RESEARCH ARTICLE

DETERMINATION OF SOME HEAVY METAL IONS AND WATER QUALITY IN GROUNDWATER OF MANY WELLS IN ASSIUT , EGYPT.

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Manuscript Info	Abstract
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Study of some heavy metal ions in the groundwater at Assiut- Egypt is an essential ingredient for a healthy. The measured ions and water quality parameters such as: (pH, conductivity, salinity , turbidity, Dissolved Oxygen (DO) ,NO_2 ,NO_3, NH_3, SO_4^{-2}, Ca^{+2}, Mg^{+2} , Pb^{+2} , Cd^{+2} , Ni^{+2}, Cu^{+2}, total Fe, Mn^{+2}, total Cr and Total Hardness (TH) were carried out on groundwater samples at different localities in Assiut city and some countryside, Egypt. Classifications of groundwater samples based on groundwater wells depth. Evaluation of the samples for different uses (drinking and domestic uses, irrigation and industrial purposes), saturation index (SI), and water quality index (WQI) indicated. A systematic calculation of correlation coefficients among was performed.

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Introduction:-

Groundwater has been considered to be a pure form of water because of its filtration through soil and its long residence time underground, it contains organic matter and some pathogenic microorganisms compared to water in lakes and rivers [1]. In addition, groundwater is very important for arid and semi-arid regions, where it is pumped directly from wells at the point of their utilization [2]. The groundwater characteristics have certain advantages over surface water for domestic use, since it usually contains no suspended materials. It contains only small amount of different types of bacteria, generally, harmless soil forms, unless contaminated by human, and it is clear and colorless unless tainted with humic materials [3].

The level of groundwater vulnerability depends on three groups of factors, i.e., natural, human-induced, and physicochemical [4]. The natural factors include:
- Groundwater depth (this is the factor of our study).
- Thickness, lithology and permeability of rocks overlying groundwater.
- Presence of relatively impermeable beds, i.e., rocks with hydraulic conductivity less than 0.01 m/day.
- Sorption properties of rocks; and
- Relationship between groundwater levels in the aquifers.

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In Egypt, ground water is considered the third water source for irrigation and other human uses after the river Nile, and irrigation canals and drains [5]. Groundwater reservoir in the Delta region is considered as one of the biggest reservoir in the world in which its capacity is estimated to be around 280 km^3 [6].

From geological point of view, the groundwater reservoir of Nile valley region consists of Tertiary and Quaternary deposits. Its thickness is estimated as 300 m at Middle Egypt and decreases to the north towards Cairo and in the south direction up to Aswan [7]. Below this aquifer, there are clayed deposits that were formed during the Pliocene, which are impermeable and prevent the connection between this aquifer and the Nubian Sandstone aquifer. However, there could be a connection between the Quaternary deposits and the surrounding limestone. The water is mainly used for domestic purposes and irrigation; its salinity is less than 1,500 ppm [8].

Many research studies [9-15] were carried out on the groundwater quality in Nile Delta ,Cairo, Assiut , Sohag, Aswan governorates (Egypt).

The main objectives of this study are to determine some heavy metal ions and evaluate the groundwater quality in Assiut city and some countryside. The monitoring of groundwater quality is necessary in order to detect pollution and prevent use of contaminated groundwater of public water supply.

Methods And Materials:-
Chemicals and reagents:-
All chemicals in this study were purchased from Sigma -Aldrich (Germany), Merck (USA), Kanto Chemical CO. (Japan), (A.R.E). The atomic absorption spectroscopic standard solutions (1.0 g/L) for the elements were purchased from (Merck) which is traceable to Standard Reference Material (SRM) from National Institute of Standards and Technology (NIST). Working standard solutions were prepared by diluting the stock solution using deionized water. Argon and acetylene gas with 99.99% purity, used in Atomic Absorption Spectrophotometer (Shimadzu Corporation) Model: (AA-6800).

Analytical procedures:-
Water quality parameters, their units, reference methods and methods of analysis are summarized in table(1). The various parameters were determined using standard procedures [16]. The temperature, pH, electrical conductivity, salinity, turbidity and DO of each water sample were measured at the sampling points by (water quality analyzer (HORIBA .LtD) Model U-10-2M), were measured on site by (Ultra meter (Myron L company) Model: 6P), SO_4^{-2} (Turbidimetry), TDS were determined gravimetrically at 105-110 ^{O}C. total hardness and Ca hardness were measured by EDTA complexo-metry titration , the indicators are Eriochrome Black T and muroxide at pH 10 and 12, respectively . alkalinity determined by acid titration using bromcresol green as indicator. Total organic carbon (TOC) was determined by TOC analyzer (Shimadzu Corporation Model: (TOC-V $_{CSN}$). NO_2^- - N, NO_3^- - N, NH_3 – N were analyzed by Colorimetric method, UV spectrophotometer, Phenate method respectively using (UV- Visible spectrophotometer (Shimadzu Corporation) Model: (UV-1650PC). Fluoride was measured using SPADNS method. . Trace and heavy metal (Cu, Fe and Mn) were determined by FAAS using acetylene air flame while (Pb, Cd, Ni and Cr) were analyzed using electro-thermal atomic absorption spectrometer (ETAAS) (Shimadzu Corporation) Model: (AA-6800).

Water Sampling:-
A total number of 44 water samples from Assiut city and some countryside were collected from selected productive wells. The selected samples were taken from the wells after they have been pumped for 10-15 min, in order to remove the stagnant water. The water samples were collected in previously rinsed three 500 mL capacity polyethylene and glass bottles. These bottles were immediately transported to the laboratory under low temperature conditions in iceboxes. The samples were stored in the laboratory at 4 ^{o}C until processed/analyzed.

For the determination of trace elements a 500 mL polyethylene bottle which are good tighted were used instead of glass bottles. This reduces the leaching of the trace element from the wall containers. Also, the storage of water samples into plastic bottles eliminates the adsorption of trace elements. The samples usually acidified with concentrated nitric acid to prevent the hydrolysis of these elements. The bottles were completely filled with water samples for protection and isolation from air. Finally, they were stored in a refrigerator. pH, salinity, electrical conductivity (EC), temperature, turbidity, dissolved oxygen (DO) and oxidation reduction potential (ORP) were determined in the site. All parameter were determined using the standard procedures (APHA, 2005) [16].

Data treatment by statistical method:-
Statistical analysis was carried out using Statistical Package for Social Sciences (SPSS) version 17.0

Table 1:- Abbreviations, Units, Reference Methods and Analytical methods.

Item	Abbreviations	Units	Reference Method	Analytical method
pH	pH	pH unit	SM 4500-H^+B	pH - meter
Salinity	Salinity	%	SM 2520 B	Electrometric
Electrical conductivity	EC	ms/cm	SM 2510 B	Electrometric
Temperature	Temp.	^oC	SM 2550 B	Electrometric
Dissolved Oxygen	DO	mg/L	SM 4500 -O-G	Membrane electrode method
Turbidity	Turb.	NTU	SM 2130 B	Nephelometric method
Nitrite nitrogen	NO_2^- - N	mg/L	SM 4500 – (NO_2^- - N)B	Colorimetric method
Nitrate nitrogen	NO_3^- - N	mg/L	SM 4500 – (NO_3^- - N)B	UV spectrophotometer
Ammonia	$NH_3 – N$	mg/L	SM 4500 – ($NH_3 – N$) F	Phenate method
Total organic carbon	TOC	mg/L	SM 5310 B	TOC analyzer
Chemical oxygen demand	COD	mg/L	SM 5220 B	Open reflux method
Sulphate	SO_4^{2-}	mg/L	SM 4500 - SO_4^{2-} E	Turbidimetric method
Total dissolved solids	TDS	mg/L	SM 2540 C	Gravimetric method
Fluoride	F^-	mg/L	SM 4500 - F^- B	SPADNS method
Chloride	Cl^-	mg/L	SM 4500 - Cl^- B	Argentometric method
Alkalinity	Alk.	mg/L	SM 2320 B	Titrimetric
Total Hardness	T.H.	mg/L	SM 2340 C	EDTA Titrimetric
Calcium	Ca^{2+}	mg/L	SM 3500- Ca B	EDTA Titrimetric
Magnesium	Mg^{2+}	mg/L	SM 3500 – Mg B	Calculation method
Oxidation reduction potential	ORP	Mv	SM 2580 B	Electrometric
Lead	Pb^{+2}	μg/L	SM - 3113B - Pb	ETAAS
Cadmium	Cd^{+2}	μg/L	SM - 3113B - Cd	ETAAS
Nickel	Ni^{+2}	μg/L	SM - 3113B - Ni	ETAAS
Chromium	Cr^{+2}	μg/L	SM - 3113B - Cr	ETAAS
Iron	Fe^{+2}	mg/L	SM - 3111B - Fe	FAAS
Manganese	Mn^{+2}	mg/L	SM - 3111B - Mn	FAAS
Copper	Cu^{+2}	mg/L	SM - 3111B - Cu	FAAS

SM: Standard Methods for Examination of Water and Wastewater 21th Edition (2005) (APHA).
FAAS: flame atomic absorption spectrophotometer.
ETAAS: electro-thermal atomic absorption spectrophotometer.

Studied area:-
The area under studied is Assiut city and some country side shows in Fig.1. Assiut lies in the middle north of Upper Egypt far about 400 km from Cairo.(27° 11$^'$ N and 31° 10$^'$E).
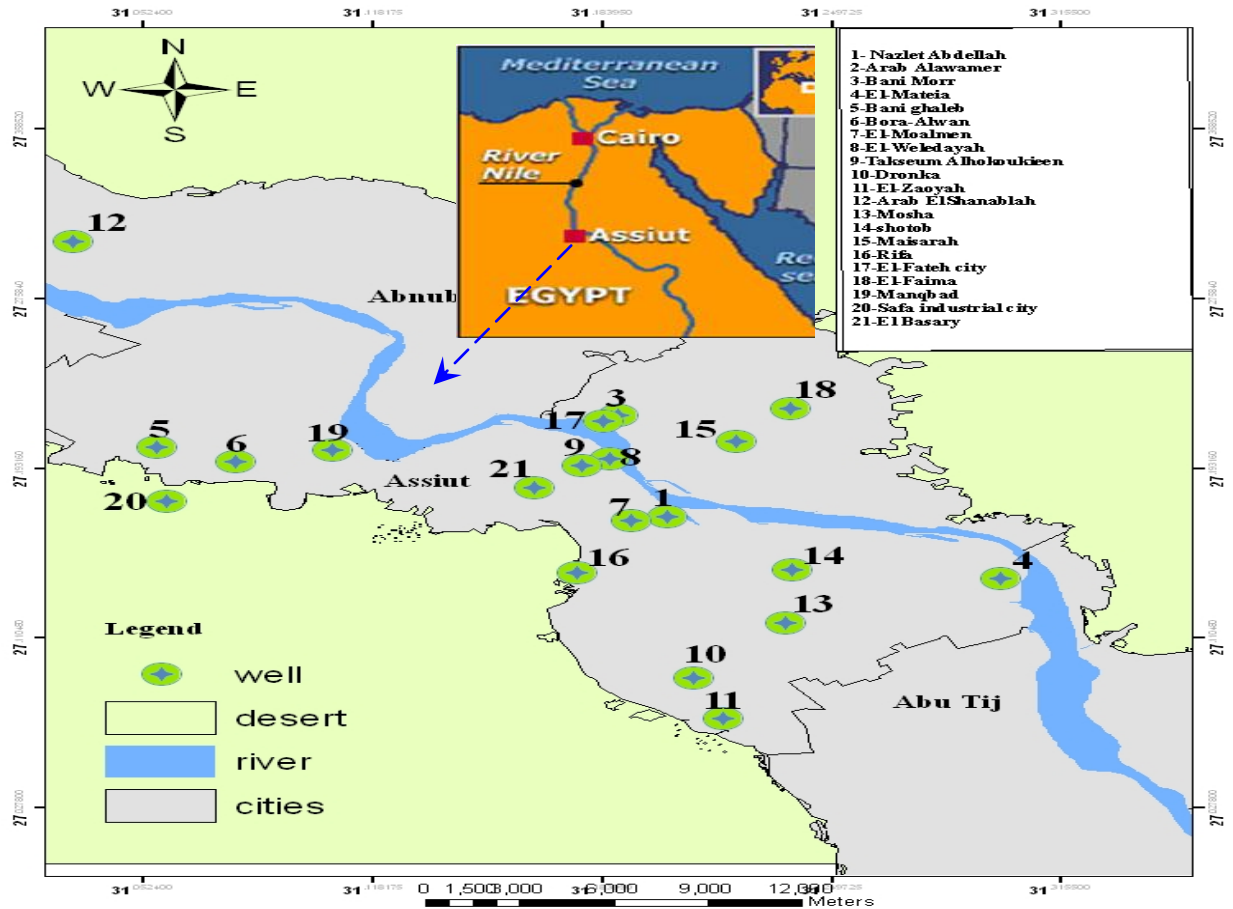
Fig.1:- The locations of the groundwater samples at Assiut city and selected country side.

Results and Discussion:-
Classification of groundwater samples:-
The level of groundwater vulnerability depends on three groups of factors, i.e., natural, human-induced, and physicochemical [4]. Groundwater depth; is one of the natural factors .

In this study we are classified the wells under investigation according to the depth of well into two group:
Group A: low depth wells (50 – 80 m)
Group B: high depth wells (80 – 100 m)

Determination of Hydro-chemical properties:-
The parameters of Hydro-Chemical such as: pH, salinity, electrical conductivity (EC), temperature, turbidity, dissolved oxygen (DO) and oxidation reduction potential (ORP) were determined in the site. The obtained data for group A, samples which collected from wells of groundwater with high depth, were recorded in Table2.

Table 2:- Hydro-chemical data from groundwater with high depth wells (Group A)

Well No.	pH	Salinity	Cond.	Temp.	Turb.	DO	NO_2^-	NO_3^-	NH_3	SO_4^{-2}
1	8.1	0.01	0.403	23.5	0.13	0.9	0.007	0.11	1.05	70
2	8.2	0.01	0.331	23	0.1	0.95	0.004	0.16	0.88	86
3	7.8	0.03	0.789	23	0.21	0.64	0.001	0.08	0.7	67
4	7.5	0.02	0.36	22.6	0.18	3.19	0.001	0.27	0.5	47
5	7.6	0.01	0.33	22.5	0.21	3.03	0.003	0.22	0.36	31
6	7.6	0.01	0.446	24.4	0.09	1.2	0.003	0.9	0.16	41
7	7.5	0.02	0.541	24	0.14	1.4	0.003	0.45	ND	23
8	8.1	0.02	0.598	24.5	0.15	0.5	0.001	0.2	0.2	100
9	7.3	0.12	2.47	25.2	0.04	1.5	0.093	1.8	0.05	799
10	7.3	0.14	2.741	25.1	0.02	2	0.052	10.2	0.09	840
11	7.4	0.09	1.859	24.5	0.01	1.6	0.095	7	0.03	562
12	8.2	0.1	1.76	25	0.8	1.5	0.06	2.4	0.04	56
13	8.3	0.1	2.17	24	0.9	1.8	0.02	1.2	0.03	73
14	7.9	0.04	1.221	27.1	0.09	0.15	0.13	0.7	0.2	127
15	7.6	0.02	1.054	27.3	0.14	0.3	0.02	1.9	0.55	121
16	7.1	0.03	1.098	27.8	0.08	0.05	0.004	0.55	0.2	143
17	7.4	0.02	1.015	27.7	0.22	0.12	0.003	0.4	0.14	130
18	7.6	0.02	1.055	28	0.16	0.1	0.003	0.4	0.22	120

Also, The obtained data for group B, samples which collected from wells of groundwater with low depth, were recorded in Table 3.

Table 3:- Hydro-chemical data from groundwater with low depth wells (Group B)

Well No.	pH	Salinity	Cond.	Temp.	Turb.	DO	NO_2^-	NO_3^-	NH_3	SO_4^{-2}
1	7.5	0.05	1.35	25.7	0.25	0.44	0.003	0.15	0.4	90
2	7.5	0.03	0.746	25.3	0.21	0.35	0.002	0.2	0.08	70
3	8	0.07	1.292	25	0.17	1.2	0.03	3.7	0.3	85
4	8	0.02	0.568	23.8	0.2	0.8	0.01	0.4	0.76	90
5	7.7	0.04	0.857	24.2	0.16	0.3	0.012	0.11	0.7	158
6	7.6	0.03	0.769	24.4	0.3	0.44	0.01	0.07	0.85	101
7	7.8	0.05	0.988	26	0.2	0.2	0.003	0.25	0.66	35
8	7.4	0.07	1.267	25	0.2	0.15	0.02	0.4	0.5	32
9	7.4	0.05	1.678	24.3	0.18	0.5	0.014	0.3	0.09	40
10	8	0.04	1.53	25.4	0.15	0.3	0.012	0.5	0.1	43
11	7.6	0.01	0.64	23	0.21	0.7	0.006	0.09	0.2	98
12	7.5	0.02	0.886	24	0.12	0.4	0.009	0.3	0.6	86
13	8.1	0.02	0.592	25.2	0.06	3.4	0.001	0.05	0.48	71
14	7.8	0.01	0.575	27.3	0.32	3.8	0.001	0.05	0.48	52
15	7.7	0.05	1.13	25	0.26	2.01	0.002	0.04	0.68	98
16	7.9	0.05	0.766	24.2	0.09	0.38	0.003	0.04	ND	377
17	8	0.03	1.23	25.3	0.14	0.23	0.004	0.05	0.18	128
18	7.8	0.01	1.106	28	0.13	3.5	0.035	0.23	0.08	460
19	7.7	0.02	1.099	26	0.11	3.7	0.046	2.46	0.15	358
20	7.9	0.02	1.133	27.5	0.24	4.11	0.02	1.96	0.2	364
21	7.7	0.04	1	22.4	0.14	0.7	0.002	0.4	0.3	427
22	7.2	0.04	1	22.5	0.05	0.3	0.01	0.5	0.1	451
23	7.8	0.01	0.36	24	0.31	0.4	0.001	1.1	ND	42
24	7.3	0.03	0.86	24	0.09	0.45	0.002	0.08	0.3	156
25	7.6	0.01	0.699	23.1	0.05	0.3	0.001	0.2	0.12	98
26	8	0.03	0.757	23.2	0.1	0.4	0.003	0.1	0.1	118

Determination of Total Dissolved Solids (TDS):-
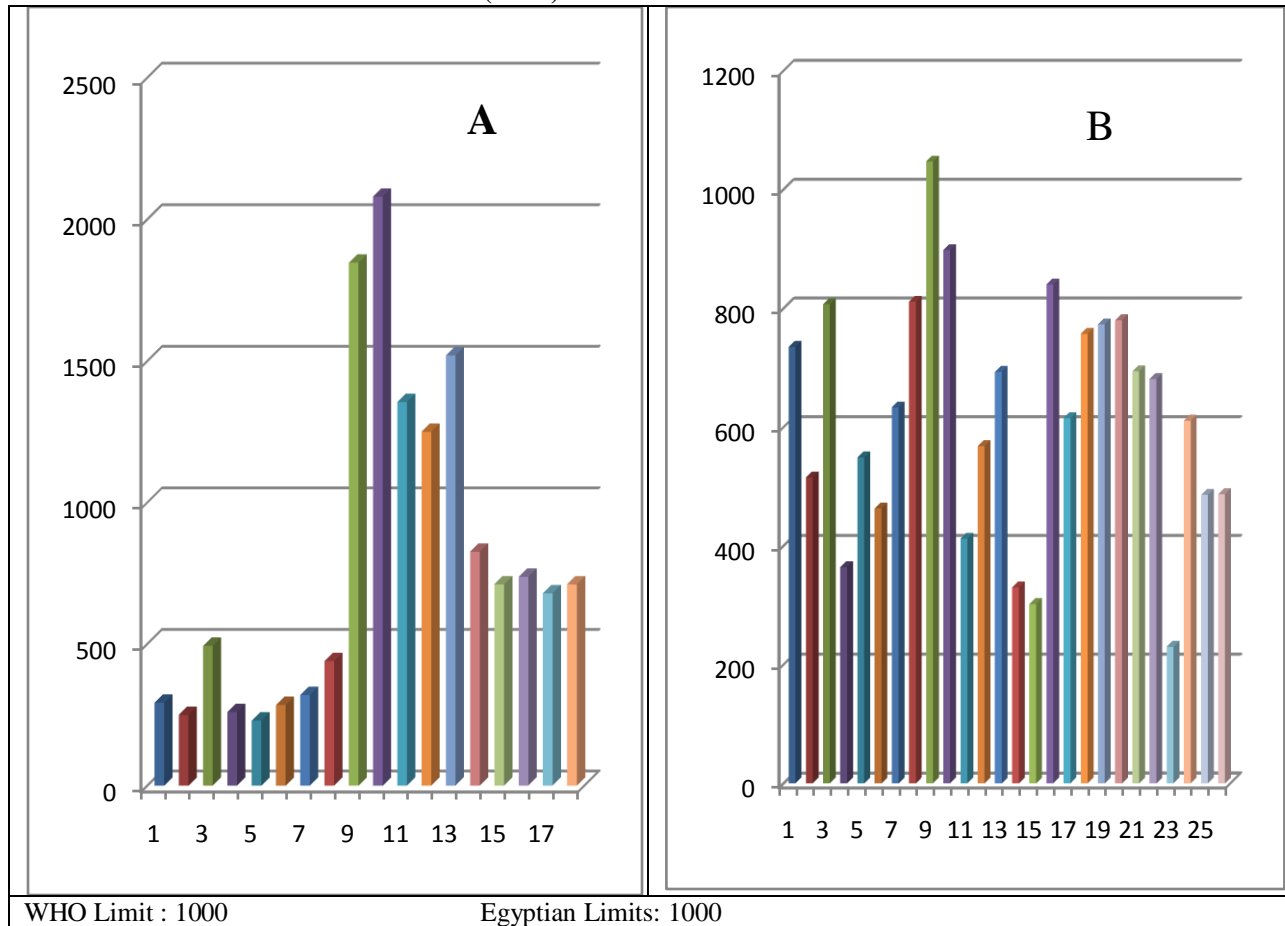
Fig. 2:- Determination of TDS in ground water: A) high depth wells , B) low depth wells.

According to a salinity classification by Rabinove et al [20], the groundwater was classified as shown in Table 4.
Table 4:- Classification of water on basis of Total Dissolved Solids (TDS).

Classification of groundwater	TDS (mg/L)
Non-saline	<1000
Slightly saline	1000-3000
Moderately saline	3000-10000
Very saline	>10000

The presence of high levels of TDS in water may be objectionable to consumers owing to the resulting taste and to excessive scaling in water pipes, heaters, boilers and household appliances [21].

Applying the classification from table 4 on the obtained data it is found that:
- On group A (high depth wells), there are 13 wells (less than 1000 mg/L) Non-Saline water. While, there are 5 wells (1000- 3000 mg/L) Slightly saline water.
- On group B, (Low depth wells), there are 25 wells (less than 1000 mg/L) Non-Saline water. While, there are only one well (1000- 3000 mg/L) Slightly-Saline water.

This means that, the depth of well can affect on the TDS of water . The low depth groundwater wells have Non-saline water more than high depth well. Relatively high salinity may be due to the lithologic composition of these locations, in addition the leaching and dissolution of the soil salts and chemical fertilizers by irrigation water.   The lower salinity was observed in the group B, wells no. (4, 5) this due to the seepage of the Nile water into these regions (the wells are near to the river Nile stream for about 400 m).

Determination of Total Hardness (T.H.):-
Water was classified according to Total Hardness, T.H., by Durfor and Becker's [22] classification, , shown in Table 5.

Table 5:- Classification of the water on the basis of Total Hardness (T.H.)

Description	Total Hardness (mg/L)
Soft	0-60
Moderately hard	61-120
Hard	121-180
Very hard	> 180

Total Hardness (T.H.) were determined for two groups of wells and summarized in Fig.3

WHO Limit : 500   Egyptian Limits: 500
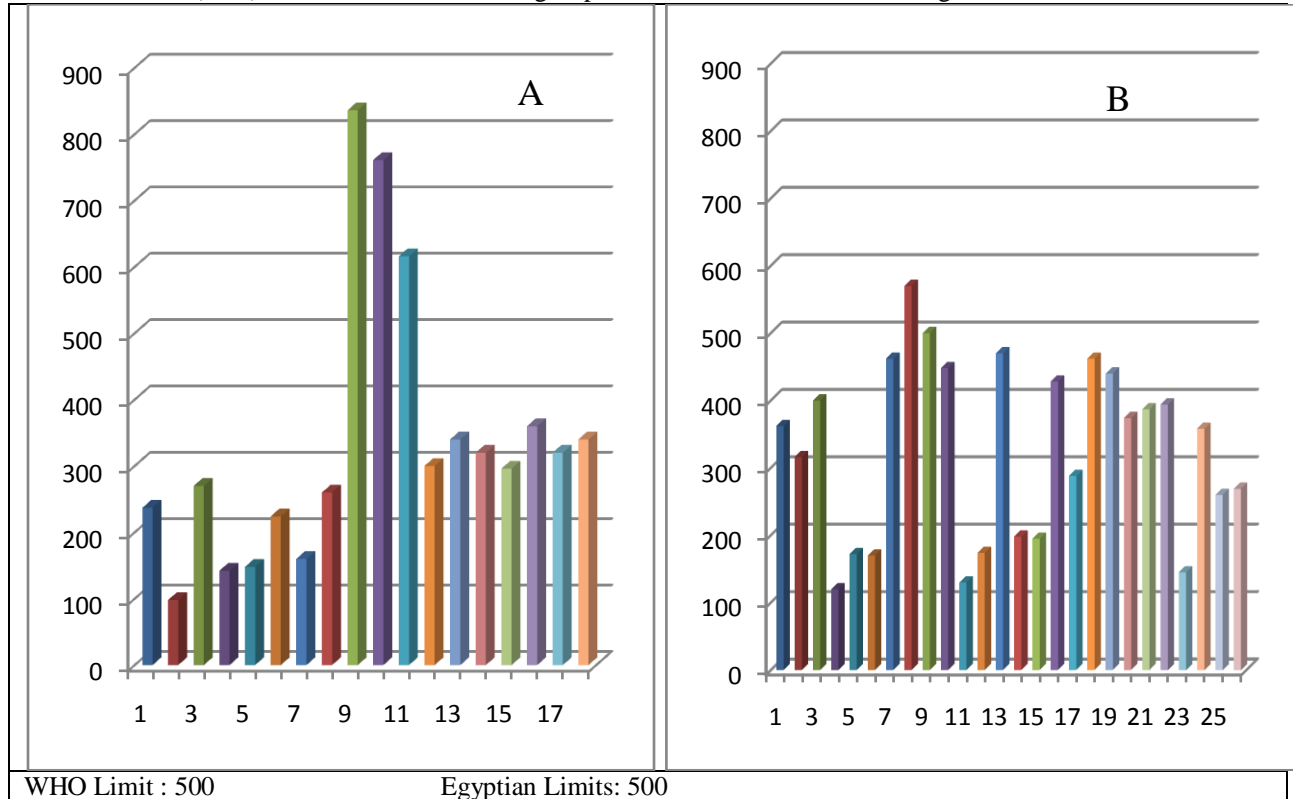
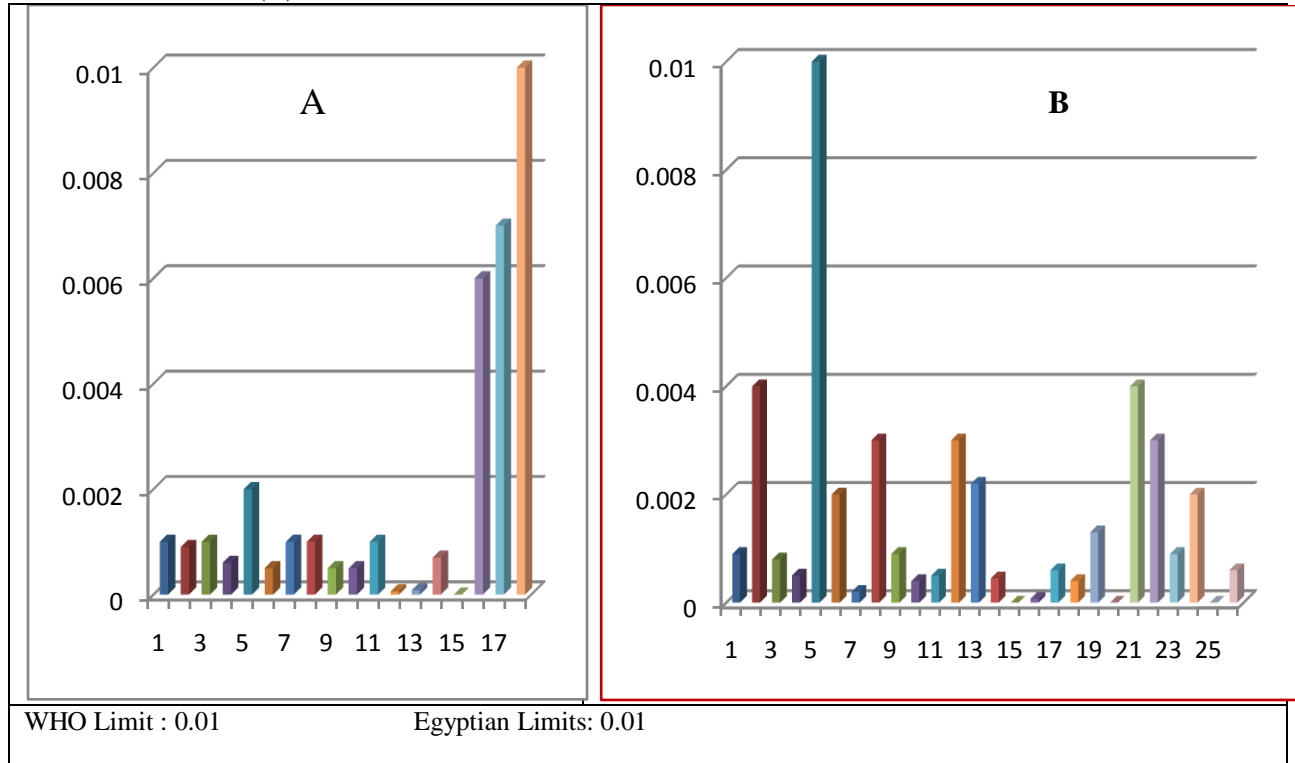**Fig. 3:-** Determination of T.H. in ground water A) high depth wells , B) low depth wells

The results show that the groundwater samples were characterized as follow:
- ❖ Group A (high depth wells) : there is no any well has soft water. One well has moderately hard . Also, there are 3 wells have hard water. While there are 14 wells have very hard water .
- ❖ Group B (low depth wells) : there is no any well has soft water. One well has moderately hard . Also, there are 5 wells have hard water. While there are 20 wells have very hard water .

**Determination of Some Metal Ions:-**
The suitability of the water from the groundwater sources for the drinking and domestic uses was analyzed by comparing the values of different water quality parameters with Egyptian guideline standard for drinking water [23]. WHO (World Health Organization) standards [24].

Determination of Pb(II) ions:-

WHO Limit : 0.01   Egyptian Limits: 0.01
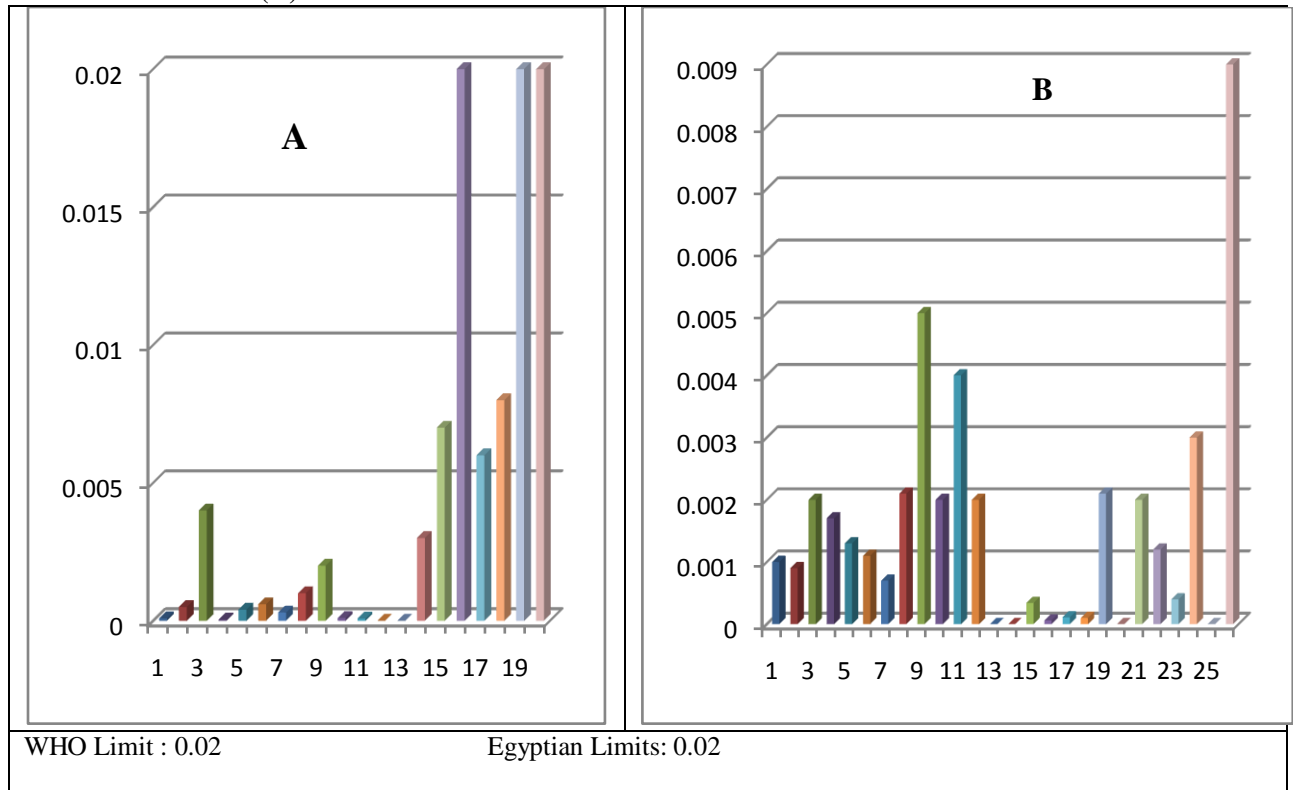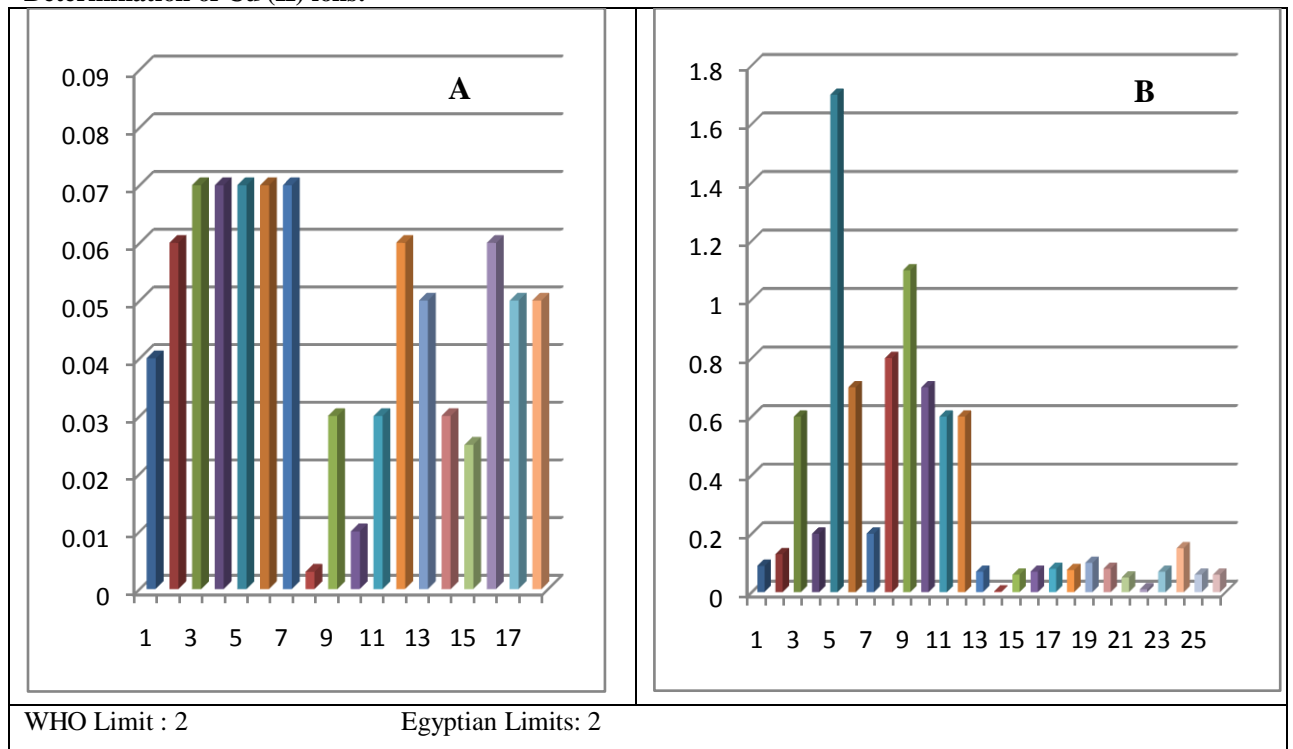
Fig. 4:- Concentration of Pb(II) ion in ground water: A) high depth wells , B) low depth wells

Determination of Cd(II) ions:-

WHO Limit : 0.003   Egyptian Limits: 0.003
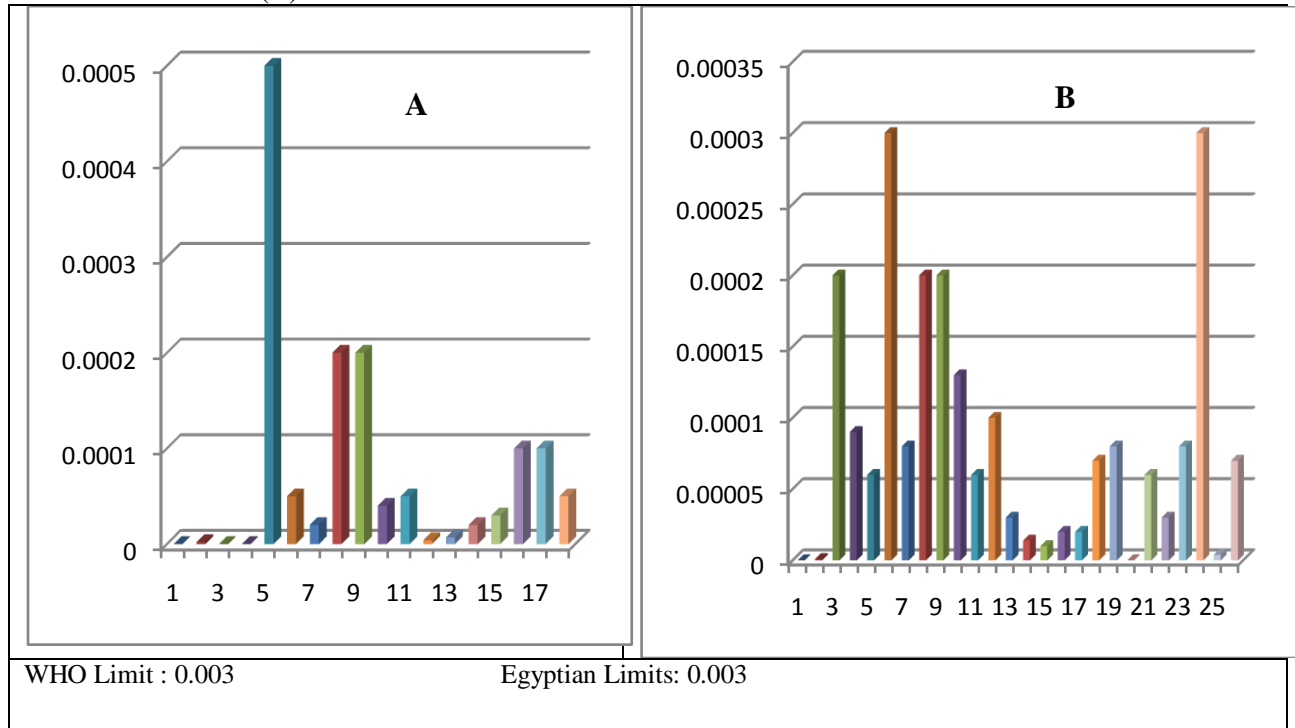
Fig. 5:- Concentration of Cd(II) ion in ground water: A) high depth wells , B) low depth wells

Determination of Ni (II) ions:-

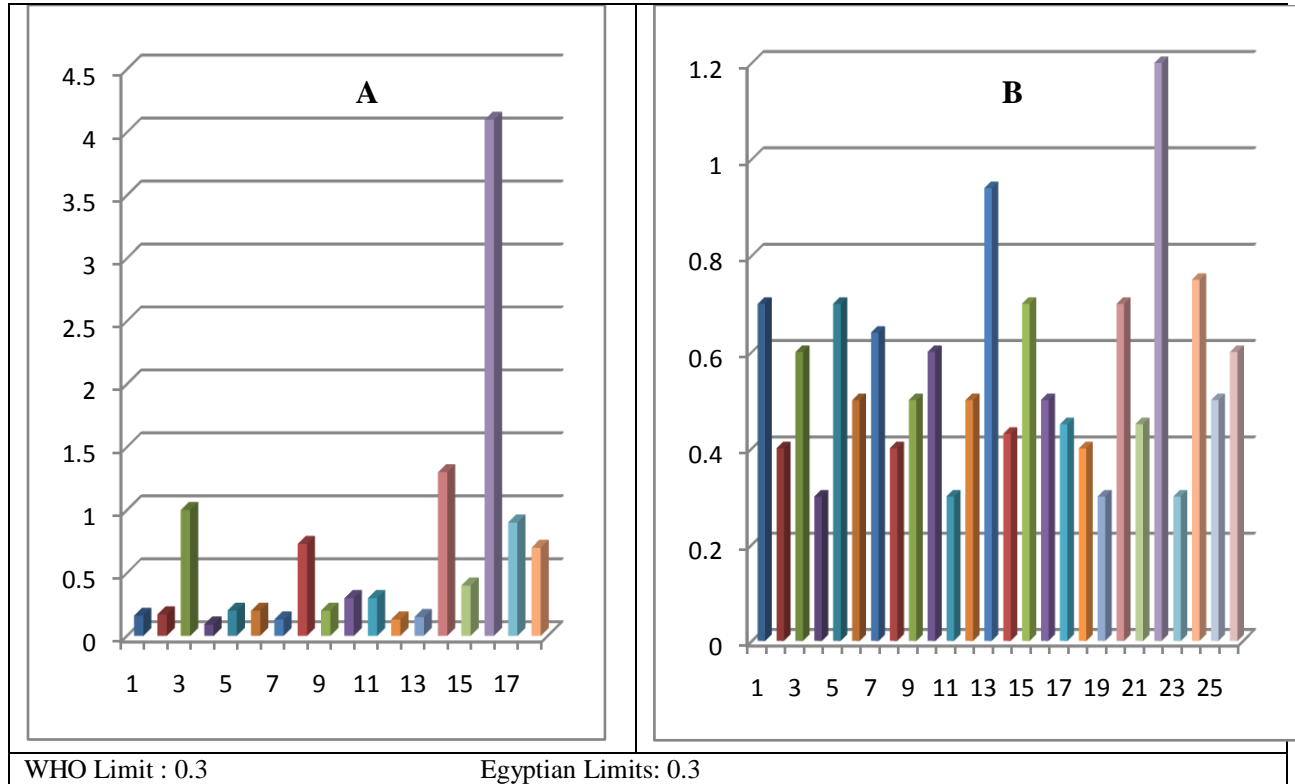WHO Limit : 0.02   Egyptian Limits: 0.02

Fig. 6:- Concentration of Ni(II) ion in ground water A) high depth wells , B) low depth wells.

Determination of Cu (II) ions:-

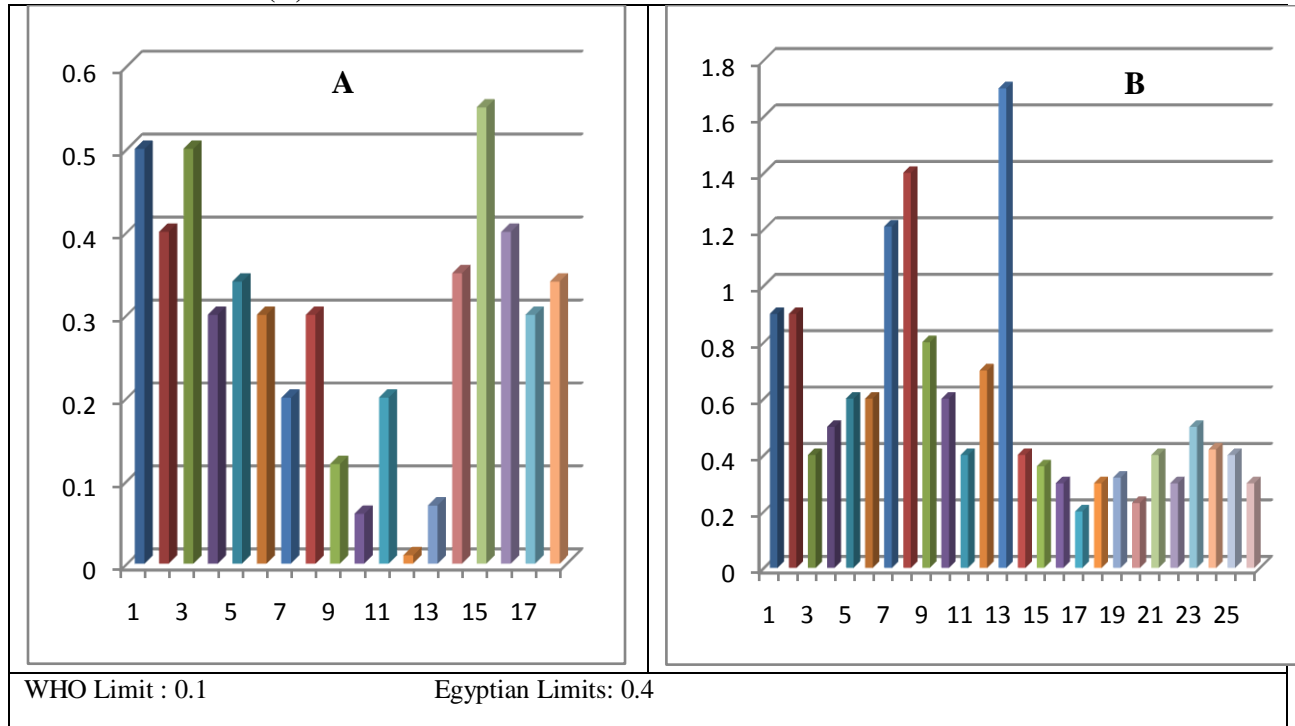

WHO Limit : 2   Egyptian Limits: 2

Fig. 7:- Concentration of Cu(II) ion in ground water: A) high depth wells , B) low depth wells

Determination of Total Fe ions:-

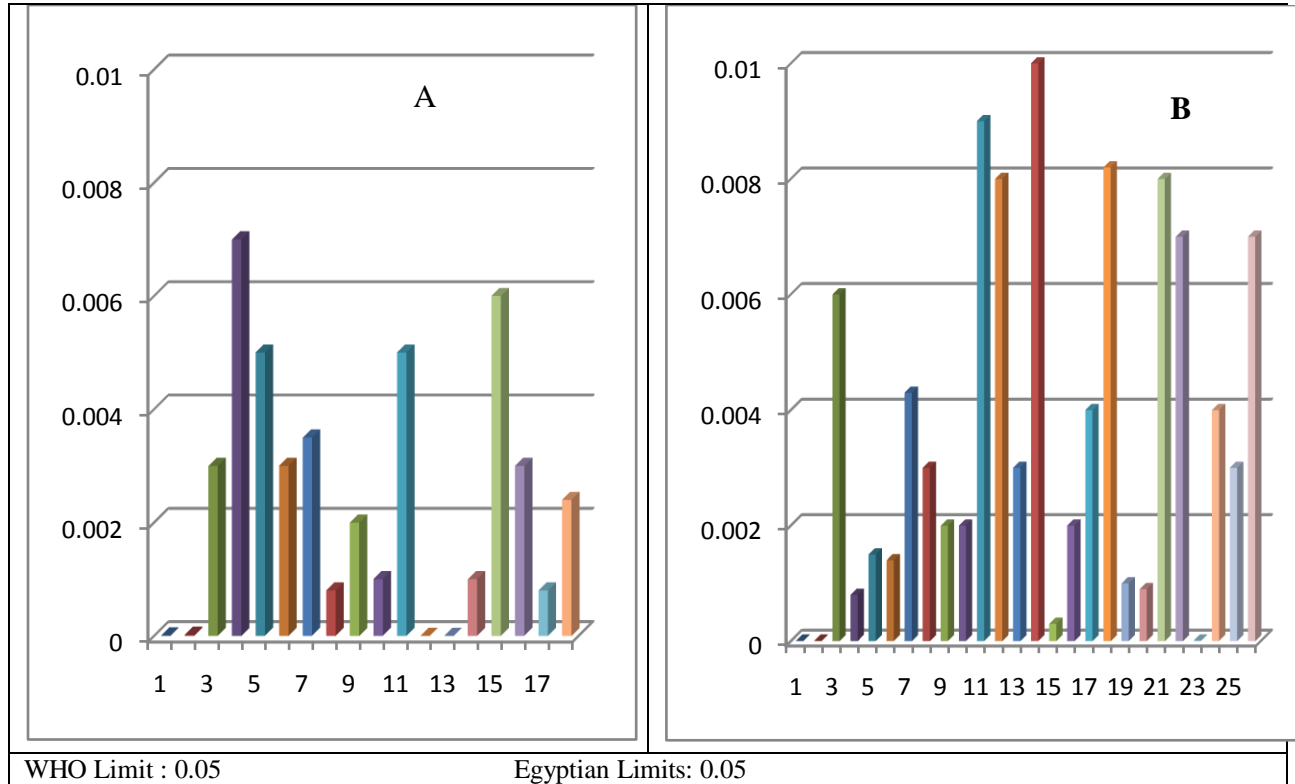WHO Limit : 0.3   Egyptian Limits: 0.3

Fig. 8:- Concentration of Total Fe in ground water: A) high depth wells , B) low depth wells

Determination of Mn(II) ions:-

WHO Limit : 0.1   Egyptian Limits: 0.4

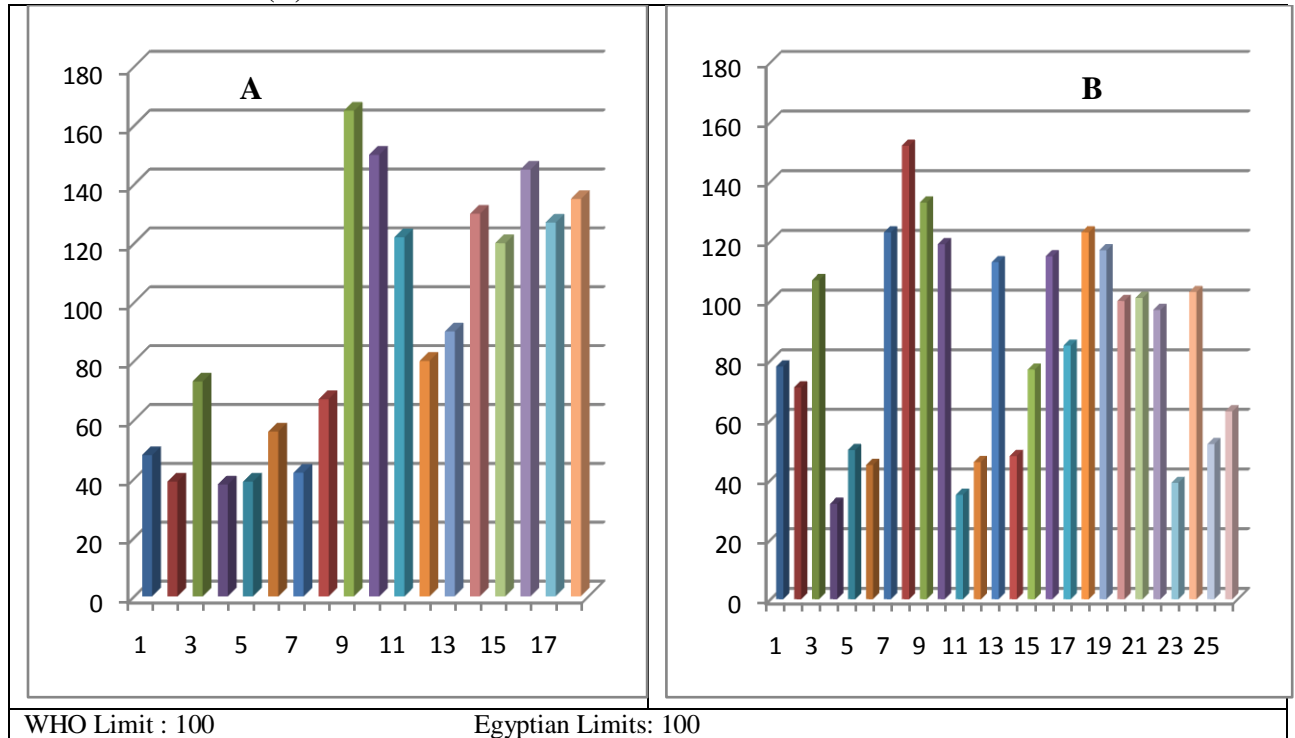**Fig. 9:-** Concentration of Mn(II) ion in ground water A) high depth wells , B) low depth wells.

Determination of Total Cr ions:-

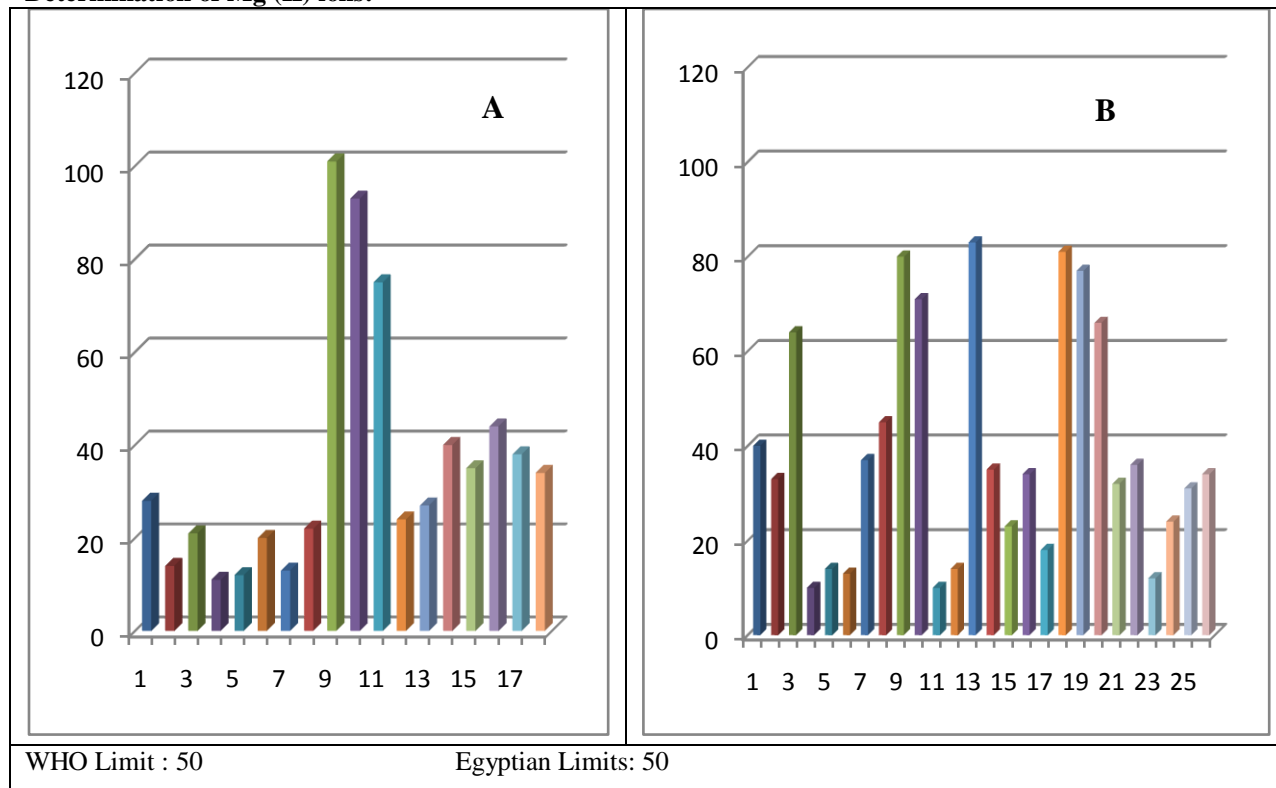| WHO Limit : 0.05	Egyptian Limits: 0.05

Fig. 10:- Concentration of Total Cr ion in ground water: A) high depth wells, B) low depth wells

Determination of Ca (II) ions:-

WHO Limit : 100	Egyptian Limits: 100

Fig. 11:- Concentration of Ca(II) ion in ground water A) high depth wells , B) low depth wells

Determination of Mg (II) ions:-

Fig. 12:- Concentration of Mg(II) ion in ground water: A) high depth wells , B) low depth wells

Among the heavy metals, low concentration of Pb (0.00006-0.01 mg/L), Cd (0.000001-0.0005mg/L), total Cr (0.00001-0.01 mg/L), Ni (0.000045-0.02 mg/L) may be due to presence of Cd, Pb, Cr and Ni as carbonates in the soil matrix. Poor reversibility of adsorbed metals can thus be attributed to incorporation into either or both of these solid components, most likely the carbonates [17].

However, concentration of total Fe (0.09- 4.1 mg/L), Mn (0.01-1.7 mg/L) and Cu (0.0024-1.7 mg/L) were relatively high, Relatively high concentration of these metal are due to the mobility of trace metals in presence of high concentration of chloride ion. Chloride complexation increases the metals mobility [18] and decreases adsorption [19].

Suitability of the groundwater in Assiut city and countryside for irrigational purposes:-
Groundwater in the study region finds intensive use in irrigation. Its suitability for irrigational purposes can be assessed using the indices for salinity [25]. Salinity index of the groundwater samples was computed using the measured electrical conductivity values. Water exhibiting low to moderate salinity (classes I and II) are not considered very harmful to soils or crops, whereas, those exhibiting high salinity (class III) are suitable for irrigating the medium and high salt tolerant crops.

High salinity water (class IV) is suitable for irrigating high salt tolerant crops, whereas, water of salinity (class V) or above is generally unsuitable for irrigation. Majority of the groundwater samples (73%) in the study region are categorized as class I or II, and thus, may be considered as suitable for irrigation. However, about 27% of the water samples are found to exhibit high salinity (classes III), and are suitable for irrigation (Figure 13).

Low salt tolerance crops are usually chloride sensitive. The chlorinity index of the groundwater sources was calculated using the measured chloride ion concentration in water (Figure 5). Majority of the groundwater samples (100%) are found to be suitable (classes I and II) for irrigation.

Low salt tolerance crops are usually chloride sensitive. The chlorinity index of the groundwater sources was calculated using the measured chloride ion concentration in water (Figure 5). Majority of the groundwater samples (100%) are found to be suitable (classes I and II) for irrigation.
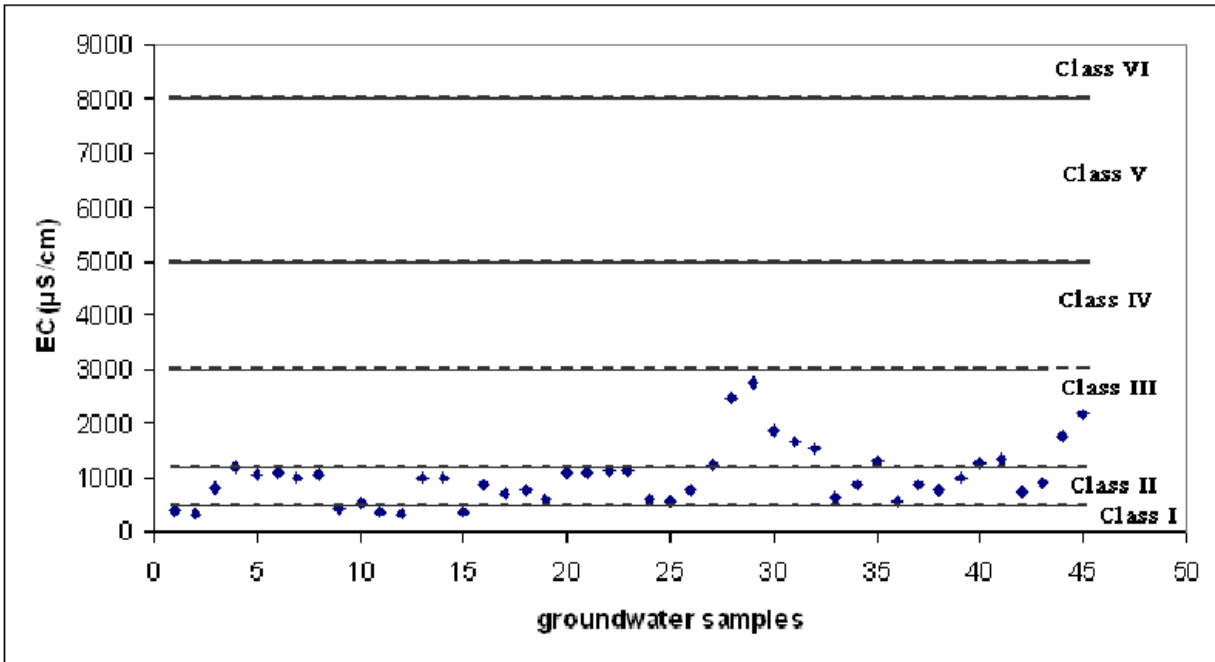

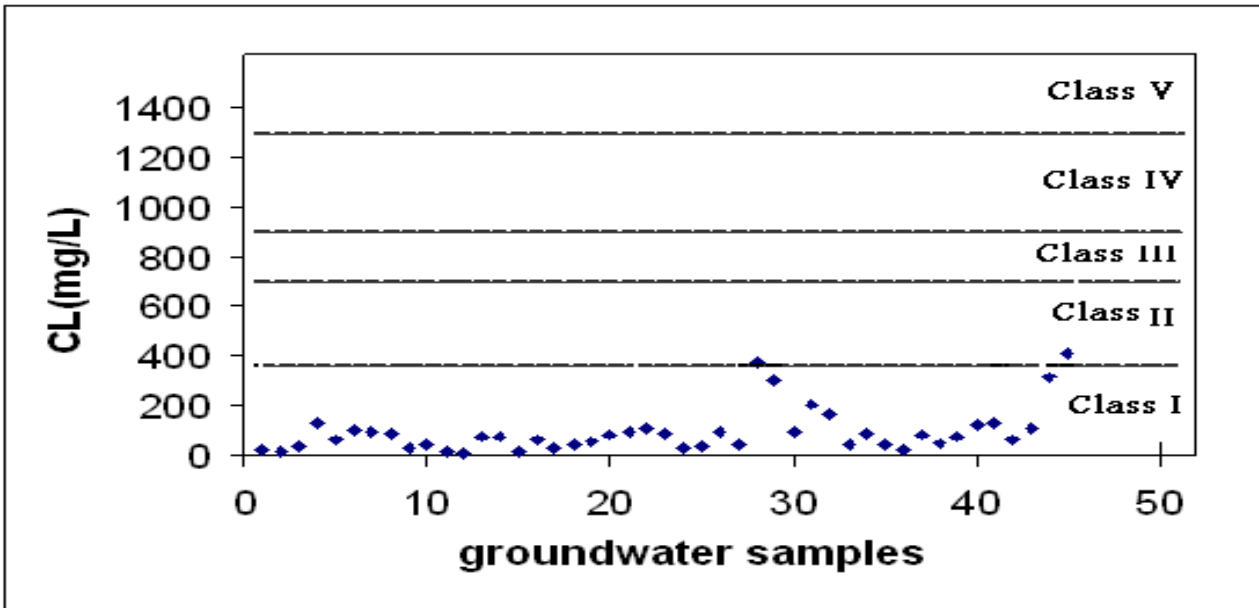**Fig. 13:-** Salinity index for groundwater sample of the study region.

Fig 14:- Cholrinity index for the groundwater samples of the study region.

Suitability of the groundwater in Assiut city and countryside for industrial purposes:-
Water is considered safe for industrial use, if it is neither scale forming nor corrosive in nature. The saturation index of water is an important parameter for assessing its tendency for precipitating out or dissolving calcium carbonate.

Two different saturation indices were calculated, The Langelier Saturation Index (LSI); and the Ryznar Stability Index (RSI) [26].

Determination of Langelier Saturation Index (LSI):-
The LSI is defined as the difference of actual measured pH of water (pH_w) and calculated pH which the water would have when in equilibrium with calcium carbonate (pH_s) as follows:
Where pH_s, the pH at saturation in calcium carbonate is calculated as
$$LSI = pH_w - pH_s \tag{1}$$
$$pH_s = (9.3 + A + B) - (C + D)$$

Where the constants $A = (Log_{10} [TDS] - 1)/10$; $B = -13.12 \times Log_{10} (^oC + 273) + 34.55$; $C = Log_{10} [Ca^{2+}$ as $CaCO_3] - 0.4$,
and $D = Log_{10}$ [alkalinity as $CaCO_3$].

A negative value of LSI indicates $CaCO_3$ dissolving nature of water, whereas, a positive value suggests for scale forming tendency of water. The negative values of LSI index indicates all the water samples would be safe for industrial purposes (electric power station and industrial boiler houses, etc; the water may be either heated or cooled). The positive values indicate the positive tendencies for the waters to dissolve any solid calcium carbonate present.

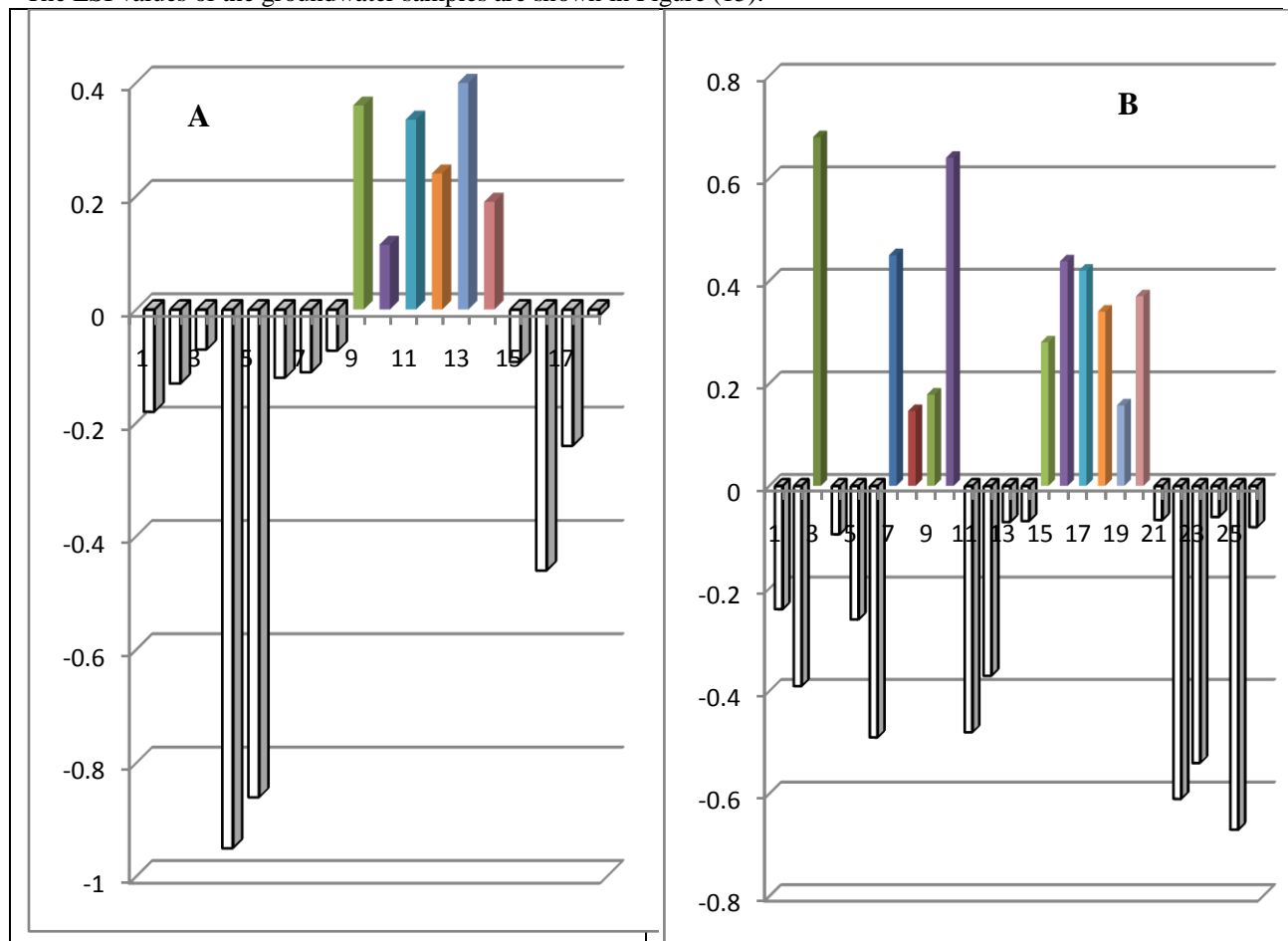The LSI values of the groundwater samples are shown in Figure (15).

Fig. 15:- The LSI values of the groundwater: A) high depth wells , B) low depth wells

It is evident that:-
- ❖ On group A, the water samples (66.7%) are $CaCO_3$ dissolving, whereas (33.3%) are $CaCO_3$ depositing in nature.
- ❖ While, On group B, the water samples (57.7%) are $CaCO_3$ dissolving, whereas (42.3%) are $CaCO_3$ depositing in nature.

Determination of the Ryznar Stability Index (RSI):-
The RSI is calculated as:
$$RSI = 2(pH_s) - pH_w \qquad (2)$$

Where pH_S is the pH at saturation in calcium carbonate and pH_w is the measured pH of water. RSI value of< 6 indicates increasing tendency for scale formation with a Decreasing index value, whereas, a value of > 7 suggests formation of no corrosion protective films. Water with RSI > 8 suggests tendency for dissolution of $CaCO_3$, and thus corrosive in nature. The RSI values of the groundwater samples are shown in Figure (16).
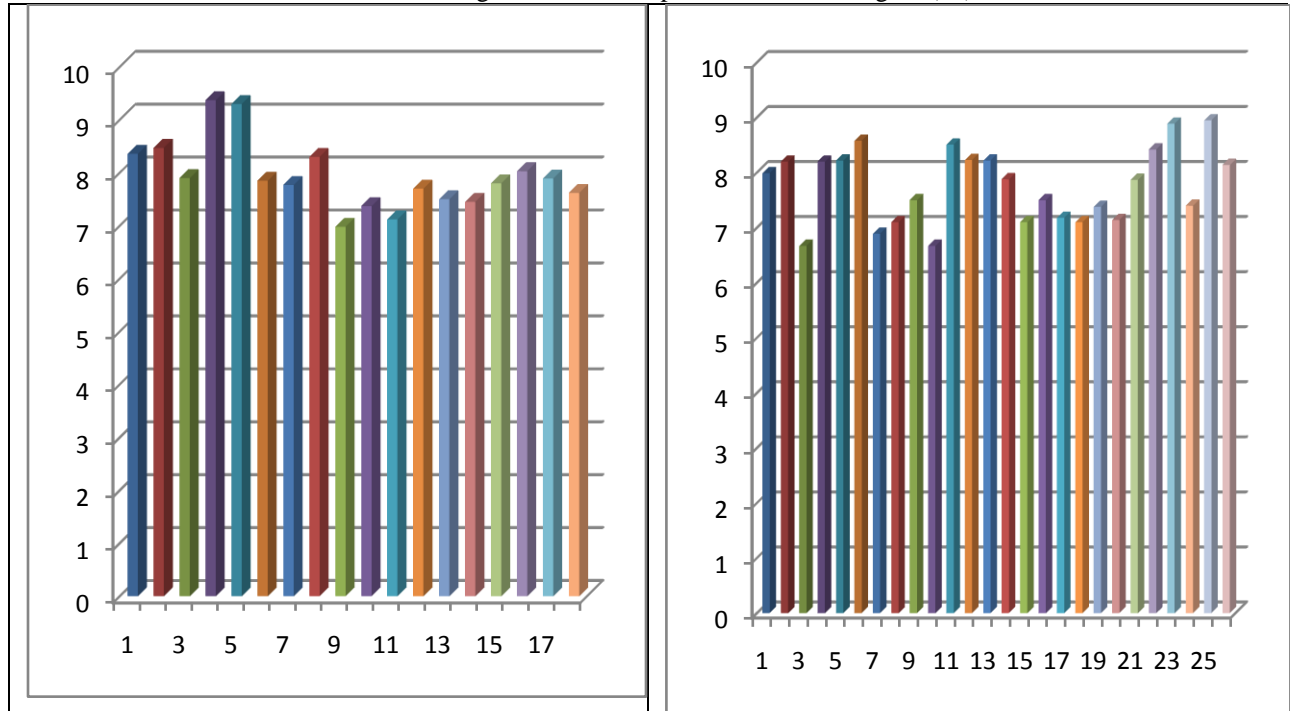
Fig. 16:- The RSI values of the groundwater: A) high depth wells , B) low depth wells

Water Quality Index(WQI):-
The water quality index (WQI) allows the reduction of vast amounts of data on a range of physico-chemical and biological parameters to a single number in a simple reproducible manner. The assessment of heavy metals is included with water quality parameters in order to assess overall pollution of water. WQI is calculated from the point of view of stream water quality criteria with regard to all uses [27-28]. Fourteen water quality parameters (NO_2^-, NO_3^-, NH_3, F^-, Cl^-, TDS, T.H, Cd, Fe, Mn, Cr, Cu, Ni, and Pb) were considered according to their importance as water quality assessment indicators. The overall water quality index can be calculated as follows:

$$WQI = \sum_{i=1}^{n} qi \qquad (1)$$

Where: n = number of parameter, qi = quality rating for the ith water quality parameter. The quality rating can be obtained by the following relation: qi = 100 (Vi/Si) where Vi = observed value of the ith parameter at a given sampling site and Si = water quality standard for i. The permissible or critical pollution index value is 100. The average water quality index (AWQI) for n parameters can be calculated using the following equation:

$$AWQI = \frac{\sum_{i=1}^{n} qi}{n} \qquad (2)$$

The AWQI = 0 when all pollutants are absent, and the AWQI = 100 when all pollutants reach their permissible limits. Values of AWQI exceeding 100 indicate that the water sample may suffer from serious pollution problems.

The computed AWQI value ranges from 18 to 137 and therefore, can be categorized into five types "excellent water" to "water unsuitable for drinking". Table (6) shows the water quality classification based on WQI,

Table 6:- Water quality classification based on WQI value**.**

WQI value	Water quality	Number of wells of group A	Number of wells of group B
< 50	Excellent	12	15
50-100	Good water	5	11
100-200	Poor water	1	-
200-300	Very poor water	-	-
>300	Water unsuitable for drinking	-	-

But the AWQI for the other wells are generally good as shown in Fig.17
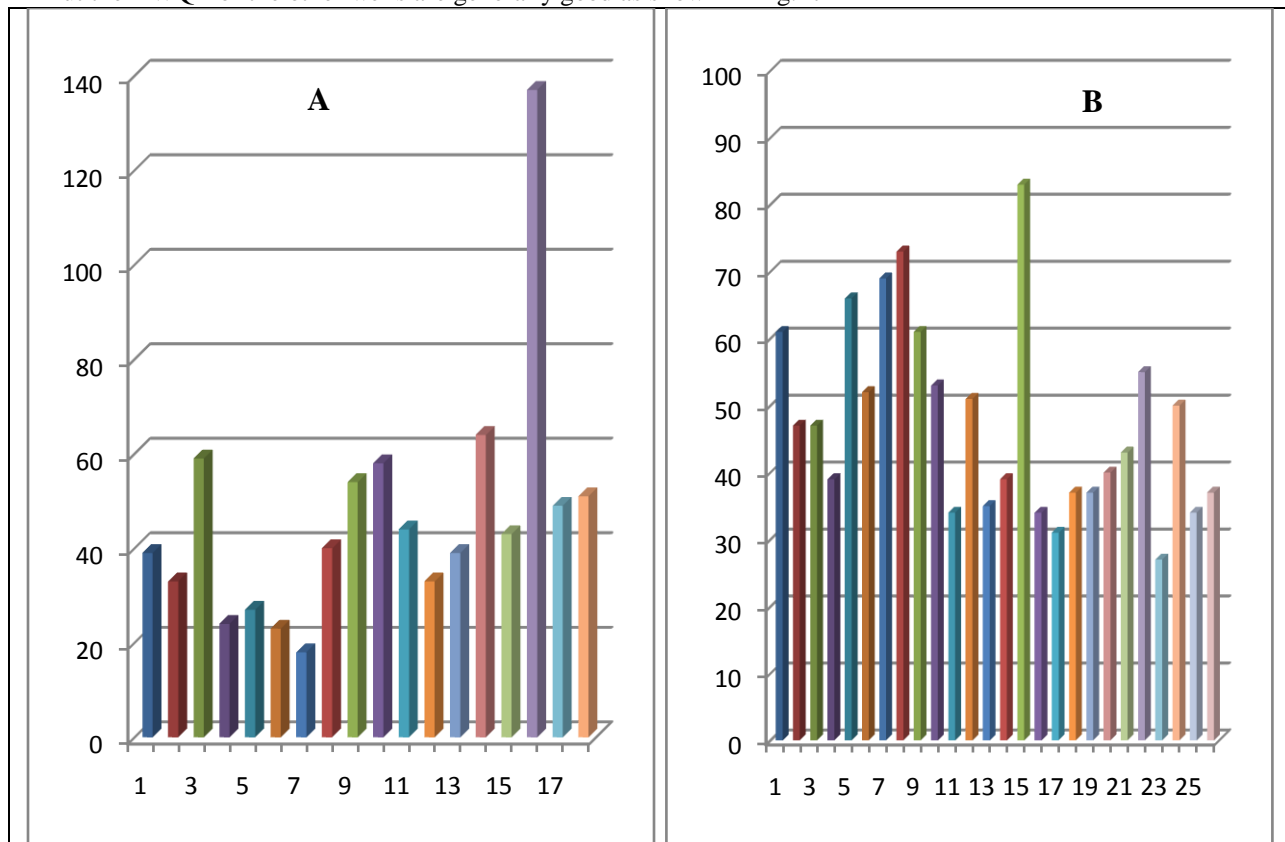
Fig. 17:- AWQI for ground water: A) high depth wells , B) low depth wells

AWQI of well no. (16 in group A) exceed 100. The high value of AWQI at this case has been found to be mainly from the higher values of iron, total dissolved solids, manganese, fluorides, and hardness. The AWQI for all wells was below the value (100) which refers to the water manly good water.

Correlation of quality variables among groundwater:-

Statistical analysis of the database of groundwater samples (table 7) exhibits excellent positive correlation values(r > 0.8) between salinity and EC, TDS, T.H, Cl⁻ indicate salinity is the total amount concentration of dissolved salts the salts present are typically dominated by cation such as [calcium (Ca^{+2}) and magnesium (Mg^{+2})] and anions such as [carbonate (CO_3^{-2}), sulphate (SO_4^{-2}), and chloride (Cl^-)].

A high correlation (r = 0.98) Between EC and TDS as the TDS values have been derived from the EC.

High positive correlation (r ranged from 0.66 to 0.98) between EC and TDS, Cl^-, T.H, Ca^{+2}, Mg^{+2}, SO_4^{-2} this is due to the fact that conductivity depends on total dissolved solids and the main constituents of TDS in water are Ca^{+2}, Mg^{+2} and Cl^-, SO_4^{-2}. High positive correlation (r ranged from 0.702 to 0.912) are observed between Ca & Mg, Ca & T.H and Mg & T.H this due to the presence of Ca & Mg as dolomite (Ca Mg CO_3) in sandstone, in addition, the Ca & Mg are a main causes for hardness [15].

Also, positive correlation value (r = 0.657) between Mg and SO_4^{-2}, indicate that the main water type in samples is (Mg SO_4).

Fe correlates inversely with ORP (r = -0.4, table 20) indicate that the concentration of dissolved Fe would be influenced principally by the redox potentials of groundwater systems. The presence of high levels of (Fe) is possibly a result from the reductive dissolution of Fe oxides under the lower redox levels of groundwater [29]. The occurrence of trace elements is possibly influenced by redox levels and nature of underlying sediment.

Fe & Mn correlates inversely with DO (r = -0.27,-0.23 respectively) indicate that the extent to which Fe and Mn dissolve in groundwater depends on the amount of oxygen in the water. When at higher dissolved oxygen levels, iron occurs as Fe^{3+}, while at lower dissolved oxygen levels, the iron occurs as Fe^{2+}.Where Fe^{2+} is very soluble in water and Fe^{3+} will not dissolve in water.

In addition, there was no correlation of Mn with other elements (Table 8) indicate that the manganese in water samples probably originated from amorphous state, [30].

No correlation of Cd with other elements, indicating that the dissolution of mineral phase could not be the source of cadmium. Where don't find any manufactures producing Cd – containing wastes in study area [30]. High positive correlation (r =0.93) are observed between TOC & COD indicate to COD and TOC specify the loading of organic matter in water samples.

Table 7:- Least square of the relation (x = A+ By) among significantly correlated parameter.

x(dependent)	y(independent)	r*	A	B
Salinity	EC	0.892	-0.14	0.051
Salinity	TDS	0.912	-0.01	7E-05
Salinity	T.H	0.749	-0.009	0.0001
Salinity	Cl^-	0.825	0.012	0.0003
EC	TDS	0.977	0.111	0.0013
EC	T.H	0.823	0.11	0.003
EC	Cl^-	0.881	0.531	0.005
EC	Ca^{+2}	0.710	0.13	0.01
EC	Mg^{+2}	0.712	0.441	0.015
EC	SO_4^{-2}	0.610	0.738	0.002
Ca^{+2}	Mg^{+2}	0.766	44.246	1.117
Ca^{+2}	T.H	0.868	20.713	0.205
Mg^{+2}	T.H	0.875	-6.953	0.135
Mg^{+2}	SO_4^{-2}	0.638	23.707	0.082
Fe	DO	-0.269	0.734	-0.137
Fe	ORP	-0.414	1.093	-0.003
Mn	DO	-0.23	0.543	-0.065
TOC	COD	0.933	-0.671	0.773

Table 8:- Correlation coefficient values of chemical parameters of groundwater

	TDS	T.H	Ca	Mg	Pb	Cd	Ni	Cu	Fe	Mn	Cr
TDS	1	0.84**	0.65**	0.74**	-0.1	-0.07	0.05	-0.02	-0.01	-0.21	-0.09
T.H		1	0.83**	0.91**	-0.1	0.04	0.02	-0.05	0.06	0.07	-0.07
Ca			1	0.7**	0.2	0.01	0.36*	-0.03	0.36*	0.13	-0.09
Mg				1	-0.1	0.09	-0.02	0.05	-0.01	0.13	-0.1
Pb					1	-0.02	0.43**	0.33*	0.4**	0.12	-0.14
Cd						1	-0.01	0.25	-0.01	0.1	-0.01
Ni							1	-0.02	0.79**	-0.01	0.1
Cu								1	-0.02	0.33*	-0.04
Fe									1	0.09	-0.08
Mn										1	-0.07
Cr											1

* Significant value at $p<0.05$,   **** Significant value at $p<0.01$**

Conclusion:-

The study clearly indicate the most ground water of Assiut city and some countryside suitable for drinking and human use in accordance with the limits of law of the Egyptian drinking water with exception of wells No.[(9, 10, 11, 12, and 13) from group A, while only well No. 9 from group B) . Most of wells should be treated for Fe and Mn. Most groundwater samples can be used for irrigation and industrial purposes (negative values of sat. index) and for different uses (WQI). The depth of well can affect on some parameters of water quality such as, the TDS of water. The low depth groundwater wells have Non-saline water more than high depth well. Statistical analyses confirm results of chemical analysis and exhibits good and interesting correlations lead to interpretation these results.

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