader Model SavantAA AAS with GF 5000 Graphite Furnace.

Statistical analysis

One-way ANOVA analysis was applied to identify significant differences for all metals among different seasons and stations for water and sediment samples. Significance levels of tests were taken as $p<0.05$ and highly significance as $p<0.01$.

Pearson's correlation analysis was performed to evaluate the potential relationships between the measured variables.ANOVA tests and Correlation Coefficient (r) between the studied elements were undertaken using the Excel-Stat software.

Resultsand Discussion

Heavy metals in water

Heavy metals play a principal role in water pollution since they are toxic to aquatic animals and may become a threat to man. The primary source of heavy metals in River Nile is the discharge of domestic sewage, industrial wastes and washing of herbicides and pesticides of the agricultural land.(14)

The contamination of freshwater with heavy metals has become a matter of great concern over last few decades, not only because of threat to public water supplies but also, their damage caused to the aquatic life**.** Also, Contamination with heavy metals may have devastating effects on the ecological balance of the aquatic environment and diversity of aquatic organisms become limited with the extent of contamination.(4)

The mean concentration values of studied heavy metals in water and sediment samples in El- Sharkawia canal and ranges during four successive seasons compared with guidelines values are presented in Table (3).

Table (3): Minimum, maximum and mean of heavy metals in water (µg/l) and sediment (µg/g) of El- Sharkawia canal compared to guidelines values.

Parameter	**Water µg/l**				**Sediment µg/g**			
	Min	**Max**	**mean**	**PL(1)**	**Min**	**Max**	**mean**	**(LEL-SEL)(2)**
Fe	**125.80**	**1478.47**	**491.29**	**300**	**11.20***	**30.64***	**26.74***	**20.00-40.00***
Mn	**1.80**	**119.00**	**54.50**	**100**	**152.02**	**677.11**	**513.44**	**460-1100**
Zn	**1.60**	**40.40**	**15.77**	**3000**	**50.20**	**248.53**	**123.03**	**120-810**
Cu		**4.12**	**1.72**	**2000**	**20.90**	**111.1**		**16.00 -110**

	0.60					**1**	**55.17**	
Ni	**1.75**	**20.20**	**9.02**	**20.00**	**23.40**	**128.22**	**75.88**	**16.00 -75.00**
Cr	**5.20**	**25.20**	**11.30**	**50.00**	**11.70**	**90.60**	**44.05**	**26.00 -110**
Co	**0.80**	**13.60**	**6.03**	**-**	**0.30**	**27.00**	**9.53**	**50.00**
Pb	**3.40**	**32.60**	**13.13**	**10.00**	**6.00**	**102.10**	**39.98**	**31.00-250**
Cd	**ND**	**1.21**	**0.56**	**3.00**	**ND**	**0.88**	**0.44**	**0.60 -10.00**

*mg/g

(1) PL=Permissible level of drinking water, according toEgypt Guidelines.(15)

(2) LEL= Lowest effect level; SEL= Severe effect level, according to OMOE.(16)

The seasonal variations of the studied trace metals in El-Sharkawiacanal water were found to be in the ranges of: Fe (125.80-1478.47, 202.60-610.80, 177.60-892.00 and 159.00-858.54 µg/l), Mn (1.80-37.80, 37.56-79.60, 41.40-101.40 and 19.20-119.00 µg/l), Zn (1.60-13.40, 12.20-30.60, 4.00-22.00 and 13.00-40.40 µg/l), Cu (0.80-3.20, 1.07-4.12, 0.60-2.40 and 0.80-3.07 µg/l), Ni (2.10-16.75, 1.75-15.90, 7.20-20.20 and 5.20-13.00 µg/l), Cr (6.17-13.28, 5.20-25.20, 7.62-14.31 and 9.16-18.24 µg/l), Co (1.98-8.16, 1.80-10.00, 1.87-13.60 and 0.80-13.18 µg/l), Pb (7.14-32.60, 4.60-20.20, 6.12-21.74 and 3.40-31.12 µg/l) and Cd (ND-1.21, ND-1.00, ND-0.83 and ND-1.02 µg/l) during autumn, winter, spring and summer seasons, respectively.

The seasonal variations of heavy metals content may be attributed to the fluctuations of the amount of agricultural drainage water, illegal untreated domestic sewage effluents and industrial wastes discharged into the canal. However, the domestic wastewaters can contain fairly high concentrations of metals, such as Al, Ni, Cu, Fe, Pb and Zn, which are derived from a wide variety of household products, such as cleaning materials, toothpaste and cosmetics.[(17)]

On the other side, the increase in metal concentrations in water during hot seasons (spring- summer) could be attributable to the reduced volume associated with higher evaporation rate induced by the increase in water temperature during dry hot seasons; and to the liberation of heavy metals from the sediment to the overlying water under the effect of both high temperature and organic matter decomposition due to the fermentation process.[(18)]

The results showed that slightly the decrease in Fe concentration during autumn may be due to the high concentration of dissolved oxygen leading to oxidation of Fe^{2+} to Fe^{3+}.[(19)]The increase in Mn concentration during winter and spring seasons may be attributed to the effect of the drought period. This result agrees with the finding by(Moustafa*et al.*, 2010).[(20)]The decrease in Zn concentration during autumn at different stations, in behavior similar to iron- may support the explanation attributed the decrease in zinc concentration to its adsorption on $Fe(OH)_3$ sedimentation and manganese oxides.[(21)]This observation was confirmed with the positive correlation of Zn with Mn ($r=0.378$, $p<0.05$). The increase in Pb concentration during autumn could be due to the decrease in the precipitation of Pb salts under low pH (7.91-8.20) and temperature values.[(22)]The heavy metal concentrations were found increased at stations (2), (5) and (10). This may be related to the slaughterhouse drainage at station 2, agricultural and domestic sewage effluents at station 5 and the canal closed end at station 10. The concentration levels of studiedheavy metals in water samples were arrangement in the order of: Fe>Mn> Zn>Pb> Cr> Ni> Co> Cu> Cd.

The positive correlation between Fe/Pb (r = 0.409, $p< 0.05$), Mn/Zn (r = 0.378, $p< 0.05$), Ni/Mn ($r=0.365$, $p<0.05$) and negative correlation between Ni/Cd ($r= -0.468$, $p< 0.01$) are revealed that these heavy metals have the same source of pollution. Also, ANOVA results show highly temporal significant differences ($p<0.01$) for manganese and zinc with an increase during summer season, but there is a spatial significant difference ($p<0.05$) for copper.

Heavy metals in sediment

The analysis of heavy metals in sediments permits us to detect pollution that could liberate to water. Also, provides information about the critical sites of the water system under consideration.[23]

The seasonal variations of the studied trace metals in El-Sharkawia canal sediment were found to be in the ranges of: Fe (12.28-30.04, 26.06-30.09, 21.02-30.64 and 11.20-29.69 mg/g), Mn (125.02-641.74, 555.35-677.11, 301.42-621.33 and 197.87-563.36 µg/g), Zn (96.73-167.50, 107.23-248.53, 50.20-193.00 and 80.43-208.20 µg/g), Cu (36.50-111.11, 40.00-99.47, 24.00-78.20 and 20.90-83.20µg/g), Ni (38.10-125.47, 31.80-128.22, 41.00-126.05 and 23.40-107.30 µg/g), Cr (31.97-88.29, 25.10-65.70, 21.14-83.28 and 11.70-90.60 µg/g), Co (4.12-13.70, 2.80-22.40, 4.18-27.00 and 0.30-12.64 µg/g), Pb (6.00-64.21, 22.40-53.70, 9.30-102.10 and 35.60-97.72 µg/g) and Cd (ND-0.76, ND-0.87, 0.24-0.76 and 0.12-0.88 µg/g) during autumn, winter, spring and summer seasons, respectively.

The positive correlations between Fe with Cr, Co, Mn and Ni (r=0.378, 0.405, 0.932 and 0.576, respectively), during different seasons, reflect that iron is considered as one of the geochemical support phase of these metals. Seasonally, the factors affecting the deposition of iron are the presence of dissolved oxygen and organic matter content.[24]The maximum value of Mn was reached to 677.11 µg/g, while the minimum value was reached to 152.02 µg/g. The increase in manganese contents may be attributed to the precipitation of Mn as MnO_2 under reducing conditions.[24] But, the decrease in manganese contents may be related to the mobilization of manganese from sediment to the overlying water due to the decomposition of organic matter.[25] The positive correlation between Mnand Fe (r=0.932, p<0.01) indicated that manganese is probably similar to the geochemical support phase of Fe which associated with Mn co-precipitate or adsorbed on manganese oxides or hydroxides.[22]The results of nickel showed that, there are wide variations among different stations during different seasons. These wide variations may be attributed to the sediment texture and its grain size,[21] as well as, the organic matter content. This is supported by the positive correlation between Ni & OM (r=0.413). On the other side, the positive correlation between Ni&Mn (r=0.544) declared that the deposition of nickel as a co-precipitate with manganese.[14]Also, there are positive correlations ($p<0.01$) between Ni with Cr ($r=0.443$) and Fe ($r=0.576$).A wide fluctuation in cobalt content was observed at different stations depending on the sediment texture, the settling of cobalt rich organic matter, the dynamics mechanism of adsorption on clay minerals and assimilation of cobalt by aquatic organisms especially macrophytes[25]. The statistical analysis showed positive correlations between Co with Fe,Mn ($r=0.405$ and 0.454) andCr with Fe ($r=0.378$) are indications the role of hydrated iron oxide in the precipitation of chromium to the sediment.[22]

The increase in Pb content may be related to the settling of lead rich plankton from the overlying water to the sediment. This result coincident with that reported by Abdel-Sattar, *et al.*,(2003).[26] The negative correlations between Pb with Fe and Mn ($r= -0.571$ & -0.466) showed the abnormal distribution dynamics of Pb than other metals in El-Sharkawia canal sediment.

There is increase in cadmium concentration during hot seasons (spring & summer). This may be attributed to the slight rise of water temperature, pH and carbonate concentration which facilitate the precipitation of Cd to sediment. On the other hand, the decrease in Cd concentrations during cold seasons (autumn & winter) may be related to the mobilization of Cd from sediment to the above water layers because of the decrease in pH values.[27]

The correlation coefficient (r) results demonstrated that, there are positive correlations between Fe &Mn ($r=0.932$) and Fe & Ni ($r=0.576$) at ($p<0.01$), but between Fe & Cr ($r=0.378$) and Fe & Co ($r=0.405$) at ($p<0.05$) during different seasons. These positive correlations indicated that, iron and manganese oxides can play a role in the retention of trace metals. These metals in solution can be adsorbed by hydroxides of these two elements or co-precipitate with them when physico-chemical conditions change.[25]

The positive significant correlation between Zn and Cu ($r=0.578$, $p<0.01$) revealed the association of metals with clay minerals or adsorption of both Cu and Zn on hydrated iron and manganese oxides. Similar situation was reported by Abdo, (2005).[25] Also,manganese is positively correlated with chromium ($r=0.341$) and cobalt ($r=0.454$), as well aspositive correlation ($p<0.01$) between Zn/Cu ($r=0.578$).According to ANOVA results, there are highly temporal significant differences ($p<0.01$) for lead and cobalt, but there is highly spatial significant difference ($p<0.01$) for copper. Also, there is temporal significant difference ($p<0.05$) for manganese.

A multiple box and whisker plot diagram were used to compare the heavy metals accumulation in the sediment of El-Sharkawia canalFig.(2). The results showed that the Fe and Cuwere higher accumulation than other elements. Mn, Zn and almost Ni were

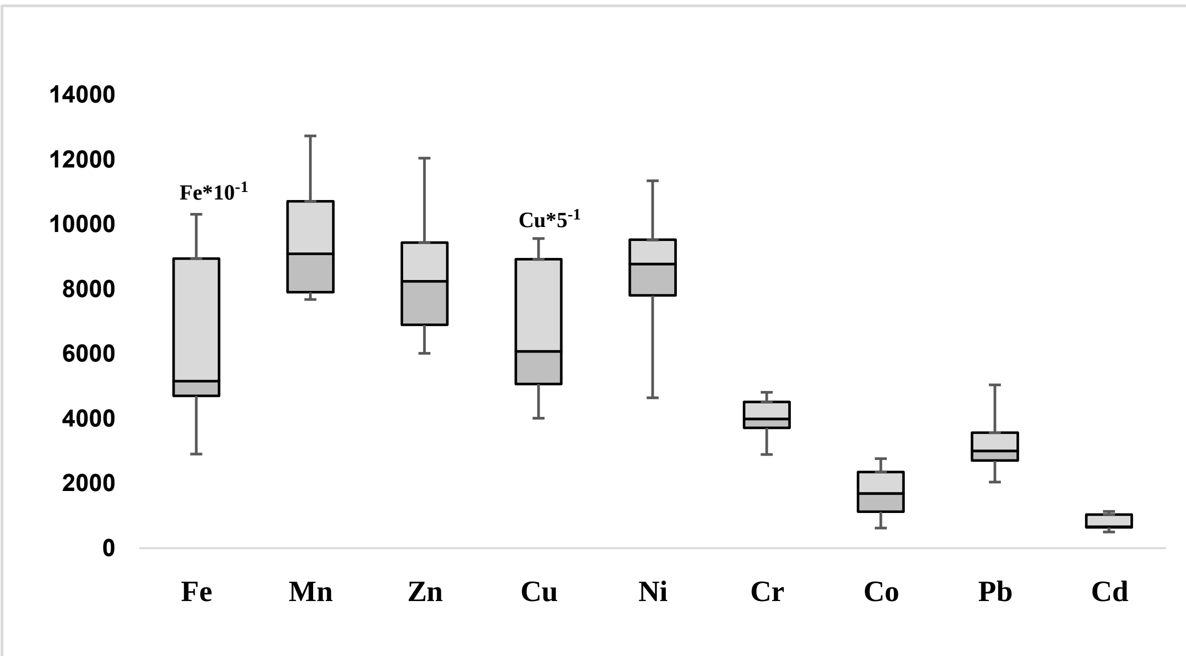

Fig. 3. Multiple box and whisker plots of measured heavy metals accumulation in sediments of the study area during 2013-2014

moderate accumulation. Co, Pb and Cd were lower accumulation.

Index of geo-accumulation (I_{geo})

The geo-accumulation index (I_{geo}) values were calculated for the studied metals as introduced by Muller (1981)[27] as follows:

$$I_{geo} = \log_2 (C_n/1.5*B_n)$$

where (C_n) is the measured concentration of examined element (n) in the sediment sample and (B_n) is the geochemical background for the element (n) which is either directly measured in pre-civilization (pre-industrial) reference sediments of the area or taken from the literature (average shale value described by Turekian and Wedepohl (1961).[28]The factor 1.5 is introduced to include possible variation of the background values that are due to lithogenic variations,[29] as well as very small anthropogenic influences[30]. Muller (1981)[27] proposed seven grades or classes of the geo-accumulation index. Different geo-accumulation index classes along with the associated sediment quality are given in Table (4); the Igeo class 0 indicates the absence of contamination while the Igeo class 6 represents the upper limit of the contamination. The highest class 6 (very strong contamination) reflects 100-fold enrichment of the metals relative to their background values.[31]

Table (4): Different geo-accumulation index classes according to Buccolieri*et al.* (2006).[32]

I_{geo}	I_{geo}class	Pollution
<0-0	0	Unpolluted
0-1	1	Unpolluted to moderated
1-2	2	Moderated polluted
2-3 3-4	3	Moderated to high polluted Highly polluted
4-5 5-6	4 5 >5	Highly to extremely polluted Extremely polluted

The pollution grade of El-Sharkawia canalsediment according to Igeo values is given in Table (5). Igeo values for all the studied trace metals exhibited a zero class or class 1 indicating unpolluted to moderately polluted sediment quality.Igeo values ranged between -0.817:0.513, -0.892:0.295, -5.187:-2.763, -0.695:0.423, -1.576:-1.229, -0.074:0.835, -1.842:-1.24, -0.873:0.077; and -0.642:0.02 for Cd, Cr, Co, Cu, Fe, Pb, Mn, Ni and Zn, respectively with adescending order of theaverage as follows: Pb> Cd> Cu> Zn> Cr> Ni> Fe>Mn> Co.

Table (5): The pollution grade of El-Sharkawia canal sediment according to Igeo values.

station	Cd	Cr	Co	Cu	Fe	Pb	Mn	Ni	Zn
2	0.25	0.182	-4.440	-0.182	-1.465	0.835	-1.597	-0.728	0.007
3	-0.039	-0.192	-3.226	-0.127	-1.260	0.427	-1.289	-0.136	-0.259
4	-0.344	-0.613	-3.187	-0.213	-1.248	0.267	-1.288	-0.381	-0.304
5	0.181	0.295	-3.564	0.423	-1.469	0.459	-1.602	-0.348	0.020
6	0.513	-0.666	-4.814	-0.246	-1.554	0.486	-1.590	-0.846	-0.166
7	-0.305	-0.597	-5.187	-0.621	-1.576	0.637	-1.842	-0.873	-0.642
8	0.096	-0.892	-4.568	-0.695	-1.367	-0.074	-1.545	-0.343	-0.381
9	-0.298	-0.372	-3.695	-0.127	-1.385	0.255	-1.370	-0.551	-0.220
10	-0.817	-0.510	-2.763	0.320	-1.229	0.249	-1.240	0.077	-0.080

1. Not available collect

Conclusionand Recommendations

The results of this study supply valuable information about some heavy metals concentrations in water and sediment from different sites along El-Sharkawia canal.The present results indicated that the concentration levels of the studied heavy metals in El-Sharkawia canal water were found within the permissible limits except for Fe, Mn, Ni and Pb according to Egypt. Guidelines, (2007),[(15)] but the concentration levels of these metals in the sediment were within the permissible limits except for Ni and Cu according to OMOE, (1993),[(16)]as shown in Table (3). The main factors which affect the distribution and concentration levels of the studied heavy metals are: 1- Climatic conditions, 2- Activities and other pollution drainage sources, 3- Nature of the sediment, and 4- Systematic investigation which is recommended to monitor heavy metals loading and changes in the canal water and sediment qualities.

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