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Geo-spatial Variability Assessment of Water Pollutants Concentration in Mariut Lake, Egypt

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WATER pollution has become a growing threat to human society and natural ecosystems in recent decades, increasing the need to better understand the spatial and temporal variabilities of pollutants within aquatic systems. Mariut Lake is one of the most heavily populated urban areas in Egypt and in the world. A total of 22 samples were collected and analyzed for determining the concentrations of chromium (Cr), manganese (Mn), iron (Fe), cobalt (Co), nickel (Ni), copper (Cu), zinc (Zn), cadmium (Cd) and lead (Pb) in winter time 2014. Inverse distance weighting analyst tools were used to explore, analyze the spatial distribution and mapping of the heavy metal concentrations.

The results revealed that all of heavy metals concentrations matched with the allowable limits to be discharged in marine environment as prescribed in Egyptian law except of Ni metal which exceeded the allowable limits. The results illustrated that the highest concentration of Mn and Fe were distributed in the upper north eastern parts of the studied stations, this may be due to human's activities and industrial area. While the eastern region has high concentrations of Pb, Ni, Cr and Co due to El-Kalaa drain discharges. However, the western part of the study area has high concentration of Zn and Cu due to El-Ommum drain discharges. The study concluded that the accurate spatial pattern of heavy metals could improve our understanding of possible sources, controlling factors and involving processes which are essential for monitoring and remediation of the contaminant sites in the lake.

Keywords: Heavy metal, Mariut Lake, Geo-Spatial

Heavy metals are common pollutants which are distributed in aquatic environment and have received considerable attention due to their toxicity (Mason, 1991). Metals generally enter the aquatic environment through atmospheric deposition, erosion of the geological matrix, or due to anthropogenic activities caused by industrial effluents, domestic sewage and mining wastes (Stephen *et al*., 2000 and Kambole, 2002).

The fact that coastal lakes generally have low water exchange (Coulibaly *et al*., 2010), favoring the accumulation of heavy metals in the ecosystem. Some of these metals such as Cu, Mn, Fe and Zn are essential elements for normal metabolism of aquatic organisms in low concentrations. Zn has a multitude of biological functions in the human body. It is an important constituent of over 100 enzymes involved in a variety of fundamental metabolic processes. It is involved in the production and function of several hormones. Excessive intake of Zn causes abdominal pain, violent vomiting, collapse, and degenerative changes in the liver. Cu is probably a functional constituent of all cells. Toxicity can result from excessive intake,which results in gastrointestinal disturbance, headache, cirrhosis, necrosis, and liver failure. However, some others like pb and cd are considered to be toxic to living organisms (Virha *et al.*, 2011). They impose serious damage to metabolic, physiological and structural systems of organisms when present in high concentrations in the environment. Accumulation of heavy metals in the food can occur either by accumulation from the surrounding medium, such as water or sediment, or by bioaccumulation from the food source (Tulonen *et al*., 2006). Aquatic organisms have been widely used in biological monitoring and assessment of safe environmental levels of heavy metals.

Pollution mapping is a time consuming process that requires intense efforts of scientists to think spatially, geographically, technically, and statistically to produce an accurate prediction map. To understand and solve a problem, particularly in the geo-environmental sciences, broad knowledge of basic sciences, environmental science, geospatial statistical analysis, geographic information system (GIS), and analytical ability are necessary requirements (Swatntra, 2013). Also, due to cost and practicality, it is not feasible to establish monitoring stations in every location of study area to measure the pollutant concentration. Therefore, prediction of values at other locations based upon selectively measured values could be one of the alternatives (Gorai, 2013).

The spatial variability of heavy elements concentration in water can play an important role in understanding of possible pollution sources, identifying critical and contaminated areas and monitoring the impacts of human activities and natural sources (Yalcin *et al*., 2007 and Fang *et al*., 2011). However, environmental protection in nature requires a good knowledge of the present conditions, and the spatial distribution of contaminants of concern. Geo-statistical and spatial analysis techniques can be used in the identification of contaminant sources (Oyarzun *et al*., 2007; Choe *et al*., 2008 and Wang & Lu, 2011).

In this research, inverse distance weighting interpolation techniques was used to extract spatial distribution of heavy metal concentrations in the studied area of Mariut lake because it was detected in little specific locations.

Study area

Lake Mariut is a 90-150 cm deep brackish water lake located in the north of Egypt southeast to the Alexandria City, belonging to the Nile River Delta and one of the most heavily populated urban areas in Egypt and in the world. By the end of the 19^{th} Century, the development of irrigation systems of the adjacent fields made of Mariut lake an intermediate water body to receive the excess of water from the irrigation channels. Then the water was pumped out to the Alexandria Bay (Miguel, 2009).

Mariut Lake, for a long time, represents a source of fish production in Egypt. Currently, some parts of the lake are used in aquaculture activities (Bakhoum, 1994).

Nowadays the lake occupies around 250 km^2 due to intense land reclamation for urban and agricultural purposes. The Lake is artificially subdivided into four basins (Fig. 1);

- The northern-west basin (1214 hectares), which receives its water from El-Ommum drain.
- The southern-west basin (2023 hectares), which also receives its water from El-Ommum Drain and Noubaria Canal and is densely, covered with Phragmites.
- The fish farm (405 hectares), which receives its water from the drainage waters of El-Ommum and El-Kallaa drains.
- The main proper basin (2428 hectares), which covers an area of about 25 km^2, has been suffering from high levels of pollution.

Currently, the main sources of pollution in this part of the lake are represented by El-Sharkawi (1999) and Kassim (2005):

a. The West Treatment Plant Outfall, which discharges about 200,000–300,000 m^3/day of settled sewage into the lake.

b. El-Kallaa Drain Outfall, which discharges about 400,000 m^3/day of agricultural waste water and sewage into the lake after primary treatment. In general, El-Kallaa Drain is considered the major source of pollution in the lake.

c. Noubaria Canal which discharges wastewaters at the western side of the basin.

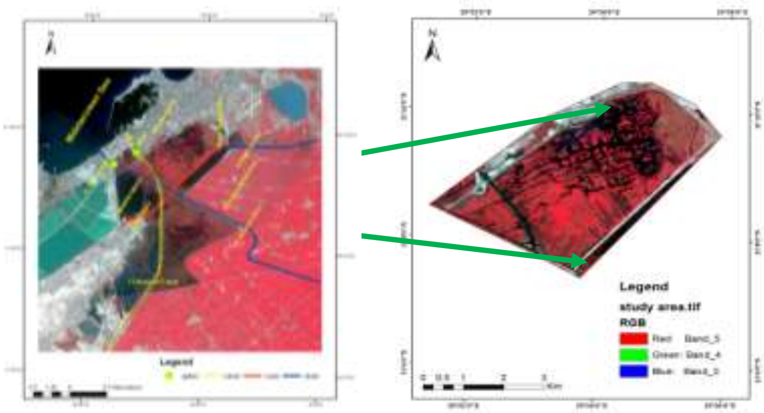

Fig. 1. Location of the studied area

Materials and Methods

Sampling and laboratory analysis of heavy metals concentrations

Water samples were collected from twenty two water stations in Lake Mariut in February 2014. The stations were selected on the basis of variation including all water bodies as shown in Fig. 2. Water samples were collected, routinely acid-treated with a solution (0.5 N HNO_3) and stored in bottles to prevent contamination. All samples collected for chemical analysis were kept at a temperature of about 4 °C by using cool boxes and cooling agents. The collected water samples were taken to laboratory for determining heavy metals concentration (Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd and Pb), according to standard method (APHA, 1992).

A quantity of 200 ml of water sample were taken, pH was adjusted from 2-3 by adding drops of 1 M HNO_3. The solution was put in 500 ml separating funnel, 1 ml of ammonium pyrolidine di thiocarbamate (APDC) was added, shaking the solution to mix and then, adding 10 or 5 ml of methyl isobutyl ketone. The mixture is shaken manually for 2 min, if an emulsion is formed at the interface of the 2 layers, centrifuged for 2 min, the extraction is repeated with another 5 ml methyl isobutyl ketone. If a precipitate is formed in the solvent phase during the extraction, 5 ml of methyl isobutyl ketone is added and the extraction is repeated with the second 10 ml of the extraction solvent. The organic layers were separated, then acidified with HNO_3 (back extraction). The aqueous acidified solution was treated with the suitable chemical modifier and aspirated directly into flame atomic absorption spectrometer (FAAS) to record the absorbance and then converted to concentration expressed in mg/L.

Inverse distance weighting interpolation method

The inverse distance weighted (IDW) method was used to map the spatial distribution of the pollutants using Arc GIS software (v.10.1) to create maps and 3D surfaces to display and interpret the data. IDW uses a specific number of nearest-neighbor points, which are then weighted according to their distance from the location being interpolated. The interpolating surface is a weighted average of the neighboring sampling sites. The weight assigned to each point diminishes as the distance from the interpolation location to the sampling sites increases. The results of the interpolation are then the expected possible values. The 3D surfaces were produced for better visualization to understand the spatial distribution of pollutants. Then each parameter was mapped and added into the GIS. (Weber and Englund, 1994) found that squared inverse distance weighting produced better interpolation results than any other method, including kriging. Kriging performance can be significantly affected by variability and spatial structure of the data (Leenaers *et al*., 1990), and by the choice of variogram models, search radius, and the number of the closest neighboring points used for estimation. In the current study, IDW interpolation method was used for mapping the spatial distribution of heavy metal in Mariut Lake.

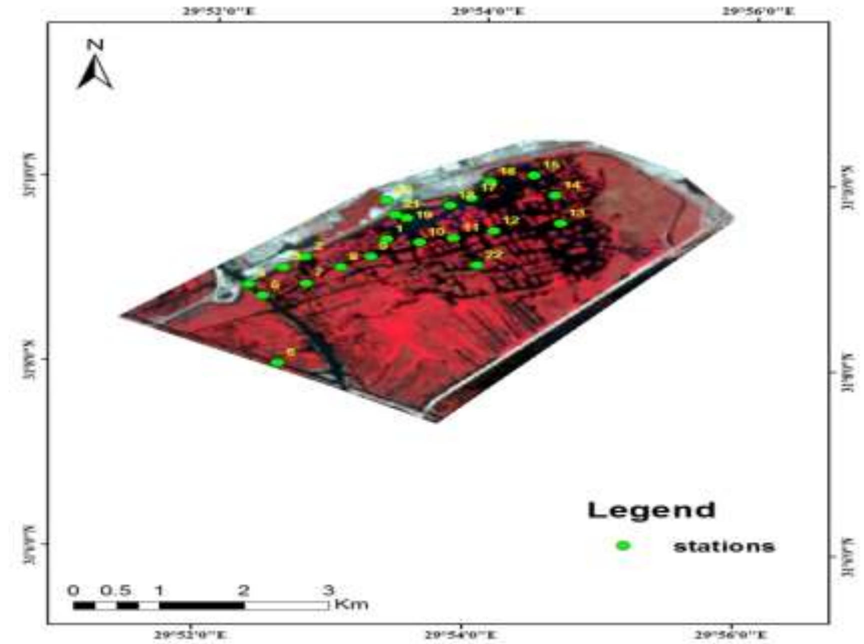

Fig. 2. Locations of sample stations in the main basin of Mariut Lake

Results and Discussion

Manganese (Mn) concentrations and its spatial distribution

Manganese occurs naturally in many surface water and groundwater sources and in soils that may erode into this water. However, human activities are also responsible for much of the manganese contamination in water in some areas.

The obtained data (Table 1) illustrated that the manganese concentrations ranged from 0.097 to 0.245 mg/L with a mean average of 0.15 mg/L. The Mn concentrations are matching with the Egyptian law No. 4/1994 which is 1 mg/L as a maximum allowable limit for manganese. The maximum concentration value of manganese was 0.245 mg/L recorded at site 21, while the minimum concentration value was 0.097 mg/L observed at site 12. The average of Mn (0.15 mg/L) are more than that reported by (Kondrashin and Khalifa, 2013) (0.084 mg/L) in Mariut Lake.

The spatial distribution of Mn concentration level in water was given in Fig. 3. As seen in the distribution map, the Mn concentration has high level on the north eastern part due to human's activities which has industrial wastes.

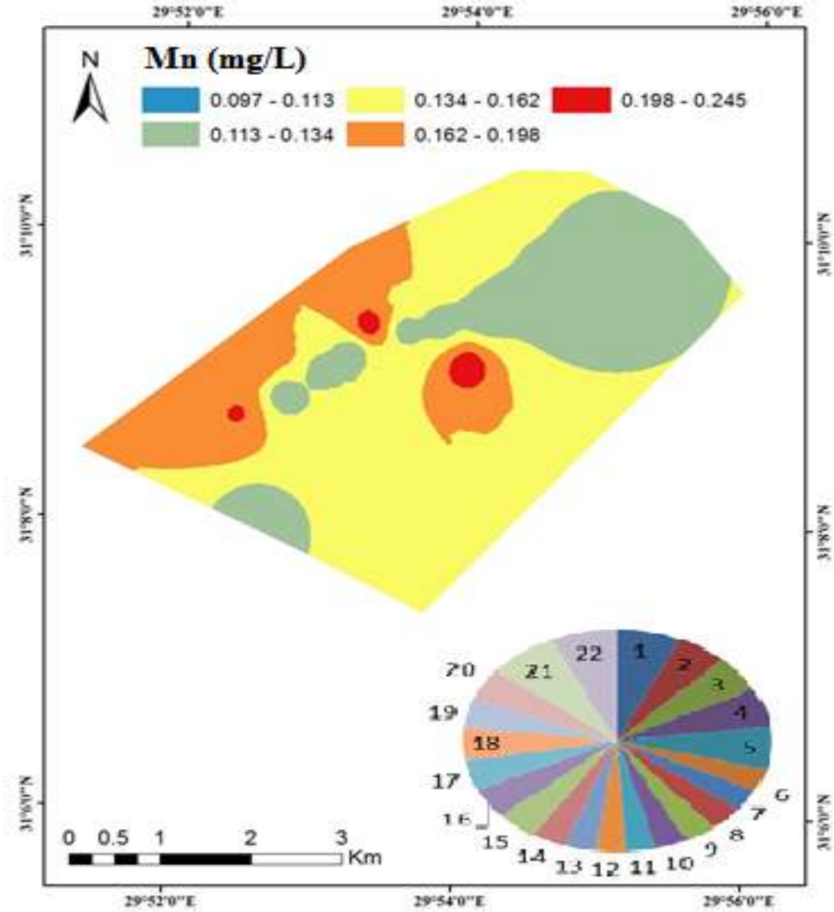

Fig. 3. Mn spatial distribution in the study area

Cobalt concentrations

Cobalt is a relatively rare element of the earth's crust with concentrations approximately 25 µg/g (Hamilton, 1994). Cobalt is essential in trace amounts for humans and other mammals as it is an integral component of the vitamin B12 complex. Cobalt is reportedly an essential element for the growth of many marine algal species, including diatoms, chrysophytes and dinoflagellates (Bruland *et al*., 1991). It is also a micronutrient essential for some blue-green algae and is required by microorganisms for nitrogen fixation in legumes. Although its essentiality in higher, non-leguminous plants is not clearly proven, there is some evidence of favourable effect of cobalt on plant growth (Kabata-Pendias and Pendias, 1984). In higher concentrations, cobalt is toxic to humans and to terrestrial and aquatic animals and plants.

The data (Table 1) indicated the cobalt concentrations ranged from 0.069 to 0.199 mg/L with a mean average of 0.133 mg/L, which is matching with the Egyptian law No. 4/1994 (2 mg/L) as a maximum allowable limit for cobalt. The maximum concentration of cobalt was 0.199 mg/L recorded at site 15, while the minimum concentrations value of cobalt was 0.069 observed at site 2. The present results of cobalt are higher than that reported by Kondrashin and Khalifa (2013) (most of the cobalt concentration values fall below the instrument detection less than 0.005 mg/L) in Mariut lake which mean that the concentration increased from 0.005 to 0.133 mg/L in one year although it is under the permissible level, it is a serious call to observe the increase in heavy metal pollutant every year to try to control the water pollutant.

The spatial distribution of Co in water is shown in Fig. 4, which illustrates the increase of Co level in the eastern region due to El-Kalaa Drain discharges.

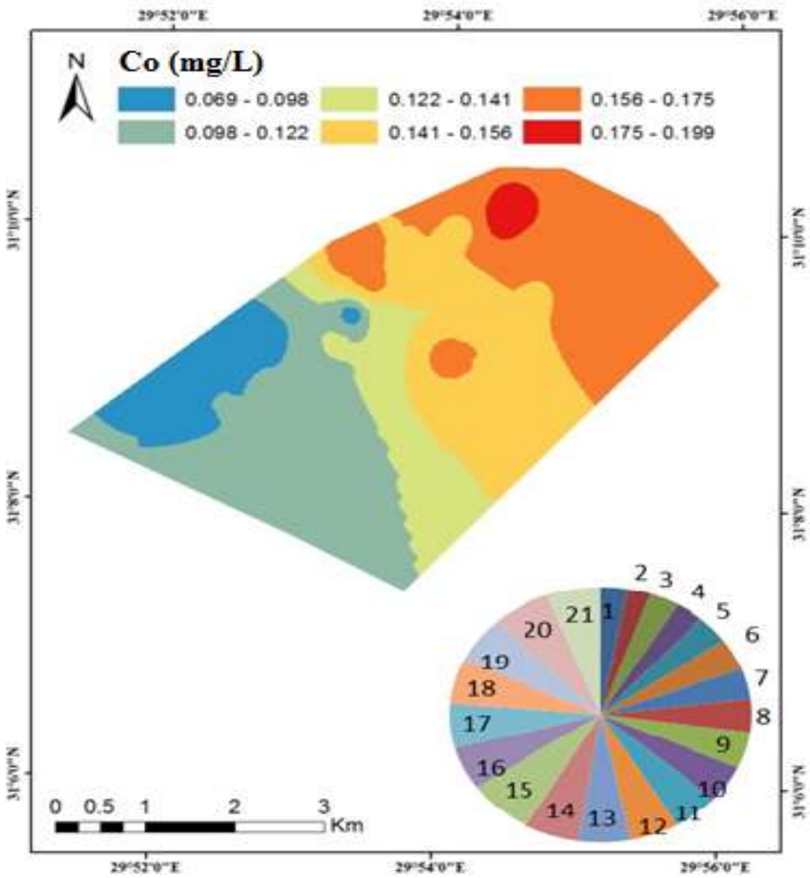

Fig. 4. Co spatial distribution in the study area

Chromium concentrations

Chromium is widely distributed in the earth's crust. It can exist in oxidation states of +2 to +6. Soils and rocks may contain small amounts of chromium, almost always in the trivalent state. In general, the chromium content of surface waters reflects the extent of industrial activity.

The results indicated that (Table 1) the chromium concentrations ranged from 0.006 to 0.12 mg/L with a mean average of 0.065 mg/L. It is observed that chromium concentrations are matching with the Egyptian law No. 4/1994 which is 1 mg/L as a maximum allowable limit for chromium. The highest concentration value of chromium was 0.12 mg/L recorded at site 20, while the lowest concentrations value of chromium were 0.006 observed at site 7. The present average result of chromium (0.065 mg/L) is higher than that reported by Kondrashin and Khalifa (2013) (0.038 mg/L) in Mariut Lake.

The spatial distribution of Cr in water was given in Fig. 5, which demonstrated that the maximum value is distributed in the eastern region of the studied area. This is attributed to effect of El-Kalaa drain discharges.

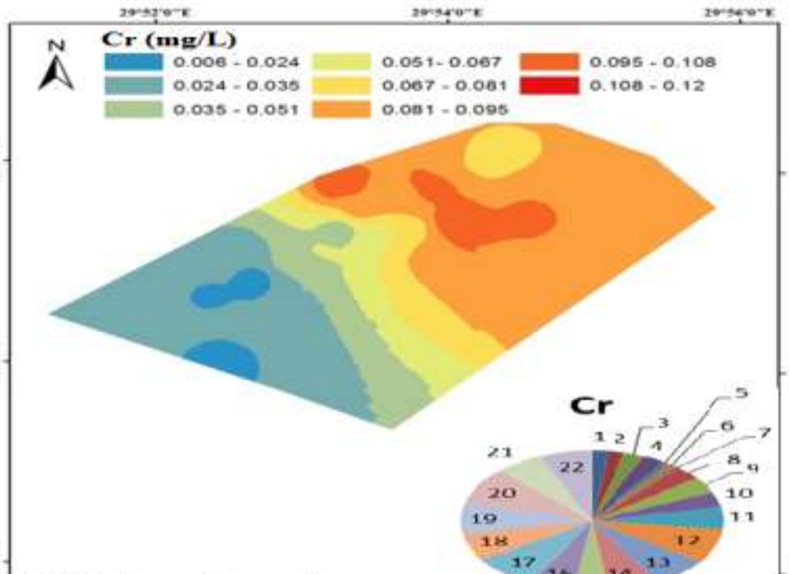

Fig. 5. Cr spatial distribution in the study area

Nickel concentrations

The primary source of nickel in drinking-water is leaching from metals in contact with drinking-water, such as pipes and fittings. However, nickel may also be present in some ground waters as a consequence of dissolution from nickel ore-bearing rocks.

As seen from the data (Table 1), that the nickel concentrations ranged from 0.395 to 0.516 mg/L with a mean average of 0.46 mg/L. It is observed that nickel concentrations are higher than the Egyptian law No. 4/1994 which is 0.1 mg/L as a maximum allowable limit for nickel. The highest concentration value of nickel was 0.516 mg/L recorded at site 20, while the lowest concentration value was 0.395 mg/L recorded at site 3. The present results of Nickel are higher than that reported by Kondrashin and Khalifa (2013) All nickel concentration values fall below the instrument detection limit (*i.e*., less than 0.001 mg/L) in Mariut Lake. The high concentrations of nickel might be due to agricultural, domestic and industrial wastewaters discharged into these sites.

The geographical distribution of Ni in the studied area is given in Fig. 6, which illustrates that the Mn concentration has high level on the eastern region due to El-Kalaa Drain discharges.

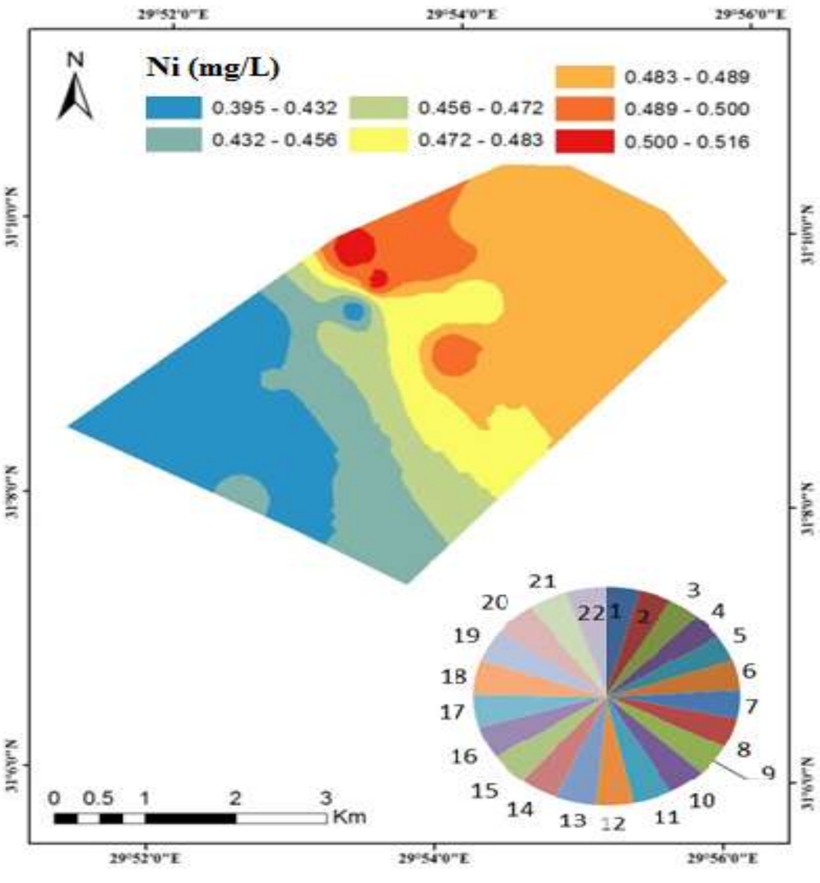

Fig. 6. Ni spatial distribution in the study area

Copper concentration

Copper is found in surface water, groundwater, seawater and drinking-water, but it is primarily present in complexes or as particulate matter. Copper concentrations in drinking-water vary widely as a result of variations in water characteristics, such as pH, hardness and copper availability in the distribution system.

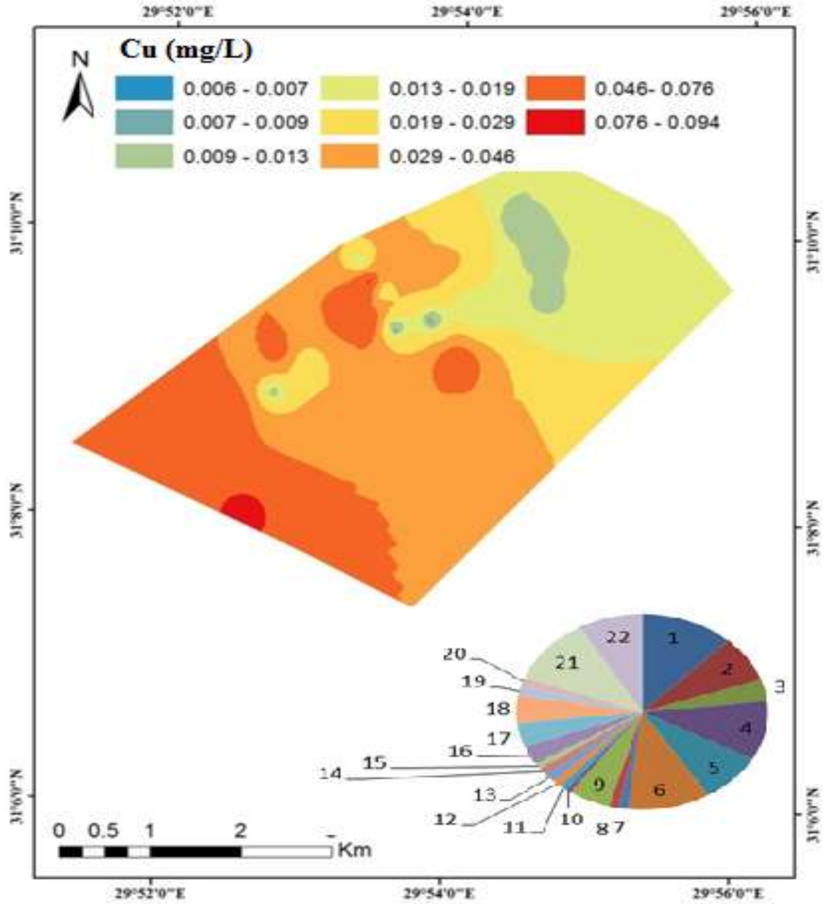

Fig. 7. Cu spatial distribution in the study area

Data showed that the copper concentrations ranged from 0.006 to 0.094 mg/L with a mean average of 0.036 mg/L. The obtained values of copper are coinciding with the Egyptian law no. 4/ 1994 which is 1.5 mg/L. The present average result of copper (0.036 mg/L) is lower than that reported by Kondrashin and Khalifa (2013) (0.048 mg/L) in Mariut Lake.

As seen in Fig. 7 the geographical distribution of Cu concentrations in the Lake water, the levels increased on the western region due to El-Ommum Drain.

Cadmium concentration

Cadmium is a metal with an oxidation state of +2. It is chemically similar to zinc and occurs naturally with zinc and lead in sulfide ores. Fertilizers produced from phosphate ores constitute a major source of diffuse cadmium pollution. The solubility of cadmium in water is influenced to a large degree by its acidity; suspended or sediment-bound cadmium may dissolve when there is an increase in acidity (Ros and Slooff, 1987). In natural water, cadmium is found mainly in bottom sediments and suspended particles (Friberg *et al*., 1986).

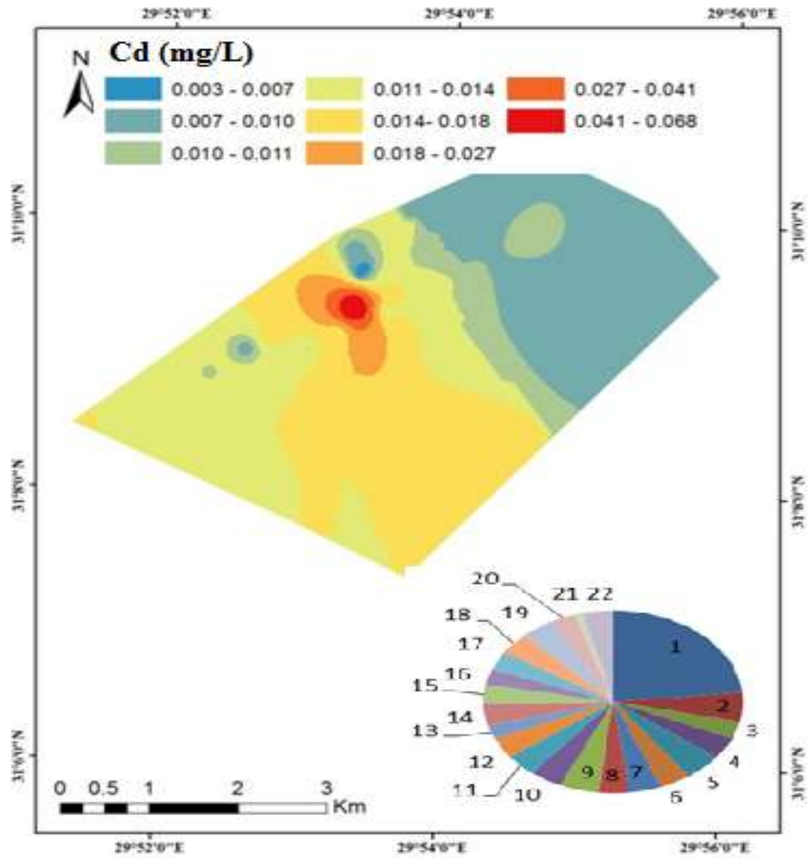

Fig. 8. Cd spatial distribution in the study area

The obtained data (Table 1) showed that the cadmium concentrations ranged from 0.003 to 0.068 mg/L with a mean average of 0.013 mg/L. It is stated that cadmium concentrations match with the Egyptian law No. 4/1994 stating 0.05 mg/L as a maximum allowable limit for cadmium. The highest concentration value of cadmium is 0.068 mg/L recorded at site 1, while the lowest concentrations value 0.009 mg/L is observed at site 20. The high concentrations of cadmium might be due to agricultural, domestic and industrial wastewater discharged into these sites. The present average result of cadmium (0.013 mg/L) is lower than that reported by Kondrashin and Khalifa (2013) (0.026 mg /L) in Mariut Lake. The spatial distribution of Cd is shown in Fig. 8.

Lead concentration

Lead is the commonest of the heavy elements, accounting for 13 mg/kg of earth's crust. The obtained data indicated that the lead concentrations ranged from 0.98 to 1.527 mg/L with an average of 1.25 mg/L. The mean concentrations of lead are below the allowable limits (5 mg/L) to be discharged in marine environment as prescribed in Egyptian law No. 4/1994.

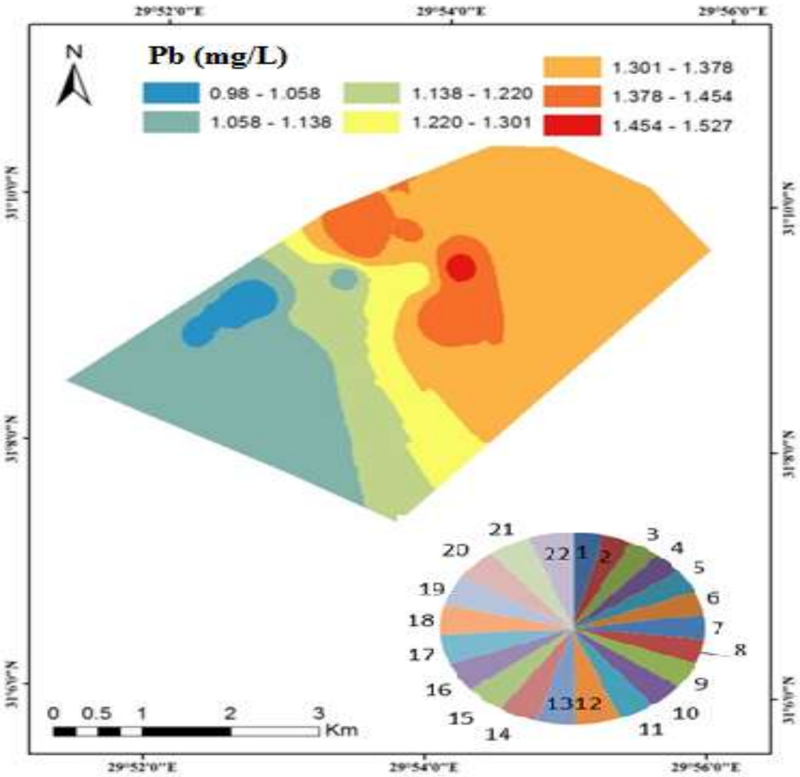

Fig. 9. Pb spatial distribution in the study area

The highest concentration level of lead 1.527, 1.464 and 1.396 mg/L is reported at sites 12, 22 and 18, respectively (Table 1). The high values of lead might be due to the high amounts of agricultural, domestic and industrial wastewater discharged into these waterways. The present average result of Pb (1.25 mg/L) is lower than that reported by Kondrashin and Khalifa (2013) (2.5 mg/L) in Mariut Lake.

The geographical distribution of Pb in water is given in Fig. 9. This element has high levels on the eastern region due to El-Kalaa Drain discharges.

Iron concentration

Iron is the second most abundant metal in the earth's crust, of which it accounts for about 5%. Elemental iron is rarely found in nature, as the iron ions Fe^{2+} and Fe^{3+} readily combine with oxygen- and sulfur-containing compounds to form oxides, hydroxides, carbonates, and sulfides. Iron is most commonly found in nature in the form of its oxides.

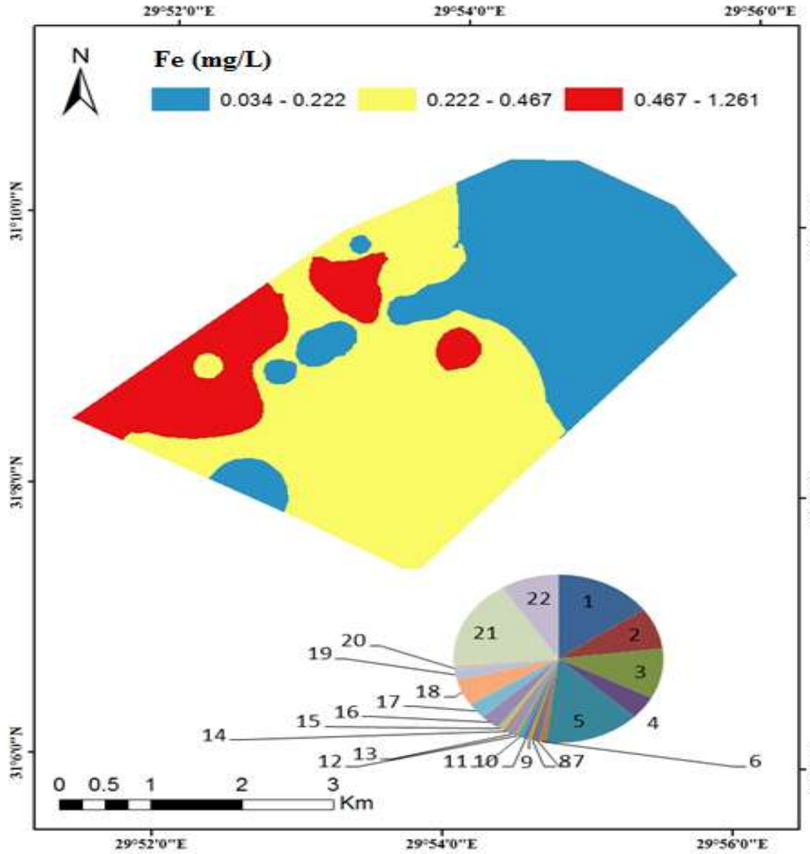

Fig. 10. Fe spatial distribution in the study area.

The obtained data (Table 1) showed that the iron concentration values ranged from 0.034 to 1.261 mg/L with an average of 0.33 mg/L. The obtained values of iron are coinciding with the Egyptian law No. 4/1994 which, 1.5 mg/L. The highest concentration of iron is 1.26 mg/L observed at site 21. High concentrations of iron might be attributed to agricultural, sewage and industrial wastewater discharged into these sites. Fluctuation of salinity is a prime factor in the coastal areas, which influences partitioning and bioavailability of metals (Mitra *et al*., 2000). The present average results of Fe (0.33 mg/L) are higher than that reported by Kondrashin and Khalifa (2013) (0.172 mg/L) in Mariut Lake.

The concentration and geographical distribution of Fe in water are given in Fig. 10. Fe element has high levels on the eastern north region because this region is near to industrial area.

Zinc concentration

Zinc occurs in small amounts in almost all igneous rocks. The principal zinc ores are sulfides, such as sphalerite and wurzite.

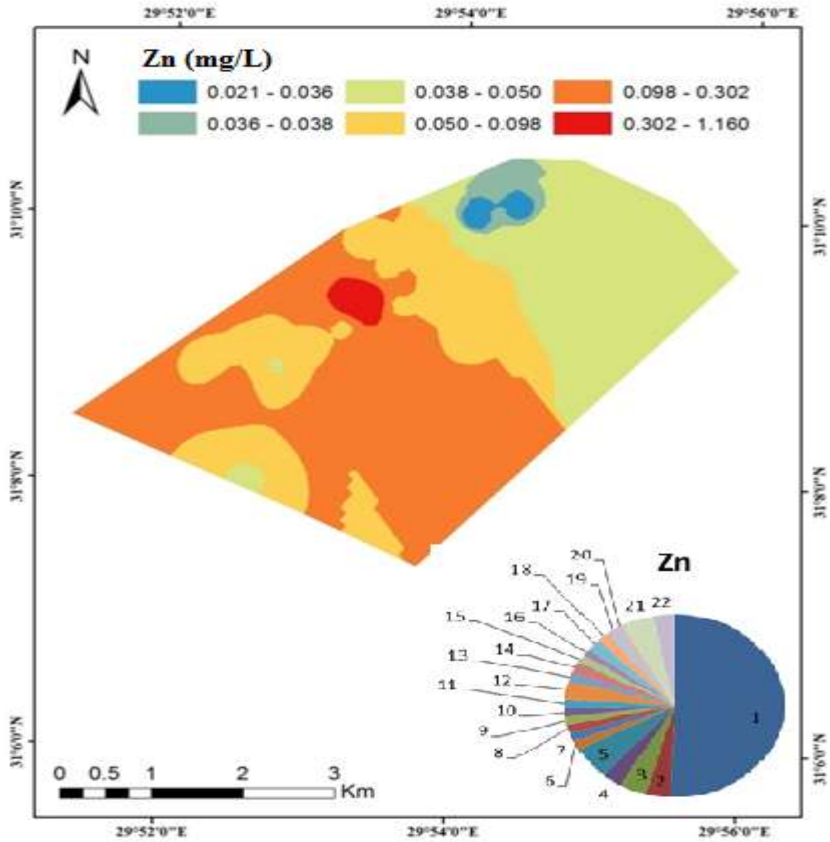

Fig. 11. Zn spatial distribution in the study area

Data showed that (Table 1) zinc concentrations ranged from 0.021 to 1.160 mg/L with an average of 0.1 mg/L. The highest concentration value of zinc, 1.16 mg/L is observed at site 1. The mean concentration of zinc is in agreement with the allowable limits to be discharged in marine environment as prescribed in Egyptian law No. 4/1994 which is (5 mg/L). The mean concentration of Zn (0.1 mg/L) in the present study is coinciding with that reported by Kondrashin and Khalifa (2013) (0.1 to 0.15 mg/L) in Mariut Lake.

The geographical distribution of Zn concentration in water is given in Fig. 11. This element has high levels on the western region due to El-Ommum Drain.

TABLE 1. Variation of heavy metal concentrations of the studied area (February 2014) .

Sample No.	Mn (mg/L)	Co (mg/L)	Cr (mg/L)	Ni (mg/L)	Cu (mg/L)	Cd (mg/L)	Pb (mg/L)	Fe (mg/L)	Zn (mg/L)
1	0.229	0.079	0.028	0.406	0.094	0.068	1.016	1.0893	1.160
2	0.171	0.069	0.029	0.407	0.060	0.015	0.980	0.576	0.085
3	0.179	0.087	0.034	0.395	0.028	0.009	1.027	0.698	0.089
4	0.191	0.086	0.038	0.398	0.077	0.0109	1.040	0.319	0.069
5	0.205	0.101	0.012	0.408	0.064	0.014	1.092	1.072	0.134
6	0.108	0.112	0.016	0.435	0.083	0.011	1.094	0.070	0.038
7	0.108	0.107	0.006	0.438	0.009	0.012	1.135	0.049	0.035
8	0.12	0.115	0.044	0.447	0.010	0.011	1.160	0.038	0.036
9	0.109	0.129	0.053	0.478	0.042	0.014	1.185	0.049	0.032
10	0.114	0.132	0.050	0.474	0.006	0.012	1.221	0.045	0.032
11	0.111	0.14	0.071	0.477	0.007	0.011	1.228	0.065	0.035
12	0.097	0.144	0.114	0.472	0.009	0.011	1.257	0.034	0.072
13	0.114	0.155	0.100	0.484	0.011	0.007	1.294	0.076	0.036
14	0.123	0.161	0.090	0.489	0.010	0.011	1.317	0.068	0.048
15	0.139	0.199	0.059	0.483	0.008	0.010	1.333	0.071	0.033
16	0.147	0.152	0.080	0.485	0.024	0.008	1.357	0.218	0.031
17	0.148	0.156	0.113	0.503	0.031	0.010	1.356	0.219	0.048
18	0.159	0.156	0.088	0.498	0.035	0.011	1.396	0.367	0.043
19	0.138	0.164	0.106	0.512	0.013	0.013	1.428	0.144	0.035
20	0.162	0.177	0.120	0.516	0.011	0.009	1.452	0.049	0.021
21	0.245	0.159	0.080	0.490	0.086	0.003	1.455	1.261	0.106
22	0.23	0.166	0.094	0.498	0.065	0.0109	1.464	0.648	0.075

Conclusion

Mariut Lake has a very important economic activity in Egypt for fish production. The results of the present study clearly demonstrate that Lake Mariut is in risk of contamination with heavy metals due to the continuous discharge of different wastes. From this study it can be concluded that using inverse distance weighting for spatial interpolation, it is possible to determine and map the heavy metals concentrations in the studied area. The result revealed that all of heavy metals concentrations matched with the allowable limits to be discharged in marine environment as prescribed in Egyptian law except of Ni metal which exceeded the allowable limits. Also, the north eastern parts of the studied area have high concentration of Mn and Fe due to human's activities and industrial area while, eastern region has high concentration of Pb, Ni, Cr and Co due to El-Kalaa drain. While, the western part of the studied area has high concentrations of Zn and Cu due to El-Ommum Drain discharges. These also, lead to conclude that the El-Qalaa canal manages to a great extent the contamination and concentration of heavy elements at Mariut Lake water.

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تقييم التوزيع المكانى لملوثات المياة ببحيرة مريوط – مصر

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أصبح تلوث المياه تهديدا متزايدا للمجتمع البشري والنظم الإيكولوجية الطبيعية في العقود الأخيرة، كما أننا فى حاجة إلى فهم أفضل للمتغيرات المكانية والزمانية للملوثات داخل النظم المائية. بحيرة مريوط هي واحدة من المناطق الحضرية الأكثر سكانا في مصر وفي العالم. تم جمع 22 عينة مائية وتحليلها لتحديد تركيزات العناصر الثقيلة مثل الكروم، المنجنيز، الحديد، الكوبالت، النيكل، النحاس، الزنك، الكادميوم والرصاص في فصل الشتاء لعام 2014. تم استخدام Inverse distance weighting analyst tools لاستكشاف وتحليل التوزيع المكاني ورسم الخرائط لتركيزات المعادن الثقيلة.

أظهرت النتائج أن جميع تركيزات المعادن الثقيلة متطابقة مع الحدود المسموح بها ليتم تصريفها في البيئة البحرية على النحو المنصوص عليه في القانون المصري ما عدا عنصر النيكل الذى تجاوز الحدود المسموح بها. كما أوضحت النتائج أن تركيز كلا من المنجنيز والحديد مرتفعة في الأجزاء الشمالية الشرقية، وهذا قد يكون راجعا إلى الأنشطة البشرية ووجود العديد من المناطق الصناعية. في حين أن المنطقة الشرقية لديها تركيزات عالية من الرصاص، النيكل، الكروم نظرا إلى مصب مصرف القلعة. ومع ذلك، فإن الجزء الغربي من منطقة الدراسة لديها نسبة عالية من الزنك والنحاس نظرا إلى مصرف العموم.

وخلصت الدراسة إلى أن النمط المكاني للمعادن الثقيلة يمكن أن يحسن فهمنا عن المصادر المحتملة، والسيطرة على العوامل المسببة للتلوث والتي تشمل العمليات التي تعتبر أساسية لرصد ومعالجة المواقع الملوثة في البحيرة .