Determination of Some Heavy Metals in water of the Southern Region of Lake Manzala, Egypt

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ABSTRACT

Lake Manzala is the largest Nile Delta, coastal ecosystem in Egypt. To examine of the pollution in the lake, the levels of some heavy metals (Fe, Mn, Zn, Cu, Pb, Ni, Cd and Co) were assessed in water samples collected from twelve stations covering the southern region of the lake area, seasonally from the spring 2014 to winter 2015. The lake has undergone substantial recent changes particularly over the last 30 years due to increasing the inflows of drainage water, land reclamation and increasing loads of pollutants.

The obtained results confirmed that, industrial, agricultural and domestic sewage drained into the lake from the main drains has a considerable impact on the water quality characteristics of the lake. The concentration of heavy metals varied in a wide range; increased in the southern region and decreased towards north eastern part of the lake. Heavy metals discharged into the lake causes a momentous environmental problem.

Keywords: Lake Manzala, heavy metals, pollution, plankton, fish.

INTRODUCTION

Lake Manzala is the largest of the Nile Delta coastal brackish ecosystem. Geographically, it is located between longitudes $31^{\circ} 45'$ and $32^{\circ} 22'$ E and latitudes $31^{\circ} 00'$ and $31^{\circ} 35'$ N. The lake is bordered by Mediterranean Sea to the North and the North-East, Suez Canal to the East, Dakahlia and Sharkia Provinces to the South and Damietta Branch of the Nile to the West (Hossen and Negm, 2016).

The lake is connected with the Mediterranean Sea by five outlets permitting exchange the water and biota between the lake and the sea (Rashad and Abdel-Azeem 2010). These outlets are El-Gamil, El-Boughdady and the new El-Gamil (Elewa *et al.*, 2007). The lake is also connected to the Suez Canal at El-Qabouti; a few kilometers to the South of Port Said, and connected with the Damietta branch of the Nile through the El-Inaniya, Souffara and El-Ratma Canals (Sallam and Elsayed, 2015).

Lake Manzala is shrinking everyday due to input from human activities (El-Saharty, 2014). Several decades ago the surface area of the lake was 1698 km² and reduced by 1988 to 770 km² (Saeed and Shaker, 2008) due to continuous land reclamation projects.

The southern region of the lake receives about 7500 million cubic meters of untreated industrial, domestic and agricultural drainage water. This amount of water was reduced to about 4000 million cubic meters after construction of El-Salam Canal (Abdel-Baky, *et al.*, 1998).

Lake Manzala is linked to six drains through the southern and western shores (Donia and Hussein, 2004), these drains discharge into the lake and affect its water quality (Mustafa *et al.*, 2015). So, the southern part of the lake water maintained high

heavy metals levels which exceed the allowable maximum concentration reported by Word Health Organization, which might cause a public health problem (Abdel-Satar, 2001).

The direction of water flow is from the Lake to the sea and vice versa and a pollutant coming from drains affects the whole area of the Lake (El-Naggar *et al.*, 2016).

The contamination by heavy metals in the aquatic environments has drawn particular attentions due to their toxicity, persistence and biological accumulation (Zahran *et al.*, 2015). Such pollutions can negatively impact human health and ecosystems through a range of accumulatory processes within the food chain (Dar *et al.*, 2015). Once they enter the food chain, ultimately humans may accumulate heavy metals from these diets (Barakat, 2011). Fish is at the top of the aquatic food chain, and during its life can accumulate large amounts of toxic elements, when heavy metals accumulate in fish, they are finally transferred to other animals within the food chain (Nwabunike, 2016). Also, fish are considered as a key species in trophic levels that concentrate large amounts of metals (Mahboob, *et al.*, 2014).

The high values of heavy metals would limit drainage water reuse or increase the mixing ratio between fresh and drainage waters (Nasr *et al.*, 2014). Existence of heavy metals either at high or low concentrations must be effectively removed from the drains (Misheloff, 2010).

Lake Manzala attracts attention of many scientists because of its important economic aspects. Several investigations have been carried out concerning its ecosystem. These studies dealt with different environmental aspects of the lake including geological aspects, hydrological regime, physico-chemical properties, bacterial indices, phytoplankton composition, benthic invertebrates, fishery status and water quality and pollution of the lake (El-Wakeel and Wahby, 1970; Dowidar and Hamza, 1983; Abdel-Mouti, 1985; Abdel-Mouti and Dowidar, 1988; Khalil and El-Awamri, 1988; Khalil and Bayoumi, 1988; Khalil, 1990; El-Ghobashy, 1990; El-Sabrouti and Mahmoud 1990; Said, 1992; El-Bokhty, 1996; Hussein 1997, Abdel-Satar, (1998, 2001 and 2009); Frihy *et al.*, 1998; Abdel-Baky and Zyadah, 1998; Dewidar and Khedr, 2001; Fathi *et al.* 2001; Flower, 2001; Lotfy, 2001 and 2007; Abdalla, 2003; Fathi and Abdelzahar, 2003; Abbassy *et al.*, 2003; El-Enany, 2004; Mabrouk, 2004; Gad, 2005; Yacoub *et al.* 2005; Ali. 2008; El-Refaie, 2010; Hamed, *et al.*, 2013; Mehanna, *et al.*, 2014; Orabi and Osman, 2015; Zahran, *et al.*, 2015 and EL-Shafei, 2016).

The main objective of this research is to determine the levels of some heavy metals (Fe, Mn, Zn, Ni, Cu, Pb, Cd and Co) in the lake water because of their health implications to human populations consuming fishes from the lake.

MATERIALS AND METHODS

Collection of samples

Samples of water were collected seasonally during the period from spring 2014 to winter 2015 from the selected station in polyethylene bottles. The bottles were previously rinsed several times with lake water before collection. The entire samples were kept in cleaned stoppered plastic bottles of two-liter capacity and have been acidified using 5 ml concentrated nitric acid at collection.

No. of station	Stations
Ι	El-Serw Drain
Π	El-Serw D.P.
III	Faraskour Drain
IV	Faraskour D.P.
V	Hadous Drain
VI	Hadous D.P.
VII	Old Bahar El-Bakar Drain
VIII	Old Bahar El-Bakar Drain D.P.
IX	New Bahar El-Bakar Drain
X	New Bahar El-Bakar Drain D.P.
XI	El-Genka
XII	El-Boom
XIII	El-Matariya

Table 1: Selected stations in Lake Manzala

Methodology:

For heavy metals analysis water samples were digested by adding 10 ml of nitric acid to 500 ml of water sample in a beaker and boiled slowly on a hot plate till the lowest volume, nearly 15 - 20 ml before precipitation occurs, until complete digestion. Beaker walls were washed carefully with distilled water then the digested samples were transferred to a 100 ml volumetric flask and completed to the mark with deionized distilled water. A portion of this solution was used for the determination of heavy metals.

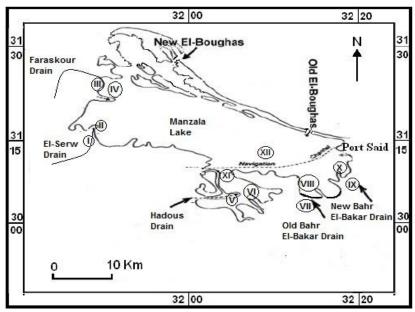


Fig. 1: A map of Lake Manzala showing the drains and collecting stations

RESULTS

Heavy Metals

The contamination by heavy metals in the aquatic environments has drawn particular attentions due to their toxicity, persistence and biological accumulation (Zahran, *et al.*, 2015).

Iron contents in the lake water fluctuated in a relatively wide range (Fig. 2). Furthermore, the results showed slight increase of Fe during spring and summer than other seasons. The values of Fe at different stations were found to be in the ranges of 0.00-18.48, 3.06-33.09, 0.00-24.45 and 2.04-35.26 μ g/l during autumn, winter, spring and summer, respectively. The highest levels of the iron (35.26 μ g/l) were found during summer in front of the New Bahar El-Bakar Drain. The lowest values occurred during autumn at El-Boom station away from the southern region which contains drains.

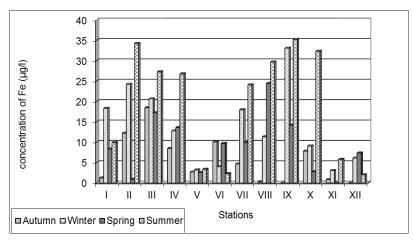


Fig. 2: Seasonal variation of iron concentration (µg/l) in Lake Manzala during 2014-2015.

Concerning the average annual values, the least value was 2.43 mg/l which recorded at El-Genka station, while the highest one was recorded at Faraskour Drain which was 20.92 mg/l.

On the other hand, manganese values exhibited a similar distribution trend as iron. The values of Manganese ranged between 0.256-1.727, 0.837-3.19, 0.198-3.7 and 0.745-6.091 μ g/l during autumn, winter, spring and summer respectively. The minimum value of manganese was recorded at El-Boom Station during winter (0.108 μ g/L), but the maximum value was recorded at El-Serw Drain Station during summer (Fig. 3).

Concerning the average annual values of Mn, the least value was 0.21 mg/l, which recorded at El-Boom station, while the highest one was recorded at El-Serw Drain which was 2.46 mg/l.

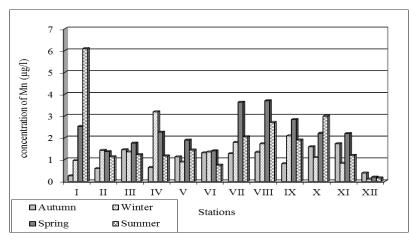


Fig. 3: Seasonal variation of manganese concentration (μg/l) in different stations of Lake Manzala during 2014-2015.

The values of zinc were varied in the range between 0.487-3.929, 1.865-3.818, 1.811-3.042 and 1.887-4.726 μ g/l during autumn, winter, spring and summer respectively.

The maximum value $(4.726\mu g/l)$ was observed at Old Bahar El-Bakar Drain during summer season, while the minimum one was recorded at New Bahar El-Bakar Drain $(0.487\mu g/l)$ during autumn (Fig. 4).

The values of copper were varied in the range between 0.00-0.030, 0.0-0.103, 0.00-0.031 and 0.00-0.163 μ g/l during autumn, winter, spring and summer respectively. The levels of copper showed a similar trend as Fe and Mn, where its values increased during summer.

Results revealed that, the maximum value of copper was recorded at Old Bahar El-Bakar D.P. during summer $(0.163\mu g/l)$. While the minimum value was recorded at Hadous D.P. during autumn $(0.004\mu g/l)$ beside the depletion of copper which present in many stations. (Fig. 5).

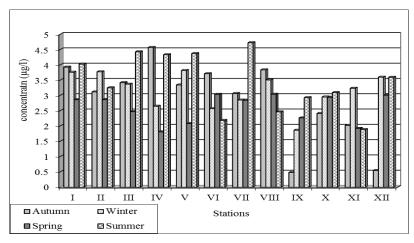


Fig. 4: Seasonal variation of zinc concentration ($\mu g/l$)) in different stations of Lake Manzala during 2014-2015.

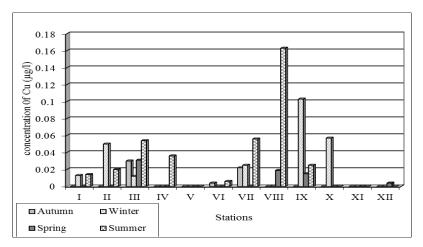


Fig. 5: Seasonal variation of copper concentration (μ g/l)) in different stations of Lake Manzala during 2014-2015.

The values of lead were varied in the range between 0.00-0.023, 0.0-0.418, 0.00-0.064 and 0.00-0.364 μ g/l during autumn, winter, spring and summer respectively. Results revealed that, the maximum value of lead was recorded at New Bahar El-Bakar D.P. during winter (0. 364 μ g/l). The minimum one was recorded at Faraskour

D.P. during summer ($0.012\mu g/l$). Beside the depletion of lead which was recorded in many stations (Fig. 6).

The values of cadmium were varied in the range between 0.00-0.014, 0.0-0.001 and 0.00 -0.028 μ g/l during autumn, winter, and summer respectively. While in spring, a total depletion of cadmium was recorded in all investigated samples (Fig. 7).

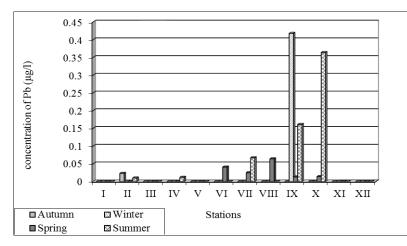


Fig. 6: Seasonal variation of lead concentration (μ g/l) in different stations of Lake Manzala during 2014-2015.

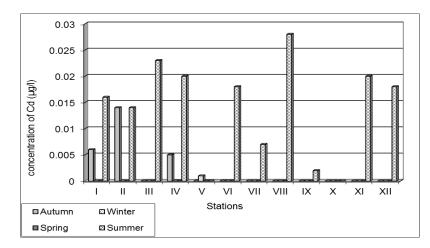


Fig. 7: Seasonal variation of cadmium concentration (μ g/l) in different stations of Lake Manzala during 2014-2015.

Results revealed that, the maximum value of cadmium was recorded at Old Bahar El-Bakar D.P. during summer (0. 028 μ g/l). The minimum one was recorded at Hadous Drain during winter season (0.01 μ g/l). The depletion of cadmium which was recorded in many stations.

The values of nickel were varied in the range between 0.00-0.084, 0.0-0.085, 0.0-0.105 and 0.00 -0.201 μ g/l during autumn, winter, spring and summer respectively (Fig. 8). Results revealed that, the maximum value of nickel was recorded at New Bahar El-Bakar Drain during summer (0. 201 μ g/l).

The values of cobalt were varied in the range between 0.00-0.051, and 0.00 - 0.126 μ g/l during winter and summer respectively. During autumn and spring a total depletion of cobalt was recorded in all investigated samples.

Results revealed that the maximum value of cobalt was recorded at New Bahar El-Bakar D.P. during summer (0. 126 μ g/l), while, the minimum value was recorded at New Bahar El-Bakar D.P. during winter (0.02 μ g/l). Depletion of cadmium which was recorded in many stations (Fig. 9).

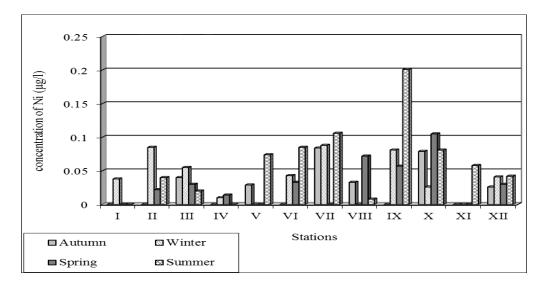


Fig. 8: Seasonal variation of nickel concentration (µg/l) in different stations of Lake Manzala during 2014-2015.

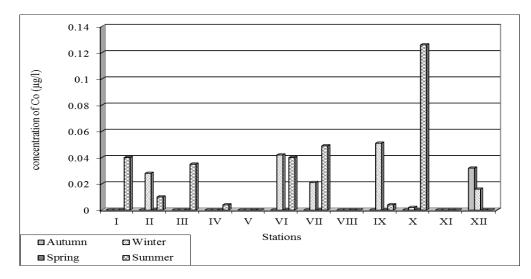


Fig. 9: Seasonal variation of cobalt concentration (µg/l) in different stations of Lake Manzala during 2014-2015.

DISCUSSION

Trace metals have a great ecological significance in aquatic ecosystem due to their toxicity and accumulation behavior. In general, the heavy metals; lead, copper, cadmium, zinc, cobalt and nickel, produce their toxicity by forming complexes or "ligands" with organic compounds (El-badry, 2016).

The increasing of Fe during spring and summer than other seasons is due to the elevation of temperature, which decreases the assimilation rate of Fe by aquatic organisms especially macrophytes (Berg *et al.*, 1995).

The occurrence of lowest values at El-Boom station which is away from the southern region may be attributed to the direct precipitation of iron and clarity of water at this station.

These results are in agreement with those obtained by Ghallab (2000), El-Enany (2004), Rasheed (2011), Bahnasawy *et al.*, 2011, Nwabueze & Oghenevwairhe, 2012 and Saad *et al.*, 2013.

The increasing of Mn during hot seasons than cold ones is mainly attributed to the mobilization of manganese from the sediment to the overlaying water due to the decomposition of organic debris by microbial activity. The high evaporation rate and the raising of water temperature and air during hot seasons causing increasing of manganese concentrations, that comes with the industrial and sewage effluents which drain to the water body (Goher, 1998).

It is clear that the concentration of zinc decreases in autumn, which may be attributed to the adsorption of zinc on iron colloids and precipitated to sediments (Maria *et al.* 2000 and El-Sayed, 2011).

The highest values of zinc concentrations were recorded at Bahr El-Bakar drain which carries higher amount of domestic, industrial and agricultural wastes. This agreed with Rasheed, (2011).

The increasing of Cu values during summer is mainly attributed to the precipitation of copper to the sediment as CuS under elevation of temperature (Hutchinson, 1957). The presence of maximum value of copper at Old Bahar El-Bakar D.P. during summer (0.163 μ g/l), is attributed the highly amount of industrial discharge in this drain.

The minimum value of copper was recorded at Hadous D.P. during autumn (0.004 μ g/l). Depletion of copper was recorded in many stations. This may be attributed to the uptake of phytoplankton and other aquatic plants. Copper concentrations of the present study are lower than those obtained by Aboul-Ezz and Abdel-Razek (1991), El-Enany(2004) and Rasheed (2011).

The maximum value of lead was recorded at the New Bahar El-Bakar D.P. during winter. This may be due to the highly amount of industrial discharge in this drain, from the effect of effluent of Bahr El-Bakar drain which carry higher amount of domestic, industrial and agricultural wastes. This result agreed with Abdo, (2002), El-Sayed (2011) and Rasheed (2011).

The presence of the maximum value of cadmium at the Old Bahar El-Bakar D.P. during summer, may be due to the highly amount of industrial discharge in this drain, or due to the effect of effluent of Bahr El-Bakar drain which carry higher amount of domestic, industrial and agricultural wastes. This result agreed with Rasheed (2011).

The decrease in cadmium concentrations during cold period may be attributed to the uptake of cadmium by aquatic plants, invertebrates accumulated during this period (Touffek, 1993).

The maximum value of cobalt was recorded at the New Bahar El-Bakar D.P. during summer. While, the minimum value was recorded at New Bahar El-Bakar D.P. during winter (0.02 μ g/l). Depletion of cadmium which was recorded in many stations (Fig. 9). This result agreed with Nagpal (2004) and Zahran *et al.*, (2015).

Mehanna *et al.* (2014) declared that, the annual variation of heavy metals (Fe, Cu, Zn, Pb, Mn, Cd and Hg) concentration in the lake water was; Iron concentration ranged from 0.32 to 1.71 ppm, copper concentration ranged from 0.01 to 0.68 ppm, zinc concentration ranged from 0.017 to 0.66 ppm, lead concentration ranged from

0.001 to 0.30 ppm, manganese concentration ranged 0.001 to 1.09 ppm and cadmium concentration ranged from 0.0001 to 0.06 ppm.

El-badry 2016 found that the highest concentrations of Cd, Pb, Ni and Zn in water were observed in the eastern portion of the lake where industrial zone of Port Said country whiles the lowest values were recorded at the western portion of the lake. Highest Cu and Co values were recorded in the western area towards el-Serw agricultural drain. The relative order of abundance of the potentially toxic metals in the lake's water is; Pb>Cu>Zn>Cd.

CONCLUSIONS

Generally, the distribution of heavy metals in Lake Manzala revealed that the highest concentrations of heavy metals were observed in the northeastern and the southern parts of the lake nearby drains. This attributed to industrial, agricultural and municipal wastes coming through the drains especially Bahr El-Bakar drain and the industrial wastes coming from Port Said area.

A monitoring program should be set up to control the pollution in this vital important ecosystem and mange it healthy fish production.

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ARABIC SUMMARY

دراسة بعض العناصر الثقيلة في مياه المنطقة الجنوبية لبحيرة المنزلة – مصر

وائل حسين رشدي حجازي 1، محمد عبد الفتاح حامد2، محمد الصديق توفيق2، بزادى خميس أمين مبروك2 1- قسم الكيمياء – كلية العلوم – جامعة السويس – السويس – مصر 2- المعهد القومي لعلوم البحار والمصايد - مصر

تعد بحيرة المنزلة أكبر بحيرة في منطقة دلتا النيل، على ساحل البحر المتوسط لتقدير التلوث في البحيرة، تم قياس تركيزات بعض المعادن الثقيلة (الحديد والمنجنيز والزنك والنحاس والرصاص والنيكل والكادميوم والكوبالت) في عينات المياه التي تم جمعها من اثني عشر محطة تغطي المنطقة الجنوبية من البحيرة بداية من ربيع 2014 وحتى شتاء 2015. وقد شهدت البحيرة تغيرات كبيرة في الفترة الأخيرة وخاصة خلال السنوات ال 30 الماضية بسبب تدفقات مياه الصرف، واستصلاح الأراضي وزيادة الأحمال من الملوثات. وترتبط كمية الملوثات ارتباطا وثيقا بوجود المصارف التي تصب في البحيرة.

وأكدت النتائج أن المصارف الصناعية والزراعية ومياه الصرف الصحي والمنزلي التي تصب في البحيرة من المصارف الرئيسية لها تأثير ملحوظ على خصائص ونوعية مياه البحيرة، مما أدى الى انحدار شديد في جودة ونوعية المياه بالبحيرة.

. وتتراوح تركيزات العناصر الثقيلة على مدى واسع، وكانت الزيادة الملحوظة في المنطقة الجنوبية التي تصب فيها المصارف مباشرة، وتنخفض التركيزات كلما اتجهنا نحو الجزء الشمالي الشرقي للبحيرة.