GROUNDWATER DETERIORATION WITH HEAVY METALS IN NORTHEAST CAIRO AREA, EGYPT

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ABSTRACT

Groundwater in northeast Cairo is used for drinking, irrigation and industrial purposes. The fast development in this region and its surroundings, as well as the diverse agricultural, industrial and domestic activities, provide many sources of groundwater pollution; such as smelters, industrial effluents, construction debris, and drainage wastes. The pollution leads to deterioration in groundwater quality which affected the human's health, plants and animals. Twenty two groundwater samples from Quaternary aquifer are collected and chemically analyzed to determine the areal distribution of heavy metals concentrations in the area between Anchas and Abu Zaabal at northeast Cairo. The concerned heavy metals include Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. High concentrations of Cd, Co and Pb are recorded in most of the collected samples.

Keywords and Phrases: Groundwater Deterioration, pollution, Heavy Metals, Cluster analysis, Egypt.

INTRODUCTION

There is a growing consensus among scientists, international organizations and lay persons that water contaminations are endemic environmental issue in fast growing cites. Continuous urbanization of the Nile Delta and surroundings has led to an increase in the contamination of soil and water resources, creating a potential health risk of epic proportions. Due to increasing population density in these areas, groundwater quality is strongly influenced by anthropogenic activities (industrial and agricultural activities). Therefore, this groundwater accumulates different types of contaminants from non-point and/or point sources pollution. Nowadays, Egypt is vulnerable to confrontation a serious problem of the shortage in water. Subsequently, the groundwater represents an important source to satisfy the urgent demand for water for different purposes such as drinking, domestic, irrigation and industrial uses.

Geochemical characteristics of groundwater, particularly the levels of heavy metals are significant factors in controlling groundwater usage and for health considerations (Baba and Tayfur, 2011 and Yehia *et al*., 2017). Assessment of the heavy metals concentrations in groundwater sources is important in protecting the population against toxicity (Yuce *et al.*, 2009). Exposure to very low levels of heavy metals such as lead, chromium, cadmium and mercury have an adverse cumulative effects on human and environment (Carter and Fernando 1979). The dreadful health effects of exposure to these heavy metals are well documented in previous literature in Egypt and worldwide (Dietrich *et al*., 2004; Salem et al., 2000; Rajappa *et al.*, 2010; Anyakora *et al*., 2011 and Mousavi *et al.,* 2013).

Owing to industrial and agricultural activities, large amounts of untreated urban municipal, industrial wastewater and rural domestic wastes discharge into the Nile River, canals or agricultural drains which become an easy dumping site for all kinds of wastes (Stahl and Ramadan, 2008). Ismailia Canal represents the most distal downstream of the main Nile River. Thus its water contains all the proceeded pollutants discharged into the Nile. Ismailia

Canal has many sources of pollution which potentially affects and deteriorates the water quality of the canal (Geriesh *et al.,* 2008; Goher *et al.,* 2014 and Safar *et al.,* 2014).

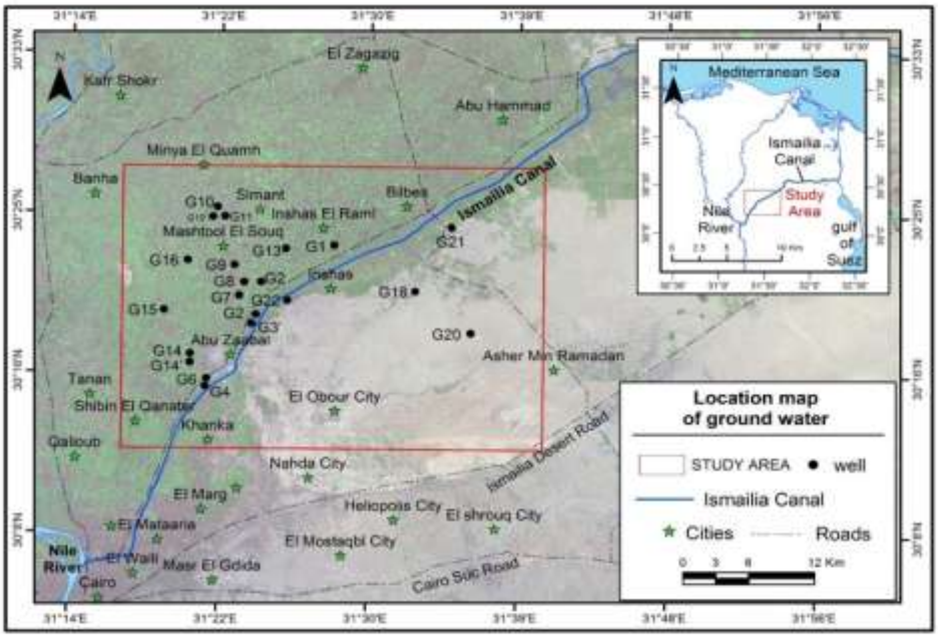
The present study aims to study the heavy metals contamination levels in the groundwater of the Quaternary aquifers in the northeast Cairo region, as well as, tracking the potential sources of these metals.

MATERIALS AND METHODS

1 Study Area: The study area lies nearly between Anshas and Abu Zaabal. It is bounded by Longitudes 31° 27’, 31° 67’ E and Latitudes 30° 20’, 30° 46’ N (Fig 1). The average temperatures in the study area depend on the time of the year. The highest degrees are recorded in July and August where they reach 38 degree centigrade. The maximum monthly precipitation recorded reached 4 mm in January and March where the lowest one reached in January and July with a value of zero, so it is considered a dry area (Meteoblue.com 2016).

Several industrial and agricultural activities are recorded in Abu Zabaal and Anshas respectively. The industrial activities in the area include the factory of phosphatic fertilizers, a great number of smelters, National company for metal industries, Mustafa Center for automotive paint, Swissy factory for chemicals, Paper Mill, Mowad Group for manufacture of glass, Chemical plant united for developed industries (Lasheen), Letos factory, Sham textile industries, Sherif factory, Grand bed Egypt factory, Warehouse Rod Line Co., LTD, Aracemco ceramics factory, Egyptian alum factory and Abu Zaabal factory.

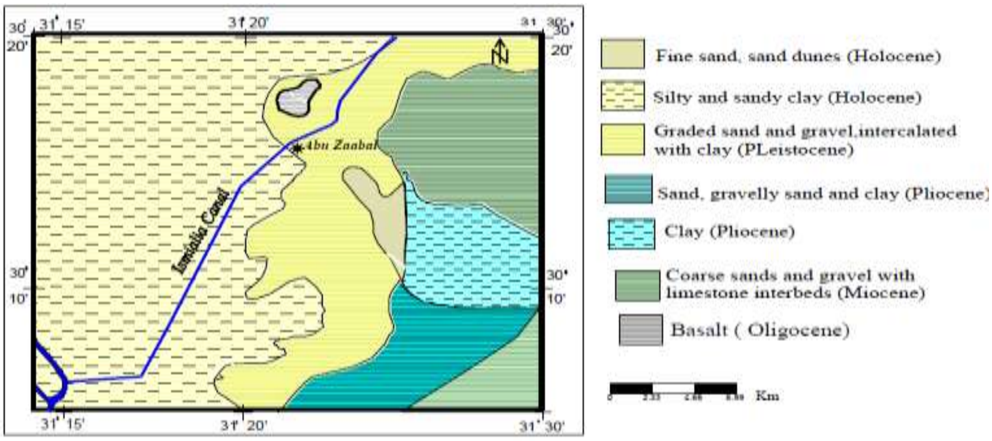
There are many villages located very close to Ismailia canal which constitute potential sources of pollution to surface and groundwater resources.



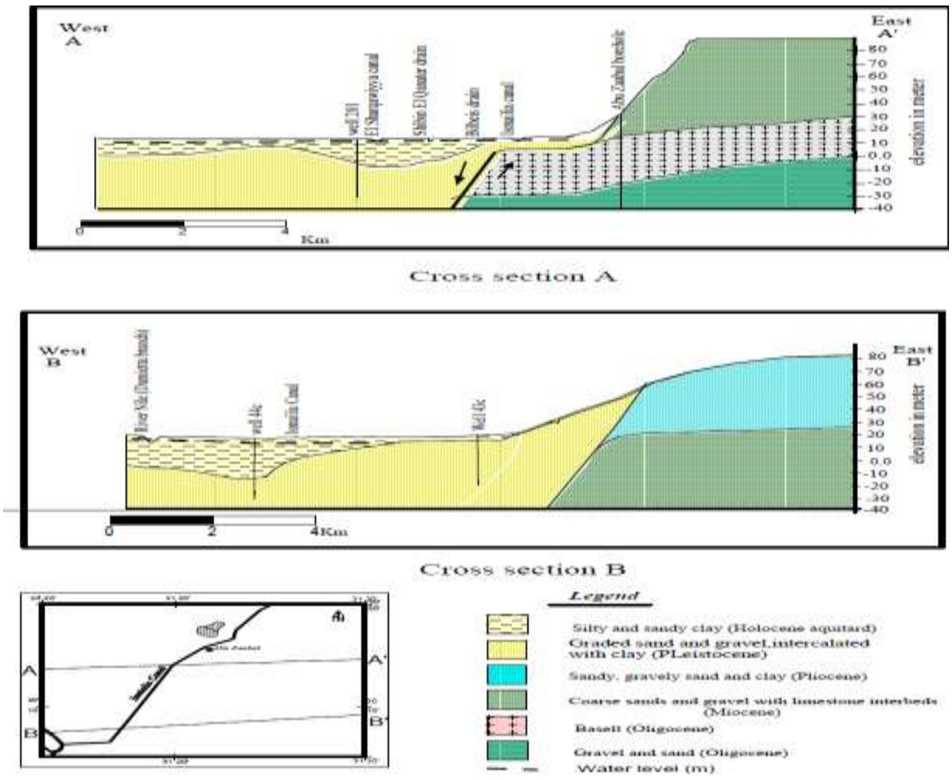
Fig(1): Location map of the study area showing groundwater samples

2 Geologic and Hyrogeologic Settings: The Quaternary sediments which belonging to the Pleistocene and Holocene cover almost all the study area. Basaltic rocks belonging to Upper Oligocene age exposed at Abu Zaabal Quarries while Miocene and Pliocene sediments outcrop at the eastern portions (Fig 2) (RIGW, 1989 and El Fakharany and Mansour, 2009).

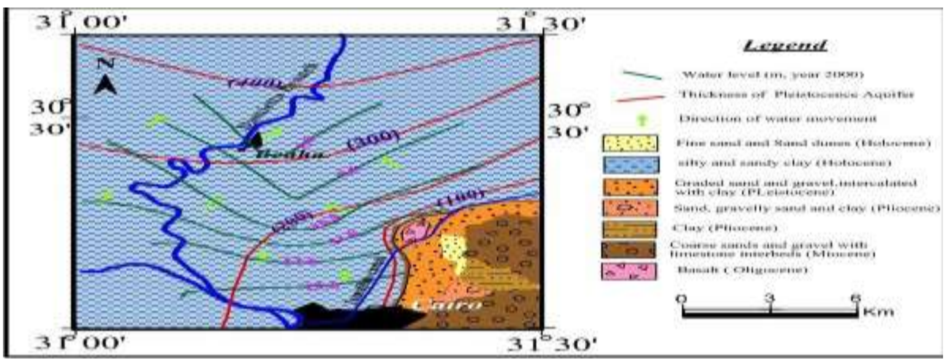
The Quaternary aquifer around the Ismailia Canal consists of two hyrogeologic units. The shallow one, especially along the eastern downstream, consists of fine sand and silts mixed with clays and evaporate with thickness varied between 10 and 30 m. The deeper one is of especial importance for the water supply in the region, which consists of fluviatile deposits forming sequence of loose gravely sands alternating with clay and mud lenses. The thickness of this sequence amounts up to 200 m along the canal course. The salinity of the groundwater in the shallow aquifer ranges between 340 mg/l and 7650 mg/l of Na-mix (no dominant anion) to Na-Cl type, respectively. The low salinity water is detected in the areas close to the canal course revealing the effect of aquifer recharge by the canal water. The salinity of the deeper aquifer rarely exceeds 1500 mg/l and is mainly of Na-mix type. The Quaternary aquifer unconformably overlies the Miocene and Oligocene rocks. Along the western side, Oligocene gravely sands and basaltic sheets are exposed on the surface along the canal enabling external recharge source for the canal water, especially during the winter (Fig 3). The groundwater flow is directed toward the east and northeast and finally discharged into the Suez Canal and its lakes to the east or into the Lake Manzala to the northeastern side (Fig 4) (Geriesh *et al*., 2008).



Fig(2): Simplified geologic map of the study area (after RIGW, 1989)



Fig(3): Hydrogeological cross sections at different locations (After RIGW, 1989).



Fig(4): Flow lines of groundwater, the Quaternary aquifer, East Cairo area, Egypt (modified after RIGW 1992; Geriesh *et al*., 2008).

3 Sampling: Twenty two groundwater samples are collected from the area of Anshas – Abu Zaabal (Fig 1). The accurate sampling locations were determined using GPS. Samples were collected after 10 min of pumping and were stored in acid-leached polyethylene bottles and preserved by adding ultra-pure nitric acid (5 mL/l). Sampling was handled according to the standard methods for examination of water (APHA, 1999).

4 Chemical Analysis: To determine the heavy metals concentrations in groundwater samples, they are filtered by using filtration system through 0.45 μm-pore-diameter filter paper. Filtration of the groundwater samples aims to minimize the effect of suspended materials on the actual concentration of heavy metals. They are analysed by using of Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) with ultrasonic Nebulizer (USN). This Nebulizer decrease the instrumental detection limits by 10%, this ICP instrument is Perkin Elmer Optima 3000, USA.

5 Statistical analysis: In order to exhibit the relationship between heavy metals, correlation coefficients and cluster analysis (CA) are identified using IBM SPSS 20. Correlation coefficient is usually used to establish the relation between independent and dependent variables (Nair *et al.*, 2005).

Cluster analysis is used to group data into hierarchies based on similarities or dissimilarities. There are two types of cluster analysis: R and Q-modes. R-mode was performed on different water quality variables. Q-mode cluster analysis was performed on the water chemistry data to group the samples in terms of water quality (Davis, 2002). In the present study, CA was applied to group groundwater samples for Cd, Cr, Cu, Fe, Mn, Ni, Pb and Zn content.

RESULTS AND DISCUSSION

1 Metal Distribution: Table (1) shows the concentrations of heavy metals in the study area including Cd, Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn. The concentrations of Cd, Cr and Pb range from 0.010 to 0.018, 0.065 to 0.271 and 0.114 to 0.184 ppm respectively. Spatial distributions of the heavy metals concentrations in the groundwater samples of the study area (Figs 5 and 6), shows that the highest values of pollution are recorded at Abu Zabaal region and its vicinity which is characterized by intensive industrial activity.

The concentration of (Cu) in the groundwater of the Quaternary aquifer in the study area ranges from 0.006 to 0.082 ppm. The spatial distribution of (Cu) in the collected samples indicate an increase of its concentration in the direction of south Abu Zaabal, but it doesn't exceed the international standards for drinking water. The concentration of (Ni) in the groundwater of the study area ranges from 0.011 to 0.247 ppm and its distribution shows high concentrations in the areas of Abu Zaabal, Mashtool, Tal El Yahoudia, Belbees Road, Shebeen El Qanater, Al Adlya Farm and Anshas, which not far from Abu Zaabal source pollution represented in the intensive industrial activity and inappropriate methods for dumping industrial wastes.

The concentration of (Zn) in the groundwater of the study area ranges from 0.003 to 0.488 ppm and shows relatively high concentration in two samples which lying in Anshas and Abu Zaabal, but within the normal range.

The concentration of (Fe) ranges from 0.058 to 2.105 ppm. The spatial distribution of (Fe) shows high concentrations in regions of Anshas El Raml, Mashtool and El Adlya, but it exceeds the standard just in Anshas El Raml (2.105 ppm). The concentration of (Mn) in the groundwater of the study area ranges from 0.007 to 1.063 ppm. The distribution of (Mn) in the groundwater of the study area shows several high concentrations such as in G1, G9, G11 and G16, while it exceeds limit only in Anshas El Raml (Figures 5 and 6). The Co is below detective level in all samples (BDL).

The results show that the duplication ratio between the recorded concentrations and the international standards varies from about 400% to 960%, 300% to 600% and 1200% to 1700 %, for Cd, Cr and Pb respectively.

There are many possible sources of contamination by heavy metals. They include wastes from industrial chemical production, metal plating operations, domestic wastewater and pesticide runoff from agricultural lands. The traditional method of collecting and discharging wastewater using septic tanks lead to wastewater leakage, which severely affect soil and groundwater properties.

Table(1): Concentration of heavy metals in groundwater samples of the study area (ppm)

Sample No.	Location	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
G1	**Anshas El Raml**	0.012	BDL	0.176	0.024	2.105	1.063	0.014	0.148	0.115
G2	**Mashtool – El Ghafarya**	0.012	BDL	0.260	0.043	0.309	0.019	0.013	0.114	0.019
G3	**Al Monier**	0.013	BDL	0.143	0.006	0.058	0.032	0.011	0.136	0.003
G3'	**Al Monier**	0.012	BDL	0.092	0.032	0.379	0.026	0.010	0.128	0.012
G4	**Abu Zaabal (fawzy Farm)**	0.014	BDL	0.188	0.295	0.188	0.038	0.020	0.170	0.272

Cont. Table(1):

Sample No.	Location	Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn
G6	**Abu Zabal Maqaber**	0.014	BDL	0.271	0.064	0.271	0.048	0.041	0.151	0.052
G7	**Mashtool (Usama Farm)**	0.010	BDL	0.160	0.020	0.409	0.035	0.023	0.125	0.011
G8	**Mastool**	0.012	BDL	0.224	0.014	0.466	0.240	0.011	0.127	0.066
G9	**Mashtool**	0.014	BDL	0.236	0.016	0.530	0.300	0.015	0.134	0.005
G10	**Mashtool (Kafr Ebrash)**	0.017	BDL	0.169	0.037	0.169	0.101	0.016	0.146	0.063
G10’	**Mashtool (Kafr Ebrash)**	0.013	BDL	0.110	0.155	0.110	0.297	0.014	0.137	0.086
G11	**Mashtool (Kafr Ebrash)**	0.013	BDL	0.153	0.020	0.153	0.522	0.018	0.133	0.020
G13	**Meniat Salamant**	0.013	BDL	0.133	0.041	0.133	0.069	0.010	BDL	0.028
G14	**Tal El Yahodya**	0.017	BDL	0.215	0.017	0.215	0.029	0.033	0.161	0.040
G14’	**Tal El Yahodya**	0.014	BDL	0.118	0.082	0.751	0.021	0.018	0.127	0.020
G15	**Shebeen El Qanater (AlAhwaz)**	0.015	BDL	0.065	0.100	0.566	0.389	0.022	0.133	0.020
G16	**Shebeen Elqanater(Kafr Saad Behairy)**	0.014	BDL	0.091	0.060	0.539	0.396	0.017	0.127	0.032
G18	**Belbees Road**	0.015	BDL	0.156	0.015	0.302	0.010	0.026	0.165	0.007
G19	**Dr Ayman El Hadidy Farm**	0.018	0.001	0.313	0.012	0.747	0.012	0.042	0.165	0.022
G20	**El Adlia Farm**	0.018	BDL	0.385	0.013	0.139	0.013	0.047	0.163	0.026
G21	**Belbees Air Base**	0.013	BDL	0.105	0.019	0.124	0.007	0.015	0.127	0.023
G22	**Anshas**	0.014	BDL	0.252	0.025	0.529	0.112	0.027	0.153	0.488
Drinking Water MAC*		0.003	NM	0.05	2	1	0.5	0.02	0.01	3

BDL = below detection limit, NM = Not mentioned, MAC = Maximum allowable limit, *= WHO (2011)

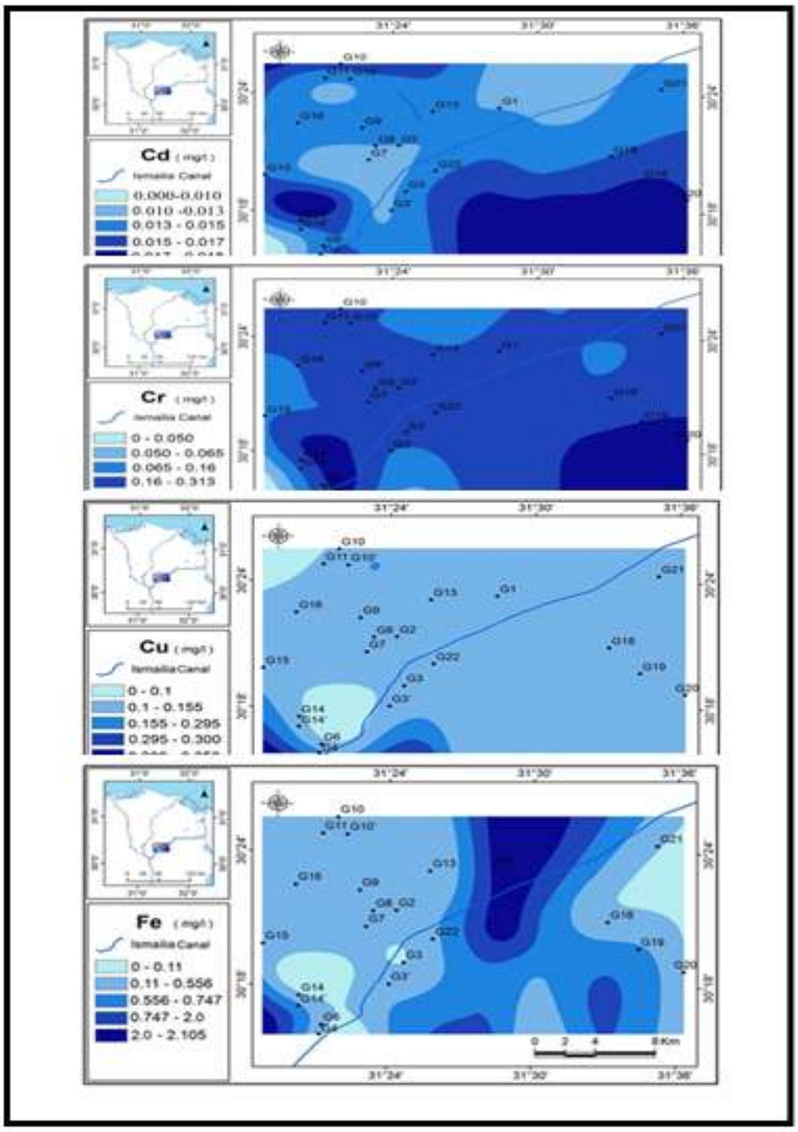


Fig.(5): Concentrations of Cd, Cr, Cu and Fe in the groundwater of the study area

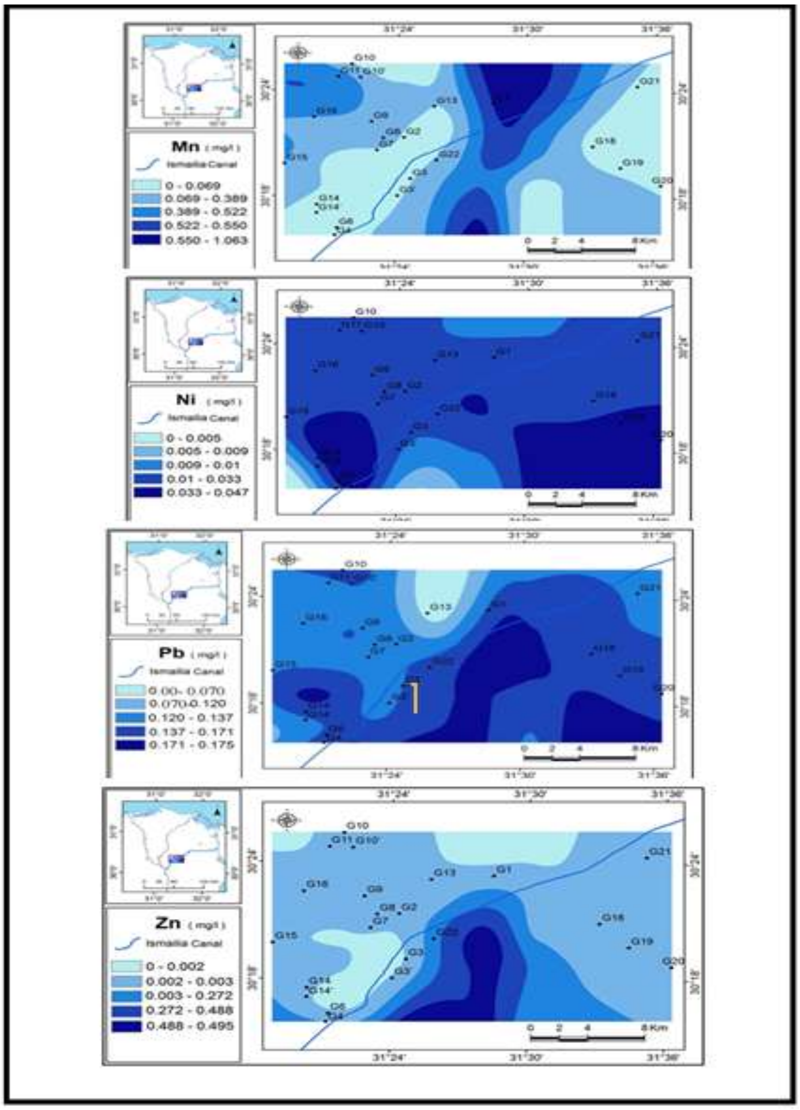


Fig.(6): Concentrations of Mn, Ni, Pb and Zn in the groundwater of the study area

2 Suitability of Groundwater for drinking: A comparison with several local and international standards and guidelines for drinking water has been done to evaluate heavy metals content in groundwater to show its suitability for drinking (Table 2).

Table(2): Suitability of Groundwater for drinking and duplication ratio based on heavy metals content

Metal	ESDW, (2007)	WHO, (2011)	ADWG, (2011)	Samples Exceed	Percentage %	Duplication Ratio to WHO standards
Cd		0.003		All Samples	100%	400-960%
Cr	0.05	0.05	0.05	All samples	100 %	300-600%
Cu	2	2	2	------	-------	---------
Fe	0.3	1	0.3	G 1	4.3 %	200%
Mn	0.4	0.5	0.4	G1 and G11	9 %	300%
Ni	0.02	0.02	0.02	8 samples	36.3 %	35-100%
Pb	0.01	0.01	0.01	Most samples	95.4 %	1200-1700%
Zn	3	3	3	------	-------	------

Groundwater samples of the study area contain high concentrations of heavy metals that exceed the recommended limits in drinking water particularly for Cd, Cr and Pb, where they exceed the recommended limits in 100%, 100% and 95.4% of the studied samples, respectively. Cu, Fe, Mn, Ni and Zn don't exceed the recommended limits in all samples, while Co is below the detective limit.

3 Comparison with different parts of the Nile Delta: A comparison between the concentrations of heavy metals in the groundwater of the present study and those of other areas are shown in Table (3). The comparison revealed that the groundwater of the study area contains higher concentrations of lead and Chromium which may be assigned to the intensive industrial activity of Abu Zaabal region and its surroundings. So, it can be said that the groundwater of the study area is heavily polluted with lead and Chromium that it is not suitable for drinking.

Table(3): A Comparisons between maximum concentrations of heavy metals in the study area and those in different parts of the Nile Delta.

Location	Heavy Metals Maximum Concentration (ppm)								Reference
	Cd	**Co**	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	
Anshas - Abu Zaabal	0.018	BDL	0.385	0.82	2.105	1.063	0.247	0.184	Present study
Northwestern Part of the Nile Delta	0.710	------	0.045	1.895	4.200	0.821	0.580	0.020	Awad et al. (2015)
Dakahlyia Governorate	0.003	------	0.004	-------	0.085	0.023	0.023	0.009	Mandour and Azab (2010)
Southeast Nile Delta	0.0007	0.0009	0.0215	0.0332	2.633	0.0864	0.003	0.014	Khalaf and Gad (2015)
East Delta	BDL	BDL	0.0308	0.2293	0.509	0.2087	0.011	BDL	GAD et al. (2015)
Western Nile Delta	0.0040	--------	0.046	0.100	4.20	0.40	3.100	0.005	Sharaky et al. (2007)
Southeast Nile Delta	0.097	-------	-------	0.760	0.531	0.58	------	0.148	Taha et al. (2004)

4 Potential Sources of Pollution with Heavy Metals: Recently, the industrial activities attract attention of many authors as point and non-point pollution sources in this area. The industrial area of Abu Zaabal and its surroundings may constitute a primary source of pollution of surface water with heavy metals which may infiltrate to the groundwater (Table 4).

Table(4): Metal concentrations related to industrial activities in the study area

Location	Type of Sample	Heavy Metals Maximum Concentration									Reference
		Cd	Co	Cr	Cu	Fe	Mn	Ni	Pb	Zn	
Awadulla Lead Smelter	Bulk Dust	9.50 mg/kg	—	338.00 mg/kg	—	—	—	—	782625.00 mg/kg	6691.50 mg/kg	Safar et al., 2014
	Soil Sample	3.25 mg/kg	—	N.D	—	—	—	—	5350 mg/kg	849 mg/kg	
Beside lead smelter	Dust	5.08 µg/g	26.2 µg/g	29.57 µg/g	—	—	—	907.5 µg/g	1102. µg/g	311.52 µg/g	Ali et al. 2011
Central of Abu Zaabal	Dust	3.95 µg/g	19.9 µg/g	26.09 µg/g	—	—	—	415 µg/g	112 µg/g	175.47 µg/g	Ali et al. 2011
100 m Eastern of Fertilizer plant	Dust	16.69 µg/g	53.3 µg/g	69.84 µg/g	—	—	—	787.4 µg/g	497.5 µg/g	786.4 µg/g	Ali et al. 2011
In front of Abu Zaabal factory	Sediment	0.29 ppm	31.2 ppm	—	37.11 ppm	—	208 ppm	33.44 ppm	37.15 ppm	158 ppm	Nour et al., 2013
Discharging point of Misr Petroleum Company	Surface Water	—	N.D.	0.053 ppm	0.58 ppm	2.608 ppm	—	—	0.166 ppm	0.80 ppm	Khalil et al., 2012
Discharging point of Abu Zaabal fertilizer and chemical Company	Surface Water	—	N.D.	0.092 ppm	0.392 ppm	3.199 ppm	—	—	0.234 ppm	0.234 ppm	Khalil et al., 2012

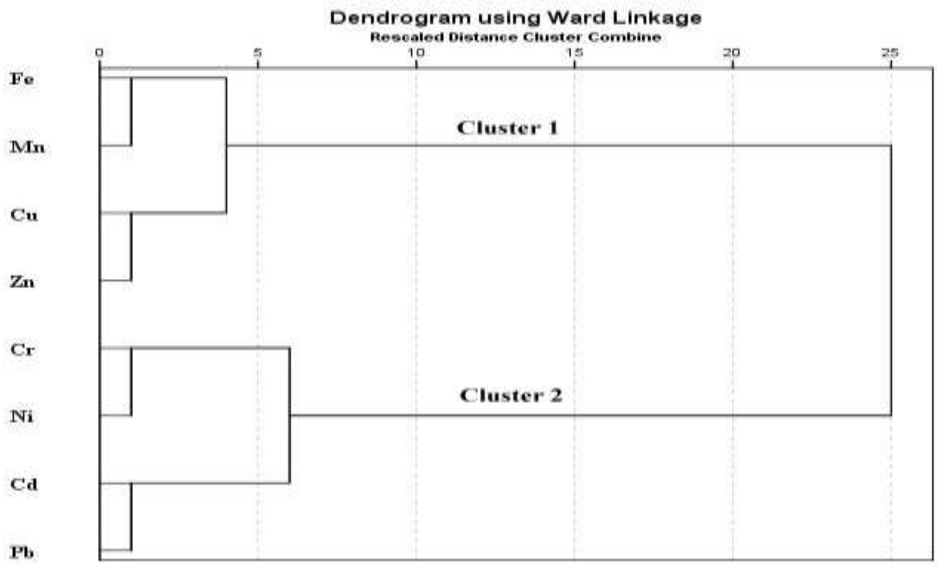
5 Statistical analysis: The groundwater samples are used for the correlation coefficient and cluster analyses. Significant positive correlations between Cd and Cr (0.451), Cd and Ni (0.675), Cr and Ni (0.692), Fe and Mn (0.726) and between Ni and Pb (0.509) are recorded (Table 5). Co was excluded due to it is not detected in more than 50% of the samples.

The results of cluster analysis (CA) are performed in Ward's method (Fig. 7). The dendrogram exhibits two groups of clusters Cluster 1 (Fe, Mn, Cu and Zn) and Cluster 2 (Cr, Ni, Cd and Pb).

The significant positive correlation between Cd, Cr, Ni and Pb and the clustering of these heavy metals in one group indicating the anthropogenic source of contamination in the studied groundwater (Moore et al., 2011).

Table(5): Correlation matrix of the heavy metals for the study area

	Cd	**Cr**	**Cu**	**Fe**	**Mn**	**Ni**	**Pb**	**Zn**
Cd	1	.451*	-.042	-.148	-.248	.675**	.406	-.007
Cr		1	-.219	.005	-.218	.692**	.345	.183
Cu			1	-.127	-.026	-.098	.127	.352
Fe				1	.726**	-.059	.139	.121
Mn					1	-.281	.021	.051
Ni						1	.509*	.076
Pb							1	.234
Zn								1
*. Correlation is significant at the 0.05 level (2-tailed).								
**. Correlation is significant at the 0.01 level (2-tailed).								



Fig(7): Dendogram for 8 variables from cluster analysis in R-mode

CONCLUSION

The concentrations of the heavy metals of the area between Anshas and Abu Zaabal, northeast Cairo, reflect the following results; the concentrations of Cadmium, Chromium and Lead in most samples are exceeding the international standards. The increase of concentration of heavy metals reflects an increase of pollution in the study area due to mainly industrial activities (Table 4). Most samples of groundwater have concentrations exceeding the international standards and not valid for drinking due to the high concentrations of these three heavy metals.

RECOMMENDATIONS

1- Law 48/1982 for the protection of the Nile River and its waterways against pollution must be enforced strictly to prevent the deterioration of water and to improve its quality.
2- Researches are required to complete the picture about the safety of groundwater and surface water of the study area for drinking, irrigation and domestic purposes.
3- Lining irrigation canals and Installing proper drainage and sewage systems in highly populated areas are highly recommended.
4- Using deep penetrated groundwater wells instead of shallow ones where pollution may be less.

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تدهور نوعية المياه الجوفية بالعناصر الثقيلة في المنطقة الواقعة شمال شرق القاهرة – مصر

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مستخلص

تستخدم المياه الجوفية في شمال شرق القاهرة للشرب والري والأغراض الصناعية. لذا يؤدي تلوث المياه الجوفية إلى تدهور نوعيتها الأمر الذي يؤثر في صحة الإنسان والنبات والحيوان. تهدف هذه الدراسة إلى توصيف تدهورالمياه الجوفية في خزان العصر الرباعي بتلوثها بالمعادن الثقيلة ولإجراء هذه الدراسة تم جمع اثنتان وعشرون عينة من المياه الجوفية من الآبار الضحلة وتحليلها

لتحديد تركيزات المعادن الثقيلة لمياه العينات التي تمت دراستها في المنطقة الواقعة بين أنشاص وأبو زعبل، شمال شرق القاهرة، حيث نوقشت تراكيزت المعادن الثقيلة التي تشمل: الكوبلت والكروم والكادميوم والرصاص والنيكل والنحاس والزنك والمنجنيز والحديد. وقد استخدم برنامج ArcGIS الإصدار ١٠,١ لتمثيل التوزيع المكاني لتركيزات هذه المعادن للإفادة من النتائج التي تم الحصول عليها من منطقة الدراسة.

وقد وجد أن الكروم والرصاص والكادميوم، على وجه الخصوص، تتعدى تركيزها النسب المسموح بها عالمياً في معظم العينات، وبذلك تكون المياه الجوفية في الآبار الضحلة للخزان الجوفي للعصر الرباعي غير صالحة للشرب، وفي حالة استخدامها يتسبب ذلك في الكثير من الأمراض الخطيرة للإنسان والحيوان على حد سواء. ويمكن تقديم بعض التوصيات للحد من تلوث المياه الجوفية بالعناصر الثقيلة أو تقليل تاثيرها ويتضمن ذلك ضرورة وضع معايير بيئية قانونية صارمة من أجل منع وصول المواد الملوثة إلى خزانات المياه الجوفية، كذلك الحفاظ على المجاري المائية وحمايتها من التلوث، ومنع تسرب الملوثات من المناطق الزراعية القديمة والمناطق المستصلحة الحديثة، ولابد من نقل المناطق الصناعية إلى خارج المدن وتجنب إلقاء المخلفات الصناعية في المجاري المائية لأنها تنقل الملوثات إلى خزانات المياه الجوفية الضحلة، كذلك ضرورة استخدام خزانات المياه الجوفية العميقة حيث يقل التلوث فيها بدلاً من الآبار السطحية.

كذلك لوحظ أن هناك مصادر عديدة أخرى للتلوث في منطقة الدراسة تؤدي إلى تدهور نوعية المياه الجوفية مثل المصاهر، والنفايات السائلة الصناعية، وحطام البناء، ونفايات الصرف.