

**Distribution of Heavy Elements and Water Chemistry
In Al-Ashar and Al-Khandak canals connected
with Shatt Al-Arab River-Basrah**

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ABSTRACT: This study is concerned with the determination and distribution of four heavy elements (Co, Ni, Mn and Fe) in dissolved and particulate phases of water from five selected stations in Al-Ashar and Al-Khandak canals which are connected with Shatt Al-Arab river.

Samples were collected monthly from the stations. Many ecological factors also were measured during the period December, 1994-November, 1995. The mean concentrations of Co, Ni, Mn and Fe in dissolved phase were 20.90, 20.90, 8.40 and 29.11 $\mu\text{g/l}$, respectively; whereas in the exchangeable phase of particulate they were non detectable (N.D.), 31.87, 909.69 and 4300.03 $\mu\text{g/g}$ dry weight respectively. However, in the residual phase of particulate they were 100.68, 204.68, 130.62 and 6068.49 $\mu\text{g/g}$ dry weight, in this order.

Seasonal and spatial variations were observed in the mean concentrations of the studied elements.

The results showed that the concentration of most of the studied elements were higher than those found by other workers, but it is, still, in the limit range of the world standards for inland water.

1. INTRODUCTION

Heavy elements, which are present in different concentrations and chemical forms, discharged into the water can severely influence aquatic ecosystems.

Concentrations of heavy elements in natural water may vary greatly locally and seasonally, such variation is due to an anthropogenic and natural sources. The major source of heavy elements in natural water is coming from the mining areas, while the heavy elements in polluted water is coming from wastewater from industrial, municipal sewage treatment facilities, .. etc.

Several authors have mentioned that domestic sewage is a potential source for contamination with heavy elements (Mustafa, 1985; Al - Saadi *et al* 1995 Al-Khafaji, 1996; Al-Saad *et al* 1997).

In the present study four stations were selected in two canals (Al - Ashar and Al -khandak) because these canals received a continuous flow of untreated municipal sewage from inhabitants of Basrah city, while the fifth station chosed on Shatt Al -Arab river were the above mentioned canals discharge, in order to illustrate the influence of pollution from these canals on the Shatt. Al - Arab river.

2. MATERIALS AND METHODS

Samples were collected from five stations, (1 & 2) in Al - Ashar canal, (3 & 4) in Al - Khandak canal and the fifth station located in Shatt Al-Arab river where the above canals discharge fig.(1).

Duplicate water samples (10 litres from station (5) and 5 litres from stations 1, 2, 3 and 4) were collected monthly, during the period December, 1994 - November, 1995, in an acid prewashed polyethelen bottles held just below the water surface.

Samples were filtered immediately using a prewashed and preweighted 0.45 μ m millipore filter paper. The filtrate was considered as dissolved phase, while those retained as particulate matters.

Heavy elements in dissolved phase were preconcentrated according to Riley and Taylors (1968) methode.

Duplicate extraction of heavy elements from particulate matter following the procedure of Chester & Voutsinou (1981) in which the exchangeable heavy elements,

which have been incorporated from the aqueous solution by processes such as adsorption and organic complexation, were extracted by added 30 ml of 0.5 N HCl and mechanically shaken for about 16 h.

The residual heavy elements, which are part of silicate matrix were digested using mixture of 4:1 HNO₃ and HClO₄ acids according to the method described by Barak and Mason (1989).

The PH was measured using PH meter (Model PH 90), and the temperature and conductivity were measured using portable digital conductivity meter (Model LF 91).

The salinity was calculated by multiplying the measured conductivity values by a factor 0.64 (APHA, 1985), while the dissolved oxygen (D.O) and biological oxygen demand (BOD₅) values were determined by some modification to Winklers method, Lind (1979) the heavy elements were extracted in duplicate from dissolved phase and particulate samples, determined by air/acetylene flame Atomic Absorption spectrophotometer (AAS) (Model Sp9 PYE - Unicam).

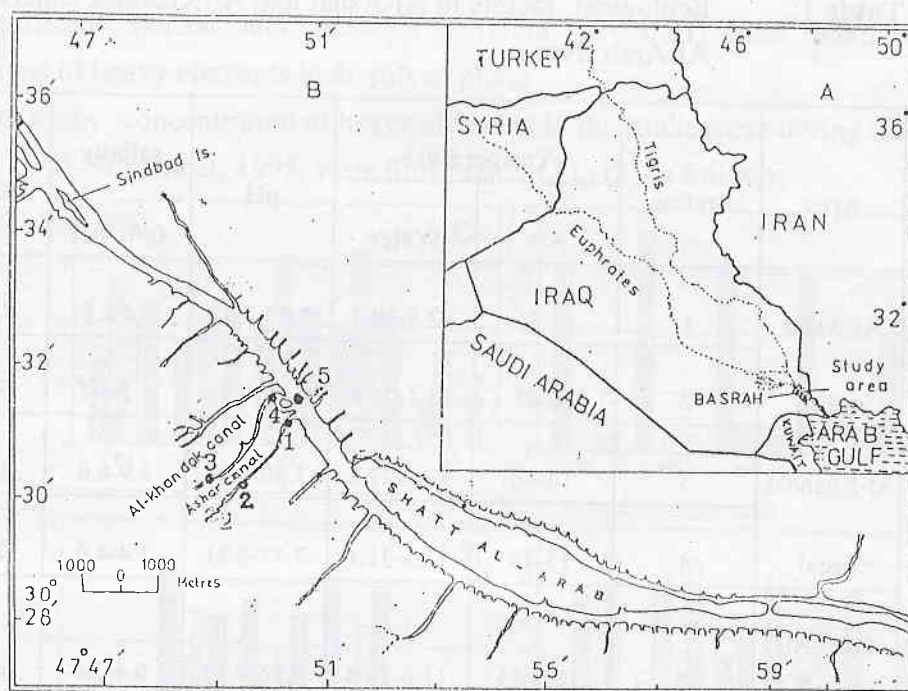


Fig.1 Map of the study area.

3. RESULTS AND DISCUSSION

The ranges of chemical and physical water factors; PH, DO, BOD₅, temperature and salinity which are the major important parameters for the distribution of heavy elements are listed in table-1.

Several workers [Parry & Hayward, 1973; Munda, 1984; Salomans, *et al* 1987; AlSaadi *et al* 1995] found that some of the above parameters (pH, DO and salinity) decrease or increase the solubility of heavy elements in water, according to the element. In the present study a nonsignificant correlations between the above parameters and the concentrations of some elements were found, Table (2), which may be attributed to the interaction between these parameters and the other environmental factors such as: variation of element concentrations flow to the area, sewage and seepage from agricultural lands, and the disposal of industrial and municipal effluents.

Table 1: Ecological factors in Al-Ashar and Al-Khandak canals as well as in Shatt Al-Arab river.

Area	Station	Temperature		pH	salinity (g/l) ‰	DO mg/l	BOD ₃ mg/l	Particulate matter
		Air	Water					
Al-Ashar canal	1	15-46	12.8-30.4	7.88-8.72	1.4-2.8	4.1-9.3	1.8-36.2	11.0
	2	16-45	13.1-28.8	7.78-8.86	3.1-4.7	0.5-6.4	5.7-47.8	21.0
Al-Khandak canal	3	14-46	13.0-27.8	7.80-8.83	3.9-6.0	1.4-8.0	5.9-49.9	25.0
	4	15-45	11.5-31.1	7.77-8.81	1.4-4.0	0.9-6.6	2.5-59.9	24.0
Shatt Al-Arab river	5	16.5-44	11.6-28.4	7.96-9.12	0.4-1.4	6.0-13.0	N.D-2.5	7.0

Table (2): Simple correlation coefficient (r) between the concentrations of studied heavy elements in dissolved phase and other parameters.

elements parameter	Co	Ni	Mn	Fe
Water	**	N.S.	**	N.S.
Temperature	0.36	-0.15	0.37	-0.00
Salinity	N.S.	N.S.	N.S.	*
	0.09	-0.15	-0.07	0.22
Ph	N.S.	N.S.	**	*
	0.09	-0.04	-0.24	-0.23
Dissolved Oxygen (D.O)	*	**	**	**
	-0.18	0.34	0.27	-0.27
Biological oxygen demand (BOD ₅)	N.S. *	*	N.S.	N.S.
	-0.00	-0.18	-0.15	0.06

(n=120, **: significant $p < 0.01$; *: significant $p < 0.05$; N.S.: Nonsignificant)

Significant spacial and seasonal variation ($p < 0.01$) were found in some concentrations of heavy elements in dissolved phase

The mean concentration of heavy elements in the studies area during the period December, 1994-November, 1995, were illustrated in Fig (2) as follows:

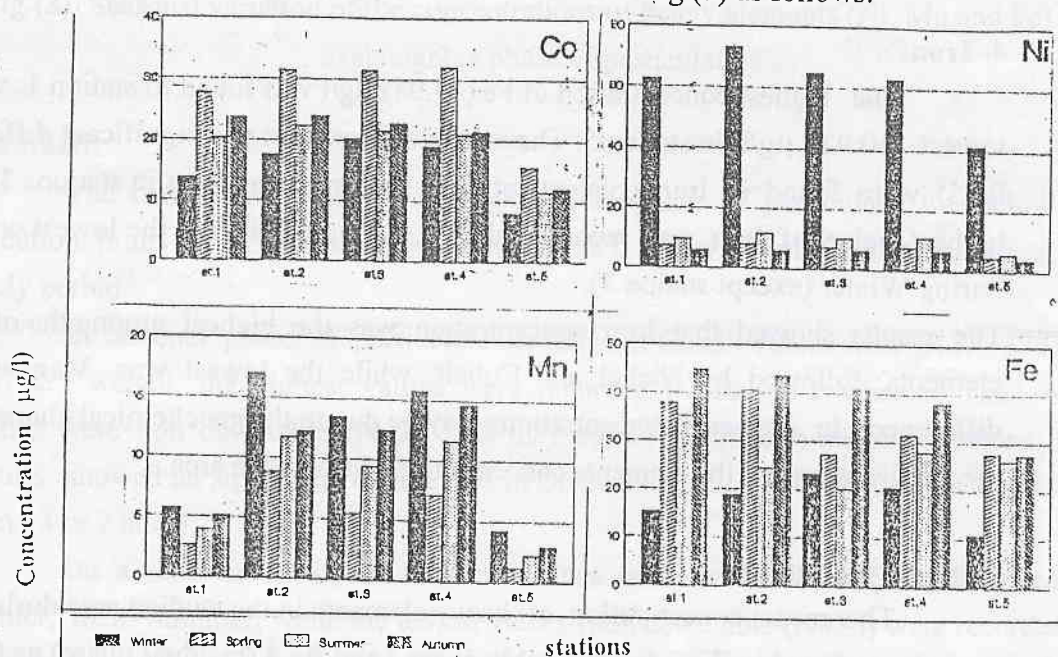


Fig.(2) The concentrations of (Co, Ni, Mn and Fe) in dissolved phase of water.

In dissolved Dhase**1- Cobalt:**

The range values were (8.07 - 32.06) $\mu\text{g/l}$ in stations 5 and 4, respectively. The highest values were recorded in Spring, whereas the lowest were in Winter. There are no significant differences ($p > 0.05$) between the concentrations recorded in Summer and Autumn.

2- Nickel:

The range values were (3.79 - 73.38) $\mu\text{g/l}$ in stations 5 and 2, respectively, station 5 was significantly different ($p < 0.01$) from the other stations. On a seasonal basis, the highest values were recorded in Winter, while the lowest were in Autumn in which the concentration had no significant difference from that in Spring or Summer.

3- Manganese:

The range of the recorded Mn values were (1.19-15.78) $\mu\text{g/l}$ in station 5 and 2, respectively. The results showed that there were no significant differences in the level of manganese in stations 2 and 4. The highest values were recorded during Winter followed by Autumn, then Summer, and the lowest was recorded in Spring.

4- Iron:

The highest concentration of Fe (44.94) $\mu\text{g/l}$ was found in station 1, whereas the lowest (10.92) $\mu\text{g/l}$ in station 5. The results showed that non significant differences ($p > 0.05$) were found in Iron concentration in stations 1 and 2, or in stations 3 and 4. The highest value of Iron was recorded during Autumn, whereas the lowest was recorded during Winter (except station 3).

The results showed that Iron concentration was the highest among the other studied elements, followed by Nickel and Cobalt, while the lowest was Manganese. These differences in elements concentrations may be due to the geochemical characteristics of the studied area and the elements concentrations flow to the area.

In particulat matter

The mean concentration of heavy elements in the studied area during the study period was found in Fig.3 (exchangable phase) and fig.4 (residual phase) as follows:-

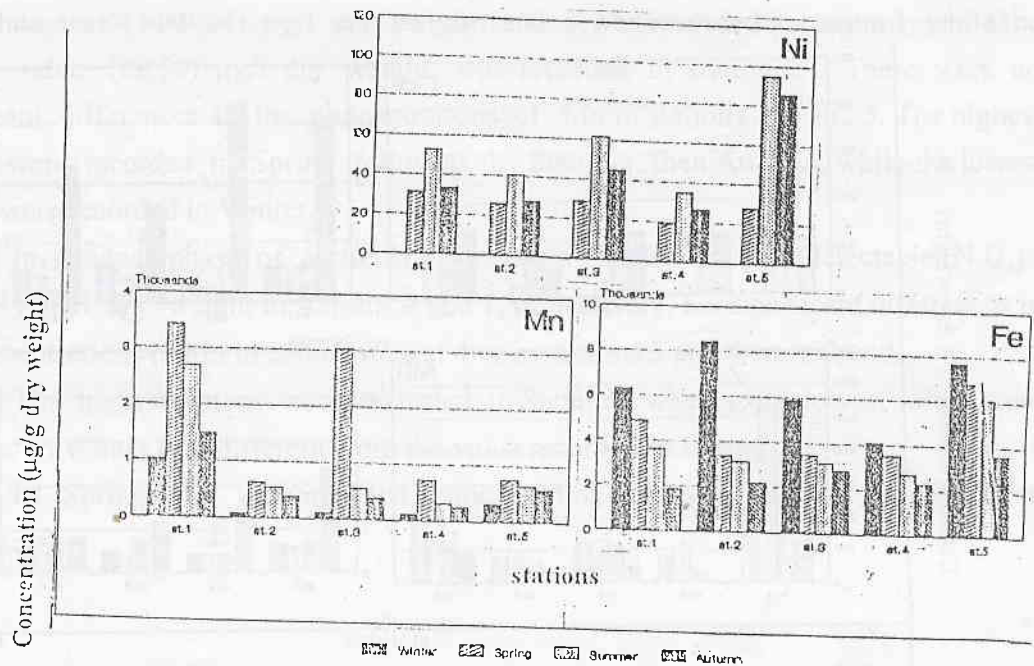


Fig.(3) Seasonal variation of the concentrations of heavy elements (Ni, Mn and Fe) in exchangeable phase of particulate.

1- Cobalt:

The concentration of Co in exchangeable phase of particulate was below the detection limits of AAS (the detection limit was $0.16 \mu\text{g/l}$) in all the stations during the study period.

In residual phase of particulate the range of Cobalt values were (N.D - $376.08 \mu\text{g/l}$ dry weight), the highest values were recorded in station 1; whereas. The lowest values were non detectable (N.D.) and they were recorded in the other stations. The results showed no significant differences in Co concentration between station 1 and 5 or 2 and 3 or 2 and 4.

On a seasonal basis, the highest values were recorded in Spring followed by Winter, then Summer, while the lowest values (non detectable (N.D.)) were recorded in Autumn.

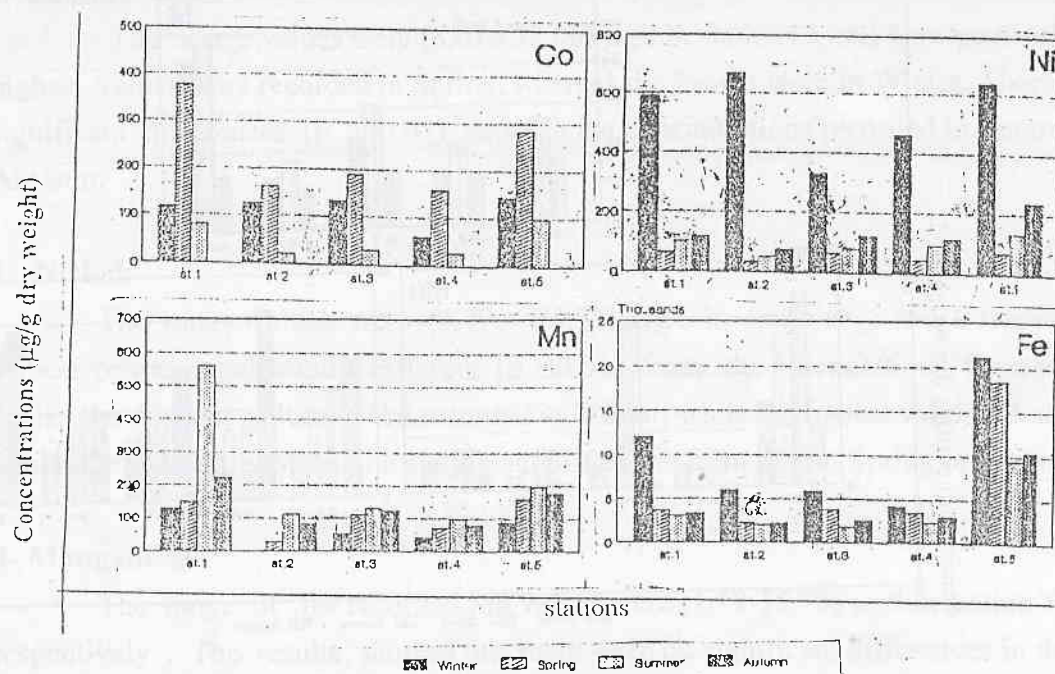


Fig.(4) Seasonal variation of the concentrations of heavy elements (Co, Ni, Mn and Fe) in residual phase of particulate.

2- Nickel:

The range values of Ni in the exchangeable phase of particulate were (N.D - 94.74) $\mu\text{g/l}$ dry weight, in station 5. Non significant differences were found in the concentration of this element in station 1 and 3 or 1, 2 and 4. The highest values were recorded in Summer followed by Autumn, then Spring, whereas the lowest value was below the detection limits of AAS (detection limit is 0.14 $\mu\text{g/l}$), and it was recorded in Winter.

The range values of Ni in residual phase of particulate were (34.44 - 669.09) $\mu\text{g/l}$ dry weight recorded in station 2, there were no significant differences in the concentration of Nickel in stations 3 and 4 or in stations 1, 2 and 5. The highest values were recorded in Winter, while the lowest values were recorded in Spring. There were no significant differences in the concentrations during Summer, Autumn and Spring.

3- Manganese:

The highest value of the concentration of Mn in exchangeable phase of particulate was (3440.24) $\mu\text{g/l}$ dry weight, and it was recorded in station 1, while the lowest value (88.59) $\mu\text{g/l}$ dry weight, was recorded in station 2. There were no significant differences in the concentrations of Mn in stations 2, 4 and 5. The highest values were recorded in Spring followed by Summer, then Autumn, while the lowest values were recorded in Winter.

In residual phase of particulate the range values were (non detectable (N.D.) - 560.8) $\mu\text{g/l}$ dry weight in stations 2 and 1, respectively. No significant differences in the concentrations of Mn in stations 2 and 4 or in stations 3 and 4 were found.

The highest values were recorded in Summer, whereas the lowest values were recorded in Winter (not different from the value recorded in Spring).

In Spring and Autumn the concentration of Mn showed no significant differences.

4- Iron

The highest value of Fe in the exchangeable phase of particulate was (8433.89) $\mu\text{g/l}$ dry weight and it was recorded in station 2.

The lowest value was (1867.57) $\mu\text{g/g}$ dry weight, and it was recorded in station 1.

Non significant differences ($p > 0.05$) were found in the concentrations of Fe in stations 1, 2 and 3, or stations 1, 3 and 4. The highest values were recorded in Winter, whereas the lowest values were recorded in Autumn. There were no significant differences in the concentrations of Fe in Summer and Spring.

In residual phase of particulate, the results showed that the highest value of Fe was (21208.49) $\mu\text{g/l}$ dry weight in station 5, whereas the lowest value (1841.64) $\mu\text{g/l}$ dry weight was recorded in station 3. Non significant differences ($p > 0.05$) were found in the concentrations of Fe in stations 2, 3 and 4.

The highest values were recorded in Winter, whereas the lowest were recorded in Summer (which are not different from the concentrations of Fe in Autumn).

The results showed that Iron concentrations in the exchangeable phase of particulate was the highest among the studied elements followed by Manganese, Nickel, whereas the lowest value was recorded for Cobalt (which was below the detection limits of AAS, this sequence may be due to the anthropogenic sources of elements in the studied area, such as untreated municipal sewage and domestic sewage which discharge

to Al-Ashar and Al-khandak canals without treatment.

A different sequence was found in residual phase of particulate ($Fe > Ni > Mn > Co$) this may be due to the natural sources of elements in the studied area. The particulate matter in the studied area consisted of [organic fraction (living planktonic organisms in particular) and inorganic fraction (clay and silt, which formed axing weathering process)].

The concentration of all studied elements were found to be higher in particulate matter compared to in dissolved phase of water. This could be attributed to the ability of particulate matter (specially the living phytoplankton) to concentrate heavy elements in their bodies more than the surrounding water (Al- Hejuje, 1997).

Comparing heavy elements concentrations in dissolved phase of this study with those given in the literature for the same area and others of nearby environments, was given in table (3), while the comparing heavy elements concentrations in particulate matter of this study with those given in literature, was given in table (4). The slightly higher elements concentration which were observed even in the part of the area may be due to an anthropogenic input of elements to the studied area possibly from the untreated municipal sewage and domestic sewage, which discharge to the studied area.

Table (3) Mean concentrations of heavy elements in dissolved phase of water from the studied area together with these in the nearby area ($\mu\text{g/l}$).

Element Locality	Co	Ni	Fe	Mn	Reference
Shatt Al-Arab River	-	0.5	-	0.074	Mustafa, 1985
Shatt Al-Arab Estuary	-	3.4	716	1.3	Abaychi & Douabul, 1985
Shatt Al-Arab Estuary	0.33	2.45	389.2	0.69	Al-Saad <i>et al.</i> 1996
Shatt Al-Arab Estuary	0.34	3.22	194	1.57	Al-Khafaji, 1996
Study area	20.90	20.90	29.11	8.403	Present study

Table (4) Mean concentrations of heavy elements in particulate matter from the studied area together with those in the nearby area ($\mu\text{g/g}$ dry weight).

Element Locality	Co	Ni	Fe	Mn	Reference
Shatt Al-Arab River	-	27.57	-	7.84	Mustafa, 1985
Shatt Al-Arab Estuary	6.0	3807	31472	1731	Abaychi & Douabul, 1985
Shatt Al-Arab Estuary	22.5	193.4	9466	63.7	Al-Saad <i>et al.</i> 1996
Shatt Al-Arab Estuary	4.92	463.8	6333.2	244.3	Al-Khafaji, 1996
Study area	100.68	236.56	10368.5	1040.31	Present study

CONCLUSIONS

- 1) Although the study showed that there was an increase in the concentrations of the studied heavy elements, still the area is considered to be unpolluted by heavy elements.
- 2) Local variations in the concentrations of the studied heavy elements depended mainly on the natural and anthropogenic sources, while seasonal variations depended mainly on the blooming of phytoplankton which has the ability to concentrate the heavy elements in their bodies more than those in the surrounding water.

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الملخص

تضمنت الدراسة الحالية قياس توزيع تراكيز اربعة عناصر ثقيلة هي: Fe، Mn، Ni، Co في الطور الذائب والعالق في الماء لخمس محطات تم اختيارها في قناتي العشار والخندق والمرتبطة بشط العرب.

تم جلب العينات في المحصت شهريا، كذلك تم قياس العوامل البيئية للمدة الممتدة من كانون الاول 1994 لغاية تشرين الثاني 1995.

وكان معدل تراكيز العناصر Fe، Mn، Ni، Co في الطور الذائب من الماء (20,90، 20,90، 8,40، 29,11) مايكغم/لتر على التوالي. بينما كان معدل تراكيز تلك العناصر في الطور المتبادل من العوالق (غير المحسوس، 31,87، 909,69، 4300,03) مايكغم/غم وزن جاف على التوالي. وفي الطور المتبقي من العوالق كان معدل تراكيز تلك العناصر (100,68، 204,68، 130,62، 6068,49) مايكغم/غم وزن جاف على التوالي.

واظهرت الدراسة وجود اختلافات فصلية وموقعية في معدل تراكيز تلك العناصر. وكانت تراكيز اغلب العناصر المدروسة اعلى مما سجل في الدراسات السابقة الا انها تقع ضمن الحدود العالمية المسموح بها في المياه الداخلية.