Original Research Article

International Journal of Bioassays
ISSN: 2278-778X
www.ijbio.com
OPEN ACCESS

FACTORS AFFECTING HEAVY METALS DISTRIBUTION IN THE RIVER NILE AT GREATER CAIRO REGION, EGYPT

Mohamed EM Hassouna*[1], Abdel-Samie A Elewa[2] and Ahmed M Ibrahim[3]
[1]Chemistry Department, Faculty of Science, Beni- Suef University, Beni-Suef, Egypt.
[2]National Institute Of Oceanography and Fishers, Cairo, Egypt.
[3]Greater Cairo Drinking Water Company, Kafr El Elw Water Treatment Plant.

Received for publication: March 22, 2014; **Revised:** April 10, 2014; **Accepted:** May 11, 2014

Abstract: In the present study, nine heavy metals (Cd, Cr, Cu, Fe, Mn, Al, Zn, Ni and Pb) were seasonally monitored through the analysis of large number of water samples collected from the River Nile in the Greater Cairo region during the period 2012 to 2013. The samples were collected from eight stations distributed in the area covering the distance from El Roda Island to El-Kanater El-khayria. Heavy metals were analyzed by inductively coupled plasma spectroscopy (ICP/OES). Results for their levels in water were compared with national and international water quality guidelines, and they proved to be within the permissible limits.

Key Words: Heavy metals, River Nile water, Greater Cairo region, Monitoring stations, ICP.

INTRODUCTION

Water is the most important natural resource on our planet. It is considered absolutely essential to sustain life since the protoplasm of many living cells contains about 80% water and any substantial reduction in this level is disastrous (Thillaiarasu *et al.,* 2014).

Heavy metals in aquatic ecosystem are transferred through food web into human beings. Some of heavy metals can cause health problems to fish consumers (Uysal *et al.,* 2008; Taweel *et al.,* 2011).

The importance of water resources, particularly surface waters (rivers), in meeting the water needs of humans, animals and industries indicates the essential need to protect them against contamination. As municipal, industrial, and agricultural wastes enter the water, biological and chemical contaminants including heavy metals also enter water resources. Although some of these metals are essential micronutrients, their high concentrations in the food chain can cause toxicity and environmental impacts and endanger aquatic ecosystems and their users (Prabu, 2009; Kane *et al.,* 2012)

Heavy metals such as copper, iron, chromium and nickel are essential metals since they play an important role in biological systems, whereas cadmium and lead are non-essential metals, as they are toxic, even in trace amounts (Fernandes *et al.,* 2008). Iron, manganese, zinc, lead, copper, cadmium, chromium and nickel metals, were detected seasonally within the period of the study.

The aim of this paper was determine some heavy metals (Cd, Cr, Cu, Fe, Mn, Al, Zn, Ni and Pb) contents in the River Nile at greater Cairo region from El Roda Island to El- Kanater El- khayria.

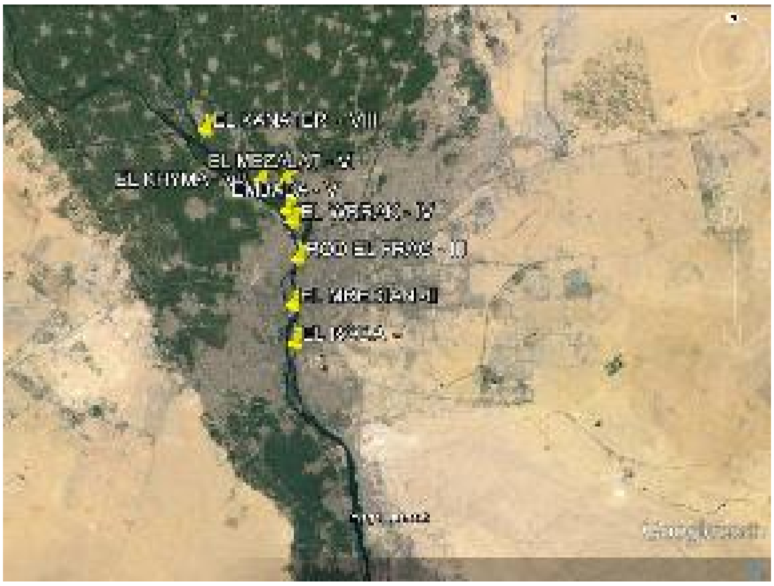

Fig.1: Map for River Nile showing the area of sampling sites (Monitoring Stations).

MATERIAL AND METHODS

Subsurface water samples were collected seasonally during the period 2012-2013 from the area under investigation. The concentrations were determined after the digestion by nitric acid as described in APHA 2012.

***Corresponding Author:**
Prof. Mohamed EM Hassouna,
Chemistry Department,
Faculty of Science, Beni- Suef University,
Beni-Suef, Egypt.

Iron, manganese, zinc, copper, cadmium, aluminum, nickel, chromium, and lead were measured by using inductively coupled plasma ICP-OES model Varian lab Liberty Series II. ICP-OES is a fast multi-element technique with a dynamic linear range and moderate-low detection limits (~0.2-100 ppb). The instrument uses an ICP source to dissociate the sample into its constituent atoms or ions, exciting them to a level where they emit light of a characteristic wavelength. Up to 60 elements can be screened per single sample run of less than one minute and the samples can be analyzed in a variety of aqueous or organic matrices. There are fewer chemical interferences than with FAAS, but some spectral interferences are possible and there are some element limitations.

Preservation and preparation of the samples

To a 1 liter sample, 5 ml conc. HNO_3 were added to preserve the sample immediately after sampling, then the solution was stored in a refrigerator at approximately 4°C for analysis. 20 mL nitric acid were added to 500 mL of the mixed sample in a beaker. Slow boiling and evaporation on a hot plate to reach the lowest volume, before precipitation occurs, until digestion is complete. The beaker walls are rinsed down with distilled water and the whole volume is transferred to a 100 mL volumetric flask, cool, dilute to mark and mix thoroughly. Take an aliquot of this solution for required determination.

RESULTS AND DISCUSSION

Iron

Iron is the fourth most abundant element in the Earth's crust and is essential for most life on the planet (Frey *et al.*, 2012). Ferrous iron is commonly found in water supplies and is soluble in water.

Iron is a redox active metal which is abundant in the Earth's crust. It has played a key role in the evolution of living systems and as such is an essential element in a wide range of biological phenomena, being critical for the function of an enormous array of enzymes, energy transduction mechanisms, and oxygen carriers. The redox nature of iron renders the metal toxic in excess and consequently all biological organisms carefully control iron levels (Hider, Kong, 2013). Fe is present in higher concentrations than Mn in most aquatic systems (Giblin, 2012).

Table 1: Seasonal variations of iron values (mg/L) in the investigated area:

Seasons stations	Summer	Autumn	Winter	Spring	Annual average
El-Roda (I)	0.3	0.431	0.164	0.391	0.32
El-Mredian (II)	0.321	0.174	0.181	0.326	0.25
Rod El- Frag (III)	0.205	0.1	0.181	0.328	0.20
El-Wrrak (IV)	0.278	0.128	0.271	0.358	0.26
Embaba (V)	0.299	0.118	0.227	0.364	0.25
El-Mezallat (VI)	0.378	0.434	0.147	0.321	0.32
El-Khyma (VII)	0.374	0.483	0.214	0.456	0.38
El-Kanater (VIII)	0.471	0.158	0.292	0.48	0.35
Seasonal avr.	0.33	0.25	0.21	0.38	

Table (1) shows the seasonal variations of iron values which were recorded during the study period. Iron values varied in the ranges of 0.205-0.471, 0.1-0.483, 0.147-0.292, 0.321-0.48 mg/L during summer, autumn, winter, and spring, respectively. The maximum value of (0.483) mg/L was recorded at station VII while the minimum one of (0.1) mg/L was recorded at station III.

The decrease in iron values may refer to the adsorption of iron by clayey minerals, suspended matter, surface microorganisms, and metal oxides as iron oxide under high temperature (Abdo, 2002). On the other hand, the relative decrease in iron concentrations during winter may be due to the oxidation of Fe^{+2} to Fe^{+3} and their precipitation as hydroxide at high pH value in presence of high dissolved oxygen according to the following equations:

$$Fe^{+2} + H_2O \longrightarrow Fe^{+3} + H_2O + (-e)$$
$$Fe^{+3} + 3H_2O \longrightarrow Fe(OH)_3 + 3H^{+}$$

(Stumm and Morgan, 1981)

The relative increase of recorded iron may be related to the flood period, which leads to the leaching of iron from the banks of the River Nile resulting in the great amount of fine grains and suspended particles containing iron element. Increasing of iron concentrations during spring, may be attributed to the dissolution of sediments and release of iron to the overlying water.

Aluminum

Aluminum makes up around 8% of the Earth's crust, making it the third most common element. It is often used in cooking utensils, containers, appliances and building materials, as well as in the production of glass, paints, rubber and ceramics. Aluminum is used in several forms, such as aluminum hydroxide (in antacids), aluminum chlorohydrate (in deodorants), and the most common form, aluminum sulphate (in treating drinking water).

At low levels, aluminum in food, air, and water is not likely harmful to our health. However, at high concentrations there is an evidence linking aluminum to effects on the nervous system, with possible connections to several diseases, such as Parkinson's, Alzheimer's, and Lou Gehrig's disease. Patients suffering from these diseases tend to have high levels of aluminum in some areas of their brains. It is not known if aluminum is causing these diseases or if the aluminum starts accumulating in people that already have the diseases. There is also some concern that aluminum may cause skeletal problems. There is no evidence to suggest that aluminum affects reproduction, or that it causes cancer.

Aluminum is a known neurotoxin and occupational exposure to aluminium has been implicated in neurological disease including Alzheimer's disease. Comprehensive and unequivocal data demonstrating significantly elevated brain aluminium content in an individual occupationally exposed to aluminium has been reported (Christopher and Thomas, 2014). Table (2) presents Aluminum values that were recorded in the study period. The values of Aluminum varied in the ranges of 0.265 - 0.736, 0.177 - 1.084, 0.339 - 1.33 and 0.377 - 0.622 mg/L during summer, autumn, winter and spring, respectively. The maximum value of (1.33) mg/L was recorded during winter at station El-Wrrak while the minimum value of (0.177) mg/L was recorded during autumn at the monitoring station of Embaba.

Table 2: Seasonal variations of Aluminum (mg/L) in the investigated area

Seasons stations	Summer	Autumn	Winter	Spring	Annual Average
El-Roda	0.478	1.037	0.5	0.476	0.62
El-Mredian	0.736	0.489	0.526	0.377	0.53
Rod El- Frag	0.265	0.314	0.339	0.492	0.35
El-Wrrak	0.289	0.257	1.33	0.465	0.59
Embaba	0.728	0.177	0.442	0.378	0.43
El-Mezallat	0.611	0.672	0.538	0.622	0.61
El-Khyma	0.601	1.084	0.426	0.56	0.67
El-Kanater	0.542	0.338	0.506	0.537	0.48
Seasonal avr.	0.53	0.55	0.58	0.49	

Aluminum values were decreased. This may be attributed to the dilution effect caused by more water comes from lake Nasser behind high dam and increasing in the water level. Increasing of the Aluminum values during winter season may be attributed to the drought period and decrease of water levels.

Manganese

Manganese is an essential nutrient for physiological functions, with most of the manganese in our body coming from food. Currently, the guideline for manganese, 0.05 mg/L, is set as an aesthetic (e.g., colour, odour, taste) objective in the Canadian drinking water quality guidelines. A maximum acceptable concentration to protect health has not been set. Studies on the possible health effects of manganese in drinking water are underway, but preliminary information indicates that any health effects would be at levels in drinking water that would be substantially higher (10 times) than those found in Winnipeg's drinking water, and would have to be associated with an exposure over a long period of time.

Manganese functions as an essential constituent for bone structure, reproduction and normal functioning of the enzymes system. It is toxic only when present in higher amount, but at low level is considered as micronutrient (El-Naggar and Tayel, 2009).Drinking water manganese (W Mn) is a potential threat to children's health due to its associations with a wide range of outcomes including cognitive, behavioral and neuropsychological effects. Although adverse effects of Mn on cognitive function of the children indicate possible impact on their academic achievement, little evidence on this issue is available (Khalid *et al.,* 2012)

Iron and manganese play major roles in determining the forms and cycling of phosphorous (P), sulfur (S), and trace metals in lakes, rivers, streams, and bogs. In some systems they also serve as important alternative oxidants for the degradation of carbon. Fe and Mn are also essential micronutrients, although they rarely appear to limit primary production in freshwater ecosystems (Giblin, 2012).

The seasonal variations of manganese values were recorded in Table (3). The maximum value of (0.08) mg/L was recorded at station IV while the minimum value of (0.05) mg/l was recorded during spring at stations I, II, III, V, VI, VII and VIII.

Table 3: Seasonal variations of Manganese (mg/L) in the investigated area:

Seasons Stations	Summer	Autumn	Winter	Spring	Annual average
El-Roda	0.34	0.046	0.039	0.07	0.05
El-Mredian	0.048	0.025	0.054	0.057	0.05
Rod El- Frag	0.084	0.022	0.063	0.044	0.05
El-Wrrak	0.095	0.027	0.144	0.057	0.08
Embaba	0.049	0.027	0.054	0.054	0.05
El-Mezallat	0.075	0.038	0.036	0.051	0.05
El-Khyma	0.044	0.041	0.045	0.059	0.05
El-Kanater	0.056	0.019	0.052	0.061	0.05
Seasonal avr.	0.06	0.03	0.06	0.06	

The results of manganese concentrations revealed that, the high values were recorded during winter and spring seasons, this may be attributed to the effect of the drought period. However, the low water level and the slow motion of water current would facilitate the excretion of manganese from dead aquatic plants in addition to dissolution of manganese sediments and release to water during spring (Abdo, 2002).

The lower values of manganese during summer and autumn may be attributed to the removal of manganese from the aqueous phase to solid phase during precipitation of Mn as MnO_2 or by adsorption on suspended particles as well as the dilution effect of the flood period (Abdo, 2002). According to (Saletovic *et al.,* 2011) Mn has an important role in the efficient utilization of other nutrients in the soil.

Zinc

Zinc is an essential trace element which plays an important role in the physiological and metabolic process of many organisms. (Mastan, 2014). Zinc is an essential element for both animals and human. It is necessary for the functioning of various enzyme systems, deficiency of which leads to growth retardation (Thillaiarasu *et al.,* 2014). Low intake of Zinc results in retardation of growth, immaturity and anemia condition known as zinc deficiency syndrome (Muthulakshmi *et al.,* 2012).

Zinc is an essential element and is a common pollutant as well. Mining smelting and sewage disposal are major source of zinc pollution. Fish take it up directly from water, especially by mucous and gills (El-Naggar and Tayel, 2009).

The relatively higher zinc concentration in the liver of the different fish species may be due to the role of zinc as an activator of numerous enzymes present in the liver (Yacoub, 2007). The seasonal variations of zinc values were recorded in Table (4). The values of zinc varied in the ranges of 18.69 – 56.762, 10.074 – 22.026, 4.439–35.537 and 56.294- 125.406 µg/L during summer, autumn, winter and spring, respectively.

The maximum value of (125.4 µg/L) was recorded during spring at station IV while the minimum value of (4.44µg/L) was recorded during winter at station VI. Increasing of Zn during hot seasons (summer and spring) more than cold seasons (autumn and winter) this is due to the high rate of evaporation during summer, besides the influence of aquatic organisms especially macrophytes. Decreasing of zinc values during autumn and winter may be attributed to its uptake by macrophytes or due to its adsorption onto the clayey particles and sedimentation to the underlying sediments.

Table 4: Seasonal variation of Zinc (µg/L) in the investigated area:

Seasons Stations	Summer	Autumn	Winter	Spring	Annual average
El-Roda	21.301	16.361	5.82	57.097	25.14
El-Mredian	56.762	16.81	4.876	56.294	33.69
Rod El- Frag	21.284	10.307	16.628	74.922	30.79
El-Wrrak	23.45	20.27	35.537	125.406	51.17
Embaba	25.488	14.345	6.981	59.705	26.63
El-Mezallat	18.69	22.026	4.439	83.566	32.18
El-Khyma	23.819	16.495	5.864	72.515	29.67
El-Kanater	27.542	10.074	10.488	89.289	34.35
Seasonal avr.	27.29	15.84	11.33	77.35	

The level of dissolved zinc in water may increase as the acidity of water increases. Fish can collect zinc in their bodies from the water they swim in and from the food they eat. Most of the zinc in soil is bound to the soil and does not dissolve in water. However, depending on the type of soil, some zinc may reach ground water, and contamination of groundwater has occurred from hazardous waste sites. Zinc may be taken up by animals eating soil or drinking water containing zinc. Zinc is also a trace mineral nutrient and as such, small amounts of zinc are needed in all animals (ATSDR, 2005).

Taking too much zinc into the body through food, water, or dietary supplements can also affect health. The levels of zinc that produce adverse health effects are much higher than the Recommended Dietary Allowances (RDAs) for zinc of 11 mg/day for men and 8 mg/day for women. If large doses of zinc (10–15 times higher than the RDA) are taken by mouth even for a short time, stomach cramps, nausea, and vomiting may occur. Ingesting high levels of zinc for several months may cause anemia, damage of the pancreas, and decrease of the levels of high-density lipoprotein (HDL) cholesterol. (ATSDR, 2005).

Copper

Copper is a metal that occurs naturally throughout the environment, in rocks, soil, water, and air. Copper is an essential element in plants and animals (including humans), which means that it is necessary for our life. Therefore, plants and animals must absorb some copper from eating, drinking, and breathing (ATSDR, 2004).

The level of copper in surface and groundwater is generally very low. High levels of copper may get into the environment through mining, farming, manufacturing operations, and municipal or industrial wastewater releases into rivers and lakes. Copper can get into drinking water either by directly contaminating well water or through corrosion of copper pipes if your water is acidic. Corrosion of pipes is by far the greatest cause for concern (ATSDR, 2004). Copper is an essential element for human body. But excessive large doses may lead to mucosal irritation, hepatic and renal damage and central nervous system (Thillaiarasu *et al.,* 2014).

Copper in the blood exists in two forms: bound to ceruloplasmin (85–95%), and the rest "free", loosely bound to albumin and small molecules. Free copper causes toxicity, as it generates reactive oxygen species such as super oxide, hydrogen peroxide, and the hydroxyl radical. These damage proteins, lipids and DNA (Brewer GJ 2010). Cu is an essential part of various enzymes necessary for the synthesis of hemoglobin (Sivaperumal *et al.,* 2007); but at higher concentrations it causes various health problems. Copper can combine with other contaminants such as ammonia, mercury and zinc to produce an additive toxic effect on fish (Yacoub, 2007).

Cu was higher in fish liver and followed by kidney, gills and muscles. While in the case of *C. striatus*, the concentration of Cu was highest in kidney followed by liver, muscles and gills (Mastan, 2014).

The seasonal variations of copper values were recorded in Table (5). The values of copper varied in the ranges of 6.23 – 16.78, 9.53– 33.95, 4.63– 8.22 and 4.44 - 5.82 µg/L during summer, autumn, winter and spring, respectively. The maximum value of (33.95 µg/L) was recorded during autumn at station I while the minimum value of (4.44 µg/L) was recorded during spring at station VI.

The results showed that, copper is increased in cold seasons (winter and autumn) and decreased in hot seasons (summer and spring). The increased values of copper in cold seasons may be attributed to adsorption of copper by humic material (El-Haddad, 2005). On the other hand, the decreased values of copper during hot seasons may be due to the removal of copper from water by the uptake by phytoplankton or may be due to adsorption on the suspended matter making complexation with organic matter leaving the water to sediment (El-Hadad, 2005). The EPA requires that levels of copper in drinking water be less than 1.3 mg of copper per one liter of drinking water (1.3 mg/L).

Table 5: Seasonal variations of Copper (µg/L) in the investigated area:

Seasons / Stations	Summer	Autumn	Winter	Spring	Annual average
El-Roda	8.862	33.954	5.936	5.208	13.49
El-Mredian	12.333	11.63	5.721	5.595	8.82
Rod El- Frag	9.311	10.115	4.633	5.252	7.33
El-Wrrak	8.579	10.408	7.936	5.75	8.17
Embaba12	8.256	9.528	5.912	4.706	7.10
El-Mezallat	7.086	10.857	5.205	4.438	6.90
El-Khyma	6.231	13.68	5.479	5.823	7.80
El-Kanater	16.78	11.728	8.221	5.303	10.51
Seasonal avr.	9.68	13.99	6.13	5.26	

Lead

Lead is one of the most commonly occurring contaminants in the environment. Lead is absorbed by plants when it is present in their environment, especially in rural localities where the soil is contaminated by exhaust from cars and in areas contaminated by fertilizers containing heavy metals (Lamhamdi *et al.,* 2013).

Plants absorb Pb from the soil solution into the root system. The highest amount of Pb^{2+} is accumulated in roots in insoluble form (Wierzbicka *et al.,* 2007).

Lead is a very toxic metal in humans and the food chain is the main pathway of lead transfer from the environment to human (El fadeli *et al.,* 2014).

Lead is used for a long time on batteries, ammunition, paint lead, fuel, and as ingredient in different alloys. It causes toxic effects on humans, animals and plants. Lead is dangerous because it tends to bioaccumulate (Censi *et al.,* 2006). Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemical's concentration in the environment (Otitoloju, 2002).The presence of lead in water causes serious health effects and symptoms such as: kidneys and heart diseases, damages of the nervous system, other epidermises and cancer.

The presence of lead in water above the maximum concentration level recommend by different environmental organizations such as: Environmental Protection Agency (EPA), World Health Organization (WHO, European Union (EU), is toxic and affect in the environment, ecosystems and human health. Presence of lead in the environment results in negative effects, depending on the level and duration of exposure (Mirela and Nikolla, 2014).

Lead poisoning has been recognized as an occupational illness for centuries and it is linked with both severe and subtle health damages. Higher concentrations of lead in drinking water has adverse effect on central nervous system, blood cell and may cause brain damage (Ponnusamy *et al.,* 2014).

Lead, a contaminant found in many water supplies across the country, is a major public health concern. Because of this concern, the U.S. Environmental Protection Agency (EPA) recently established a new National Primary' Drinking Water regulation for lead, reducing the accepted lead level to 15 ppb. The seasonal variations of lead values were recorded in Table (6). The values of lead varied in the range of 1.33 – 3.49, 2.32– 4.82, 2.39 – 5.99 and 0.31-

3.05 µg/L during summer, autumn, winter and spring, respectively. The maximum value of (5.99 µg/L) was recorded during winter at station IV while the value reached (0.31 µg/L) was during spring at station VI. The permissible limit for lead in drinking water is (0.05 mg/L).

Table 6: Seasonal variations of Lead (µg/L) in the investigated area

Seasons Stations	Summer	Autumn	Winter	Spring	Annual average
El-Roda	1.937	4.798	5.169	0.581	3.12
El-Mredian	3.489	4.037	2.397	3.052	3.24
Rod El- Frag	2.752	4.305	4.405	0.398	2.97
El-Wrrak	1.983	2.317	5.995	2.102	3.10
Embaba	2.019	3.556	4.243	0.955	2.69
El-Mezallat	1.333	3.483	3.334	0.309	2.11
El-Khyma	2.337	4.819	2.658	1.451	2.82
El-Kanater	2.921	3.627	2.75	1.229	2.63
Seasonal avr.	2.35	3.87	3.87	1.26	

These results revealed that, the values of lead concentrations are increased during cold seasons (winter and autumn) and decreased during hot seasons (summer and spring).

The lower values of lead content during hot seasons, may be attributed to the precipitation of lead salts under high pH and temperature values, most of these salts may be present in the forms of lead carbonate agreed with what reported by (Ghallab, 2000 and Abdo, 2002), Also The decreasing of lead during spring and summer may be attributed to adsorption of lead onto organic matter which descending to the bottom sediment especially with high temperature.

The higher values of lead concentrations were observed during winter may be attributed to the drought period, whereas, the water levels decreased and the degradation of the most aquatic organisms and organic matter would be increased. This results in release of the lead to the above water layers due to the microbial activities. Or may be attributed to the high amount of agricultural runoff.

The relative increase of lead concentrations during autumn, may be attributed to the flood period, leading to leaching of lead rocks and dissolution of sediments containing lead which facilitate the mobilization of lead from sediment into the above water layers.

Cadmium

Cadmium is highly toxic and responsible for several cases of poisoning through food. Small quantities of cadmium cause adverse changes in the arteries of human kidney. It replaces zinc biochemically and causes high blood pressures (Crnkić *et al.*, 2014)

In nature, Cd is always associated with zinc ores (ZnS) due to its similarity with Zn. The Cd concentration in lake water and fishes has been reported by various workers (Malik *et al.*, 2010; Bhupander *et al.*, 2011).

Cadmium enters the human body through ingestion of contaminated food and drink (Sudarwin 2008). Cd could be harmful to fishes. High accumulations of cadmium in liver may be due to its strong binding with cystine residues of metallothionein (Tayel *et al.*, 2008)

Smokers are the most exposed due to the amount of cadmium in cigarettes (Florek *et al.*, 2004; Falcon *et al.*, 2003). Elevated concentrations of cadmium in the human body cause severe stomach and lung alterations, which in turn increase the risk of death due to respiratory insufficiency (Nordberg, 2004).

The seasonal variations of cadmium values were recorded in Table (7). The values of cadmium varied in the ranges of 0-0.096, 0.141 – 0.241, 0 – 0.083 and 0–0.056 µg/L during summer, autumn, winter and spring, respectively.

The maximum value of 0.241µg/L was recorded during autumn at station VIII while the Zero value was recorded in most of sampled stations during all season except autumn. The lower values of cadmium content during hot seasons, may be attributed to the precipitation of cadmium salts under high pH and temperature values most of this salts may be present in the forms of cadmium carbonate. The higher values of cadmium concentrations during autumn, may be attributed to the flood period, leading to leaching of cadmium rocks and dissolution of sediment containing cadmium which facilitate the mobilization of lead from sediment into the above water layers.

Table 7: Seasonal variations of Cadmium (µg/L) in the investigated area:

Seasons stations	Summer	Autumn	Winter	Spring	Annual average
El-Roda	0	0.141	0.077	0.033	0.06
El-Mredian	0.024	0.217	0	0.041	0.07
Rod El- Frag	0.033	0.205	0.083	0.00	0.08
El-Wrrak	0.04	0.188	0.005	0.056	0.07
Embaba	0	0.169	0.019	0.00	0.05
El-Mezallat	0.033	0.218	0	0.00	0.06
El-Khyma	0	0.183	0.068	0.047	0.07
El-Kanater	0.096	0.241	0.047	0.00	0.10
Seasonal avr.	0.03	0.20	0.04	0.02	

Chromium

Chromium is an essential nutrient for plant and animal metabolism (Thillaiarasu *et al.*, 2014). Chromium is a naturally occurring element found in rocks, animals, plants, and soil. It can exist in several different forms.

Depending on the form it takes, it can be a liquid, solid, or gas. No taste or odor is associated with chromium compounds. The chromium metal, which is the chromium (0) form, is used for making steel. Chromium (VI) and chromium (III) are used for chrome plating, dyes and pigments, leather tanning, and wood preserving.

Chromium can be found in air, soil, and water after release from the manufacture, use, and disposal of chromium-based products, and during the manufacturing process. The International Agency for Research on Cancer (IARC), and the EPA have determined that chromium (VI) compounds are known human carcinogens. In workers, inhalation of chromium (VI) has been shown to cause lung cancer. Chromium (VI) also causes lung cancer in animals. An increase in stomach tumors was observed in humans and animals exposed to chromium (VI) in drinking water (ATSDR, 2012). Excess of Chromium present in human body causes bronchial cancer in human (Thillaiarasu *et al.,* 2014).

The criteria for total chromium in a domestic water supply is 0.05 mg/L The aquatic life criteria is less than 0.011 mg/L for chromium VI and less than 0.207 mg/L for chromium III. (The second value is based on a formula involving hardness).

Table (8) Seasonal variations of Chromium (µg/L) in the investigated area:

Seasons / Stations	Summer	Autumn	Winter	Spring	Annual average
El-Roda	1.449	1.248	1.124	0.532	1.09
El-Mredian	1.86	0.88	1.373	0.397	1.13
Rod El- Frag	1.422	2.412	0.938	0.464	1.31
El-Wrrak	1.645	1.639	7.513	0.862	2.91
Embaba	1.867	0.592	1.98	0.979	1.35
El-Mezallat	1.862	2.406	1.028	0.786	1.52
El-Khyma	1.447	2.626	0.963	1.053	1.52
El-Kanater	1.911	2.365	1.025	0.581	1.47
Seasonal avr.	1.68	1.77	1.99	0.71	

The seasonal variations of chromium values were recorded in Table (8). The values of chromium varied in the range of 1.42 – 1.91, 0.59 – 2.63, 0.94 – 7.51 and 0.39 - 1.05 µg/L during summer, autumn, winter and spring, respectively.

The maximum value of (7.51 µg/L) was recorded during winter at station IV while the minimum value of (0.39) µg/L was recorded during spring at station II.

These results revealed that, the values of chromium concentrations increased during cold seasons (winter) and decreased during mild seasons (spring).

The relative increase of chromium concentrations during winter may be attributed to the drought period, whereas, the water levels decreased and the degradation of the most aquatic organisms and organic matter would be increased. This results in release of the chromium to the above water layers due to the microbial activities. Or may be attributed to the high amount of agricultural runoff. The higher values of chromium concentrations were observed during autumn may be attributed to the flood period, leading to leaching of chromium rocks and dissolution of sediment containing chromium which facilitate the mobilization of chromium from sediment into the above water layers.

EPA has found chromium to potentially cause the following health effects when people are exposed to it at levels above the Maximum Contaminant Level (MCL) for relatively short periods of time: skin irritation or ulceration.

Long-term: Chromium has the potential to cause the following effects from a lifetime exposure at levels above the MCL: damage to liver, kidney circulatory, nerve tissues and skin irritation.

Nickel

Nickel is a very abundant natural element. Pure nickel is a hard, silvery-white metal. Nickel can be combined with other metals, such as iron, copper, chromium, and zinc, to form alloys. These alloys are used to make coins, jewelry, and items such as valves and heat exchangers. Most nickel is used to make stainless steel. Nickel can combine with other elements such as chlorine, sulfur, and oxygen to form nickel compounds. Many nickel compounds dissolve fairly easy in water and have a green color. Nickel compounds are used for nickel plating, to color ceramics, to make some batteries, and as substances known as catalysts that increase the rate of chemical reactions. Nickel is found in all soils and is emitted from volcanoes. Nickel is also found in meteorites and on the ocean floor. Nickel and its compounds have no characteristic odor or taste (ATSDR, 2005), but is slowly attacked by dilute hydrochloric or sulfuric acid and is readily attacked by nitric acid. Fused alkali hydroxides do not attack nickel. Several nickel salts, such as the acetate, chloride, nitrate, and sulfate, are soluble in water, whereas carbonates and hydroxides are far less soluble and sulfides, disulfides, sub sulfides, and oxides are practically insoluble in water.

In fact, in some cases Ni alloys provide the only suitable candidate material that can provide the required level of high-temperature strength and corrosion resistance (JOHN, 2013).

Nickel concentrations in groundwater depend on the soil use, pH, and depth of sampling (Adebola *et al.*, 2014). The seasonal variations of nickel values were recorded in Table (9).

The values of nickel varied in the ranges 1.72 – 3.14, 0.79 – 9.93, 1.43 – 3.95 and 0.98 - 14.59 µg/L during summer, autumn, winter and spring, respectively. The maximum value of (14.59 µg/l) was recorded during spring at station VI while the minimum value of (0.79 µg/l) was recorded during autumn at station II. These results revealed that values of nickel concentrations increased during spring and decreased during summer.

Table 9: Seasonal variations of Nickel (µg/L) in the investigated area

Seasons stations	Summer	Autumn	Winter	Spring	Annual Average
El-Roda	1.749	1.643	2.433	0.977	1.70
El-Mredian	1.934	0.785	2.558	1.61	1.72
Rod El- Frag	1.723	1.463	1.767	5.309	2.57
El-Wrrak	1.832	2.566	2.634	1.455	2.12
Embaba	1.757	1.095	1.908	1.082	1.46
El-Mezallat	2.069	9.93	1.431	14.586	7..00
El-Khyma	1.769	1.887	1.932	7.419	3.25
El-Kanater	3.142	3.535	3.953	1.137	2.94
Seasonal avr.	2.00	2.86	2.33	4.20	

Increasing of nickel concentrations during spring may be attributed to decreasing the water levels and increasing degradation of the most aquatic organisms and organic matter. This results in release of the chromium to the above water layers due to the microbial activities. Or may be attributed to the high amount of agricultural runoff whereas the relative increase of nickel concentrations during autumn, may be attributed to the flood period, leading to leaching of nickel rocks and dissolution of sediments containing nickel which facilitate the mobilization of nickel from sediment into the above water layers.

On the other hand, the relative decrease recorded during summer may be attributed to the dilution effect caused by more water comes from Nasser's lake behind high dam and increasing in the water level.

The human body contains approximately 10 mg nickel. Nickel is a dietary requirement for a number of organisms; therefore it might be of significance to humans. The human dietary need is estimated at only 5µg, which is the result of a 150µg intake. Nickel probably has a function in urea to ammonia conversion by the urease enzyme. Nickel cannot be resorbed in the digestive gland, unless it is complexed. Nickel inhalation poses a greater risk than nickel in water. This may cause lung cancer, or nasal tumors. Nickel carcinogenity is probably caused by nickel replacing zinc and magnesium ions on DNA-polymerase.

Table 10: Correlation coefficient matrices of heavy metals of water during summer in the investigated area:

	Al	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr
Al	1								
Fe	0.48	1							
Mn	-0.67	-0.3	1						
Zn	0.5	0.06	-0.3	1					
Cu	0.07	0.46	-0.1	0.44	1				
Pb	0.11	0.03	-0.2	0.77	0.67	1			
Cd	-0.25	0.51	0.39	0.03	0.8	0.31	1		
Ni	0.11	0.8	-0	0.07	0.83	0.28	0.89	1	
Cr	0.6	0.54	-0	0.4	0.49	0.09	0.45	0.56	1

The statistical analysis showed positive correlation in the summer season between Pb and Zn (r =0.77); Positive correlation between Cd and Cu (r =0.8); Positive correlation between Ni and Cu (r =0.83); Positive correlation between Ni and Cd (r =0.89). Ni showed positive correlation with Fe (r =0.8) which is considered highly significant correlation. Cr showed positive correlation with Al (r =0.6) and with Fe (r =0.54) moderate correlation. Ni and Cr showed insignificant correlation with Zn and Mn.

Table 11: Correlation coefficient matrix of heavy metals of water during autumn in the investigated area

	Al	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr
Al	1								
Fe	0.94	1							
Mn	0.88	0.91	1						
Zn	0.3	0.48	0.55	1					
Cu	0.15	0.44	0.31	0.59	1				
Pb	0.7	0.52	0.47	-0.4	-0.2	1			
Cd	-0.41	-0.3	-0.65	-0.2	0.29	-0.3	1		
Ni	0.11	0.42	0.23	0.52	0.96	-0.3	0.39	1	
Cr	0.27	0.34	0.05	-0.1	0.32	0.14	0.45	0.47	1

In the autumn season, there are positive correlation between Fe and Al (r = 0.94), Mn with Al (r =0.88), and Mn with Fe(r =0.91), high significant positive correlation. Cd and Mn showed negative correlation (r = -0.7), Ni and Cu showed high significant positive correlation (r = 0.96). Pb positive correlation with Al(r = 0.7). Cr showed insignificant correlation with most metals in the autumn season.

Table 12: Correlation coefficient matrix of heavy metals of water during winter in the investigated area

	Al	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr
Al	1								
Fe	0.45	1							
Mn	0.91	0.55	1						
Zn	0.84	0.53	0.97	1					
Cu	0.63	0.87	0.55	0.51	1				
Pb	0.59	0.09	0.63	0.69	0.19	1			
Cd	-0.5	-0.1	-0.3	-0.1	-0.3	0.08	1		
Ni	0.23	0.73	0.2	0.19	0.84	-0.1	0.02	1	
Cr	0.96	0.5	0.96	0.9	0.57	0.67	-0.4	0.14	1

During winter season Mn showed positive correlation with Al (r = 0.91) and with Fe (r = 0.55), Zn showed positive with Al (r = 0.84) and with Mn (r= 0.97) highly significant correlation, Cu showed highly significant positive correlation with Fe (r=0.87) and positive correlation with Al (r=0.63). Pb showed positive correlation with Zn (r=0.69) which is high significant correlation.

Ni showed positive correlation with Fe (r= 0.73) and with Cu (r=0.84). Cr showed positive correlation with Al and Mn (r=0.96) and positive correlation with Zn (r = 0.9) and with Pb (r=0.67) which is high significant correlation. Cd showed insignificance correlation with most metals in the winter season.

Table 13: Correlation coefficient matrix of heavy metals of water during spring in the investigated area

	Al	Fe	Mn	Zn	Cu	Pb	Cd	Ni	Cr
Al	1								
Fe	0.29	1							
Mn	-0.1	0.55	1						
Zn	0.33	0.07	-0.15	1					
Cu	-0.2	0.37	0.28	0.26	1				
Pb	-0.5	-0	0.19	0.11	0.66	1			
Cd	-0.2	0.08	0.45	0.24	0.79	0.67	1		
Ni	0.77	-0.3	-0.45	0.07	-0.4	-0.4	-0.26	1	
Cr	0.21	0.27	-0.02	0.27	-0.1	-0.1	0.15	0.26	1

During spring season Mn showed positive correlation with Fe (r=0.6). Pb showed positive correlation with Cu (r=0.7), Cd showed significant positive correlation with both Cu and Pb (r = 0.8) and (r =0.7) respectively, Ni showed highly significant positive correlation with Al (r=0.8). Zn, Cu and Cr showed insignificant correlation with most metals in the spring season.

The significant positive correlation between Fe and Mn during most seasons indicate that the association of the two elements originates from a common source during transportation and/or depositional reactions (Abdel-Satar and Elewa, 2001).

CONCLUSION

The findings of the study can be said that the concentrations of heavy metals in the River Nile water are in the permissible limits according to WHO (2008), EPA (2008). The water of River Nile is considered as fresh water according to all the four standards in which the discharge of some effluents to the river did not affect the life of aquatic organisms specially fish production. On the other hand Iron and aluminum concentrations are higher than the permissible levels which may be due to the effluents of iron and steel drain or another human activities at the area under investigation.

REFRENCES

1. Abdel-Satar AM & Elewa AA (2001) Water quality and environmental assessments of the River Nile at Rossetta Branch, The Second International Conference and Exhibition for life and Environment, 3-5 April:136-164
2. Abdo MH (2002) Environmental studies on Rosetta Branch and some chemical applications at the area extends from El-Kanater El-Khayria to Kafr El-Zyat City. Ph.D. Thesis, Fac. Sci. Ain Shams Univ., Egypt.
3. Adeyi AA & Torto N (2014). Profiling Heavy Metal Distribution and Contamination in Soil of Old Power Generation Station in Lagos, Nigeria. American Journal of Science and Technology. 1(1) 1-10.
4. Agency for Toxic Substances and Disease Registry ATSDR (2004). Toxicological Profile for Copper. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
5. Agency for Toxic Substances and Disease Registry ATSDR (2005), Department of Health and Human Services, Public Health Service.
6. Agency for Toxic Substances and Disease Registry ATSDR (2005). Toxicological Profile for Nickel (Update). Atlanta, GA: U.S. Department of Public Health and Human Services, Public Health Service.
7. Agency for Toxic Substances and Disease Registry ATSDR (2012). Toxicological Profile for Chromium. Atlanta, GA: U.S. Department of Health and Human Services, Public Health Service.
8. Aida C, Šestan A, Kesić A, Hodžić Z & Šestan I (2014) Physico–Chemical Properties and Some Heavy Metal Contents in Public Water Sources in Tuzla and its surrounding, Bosnian and Herzegovina, 3 (8), 1050-1056.
9. Alushllari M & Civici N (2014). Analyses of Lead in Water Depend the Weather, near the Ex-Factory Production of Batteries Region, Berat, Albania, App. Sci. Report.1(3), 122-125.
10. APHA (2012). Standard methods for examination of water and waste water. 22nd, (Edn.) APHA, AWWA, WPCF, Washington DC, USA.
11. Bhupander K, Mukherjee DP, Sanjay K, Meenu M, Dev Prakash SK, Sharma CS (2011). Bioaccumulation of heavy metals in the muscle tissue of fishes from selected aquaculture ponds in east Kolkata wetlands. Ann. Biol. Res. 2(5), 125-134.

12. Brewer GJ (2010). Copper toxicity in the general population. Clin Neurophysiol. 121(4), 459-60.

13. Censi P, Spoto SE, Saiano F, Sprovieri M, Mazzola S, Nardone G, Di Geronimo SI, Punturo R, & Ottonello D.(2006). Heavy metals in coastal water system. A case study from the north-western Gulf of Thailand. Chemosphere, 64, 1167-1176.

14. Dupont JN (2013) Welding of Nickel-Based Alloys for Energy Applications .Welding Journal, 93, 31-45.

15. El fadeli S, Bouhouch R, El abbassi A, Chai M, Aboussad A, Chabaa L, Lekouch N, Hurrell RF, Zimmermann MB & Sedki A (2014). Health risk assessment of lead contamination in soil, drinking water and plants from Marrakech urban area, Morocco. J. Mater. Environ. Sci. 5(1), 225-230.

16. El-Haddad ESM (2005). Some environmental studies on water and sediment of Ismailia Canal from El-Mazallat to Anshas Region, Cairo, Egypt, Fac. of Sci., Al-Azhar Univ., M. Sci. Thesis.

17. El-Naggar A, Mahmoud S & Tayel S (2009) "Bioaccumulation of Some Heavy Metals and Histopathological Alterations in Liver of Oreochromis Niloticus in Relation to Water Quality at Different Localities along the River Nile, Egypt," World Journal of Fish and Marine Sciences. 1(2), 105-114.

18. EPA United States (Environmental protection Agency) EPA 816-F-09-004 May (2009). http://www.epa.gov/safewater/consumer/pdf/mcl.pdf

19. Exley C & Vickers T (2014) Elevated brain aluminium and early onset Alzheimer's disease in an individual occupationally exposed to aluminum: a case report *Journal of Medical Case Reports* 2014, 8:41.

20. Falcon M, Vinas P, Perez-Carceles MD & Luna A (2003). Placental cadmium and lipid peroxidation in smoking women related to newborn anthropometric measurements. Arch Environ. Contam. Toxicol. 45, 278-82.

21. Fernandes C, Fontaínhas-Fernandes A, Cabral D & Salgado MA, (2008). Heavy metals in water, sediment and tissues of *Liza saliens* from Esmoriz–Paramos lagoon, Portugal. Environ. Monit. Assess. 136, 267–275.

22. Florek E, Piekoszewski W, Kornacka MK, Koroniak H, Wolna M & Krol A (2004). Determination of cadmium in urine oftobacco smoking pregnant women. Przegl Lek. 61:1109-12.

23. Frey PA & Reed GH (2012) The ubiquity of iron. ACS Chem. Biol. 7, 1477–1481.

24. Ghallab MHM. (2000) Some physical and chemical changes on River Nile down stream of Delta Barrage at El- Rahawy drain. M. Sc. Thesis Fac. of Sci. Ain Shams Univ. Cairo, Egypt.

25. Giblin AE (2012) Reference Module in Earth Systems and Environmental Sciences. Encyclopedia of Inland Waters .

26. Hider RC & Kong X, (2013) Iron: effect of overload and deficiency. Met Ions Life Sci.; 13, 229-94.

27. Kane S, Lazo P & Vlora A, Eds., Ohrid (2012), Assessment of heavy metals in some dumps of copper mining and plants in Mirdita Area, Albania, in Proceedings of the 5th International Scientific Conference on Water, Climate and Environment, Macedonia.

28. Khan K, Wasserman GA, Liu X, Ahmed E, Parvez F, Slavkovich V, Levy D, MA & Graziano JH (2012). Manganese exposure from drinking water and children's academic achievement Neuro Toxicology. 33, 91-97.

29. Lamhamdi M, El Galiou O, Bakrim A, Novoa-Munoz J C, Arias-Estevez M, Aarab A & Lafont R. (2013). Effect of lead stress on mineral content and growth of wheat (Triticum aestivum) and spinach (Spinacia oleracea) seedlings. Saudi J Biol. Sci. 20 , 29-36.

30. Malik N, Biwas AK, Qureshi TA & Borana K (2010). Bioaccumulation of heavy metals in fish tissues of a freshwater lake of Bhopal. Environ. Monit. Assess. 160, 267-276.

31. Mastan S A (2014). Heavy metals concentration in various tissues of two freshwater fishes, *Labeo rohita* and *Channa striatus* African Journal of Environmental Science and Technology. 8(2), 166-170.

32. Morgan SWJ (1981) Aquatic Chemistry. An Introdution Emphasizing Chemical Equilibria in Natural Waters. John Wiley & Sons, New York

33. Muthulakshmi L; Ramu A and Kannan N (2012) Seasonal distribution of some heavy metal concentrations in ground water of Virudhunagar district, Tamilnadu, South India. Electronic Journal

of Environmental, Agricultural and Food Chemistry EJEAFChe, 11(2), 32 – 37.

34. Nordberg GF (2004). Cadmium and health in the 21st century historical remarks and trends for the future. Biometals.17, 485-9.

35. Otitoloju AA. (2002).Evaluation of the joint action toxicity of binary mixtures of heavy metals against the mangrove periwinkle Tympanotonusfuscatusvarradula Ecotoxicology and Environment Safety.53, 404-415.

36. Prabu PC (2009). "Impact of heavy metal contamination of Akaki river of Ethiopia on soil and metal toxicity on cultivated vegetable crops," Electronic Journal of Environmental, Agricultural and Food Chemistry. 8(9) 818–827.

37. Saletovi M, Hodzi Z, Banjanin B & Kesi A (2011): Bioavailability of microelements (Cu, Zn, Mn) in medicinal plants. Health MED, 5/5, 1358–1364.

38. Sivaperumal P, Sarkar TV & Viswanathan PGN (2007). Heavy metal concentration in fish, shellfish and fish products from international markets of India vis-à-vis international standards. Food Chem. 102,612-618.

39. Sudarwin, (2008) [Spatial analysis of the pollution of heavy metals (Pb and Cd) on the sedimentary basins of landfill trash jatibarang Semarang] (Thesis). University of Diponegoro, Semarang, 106 pp.

40. Taweel A, Shuhaimi-Othman M & Ahmad AK (2011). Heavy metal concentration in different organs of tilapia fish (*Oreochromis niloticus*) from selected areas of Bangi, Selangor, Malaysia. Afr. J. Biotechnol. 10(55):11562-11566.

41. Tayel S, Yacoub AM and Mahmoud S, (2008) "Histopathological and Haematological Responses to Freshwater Pollution in the Nile Catfish Clarias Gariepinus," Journal of Egyptian Academic Society for Environmental Development. 9, 43-60.

42. Thillaiarasu P, Murugan A & Inba JK (2014). Atomic Absorption Spectrophotometric Studies on Heavy Metal Contamination in Groundwater in andaround Tiruchendur, Tamilnadu, India. Chemical Science Transactions. 3(2), 812-818.

43. Uysal K, Emre Y & Kose E (2008). The determination of heavy metal accumulation ratio in muscle, skin and gills of some migratory fish species by inductively coupled plasma-optic emission spectrometry in Beymelek Lagoon, Antalya/Turkey. Microchem. J. 90(1), 67-70.

44. WHO, (2008): "Guideline for drinking water quality, 3 rd edition, vol. 1, Recommendations". World Health Organization, Geneva.

45. Wierzbicka MH, Przedpelska E, Ruzik R, Ouerdane L , Polec-Pawlak K, Jarosz M, Szpunar J, & Szakiel A. (2007). Comparison of the toxicity and distribution of cadmium and lead in plant cells. Protoplasma, 231, 99–111.

46. Yacoub A (2007), "Study on Some Heavy Metals Accumulated in Some Organs of Three River Nile Fishes from Cairoand Kalubia Governorates," African Journal of Biology Science. 3, 9-21.

Source of support: Nil
Conflict of interest: None Declared