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USING HEAVY METALS CONCENTRATIONS AS AN INDICATOR FOR ENVIRONMENTAL CONTAMINANT TRANSPORT IN EGYPTIAN SANDY SOIL

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ABSTRACT

The available heavy metals concentrations were measured in two cores of sandy soil in Abu Rawash area by DTPA extraction techniques using ICP-MS instrument and it was noted that the top cultivated soil is higher in content of the heavy metals than the other subsurface units and sewage water led to increase the concentration of available heavy metals according to the following order, Cu (34.72 fold) > Cd (22.86 fold) > Pb (5.91 fold) > Zn (4.98 fold) > Ni (4.86 fold) > Fe (3.44 fold) > Co (2.67 fold) > Mn (1.62 fold) than the un irrigated soil. The accumulation of trace elements concentrated in the root zone up to 30cm more than in the other sub layers. On the other hand, Sewage irrigation led to increase soil acidity and soil organic matter percentage in the top layers.

Key words: Abu Rawash, pollution, trace elements, sewage sludge

INTRODUCTION

Holdgate (1979, cited in Alloway, 1990) defined pollution as 'The introduction by man into the environment of substances or energy liable to cause hazards to human health, harm to living resources and ecological systems, damage to structures or amenity, or interference with legitimate uses of the environment'. Similarly, Bowen (1979, cited in Pendias and Pendias, 1992), suggested that when the rate of mining of a given element exceeds the natural rate of its cycling by a factor of ten or more, the element must be considered a potential pollutant. Soil pollution has become one of the most important environmental issues in the last decade and as a result more research is now being carried on this problem.

Of the various pollutants now found in soils, heavy metals are gaining increasing attention because, unlike most organic pollutants, they do not degrade in soils but rather accumulate and thus may increase in toxicity.

Abu Rawash area (Figure 1) is one of the Egyptian areas that is subjected to some environmental contamination due to the prolonged time of wastewater disposal during irrigation that practices environmental contamination in soil and groundwater. Heavy metals are a type of these contaminants that may be found in both polluted and unpolluted soils.

Although these metals occur naturally in the earth's crust, they tend to accumulate in agriculture soil because of irrational application of commercial fertilizer, manures, and sewage sludge that contains heavy metals as well as contamination caused by mining and industry. Potential hazards associated with heavy metals pertain to their accumulation in soils which may (1) lead to a plant toxicity condition or (2) result in increasing uptake of metals into the food chain. Ten elements of primary concern are arsenic, boron, cadmium, copper, mercury, molybdenum, nickel, lead, selenium, and zinc. Cadmium has the most dangerous long-term effects on human health; many of these are amplified in the food chain.

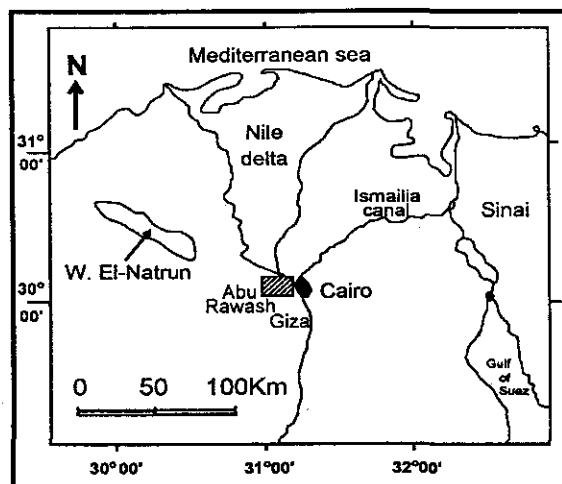


Figure (1): Location map of the study area

In recent years, however, public concern has steadily risen about the safety of this practice and about the potential for metals to accumulate in soils to levels causing phytotoxic conditions or to accumulate in plants at levels that adversely affect the health of consumers (McGrath *et al.*, 1994; McBride, 1995).

Soil pH and organic matter are the most agents that control the concentration of these heavy metals and its distribution in soil. Soil pH is an indicator for the soil chemistry and fertility. The soil pH affects the chemical activity of the elements in the soil, as well as many of the soil properties. The pH of soil control many of the chemical and biological activities that take place in soil and also reflect changes in climate, vegetation and hydrologic conditions under which the soil formed. The pH of soil horizon is affected by the parent material, and the activity of organisms (plants, animals, and microorganisms) living in the soil

More recently, there has also been concern that heavy metals may be leached below plant rooting zones and contaminate groundwater supplies (McBride *et al.*, 1997; Richards *et al.*, 1998). Heavy metal concentration in subsoil depend on short and long term sludge applications that usually did not show significant increases in total heavy metal concentrations below an approximately 30-cm depth in the profiles (Chang *et al.*, 1984). In the few cases where transport of heavy metals was noticeable below the root zone, penetration usually remained shallow (Campbell and Beckett, 1988), for example, found significant increases of Cu and Zn concentrations to a depth of merely 40 : 60 cm.

It has been proposed that the diethylene triamine pentaacetic acid (DTPA) extracted fraction of micronutrients from soils is a good estimate of that which is available for plant uptake (Lindsay and Norvell, 1978). Some reports demonstrated that the DTPA-extraction of soil could be used to evaluate the available level of heavy metals for plant.

Trace metals, often referred to as heavy metals are found naturally in soils usually in amounts less than 1% (Alloway, 1990). They originate in geological materials, mainly igneous and metamorphic rocks, and are gradually released to the soil through chemical and physical weathering of rocks and the pedogenic processes (Kabata-Pendias, 1992). Anthropogenic activities have also contributed to metals in soils (Ross, 1994).

The major anthropogenic sources include mining and smelting activities, industrial practices and materials (plastics, textiles, wood preservation, refineries), atmospheric deposition (incineration, automobile exhausts, fossil fuel and coal combustion), agricultural inputs (fertilizers, liming materials, pesticides, manures, irrigation waters), and disposal of wastes (sewage sludge, leachate from landfills, swap heaps) (Alloway, 1990; Ross, 1994). Many of these sources result in release or deposition of metals onto the surface of the soils where they tend to accumulate and interact with soil constituents including soil organisms (Vernet and Friedland, 1992).

Soil is an important sink for trace metals such that most of the trace metal inventory in an ecosystem is in the soil (Adriano, 1986). Geochemically, when metals are introduced into soil, they end up in one of the following fractions:

- (1) Dissolved in soil solution as simple or complexed ions.
- (2) Adsorbed onto exchange sites of oxides and hydroxides of Mn, Fe, and Al.
- (3) Precipitated in compounds such as carbonates, phosphates, sulfides.
- (4) Adsorbed on exchange sites with organic matter.
- (5) Adsorbed on the clay-humus colloidal complex.
- (6) Fixed in the crystal lattice-structure of soil minerals.
- (7) Included in the stable organic complexes in humus (Alloway, 1990; Lake *et al.*, 1984).

Another important soil property influencing metal behavior is the type and amount of organic matter present in the soil. Organic matter can have a wide variety of functional groups including carboxyl, phenolic, hydroxyl, carbonyl, ester and possibly quinone and methoxy groups which all possess exchange sites for binding or chelating metals (Alloway, 1990).

MATERIALS AND METHODS

After surveying the study area, some agricultural sites were selected for soil sampling on the studied area during which two cores of sandy soil (0-100 cm depth) were collected. Sewage sludge was the main source of irrigation in the first core and groundwater (105m depth) was the main source of irrigation in the second one. Every core was divided to 10 layers with 10cm thickness. All soil samples were

air dried, passed through a sieve of 2-mm mesh width and homogenized.

Soil pH was measured for all samples in (1:1) soil water extraction by pH meter (W.T.W) instrument according to (McLean, 1982), organic matter was measured according to by chromic acid oxidation method according to (Walkly, 1947).

Available Fe, Mn, Cu, Ni, Co, Pb, Cd, and Zn contents were demonstrated by using the extract with the aid of DTPA extraction solution (0.005 M DTPA, 0.01 M CaCl₂, and 0.1 M triethanolamine TEA) buffered at pH 7.30. The DTPA extraction involved a soil-solution ratio of 1:2 and reaction time was 2 h. The extracting solution was that developed by Lindsay and Norvell (1978). Trace elements were determined by ICP-MS. Two reference materials, which have DTPA extractions certified values for several heavy metals, were analyzed in parallel to ensure the quality of the results obtained.

RESULTS AND DISCUSSIONS

Soil pH:

Data in Table (1) and Figures (2 and 3) revealed that the pH value was depending on the source of irrigation as sewage water causes a detectable decrease in pH values (increase soil acidity) in the top layer in core one by about 1 pH unit than the normal pH values in most soil samples. Below the root zone in core one, the pH values increased gradually to reach the normal pH with depth. These results were in agreement with those obtained by El-Gamal (1980) i.e. the pH value ranges from 6.55 in core one (polluted with sewage water) to 7.81 in core two (groundwater irrigation). The decrease in pH values of soil irrigated with sewage water is due to the CO₂ released from the microbial activity during the decomposition of organic residues and also to the organic and inorganic acids introduced into the soil system from sewage water (Kononove, 1961). These result agreed with this obtained by Omar 2003.

Soil organic matter:

The obtained results of SOM of the two cores are presented in table (1) and figure (3), the data explained that the percentage of soil organic matter is high in the top layer, 0-10cm, in core one (1.79%) in comparison with the same layer in core two (0.68). It followed by a decrease in soil organic matter percentage with depth up to 40 cm

depth. Below 40 cm depth (root zone) there are no variations between the two cores in SOM%.

Table (1): The pH values and SOM percentage in sandy soils.

Sample depth (cm)	pH		SOM	
	Core one	Core two	Core one	Core two
0-10	6.85	7.81	1.79%	0.68%
10-20	6.94	7.85	1.02%	0.34%
20-30	6.81	7.74	0.27%	0.20%
30-40	6.88	7.79	0.20%	0.17%
40-50	7.22	7.84	0.17%	0.17%
50-60	7.38	7.88	0.17%	0.17%
60-70	7.72	7.91	0.17%	0.17%
70-80	7.82	7.94	0.17%	0.17%
80-90	7.81	7.95	0.17%	0.17%
90-100	7.84	8.02	0.17%	0.17%

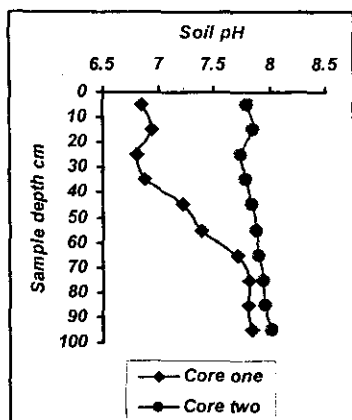


Fig (3): Variation in pH values with depth in core one compared with core two.

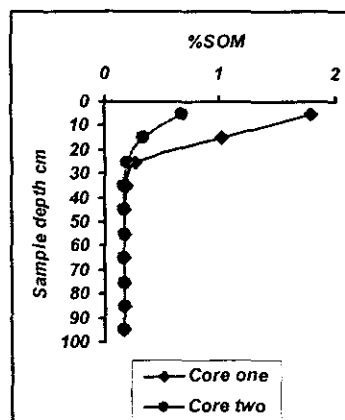


Fig (3): Variation in TOM % with depth in core one compared with core two.

The results can be expounded by the following factors:

- 1- The variation between the two cores is related to the source of irrigation. In core one the source of irrigation is Abu Rawash drain (sewage water) while in core two the source of irrigation is groundwater (low in organic matter) that was the main reason for that variation

- 2- The accumulation of organic matter was pronounced in the surface layer (0-10cm) and decrease with depth up to 40cm depth (root zone) because the sewage water contains an appreciable amount of rather coarse and hardly decomposable materials, which upon application was deposited on the surface layer, where fine parts pass to the subsurface layers.
- 3- Many types of microorganisms found in sewage water concentrated in the top layers causes the decomposition process of organic matter to become faster.

Trace elements results

Data in table (2) and figures (4) represent the difference of the available heavy metal concentration in two sandy soil cores where sewage water is the main source of irrigation in the first core and groundwater is used for irrigation in the second one. These variations are classified as:

Cobalt: High concentration of Co in core one was detected in layer two from 10:20cm depth (0.105 mg/kg soil) and gradually decreases till layer seven, followed by a relative increased till the bottom of the core. In the second core cobalt concentration is relatively high along the core depth with respect to the first one; the highest concentration appeared in layer one (0.123 mg/kg soil) whereas the lowest concentration was detected at layer nine 80:90cm depth (0.045 mg /kg soil).

Cadmium: The highest concentration of Cd in core one was found in layer one within 0:10cm depth (0.119 mg/kg soil), followed by gradual decrease downward to layer five 40:50cm depth (0.005 mg/kg soil) and disappeared (or not detected) till layer 10. On the other hand in core two, cadmium is only appeared in the first layer with very low concentration (0.007 mg/kg soil).

Copper: The maximum concentration of Cu in core one reaches 3.32 mg/kg soil in the first two layers 10:20cm depth and gradually decreased till the bottom of the core. Whereas, Cu is only presented in core two at the first layer with low concentration (0.249 mg/kg soil), that similar to that detected of cadmium ion.

Iron: In core one Fe was detected in high concentration in layer two from 10:20cm depth (38.82 mg/kg soil) and the minimum value was detected in layer seven (60:70 cm depth) reaches 5.098 mg/kg soil. These concentration are relatively high if compared with that present

in core two where the highest concentration was found in layer one (12.73 mg/kg soil) and decreased downward at layer eight (1.192 mg/kg soil).

Manganese: Like iron, the highest concentration of manganese in core one was detected in layer two (34.26 mg/kg soil) and the lowest concentration in layer seven reached 2.23 mg/kg soil. Mn concentration is relatively high if compared with its concentration in core two where the highest concentration (23.88 mg/kg) was detected in layer one and the lowest concentration (3.318 mg/kg) in layer nine.

Table (2): The available concentration of Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn in sandy soil samples in mg/kg soil

Depth (cm)	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Core no. (1) sandy soil								
0-10	0.119	0.028	2.954	14.550	10.164	0.448	0.826	7.806
10-20	0.035	0.105	3.320	38.820	34.260	0.918	1.494	13.144
20-30	0.008	0.023	2.406	8.462	4.788	0.386	0.396	2.022
30-40	0.004	0.012	3.196	7.466	2.536	0.078	0.157	0.614
40-50	0.005	0.014	2.652	7.220	2.450	0.050	0.156	0.520
50-60	0.000	0.009	1.612	5.648	2.420	0.055	0.146	0.583
60-70	0.000	0.008	1.308	5.098	2.230	0.047	0.157	0.471
70-80	0.000	0.029	0.221	13.624	4.136	0.061	0.209	1.103
80-90	0.000	0.039	0.263	13.876	4.994	0.078	0.175	0.917
90-100	0.000	0.035	0.343	7.344	5.566	0.096	0.523	1.016
Core no. (2) sandy soil								
0-10	0.007	0.132	0.249	12.730	23.880	0.207	0.372	2.970
10-20	0.000	0.081	0.000	3.152	9.748	0.085	0.089	0.746
20-30	0.000	0.053	0.000	2.064	6.068	0.071	0.000	0.889
30-40	0.000	0.059	0.000	3.274	4.106	0.110	0.049	0.523
40-50	0.000	0.049	0.000	1.381	3.376	0.042	0.000	0.267
50-60	0.000	0.058	0.000	3.226	4.572	0.067	0.046	0.489
60-70	0.000	0.050	0.000	1.240	3.384	0.081	0.000	0.300
70-80	0.000	0.050	0.000	1.192	3.456	0.065	0.000	0.240
80-90	0.000	0.045	0.000	1.258	3.318	0.060	0.000	0.279
90-100	0.000	0.055	0.000	1.741	3.648	0.068	0.068	0.574

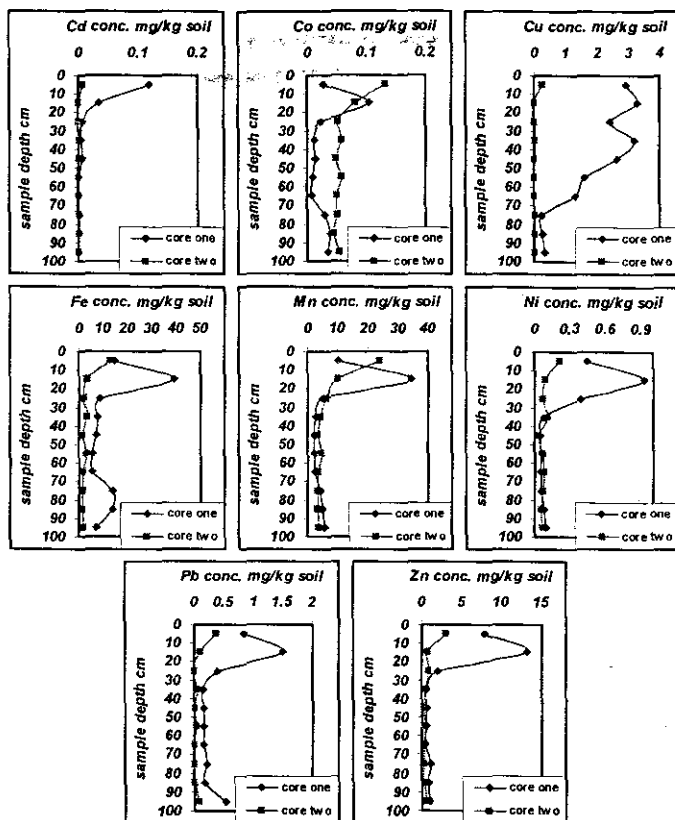


Figure (5): The available concentration of (Cd, Co, Cu, Fe, Mn, Ni, Pb, and Zn) in core one in comparison with core two..

Nickel: The highest concentration of Ni in core one was detected in layer two 10:20 cm depths (0.918 mg/kg soil) and gradually decreased till layer seven 60:70 cm depth (0.047 mg/kg soil). That concentration is considered too high if compared with the concentration of nickel in the core two where the highest concentration 12.73 mg/kg soil in layer one and the lowest concentration was found in layer eight (0.042 mg/kg soil).

Lead: The maximum concentration of Pb was detected in layer two (1.494 mg/kg soil) and the lowest concentration was in layer six (0.146 mg/kg soil). These concentrations were very high if compared with the data obtained in the unpolluted area where the highest concentration was 0.372 mg/kg soil. Lead concentration was under the detection limit in most layers (from layer three to layer nine).

Zinc: Zinc was found in layer two in high concentration (13.144 mg/kg soil) and gradually decreased till layer five (0.146 mg/kg soil). Also the highest concentration in the unpolluted sandy soil reaches 2.97 mg/kg soil in layer one and the lowest concentration was in layer five (0.267 mg/kg soil).

In order to know more about the contribution of the water of irrigation on heavy metals concentrations in root zone, summation of available trace elements amounts in core one and core two were calculated in table (3).

Table (3): The amounts of heavy metals (mg/kg) in the root zone of core one in compare with core two.

Core name	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
Core one	0.16	0.72	8.68	61.83	64.21	1.75	2.72	22.97
Core two	0.01	0.27	0.25	17.95	39.67	0.36	0.46	4.61
Folds	22.86	2.67	34.72	3.44	1.62	4.86	5.91	4.98

The data indicated that sewage water increased the concentration of available heavy metal according to the following order, Cu (34.72 fold) > Cd (22.86 fold) > Pb (5.91 fold) > Zn (4.98 fold) > Ni (4.86 fold) > Fe (3.44 fold) > Co (2.67 fold) > Mn (1.62 fold).

Summation of available heavy metals amounts in root zone (0-30cm) divided by the summation of available trace elements amounts in the profile (0-100 cm) was calculated in table (4) and (5). It was very useful indication for accumulation and mobility of the elements in the soil.

Table (4): Accumulation percentage of available heavy metals in root zone of core one

Profile layers	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
0-100 cm	0.17	0.96	18.28	122.11	88.54	2.22	4.24	28.2
0-30 cm	0.16	0.72	8.68	61.83	64.21	1.75	2.72	22.97
Accum. percentage	94.7%	75.5%	47.5%	50.6%	72.5%	79.0%	64.0%	81.5%

The data in table (4) illustrate that most of the elements were concentrated in the root zone. The accumulation in this zone was high for Cd, Zn, and Ni and mediated for Mn, Co, and Pb. There was low accumulation in root zone for Fe and Cu.

Table (5): Accumulation percentage of available heavy metals in root zone of core two.

Profile layers	Cd	Co	Cu	Fe	Mn	Ni	Pb	Zn
0-100 cm	0.007	0.63	0.25	31.26	65.56	0.86	0.63	7.28
0-30 cm	0.007	0.27	0.25	17.95	39.67	0.36	0.46	4.61
Accum. percentage	100.0%	42.0%	100%	57.4%	60.6%	42.4%	73.9%	63.3%

The data in table (5) showed that only cadmium and copper was highly accumulated in the root zone and mediated for Mn, Pb, and Zn .on the other hand there was low accumulation for Fe, Ni, and cobalt in the root zone.

CONCLUSION

Considering the distribution of organic matter through the soil profiles, a relation between soil pH and soil organic matter content that the tendency could be drown, layers that contain higher percentage of organic matter persisted to show lower values of pH. Such negative relation could be noticed clearly upon comparing the values of surface layer with those of lower ones.

Sewage water has a crucial role in transporting metals through core one. Sewage water affects all trace elements concentrations in this core. The highest values of trace elements were exhibited by Fe, Mn, Cu, and Zn while the lowest were exhibited by Pb, Ni, Cd, and Co.

Heavy metals in the sandy soil were arranged according to the following decreasing order: Fe > Mn > Zn > Cu > Pb > Ni > Cd > Co.

The highest concentration of most heavy metals in core one were observed in layer two because the source of these metals is sewage sludge precipitate which tend to accumulate in layer two. On the other hand, the highest concentration of all heavy metal was observed in layer one and the concentration decreases with depth.

The concentration of available heavy metal for plant don't exceed the recommended limits for plant, but it also represent that heavy metals form could represent the higher potential load of metal contamination.

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استخدام تركيزات العناصر الثقيلة كدليل على انتقال الملوثات البيئية في الأراضي الرملية المصرية

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يعد تلوث التربة من أحد المصادر التي تسبب خطورة على صحة الإنسان ، خاصة الذين يعيشون في المدن فالتلوث الناشئ عن الأنشطة الحيوية للإنسان أو استعمال مياه الصرف الصحي في عملية الري ينتقل إلى النبات ومنه يدخل خلال السلسلة الغذائية مسببا مخاطر على صحة الإنسان. وتعد منطقة أبو رواش أحد المناطق التي تستخدم فيها مياه الصرف الصحي في عملية الزراعة. وقد زادت أهمية تقدير العناصر الثقيلة في التربة نتيجة للاتجاهات الحديثة التي تهتم بدراسة تأثيرها على الإنسان والبيئة. وفي هذه الدراسة تم تقدير تركيزات العناصر الثقيلة في قطاعين رأسيين من التربة الرملية بمنطقة أبو رواش عن طريق الاستخلاص بمادة DTPA على جهاز ICP-MS وقد وجد أن الطبقة السطحية من القطاعين هي الأعلى من حيث تركيز العناصر الثقيلة عن الطبقات تحت سطحية، كما وجد أيضا أن استعمال مياه الصرف الصحي في الري أدى إلى زيادة تركيز العناصر الثقيلة تبعا للترتيب التالي: النحاس تضاعف ٣٤,٧٢ ضعف ، والكاديوم تضاعف ٢٢,٨٦ ضعف، والرصاص تضاعف ٥,٩١ ضعف، والزنك تضاعف ٤,٩٨ ضعف، والنيكل ٤,٦٨ ضعف والحديد تضاعف ٣,٤٤ ضعف، والكوبالت تضاعف إلى ٢,٦٧ ضعف وأخيرا المنجنيز تضاعف إلى ١,٦٢ ضعف مقارنة بالقطاع الغير مروى بمياه الصرف الصحي. وقد لوحظ أيضا أن تراكم العناصر الثقيلة كان مركزا في المنطقة الجذرية حتى عمق ٣٠ سم عن الطبقات التي تليها. على الجانب الآخر وجد أن استعمال مياه الصرف الصحي في الري أدى إلى زيادة الحموضة وزيادة نسبة المادة العضوية في الطبقات السطحية حتى عمق ٣٠سم.

قام بتحكيم هذا البحث: ا.د/ حمدي علي عطية النجار و ا.د/ صفاء محمد