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Assessment of Groundwater Quality for Different Uses Case Study: El Minya Governorate, Egypt

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ABSTRACT

The prime goals of the present study are to assess trends in the concentrations of the groundwater quality and evaluate this water for domestic, agriculture and various industrial processes. Groundwater quality indicators were monitored, for the first time, for4 years (2011, 2013, 2014 and -2015) from three wells constructed in El-Sheikh Fadl, Bani Mazar, El Minya Governorate, Egypt. Quality indicators included pH, alkalinity, TDS, hardness, Na⁺, k⁺, Mg²⁺, Ca²⁺, Cl⁻, SO₄²⁻, NO₃⁻, S²⁻, Al³⁺, Cu²⁺, Fe²⁺, Mn²⁺ and Ni²⁺ concentrations. Based on the outcomes, groundwater was classified as brackish water. Elevated pH, alkalinity, Ca²⁺, SO₄²⁻, NO₃⁻, S²⁻, Al³⁺, Cu²⁺, Fe²⁺, Mn²⁺and Ni²⁺ concentrations were observed over monitoring years. Three main Varimax-rotated factors counted for 82.53 % of the total variance of the quality variables revealing how process like water-rock interaction, salinization and industrial pollution influence groundwater quality. The groundwater samples have a mixed mineralization that is possibly pure marine water affected by leaching and dissolution and cation exchange of both meteoric water (rainy water containing cement dust) and terrestrial salts. Groundwater is generally supersaturated with respect to calcite, dolomite and aragonite minerals. The water wells are not suitable for drinking and irrigation. For industrial, the groundwater needs further treatment.

INTRODUCTION

Monitoring of the concentrations of physical and chemical parameters in groundwater is required for various functions, i.e. to describe the chemical composition of groundwater, to become aware of the presence and spatial distribution of pollutants and to identify trends in pollutant concentrations and natural substances through the years (Quevauviller *et al.*, 2009).Groundwater quality is controlled by the composition of its recharge components in addition to geological and hydrological

variations within the aquifers (Shahnawaz and Singh, 2009). Establish new production enterprise impact on the water resources in the surroundingarea, for example groundwater wells. The effect relies upon the quality of both baseline water resources and the discharge effluent from that industry.

The cement industry has been recognized to be playing a critical role in the imbalances of the surroundings and producing air pollutant hazards. The industries of cement are commonly related to excessive dust emissions by the handling and storage of intermediate and final materials, into the atmosphere (Bilen, 2010). Dusts emitted are naturally removed as deposits to the earth's surface through dry or wet deposition in rainfall (Olaleye, 2005). The dust of cement spreads along large area through rain, wind, etc. and is accumulated in and on soils, plants and animals. Those dusts could cause destructive effects on human health. The harmful effects of dust fall, is characterized via enriched toxic trace elements such as arsenic, cadmium, chromium, copper, lead, manganese, nickel, and zinc (Schuhmacher *et al.*, 2002). At low levels some of these elements are essential for human beings, but at high levels they can also mean a toxicological risk (Domingo, 2001).

Arab National Cement Company (ANCC), a subsidiary of regional cement producer ASEC (Annual Social and Economic Cement (ASEC) Supplement), is located some 220 kilometers south of Cairo, El-Minya governorate. ANCC constructed to cover the cement demand for projects held by the government. Production capacity of ANCC is 2 million tons/ year of high-quality gray cement. Production of high quality Portland cement ANCC is enhanced by the abundance of limestone in this area. The company constructed three wells in 2011 to cover the water demand of the company. Dust emissions from cement factory have not only affected the environment, but also on water quality from wells.

The current study concerned with three groundwater wells constructed in El-Sheikh Fadl, Bani Mazar, Minya Governorate, Egypt. No study has been done yet on these wells. The research aims at determining physico-chemical properties of the groundwater during period of four years (2011, 2013, 2014 and 2015), assess how groundwater quality parameters are varied, identify significant sources of quality variation and determine the origin of groundwater. Finally, investigate the suitability and acceptability of groundwater for drinking, irrigation and industrial uses.

MATRIALS AND METHODS

Study area:

The study area of the research presented here is located (between latitudes 28° 24' and 28° 25' N and longitudes 30° 57' and 30° 58' E) at the Eastern bank of River Nile, El-Sheikh Fadl, Bani Mazar, El-Minya Governorate, Egypt (Fig. 1). Table 1 shows groundwater wells coordinates and their hydraulic characteristics (obtained from the Arab National Cement Company).



Fig.1: Groundwater wells site locations (modified after Google earth).

Sampling:

Monitoring of three wells was carried out four times yearly during four years (2011, 2013, 2014 and 2015). The year 2011 represents the baseline (control), while 2013, 2014 and 2015 represent the monitoring years to determine the temporal quality variation. The samples were collected from all wells (three) present in the study area to compare between them and determine the spatial quality variation. Forty eight (48) groundwater samples were collected from well 1, well 2 and well 3 during four years (2011, 2013, 2014 and 2015) according to guidelines (EPA, 2002). Three surface water samples were collected from River Nile, El Minya governorate to determine the origin of water. For each sample three bottles were needed to perform the analysis. For major cations and trace elements, the samples filtered by the filtration system through a membrane filter of pore size 0.45 μ and acidified with nitric acid to pH <2, to prevent any change in the chemical composition of the sample before analysis, and the other two bottles were free from any additives.

| Arab National Cement Company "Minya Governorate" | | | | | | | |
|--|--|---|--|--|--|--|--|
| | Well 1 | Well 2 | Well 3 | | | | |
| Coordinates | N 28° 25' 00.9" | N 28°24' 51.8" | N 28° 24'59.2" | | | | |
| Coordinates | E 30° 57' 38.5" | E 30° 58' 09.8" | E 30° 57' 55.6" | | | | |
| Well total depth | 210 m | 216 m | 250 m | | | | |
| Materials (Casing & Screen) | Steel | UPVC (unplasticized polyvinyl chloride) | PVC (polyvinyl chloride) | | | | |
| Formation loss | $7.7\times10^{\text{-3}}~\text{d/m}^2$ | $9.5 \times 10^{-3} \text{ d/m}^2$ | $1.6 \times 10^{-2} \text{ d/m}^2$ | | | | |
| Well loss | $5.01\times 10^{\text{-6}}~d^2\!/m^5$ | $1.04 \times 10^{-5} d^2/m^5$ | $1.52 \times 10^{\text{-6}} \ \text{d}^2\!/\text{m}^5$ | | | | |
| Well safe yield | 60 m ³ /h | 50 m ³ /h | 70 m ³ /h | | | | |
| Pump setting depth | 145 m | 160 m | 160 m | | | | |

| fable (1): Some hydraulic parameter | s of the studied wells in El-Sheik | kh Fadl, Bani Mazar, El- Minya |
|-------------------------------------|------------------------------------|--------------------------------|
|-------------------------------------|------------------------------------|--------------------------------|

Reagents and Quality assurance:

Analytical reagent grade chemicals and deionized water were used for preparing all solutions. All plastic bottles were cleaned by soaking in 10% HNO₃. Procedural blanks, preparation of standard solutions were done under clean laboratory environment. Stock standard solutions of aluminum (Al), copper (Cu), iron (Fe), manganese (Mn) and Nickel (Ni), were obtained from Merck in concentrations of 1000 mg/L (Merck, Darmstadt, Germany). Recovery studies for the trace and major elements analyzed using ICP-OES & ICP-MS (inductively coupled plasma-optical emission spectrometry and inductively coupled plasma-mass spectrometry) ranged between 96 and 103%. The samples were analyzed in a thrice, while the mean value and standard deviation (SD) were calculated.

Water analysis:

The physico-chemical parameters were determined according to standard methods for examination of water and wastewater (APHA, 2005). Field tests on all samples including sulfide analysis and chlorine residual. Hydrogen sulfide was measured in the field using Methylene Blue Method (APHA, 2005) by HACH field spectrophotometer DR/2400. Chlorine demand was determined by applying different doses of chlorine to the samples according to method No. 10223, HACH company manual (HACH, 2012). Residual chlorinewas measured in the field (APHA, 2005), by Pocket Colorimeter II. pH measured at 25°C using pH meter InoLab WTW level 1. Alkalinity [Carbonate (CO_3^{2-}) and bicarbonates (HCO_3^{-}) ions] was determined titrimetrically against 0.2 N-H₂SO₄, using phenolphthalein and methyl orange indicators. Total dissolved solids (TDS) were determined by weighing the solid residue obtained by evaporating a measured volume of filtered water sample to dryness at 103-105°C. Chloride (Cl⁻), sulfate (SO₄²⁻) and nitrate (NO₃⁻), were measured using Ion Chromatography (IC), Dionex product, model DX5000. Calcium (Ca^{2+}) , potassium (K^+) , magnesium (Mg^{2+}) and sodium (Na^+) were measured by inductively coupled plasma-optical emission spectrometry (ICP-OES) Perkin-Elmer product, model Optima 5300 DV. Trace elements (aluminum Al³⁺, Copper Cu²⁺, Iron Fe^{2+} , manganese Mn^{2+} and nickel Ni²⁺) were measured in water by using the inductively coupled plasma-mass spectrometry (ICP-MS), SCIEX ELAN 9000. **Programs used for interpretation and reporting:**

Basic descriptive parameters (mean values and standard deviation (SD)) were obtained using SPSS, ver. 15, 2006, statistical software. Analysis of variance (ANOVA) and multiple component tests were applied to all parameters to identify significant spatial and temporal differences (p<0.05), using Cost at statistical program, ver. 6.400, USA. Principle component analyses (PC) of significant parameters (p<0.05) were made to find the degree of influence factors using XLSTAT, an Excel statistical add-on was used. Saturation indices (SI) were calculated using Aquachem v. 4.0.265 - PHREEQC modeled.

RESULTS AND DISCUSSION

Chemical compositions of collecting groundwater samples, their statistical and modeling plots are presented in Figs. 2 to 6 and Table 2 to 8. For investigating the status and trends of groundwater quality, the following procedures were applied to the water quality data; study spatial quality variables, temporal quality variations, interpretation spatio-temporal quality changes, detection variation factors and determine the origin of water. Finally, the results have been discussed in the light of drinking, irrigation and industrial usages.

Spatial water quality parameters variation

Spatial quality variation is controlled by rock-water interaction along distinct subsurface flow paths. Comparing physico-chemical water quality for the studied wells as shown in Table (2) which indicated that:

- Comparing water quality parameters of well1 with well2 (or well3) demonstrated that pH, sulphate and chloride didn't show significant spatial variation (p>0.05). While all the remains of water quality parameters showed significant spatial quality variation (p<0.05). Aluminum, copper, iron, manganese and zinc were found at high levels in well 1 with respect to their levels in wells 2 & 3.
- Comparing water quality parameters of well 2 & well 3 indicated that calcium showed significant spatial variation (p<0.05). The other parameters of well 2 and well 3, showed non significant spatial variation (p>0.05).
- Finally, the sequence of spatial pollution for TDS, hardness, calcium, sodium, chloride & sulphatewasWell3> Well 2> Well 1, while for pH, alkalinity, nitrate & sulfide were Well 2 > Well 3 > Well 1, but for potassium, magnesium, aluminum, copper, iron, manganese & nickel were Well 1 > Well 2 > Well 3.
- At the end, calcium demonstrated significant spatial variation (p<0.05) with respect to three wells. While alkalinity, calcium, potassium, magnesium, sodium, nitrate, sulfide, aluminum, copper, iron, manganese and nickel demonstrated significant spatial variation (p<0.05) at two studied locations (well 1 and well2) or (well 1 and well 3).

| Wells | Well 1 | Well 2 | Well 3 | | | | | |
|-----------------------|-------------------------------------|-------------------------|------------------------------|--|--|--|--|--|
| Parameters | Mean \pm SD (n=16) | | | | | | | |
| pН | $7.7^{a} \pm 0.32$ | $7.76^{a} \pm 0.3$ | $7.76^{a} \pm 0.24$ | | | | | |
| Alkalinity | 247.81 ^b ± 31 | $271.94^{a} \pm 22.9$ | 270.38 ^a ± 18.4 | | | | | |
| TDS | $4820.07^{b} \pm 298$ | $5206.81^{a} \pm 491.6$ | $5250.63^{a} \pm 407.8$ | | | | | |
| Total Hardness | $1308^b\pm74.6$ | $1367.97^{ab}\pm 170.1$ | $1431.68^{a}\pm 106.9$ | | | | | |
| Calcium | $261.57^{\circ} \pm 65.4$ | $307.87^{b} \pm 45.6$ | $375.66^{a} \pm 77.5$ | | | | | |
| Potassium | $20.81^{a}\pm2.4$ | $17.08^{b} \pm 3.1$ | $16.61^{b} \pm 2.7$ | | | | | |
| Magnesium | $173.25^{a} \pm 56.6$ | $146.66^{ab} \pm 38.7$ | $116.83^{b} \pm 45.5$ | | | | | |
| Sodium | $1180.05 \ ^{\mathrm{a}} \pm 102.0$ | $1285^{b} \pm 118.2$ | $1294.35^{b} \pm 105.7$ | | | | | |
| Chloride | $1957.73^{a} \pm 334.3$ | $2036.26^{a} \pm 411.9$ | 2040.94 ^a ± 365.7 | | | | | |
| Nitrate | $4.05^{b} \pm 4.48$ | $33.69^{a} \pm 27.2$ | $30^{a} \pm 24.2$ | | | | | |
| Sulfate | $946.06^{a} \pm 232.4$ | $1010.49^{a} \pm 269.1$ | $1089.47^{a} \pm 277.2$ | | | | | |
| Sulfide | $0.14^{b} \pm 0.11$ | $0.99^{a} \pm 0.78$ | $0.68^{a} \pm 0.39$ | | | | | |
| Aluminum | $0.038^{a} \pm 0.003$ | <0.005 ^b | <0.005 ^b | | | | | |
| Copper | $0.052^{a}\pm0.003$ | $0.007^{b} \pm 0.003$ | $0.0078^{b} \pm 0.0005$ | | | | | |
| Iron | $0.189^{a} \pm 0.18$ | $0.008^{b} \pm 0.0007$ | $0.008^{b} \pm 0.0004$ | | | | | |
| Manganese | $0.018^a\pm0.005$ | $0.007^{b} \pm 0.003$ | $0.005^{b} {\pm} \ 0.00005$ | | | | | |
| Nickel | $0.028^{a} \pm 0.037$ | <0.001 ^b | <0.001 ^b | | | | | |

 Table (2): Spatial variation for physio-chemical parameters at significance level 0.05 (n=16)

* pH is unitless, while the unit of other parameters is mg/L. Data represented as men \pm SD of 16 individuals, variations between different single letters (a, b, c) in each year is significant.

Temporal water quality parameters variation

Temporal variation is controlled by mixing principally dilution during wet periods. Comparing the monitoring years (2013, 2014 and 2015) with the baseline (control) year 2011, Table (3) & Fig. (2), indicated that:

• Concentration of pH, alkalinity, calcium, potassium, magnesium, sodium, chloride, sulfate, nitrate, sulfide, hardness, copper and nickel demonstrated a significant

temporal variation (p < 0.05). This implies the monitoring years are different from control for these parameters.

- Concentrations of TDS, aluminum, iron and manganese demonstrated non significant temporal variation (p> 0.05).
- In general, pH, alkalinity, sulfide, calcium, nitrate, sulfate, hardness, copper, iron, and nickel indicated temporal deterioration trends over the years with significant variation (p<0.05).

Table (3): Temporal variations in the physico-chemical parameter for three wells at during 2011, 2013, 2014 & 2015 (n = 12 samples [4 per year]).

| Years | 2011 base (control) | 2013 | 2014 | 2015 | | | |
|-------------------------------|------------------------------|-----------------------------|-----------------------------|-----------------------------|--|--|--|
| Parameters | | $Mean \pm SD (n=12)$ | | | | | |
| \mathbf{pH}^{*} | $7.32^d \pm 0.1$ | 7.73 ^c ±0.13 | $7.88^{b} \pm 0.06$ | 8.02 ^a ±0.11 | | | |
| Alkalinity | $236.33^{\circ} \pm 24.4$ | $252.01^{b} \pm 8.8$ | 272.5 ^b ±17.9 | $292.67^{a} \pm 8.1$ | | | |
| TDS | $5155.76^{a} \pm 433.4$ | $4954.25^{a} \pm 348.4$ | $5075.08^{a}{\pm}409.7$ | 5150.25 ^a ±451.0 | | | |
| Sulfide (as S ²⁻) | $0.13^{c} \pm 0.1$ | $0.34^{b} \pm 0.2$ | $0.75^{\text{b}}\pm0.4$ | $1.2^{a}\pm0.7$ | | | |
| Calcium | $225.04^{b} \pm 51.6$ | $316.08^{a} \pm 67.5$ | $369.12^{a} \pm 58.23$ | 349.88 ^a ±50.01 | | | |
| Potassium | $21.96^{a} \pm 2.1$ | $16.32^{b} \pm 3.7$ | $17.7^{b} \pm 2.1$ | 16.7 ^b ±1.37 | | | |
| Magnesium | $221.75^{\mathrm{a}}\pm37.2$ | $113.02^{b} \pm 25.1$ | $120.39^{b} \pm 22.8$ | $127.18^{b} \pm 21.4$ | | | |
| Sodium | $1351.88^{a} \pm 104.3$ | $1232.14^{b} \pm 86.6$ | $1198.12^{b}\pm 105.5$ | $1230.37^{b} \pm 125.4$ | | | |
| Chloride | $2502.32^{a} \pm 181.9$ | $1625.07^{c} \pm 135.6$ | $1851.17^{\rm c} \pm 138.5$ | $2068.01^{b} \pm 211.4$ | | | |
| Nitrate | $4.68^b{\pm}3.5$ | $45.67^{\mathrm{a}}\pm33.9$ | $28.66^{a} \pm 17.5$ | 11.19 ^b ±0.96 | | | |
| Sulfate | $685.7^{c} \pm 64.4$ | $1337.15^{a} \pm 125.7$ | $1125.82^{a}\pm 103.3$ | $912.59^{b} \pm 71.9$ | | | |
| Total Hardness | $1430.06^{a} \pm 131.3$ | $1248.18^{b} \pm 121.4$ | $1397.6^{a} \pm 107.7$ | $1401.14^{a} \pm 90.2$ | | | |
| Aluminum | $< 0.005^{a}$ | $0.015^{a} \pm 0.004$ | $0.015^{a} \pm 0.001$ | $0.017^{a}\pm0.001$ | | | |
| Copper | $0.003^{b}\!\!\pm 0.0005$ | $0.028^{a} \pm 0.034$ | $0.028^{a} \pm 0.028$ | $0.031^{a}\pm0.028$ | | | |
| Iron | $0.01^{b} \pm 0.0017$ | $0.105^{ab} \pm 0.144$ | $0.105^{ab} \pm 0.144$ | $0.147^{a}\pm0.201$ | | | |
| Manganese | $0.008^{a} \pm 0.003$ | $0.0101^{a} \pm 0.0083$ | $0.0101^{a}\pm0.0083$ | $0.010^{a} \pm 0.0084$ | | | |
| Nickel | <0.001 ^b | < 0.001° | $0.007^{\rm b} \pm 0.0008$ | $0.03^{a}\pm0.002$ | | | |

^{*} pH is unitless, while the unit of other parameters is mg/L. Data represented as mean \pm SD of 12 individuals, variations between different single letters (a, b, c) in each year is significant.



Fig 2: Temporal variation of the studied water quality parameters (n=12).

Spatio-Temporal water quality parameter variations

Spatio-temporal variations of well 1, well 2 & well 3 in 2011, 2013, 2014 & 2015 were presented in Table 4 and figured in Fig. 3 & Fig. 4.

- For well 1, all parameters in table (5) demonstrated temporal variation except TDS and hardness because there was significant variation (p<0.05) for these parameters in four years so that the monitoring years are different than the control year.
- For well 2, pH, alkalinity, calcium, potassium, magnesium, chloride, sulphate, nitrate, sulfide, iron, copper showed significant temporal variation (p<0.05), so that the monitoring years are not the same the control year for these parameters. Aluminum & nickel were lower than the detection limit, Table 4. Manganese, TDS & sodium demonstrated non significant temporal variation (P>0.05).
- For well 3, pH, alkalinity, calcium, potassium, magnesium, chloride, sulphate, nitrate, sulfide and iron showed significant temporal variation (p<0.05). This implies the previous parameters demonstrated temporal variation, so that the monitoring years are different than the control years for these parameters. Aluminum & nickel were lower than the detection limit, Table 4. Manganese, copper, TDS, sodium & hardness demonstrated non significant temporal variation (P>0.05).
- In general, for three wells, all water quality parameters showed spatio-temporal variation (p<0.05) except TDS. This implies pH, alkalinity, calcium, potassium, magnesium, sodium, chloride, sulphate, nitrate, sulfide, hardness, aluminum, copper, iron, manganese & nickel demonstrated significant spatio-temporal variation.

| Wells | Well 1 | | | | Well 2 | | | | Well 3 | | | |
|---------------------------|-----------------------------|-----------------------------|------------------------------|---------------------------|-------------------------------|------------------------------|--------------------------|---------------------------|---------------------------------|----------------------------------|----------------------------|--------------------------|
| Years | 2011 | 2013 | 2014 | 2015 | 2011 | 2013 | 2014 | 2015 | 2011 | 2013 | 2014 | 2015 |
| Parameters | | Mean | n ± SD | | | Mear | n ± SD | | | Mear | n ± SD | |
| pH* | 7.25 ^d ±0.03 | 7.68 ^b ±0.18 | $7.88^{b} \pm 0.1$ | 7.99 ^{ab} ±0.18 | $7.3^{\textbf{d}}{\pm}~0.07$ | 7.79 ^b ±0.04 | 7.9 ^b ±0.02 | $8.06^{a} \pm 0.04$ | 7.42 ^c ±0.09 | 7.74 ^b ±0.12 | 7.89 ^b ±0.05 | $8^{ab}\pm0.1$ |
| Bicarbonate | $204^{\mathbf{d}}\pm 4.08$ | $244^{\texttt{c}} \pm 1.41$ | $256^{\circ}\pm 6.7$ | 287 ^{ab} ±8.0 | $252^{c} \pm 7$ | 252 ^{ab} ±7.07 | 285 ^{ab} ±17.7 | 298 ^a ±7.62 | $252^{e} \pm 7$ | $260^{b} \pm 8$ | $276.5^{\text{b}} \pm 15$ | $293^{ab}\pm 5$ |
| TDS | 4886 ^{abc} ±38 | 4886 ^{bc} ±424 | 4784 ^{bc} ±151 | 4679 ^c ±120 | 5206 ^{ab} ±620 | 4973 ^{abc} ±322 | 5175 ^{abc} ±461 | 5333 ^{ab} ±431 | $5250^{a}\pm427$ | 5003 ^{abc} ±389 | 5265 ^{abc} ±453 | 5438 ^a ±310 |
| Hardness | 1324 ^b ±10 | 1222 ^{ab} ±106 | 1348 ^{ab} ±42 | 1336 ^{ab} ±34 | 1500 ^a ±164 | 1164 ^{ab} ±75 | 1378 ^{ab} ±122 | 1427 ^{ab} ±115 | $1464^{ab} \pm 113$ | 1357 ^{ab} ±105 | 1465 ^{ab} ±126 | 1439 ^{ab} ± 82 |
| Calcium | 159 ^e ±1.26 | $264^{\text{bc}}\pm22$ | 322 ^{bc} ±10 | 300°±7 | $260^{\mathbf{d}} \pm 28$ | $282^{b} \pm 18$ | 347 ^b ±30 | 341 ^b ±27 | 255 ^d ±19 | 401 ^a ±31 | 438 ^a ±37 | $407^{a}\pm23$ |
| Potassium | $24^{\mathbf{a}} \pm 0.001$ | $21.1^{\rm b} {\pm}~1.9$ | 20.1 ^b ±0.6 | 18.1 ^c ±0.6 | $21.4^{\texttt{b}}\ \pm 2.3$ | $14^{\text{cd}}\pm0.9$ | $16^{cd} \pm 1$ | $15.9^{d} \pm 1$ | $20.5^{\text{b}}\pm1$ | $13.8^{\text{cd}}\pm1$ | $16.1^{\text{cd}} \pm 1.5$ | $16^{\text{cd}}\pm0.9$ |
| Magnesium | 267 ^a ±2 | $138^{\text{de}}\pm12$ | $141^{de} \pm 4$ | $144^{\mathbf{d}} \pm 3$ | 206 ^b ± 22 | 116.5 ^e ±7 | 126 ^e ±11 | $136^{de} \pm 10$ | 191°±14 | $83^{f}\pm 6$ | $92^{f}\pm 8$ | $100^{f} \pm 5$ |
| Sodium | $1300^{a} \pm 9$ | 1220 ^{bc} ±106 | 1110 ^{bc} ±35 | 1090 ^c ±28 | $1379^{a}\pm151$ | $1250^{\mathbf{abc}} \pm 80$ | 1229 ^{abc} ±109 | 1280 ^a ±106 | $1375^{a}\pm107$ | 1226 ^{ab} ±95 | 1254 ^{ab} ±107 | 1320 ^a ±75 |
| Chloride | 2500 ^a ±18.3 | 1723°±149 | 1776 ^e ±56 | 1830 ^c ±47 | 2550 ^a ±280 | 1569 ^c ±101 | 1864 ^e ±166 | 2159 ^b ±174 | 2456 ^a ±191 | 1581°±123 | 1911°±164 | 2214 ^b ±126 |
| Nitrate | <0.2 ^f | $0.23^{\text{e}}{\pm}0.2$ | 5.4 ^e ±0.1 | $10.5^{cd} \pm 0.3$ | $7.5^{\text{de}}\pm0.7$ | $72.7^{\mathbf{a}} \pm 4.8$ | 42.4 ^a ±3.8 | 12 ^c ±0.9 | $6.4^{e}{\pm}0.56$ | $64^{b}\pm 5$ | $38^{b}\pm3.2$ | $11^{\circ} \pm 0.8$ |
| Sulfate | $640^{f}\pm 4.7$ | 1232 ^{bc} ±107 | 1048 ^{bc} ±33 | 864 ^e ±22 | $679^{f_{\pm}}74$ | $1349^{ab} \pm 87$ | 1120 ^{ab} ±99 | 891°±71 | $737^{\text{f}}{\pm}57$ | 1430 ^a ±111 | 1208 ^a ±104 | $982^{cd} \pm 56$ |
| Sulfide(S ²⁻) | <0.2 ^e | $0.08^{c} \pm 0.01$ | 0.2 ^b ±0.01 | 0.29 ^a ±0.01 | $0.2^{\textbf{d}}\ \pm 0.02$ | 0.43 ^b ±0.02 | 1.25 ^b ±0.11 | 2.1 ^{de} ±0.17 | $0.2^{\texttt{d}}{\pm}0.02$ | 0.51°±0.04 | 0.81°±0.07 | 1.22 ^b ±0.07 |
| Aluminum | < 0.005 ^c | $0.051^{b} \pm 0.004$ | $0.045^{b} \pm 0.001$ | $0.051^{a} \pm 0.001$ | $< 0.005^{c}$ | $< 0.005^{\circ}$ | < 0.005° | < 0.005 ^c | < 0.005° | < 0.005° | $< 0.005^{\circ}$ | < 0.005 ^c |
| Copper | $< 0.001^{f}$ | 0.07 ^b ±0.006 | $0.067^{b} \pm 0.002$ | 0.07 ^a ±0.001 | <0.001 ^f | $0.01^{d} \pm 0.001$ | $0.01^{d} \pm 0.001$ | 0.015 ^e ±0.001 | $0.007^{e} \pm 0.01$ | $0.008^{e} \pm 0.01$ | $0.008^{e} \pm 0.01$ | 0.007 ^e ±0.01 |
| Iron | 0.011 ^e ±0.001 | 0.024 ^b ±0.002 | 0.301 ^b ±0.009 | 0.419 ^a ±0.01 | 0.011 ^c ± 0.001 | <0.008 ^e | <0.008 ^e | 0.011°±0.01 | <0.008 ^e | <0.008 ^e | <0.008 ^e | 0.011°±0.000 2 |
| Manganese | 0.01 ^b ±0.001 | 0.021 ^a ±0.001 | 0.021 ^a ±0.001 | 0.021 ^a ±0.001 | $0.01^{\rm b}{\pm}0.001$ | 0.007°±0.01 | 0.005°±0.001 | 0.005 ^e ±0.001 | 0.0057 ^c ±0.00 05 | 0.0058 ^c ±0.00 005 | $0.006^{c} \pm 0.0008$ | $0.0057^{c} \pm 0.0005$ |
| Nickel | <0.001 ^c | <0.001 ^c | 0.02 ^b ±0.0008 | $0.09^{a} \pm 0.002$ | <0.001° | <0.001° | <0.001 ^c | <0.001° | <0.001 ^c | <0.001 ^c | <0.001° | <0.001 ^c |

Table (4): Spatio-temporal variation in the physico-chemical parameter for wells at significance level 0.05.

* pH is unitless, while the unit of other parameters is mg/L. Data represented as mean ± SD of 4 individuals, variations between different single letters (a, b, c, d) in each year is significant (p<0.05).



Fig. (3): Spatio-temporal variation of physico-chemical parameters for three wells over the studied years (n=4).



Fig. (4): Concentration (mean±SD) of physico-chemical parameters for three wells over the studied years (n=4) compared with drinking water guideline.

Interpretation of Spatio-temporal water quality parameter variation

The pH showed an elevation over years and the highest pH was recorded in 2015, possibly due to the presence of considerable amounts of NaOH, KOH and Ca $(OH)_2$ formed from cement leachate during rainy season leached through the layer of earth, Equation 1. Fig. (4), showed that all recorded pH values were within the safe limits set by Egyptian National Guidelines for Drinking (ENGD, 2007).

 $2 \text{ Ca}_3 \text{SiO}_5 + 7 \text{H}_2 \text{O} \rightarrow 3 \text{CaO}_2 \text{SiO}_2$. $4 \text{H}_2 \text{O} + 3 \text{ Ca}(\text{OH})_2 + 173.6 \text{ KJ}$ Equation 1

Carbonate concentrations in all water samples were less than 0.2 mg/L. The source of bicarbonate in the samples collected from the three wells in 2011 and 2013 could be attributed to the dissolution of calcite from the Eocene aquifer. Because there is a significant positive correlation (p<0.05) between bicarbonate ions and calcium ions concentration showed in Fig. (5). Such correlation is interpreted by Kura *et al.*, (2013) as arising from the fact most of bicarbonate ions derived from the dissolution of calcite, Equation 2. Water samples collected from three wells in 2014 and 2015 showed no significant correlation between ions of bicarbonate and calcium or magnesium. So that, bicarbonate could be resulted from the limestone [CaCO₃ (75-90%), MgCO₃& impurities] used for cement manufacturing (Equations 2 & 3) and CO₂ which is emitted from the calcinations process of limestone and combustion of fuels in kiln (Madlool *et al.*, 2011).

 $CaCO_3 + H_2CO_3 \rightarrow Ca^{2+} + 2HCO_3^{--}$ Equation 2 $MgCO_3 + H_2CO_3 \rightarrow Mg^{2+} + 2HCO_3^{-}$ Equation 3 Well 1, well 2 & well 3 in 2013 Well 1, well 2 & well 3 in 2011 carbonate œ 220 24 Calcium

Fig. (5): Correlation between calcium and bicarbonate ions

The trend of TDS showed fluctuations over the studied years (Fig. 4 & 5). According to groundwater TDS classification of Robinove *et al.* (1958), theses three groundwater wells categorized as brackish water. All the water samples analyzed have TDS higher than the safe limits set by ENGD (2007). All the water samples analyzed have TDS higher than the safe limits set by ENGD (2007). Pearson's correlation coefficients (n = 48) clarified that TDS was positively strongly correlated with Na⁺ (r=0.86) and with Cl⁻ (r = 0.50), indicating that sodium and chloride are the main factors contributing to the emerging groundwater salinization. The high TDS ascribed to groundwater wells of the present study located in the Eocene fractured layers and the groundwater potential depends mainly on the secondary porosity. As well as the relatively low rate of recharge since the recharge sources to the Eocene aquifer include percolation of the modern precipitation, occasional flash floods and local seepage from the quaternary aquifer and probably upward leakage from the Nubian sandstone aquifer (Ibrahim and Lyons (2017). The high values of TDS in the control year (2011) in comparison with the monitoring years are in agreement with US EPA (2013) due to the intrusion of cement grout into the screened intervals during the construction of wells.

All collected water samples have hardness higher than 500 mg/l, WHO (1996) recommended the value of (100-500) mg/l as a safe limit for hardness. Water with hardness above 200 mg/L may cause scale deposition in the water distribution system (Maruthi and Usha, 2011). Such scaling can shorten the lifetime of these appliances (Aqueel *et al.*, 2010). The variations of hardness in the studied wells yearly are related to calcium and magnesium concentrations.

The sources of calcium concentrations in 2011 &2013 were dissolution of calcite, due to the significance correlation (p<0.05) between calcium and bicarbonate in samples collected in 2011& 2013, Equation 2. While in 2014 &2015, the increase of calcium can be attributed to calcium hydroxide leaches out of the cement paste, releasing Ca^{2+} and OH⁻, plus alkalis (Kamali *et al.*, 2008). Calcium concentrations in most of collected samples are higher than the recommended limit by ENGD (2007).

The magnesium reduction in three wells over the studied years could be ascribed to reaction of calcium hydroxide (from cement pore water) with magnesium, sulfate in groundwater to produce magnesium hydroxide (brucite), and gypsum, according to the reaction shown in Equation 4, (Whittaker and Black, 2015). Brucite is relatively insoluble and precipitates under the high pH conditions prevailing in the cement pore water and induces a lower pH. Furthermore, in the case of comparing all the data with the Egyptian national guidelines, the result indicated that magnesium concentrations are higher than the recommended limit in 2011, and are within the safe limit recommended by ENGD (2007).

Mg²⁺ + SO₄²⁻ + Ca(OH)₂ + 2H₂O →Mg(OH)₂ + CaSO₄. 2H₂O Equation 4 Potassium concentrations reduced significantly (p<0.05) over the years in wells water. This reduction could be ascribed to the precipitation of syngenite, K₂Ca(SO₄)₂·H₂O, (Kunther *et al.*, 2013) during the reaction of potassium from groundwater with cement pore water (intrusion of cement during construction of wells). Moreover, there is no guideline in comparing the data with ENGD (2007).

Sodium concentrations in all water wells were higher the safe limit by ENGD (2007). The reduction of sodium concentration over the studied years could be explained by Jeen *et al.* (2001), Na^+ in groundwater is taken up by the exchanger-Ca, while Na^+ is adsorbed onto the sediment by cation exchange process, and accompanied by an increase of calcium concentration, Equation 5.

 $\frac{1}{2}$ Ca - Clay₂ + Na⁺ $\rightarrow \frac{1}{2}$ Ca²⁺ + Na - Clay Equation5

Chloride concentrations in water samples were higher than the recommended limit by ENGD (2007). High chloride concentration in groundwater may reveal pollutions from sewage, industrial wastes or salt water intrusions. The reduction of chloride concentration could be attributed to chloride binding from the environment of groundwater with cement pore water (ferroaluminate phase) and produced Friedel's salt ($3CaO \cdot Al_2O_3 \cdot CaCl_2 \cdot 10H_2O$) and Kuzel's salt ($3CaO \cdot Al_2O_3 \cdot 0.5CaSO_4 \cdot 0.5CaCl_2 \cdot 10(11) H_2O$) compounds (Matschei *et al.*, 2007). The increasing of chloride after that in the years 2014 and 2015 was depending on the stability of Friedel's salts.

Sources of sulphate in groundwater are dissolution of sulfate minerals such as gypsum and anhydrite. Sulphate concentrations in all samples were higher than the safe limit of ENGD (2007). Sulfate concentrations fluctuated, where it increased significantly (p<0.05) from 2011 to 2013 and then showed a significant reduction (p<0.05) in the monitoring years 2014 & 2015. The increase of sulfate concentration could be resulted from oxidation of SO₃ in cement (contain about 2.5% SO₃) pore water leached to the aquifer or sulfates are largely recycled from the atmosphere via reaction of SO₂fromthecement dust (Melki *et al.*, (2017) with water vapor, Equation 6. While the reduction of sulfate concentration could be attributed to sulphate reducing bacteria which reduces sulphate to hydrogen sulfide (increase the odor of rotten egg and sulfide concentration), Equation 7 (Christensen *et al.*, 2000).

$SO_2 + \frac{1}{2}O_2 + 2H_2O \rightarrow 2H^+ + SO_4^{2-}$ Equation 6 $SO_4^{2-} + 2H^+ + 8e^- \rightarrow HS^- + 4H_2O$, Equation7

Nitrate concentrations of well2 and well3 (in 2013) were higher than the recommended limit by ENGD (2007) and reduced significantly (p<0.05) in 2014 and 2015 to be in the acceptable limit of 50 mg/L. The presence of nitrate could be attributed to precipitation, decay and minerlization of organic substances (Namiesnik *et al.*, 1993). The low nitrate concentrations are concide with suboxic conditions due to the presence of Mn²⁺(Buschmann *et al.*, 2007).In well 2 & well 3, comparison of nitrate levels with Fe²⁺& Mn²⁺, the result indicated that the low nitrate concentrations have commonly associated with high maxima of Fe²⁺, Mn²⁺ indicating oxygen-poor groundwater. In wells 2 and 3 over years, there is a positive significant (P <0.05) correlation between SO₄²⁻ and NO₃^{-,} indicating that these ions have the same source, which is the combustion of fuels at high temperature in cement kilns results in the release of SO₄²⁻ and NOx emissions (Mousavi *et al.*, 2014; and Melki *et al.*, 2017). Sulfur and nitrogen oxides dissolve in the rainwater and drop on soil and reach the aquifer, Equations 6, 8 & 9. **2NO + O₂ → 2NO₂**

$$\frac{1}{2}O_2 + H_2O + NO_2 \rightarrow H^+ + NO_3^-$$

Equation 9

On the other hand, all forms of sulfur in water are sulfide or bisulfide due to the pH of the studied water wells is higher than 7 and less than 12 (Table 4 & Fig. 4 & 5). Currently, hydrogen sulfide in drinking water standard is not regulated directly. The rotten egg smell was occasionally noticed in three wells over the years, especially from 2013 to 2015. This may occur as a result of the amount of recharge water (rainwater) arriving at the aquifer from the surface, or in the summer because the extent of drawdown of the water table results in a deeper portion of the aquifer being tapped. Applying of Florida Department of Environmental Protection recommendations, (FDEP, 2010), on water wells to control the hydrogen sulfide as a function of sulfide & iron concentration and water pH, the following steps were applied:

- 1. In 2011, control year, sulfide concentrations were <0.3 mg/l inwaterwells1, 2 &3, so that the doses of chlorine required for treatment were 0.8, 2.0 & 1.8 mg/L, respectively.
- 2. In 2013, sulfide concentrations ranged between 0.3 and 0.6 mg/l (pH > 7.2) in wells 2 & 3, water wells was treated by conventional aeration (until the odor disappeared) followed by pH adjustment.
- 3. In 2014 & 2015, sulfide concentrations ranged between 0.3 and 0.6 mg/l (pH > 7.2) in wells 2 & 3, water wells was subjected to forced Draft aeration until (until the odor disappeared) followed by In pH adjustment.

Trace element: Fig 4 depicted spatio-temporal variation of trace elements present in groundwater of three wells. For well 1, concentrations of Al^{3+} , Cu^{2+} , Fe^{2+} , Mn^{2+} & Ni^{2+} showed a significant temporal difference (p<0.05) with respect to their concentrations in 2011. Concentrations of Fe^{2+} & Ni^{2+} collected from well1 in 2015 were higher than the safe limit 0.3 and 0.02 mg/l (ENGD, 2007), respectively. For well 2 & well 3, aluminum and nickel didn't show any significant (p>0.05) change in the concentration over studied years. While copper, iron and manganese showed an elevation in the monitoring years 2014 & 2015. All trace elements monitored in well 2 and well 3 are less than the safe limit by ENGD (2007).

The presence of Cu, Mn & Ni could be ascribed to tires utilized as combustible waste in cement plants could be the reason of the presence of some of these trace elements since tire rubber is rich in Zn and also in Cu, Pb, Mn, Co, Ni, and Cd (Melki *et al.*, (2017).For Al, Fe, known as common crustal elements, different concentrations of these elements were seen at the three wells. Similar concentrations were noticed in well 2 & well 3, this suggested that their presence was rather related to a regional background than to an industrial origin, with equal contribution of crustal particles at the two sites.

Water collected from well 1 had higher concentrations of trace element with respect to their concentrations in well 2 and well 3, which suggested other sources related to industrial

and corrosion processes. The first reason could be an intrusion of raw materials (lime, silica, alumina, and iron) or fly ash to aquifer during wet season since some cement plants of depositing their raw materials or fly ash outdoors, which could be occurred in the area of well 1. The second reason could be attributed to the corrosion product of steel casing material well1, while casing materials for well 2 and well 3 were plastic materials, Table 1. The second reason was in line with Youssef *et al.*, (2006), the corrosion product of steel subjected to artificial brackish and seawater was lead, cobalt, nickel, zinc, manganese and iron.

Variability factors (Factor analysis)

Principle component (PC) analysis was performed on the data set of 17 water quality parameters. Treatment of dataset with PC, Table (5), showed that three significant factors accounted for 82.53% of the variation (with eigen values% > 1). These three factors could be used as an indicator for potential contamination, characterizing the data and presented a unique contribution to the discrimination of the process controlling the variability.

| Indicator | PC1 | PC2 | PC3 |
|------------------------------------|---------|---------|---------|
| рН | 0.8728 | 0.3129 | -0.2074 |
| Alkalinity | 0.9374 | 0.1298 | 0.0868 |
| TDS | 0.1741 | -0.5107 | 0.5237 |
| Sulfide (mg/L as S ²⁻) | 0.7932 | -0.2949 | 0.1934 |
| Calcium | 0.8770 | -0.0987 | -0.2240 |
| Potassium | -0.7696 | 0.2061 | 0.5421 |
| Magnesium | -0.7987 | 0.0012 | 0.5177 |
| Sodium | -0.2464 | -0.6636 | 0.5415 |
| Chloride | -0.3615 | -0.3013 | 0.8702 |
| Nitrate | 0.3168 | -0.4519 | -0.7070 |
| Sulfate | 0.3956 | -0.0766 | -0.8494 |
| Hardness | 0.2914 | -0.1690 | 0.6529 |
| Aluminum | -0.1130 | 0.9362 | -0.1301 |
| Copper | 0.0067 | 0.9331 | -0.0941 |
| Iron | 0.0720 | 0.9124 | 0.0556 |
| Manganese | -0.2669 | 0.9239 | -0.0603 |
| Nickel | 0.1232 | 0.8144 | 0.0816 |
| Eigenvalue | 6.1402 | 5.5326 | 2.3567 |
| Variability (%) | 36.1186 | 32.5449 | 13.8629 |
| Cumulative % | | | 82.5264 |

 Table (5): Rotated component matrix of water quality data (Rotation method: Varimax with Kaiser normalization).

Where, PC1, PC2 & PC3 are factors 1, 2& 3 of Principle Component (PC) analysis.

The first component (PC1), accounting 36.11% of the variation in the whole data set, was positively significant highest loads for alkalinity, calcium, pH & sulfide, while negatively loaded by potassium & magnesium. The second component (PC2) accounting for 32.54% of the whole total variation, with significant positively highest loads for aluminum, copper, iron, manganese & nickel, while negatively loaded by sodium. The third component (PC3) accounting for 13.86% of the whole total variation, with significant positively loaded by sulphate & nitrate, while chloride loaded by chloride, hardness & TDS, while negatively loaded by sulphate & nitrate, while chloride loaded with moderately positive.

The negatively loaded of potassium, magnesium, sodium, sulphate & nitrate ions did not contribute significantly to the groundwater hydrochemistry. PC1 was characterized by complex process derived from the dissolution of calcite through water-rock interaction, and reduction of sulphate by SRB. The positive loading of pH values suggested that the dissolution

and reduction reactions are controlled by pH variation. PC2 was generated from combustible waste in cement plant (tire rubber, raw materials& fly ash), crustal elements and corrosion product. PC3 could be interpreted as the salinization factor. Salinization refers to an increase in the concentration of TDS in water and can often be detected by an increase in chloride, which was proportionally correlated to the cations like sodium, calcium and magnesium. In conclusion, aluminum, copper, nickel, iron, manganese, alkalinity, calcium, pH, sulfide, chloride, hardness & TDS are specified as the dominant indicators controlling the variations in groundwaterquality.

Origin of groundwater over years

Origin of groundwater was determined by estimating hydrochemical ionic ratios $(rNa^+/rCl^-, rCa^{2+}/rMg^{2+} \text{ and } rSO_4^{2-}/rCl^-)$ over the studied years. The hydrochemical ions $(rNa^+, rCl^-, rCa^{2+}, rMg^{2+} \text{ and } rSO_4^{2-})$ are miliequivalent concentrations (meq/l). The molar equivalent ratios of rNa^+/rCl^- , rCa^{2+}/rMg^{2+} and rSO_4^{2-}/rCl^- in most of groundwater wells are less than the estimated values of the collected Nile water from the River Nile in the study area, and this mean that there no recharge from the River Nile (Table 6).

| Code | rNa ⁺ /rCl ⁻ | rCa ²⁺ /rMg ²⁺ | rSO ₄ ²⁻ /rCl ⁻ |
|-----------------------|------------------------------------|--------------------------------------|--|
| Well 1-2011 | 0.80 | 0.36 | 0.19 |
| Well 1-2013 | 1.09 | 1.15 | 0.53 |
| Well 1-2014 | 0.96 | 1.38 | 0.44 |
| Well 1-2015 | 0.92 | 1.26 | 0.35 |
| Well 2-2011 | 0.83 | 0.76 | 0.20 |
| Well 2-2013 | 1.23 | 1.47 | 0.63 |
| Well 2-2014 | 1.02 | 1.66 | 0.44 |
| Well 2-2015 | 0.91 | 1.52 | 0.30 |
| Well 3-2011 | 0.86 | 0.81 | 0.22 |
| Well 3-2013 | 1.20 | 2.91 | 0.67 |
| Well 3-2014 | 1.01 | 2.87 | 0.47 |
| Well 3-2015 | 0.92 | 2.47 | 0.33 |
| Nile Water (Measured) | 2.40 | 2.12 | 0.89 |
| Sea Water (Standard) | 0.84 | 0.18 | 0.08 |

Table (6): Mean values of hydrochemical ratios of the different groundwater samples (n=4).

The rNa⁺/rCl⁻ equivalent ratios are less than unity(<1) in water wells collected in 2011 and 2015 indicating that water was marine origin (Starinsky *et al.*, 1983). Water wells collected in 2013 & 2014 have rNa⁺/rCl⁻ somewhat higher than 1 indicating that the water was affected by meteoric water via leaching and cation exchange process.

The rCa²⁺/rMg²⁺ ratio was less than unity (<1) in the samples collected in 2011 may reflect the interaction between the groundwater and the host rock contains dolomite (Plummer *et al.*, 1976). Well 1 and well 2 (in 2013, 2014 & 2015), have a ratio higher than one (>1), clarify the dissolution of calcite, which suggest that water moves in limestone or that limestone is rich with dolomite, Equations 2 & 3. Well 3 (2013, 2014 & 2015) has ratio greater than > 2, this indicates the dissolution of silicate minerals into the groundwater, Equation 1. Finally, the source of calcium in monitoring wells was the calcite, limestone and dissolution of silicate minerals (calcium leached from cement pore water).

The rSO₄^{2-/} rCl⁻ ratio was less than unity. In 2011, 2013, 2014 & 2015, the ratios for the three wells are more than the value of sea water and less than the Nile water. This reflects the dissolution of local terrestrial salts rich in sulfate such as gypsum, anhydrite, glauberite (Na₂SO₄.10H₂O) and epsomite (MgSO₄.7H₂O). The non-cyclic sulfate (NCS) was calculated from this formula (El Hinnawi, 1972): NCS = (Cl⁻/7.2) - (SO₄²⁻), where the ions will be taken

in mg/L. The data affirm that all groundwater samples have been negative values of NCS indicates that the sulfate is terrestrial origin.

Evaluation of groundwater wells for different uses:

Water samples collected from the three wells in 2015 are evaluated for drinking, irrigation and industrial uses as follows:

1. Suitability of well water for drinking water:

According to salinity (TDS) and major ions groundwater, all samples were unacceptable for human drinking. According to minor and trace constituent, groundwater samples from wells 2 and 3 were suitable for drinking water due to low concentration of aluminum, copper, iron, manganese& nickel, while groundwater of well 1 was unsuitable for drinking due to the higher concentration of iron and nickel more than the recommended limit by ENGD (2007).

2. Suitability of water wells for Irrigation:

- Based on TDS: The increase in TDS of irrigation water leads to an increase of its percentage in the soil and lead to decrease the growth and yield of the plants. Regarding to TDS content, water is considered satisfactory, fair and inferior when Its TDS value was 1000 mg/L, 1000 to 2000 mg/L, and exceeds 2000 mg/L, respectively (Ayers and Westcot, 1985). At the end, the studied wells were unsuitable for irrigation under normal conditions.
- Sodium Adsorption Ratio (SAR) is an important parameter for the determination of suitability of water for irrigation. The SAR values were calculated by using Richard (1954) formula in which all concentration values are expressed as meq/l. In the present study, SAR values for the three wells were higher than >10; Table 7, indicating that the three water wells were suitable for coarse textured or organic soil with good permeability.

$$SAR = \frac{Na^{+}}{\sqrt{\frac{(Ca^{2+} + Mg^{-2+})}{2}}}$$

-Kelly's Index (KI) is used for the classification of water for irrigation purposes. The concentration of N^{a+}, C^{a2+}& M^{g2+} in water are representing the alkali hazard. The values of KI < 1 indicate good quality water for irrigation &> 1 indicate bad water (Kelly, 1940). The values of KI in this study, Table 7, varied from 1.8 to 2.0. Therefore, according to KI all water samples were bad for irrigation.

$$KI = \frac{Na^{+}}{(Ca^{2+} + Mg^{-2+})}$$

| | Table | (7): The Value of S | SAR and I | KI for the | e studied groundwa | ater wells | in 2015. | |
|--------|-------|---------------------|-----------|------------|--------------------|------------|----------|-----|
| Well | SAR | KI | Well | SAR | KI | Well | SAR | KI |
| Well 1 | 12.9 | 1.8 | Well 2 | 14.8 | 2.0 | Well 3 | 15.2 | 2.0 |

3. Suitability of water for industrial use:

Water quality requirements vary greatly depending on the type of industries and even for different plants within the same industry. As for testing the groundwater suitability of this study for industrial purposes, Saturation Index (SI) was calculated to all samples and the results were compared with the standard of industrial uses (USEPA, 2004; Asano *et al.*, 2007):

• SI was used to mediate the extent to which water flowing through the pipes will precipitate or dissolve calcium carbonate. Such finding exhibit tendency of all groundwater samples to precipitate CaCO₃ in pipes (Stumm and Morgan, 1981). Fig. (6) showed that, all groundwater samples collected from wells were supersaturated with carbonate minerals (calcite, dolomite and aragonite). Therefore, almost all groundwater wells in this study appeared to be unsuitable for industrial purposes.



Fig. (6): Saturation indices (SI) for studied wells.

• Comparing standard limits (Table 8), with the concentration of some minor elements in the investigated water of the study area. Wells water samples are unsuitable for all industries as; pulp and papers, petrochemical and coal, cement and textiles until treated as desalination required) due to their high salinity, alkalinity and hardness.

Table 8 Guidelines for water quality requirements for various industrial processes (Asano et al., 2007).

| | Pulp and paper | | | | | | Textiles | | |
|-------------------------------|--------------------|------------------------|----------|---------------------------|-------------|------|----------|----------------------|----------------------------|
| | Mechanical pulp | chemical unbleached | Bleached | Petrochemical and coal | Chemical | | Cement | Sizing suspension | Scouring bar and dye |
| pН | 6-10 | 6-10 | 6-10 | 6-10 | 6.2- 8.3 | 6-9 | >3 | 5 | 5 |
| Hardness | _ | 100 | 100 | 100 | 250 | 350 | _ | 5 | 5 |
| Alkalinity | _ | _ | _ | _ | 125 | 500 | 1000 | | 400 |
| Mn ²⁺ | 0.1 | 0.5 | 0.05 | 0.05 | 0.1 | _ | 500 | 0.05 | 0.01 |
| HCO ₃ ⁻ | _ | _ | _ | _ | 125 | 480 | 400 | _ | _ |
| Ca ²⁺ | _ | 20 | 20 | 20 | 69 | 75 | 2000 | _ | _ |
| Mg^{2+} | _ | 12 | 12 | 12 | 19 | 30 | 2000 | _ | _ |
| TDS | _ | _ | _ | _ | 1000 | 1000 | 2000 | 100 | 600 |
| Fe ²⁺ | 0.3 | 1 | 0.1 | 0.1 | 0.1 | 0.1 | 2.5 | 0.3 | 0.1 |
| Cl | 1000 | 200 | 200 | 200 | 500 | 500 | 250-360 | _ | _ |
| SO4 ²⁻ | _ | _ | _ | _ | 100 | 100 | 600 | _ | 250 |
| NO ₃ . | _ | _ | _ | _ | 5 | _ | _ | _ | _ |

All parameters have concentrations (mg/l) except pH is unitless.

CONCLUSION AND RECOMMENDATION

Based on the results, groundwater was classified as brackish water. From all the studied water quality parameters, calcium displayed significant spatial variation (p<0.05) with respect to three wells, while 12 parameters showed significant spatial variation (p<0.05) at two studied locations. Four parameters (potassium, magnesium, sodium & chloride) showed temporal improvement trends with significant variation (p<0.05). Ten parameters (pH, alkalinity, sulfide, calcium, nitrate, sulfate, hardness, copper, iron and nickel) showed temporal deterioration trends significant variation (p<0.05). While 15 parameters (pH, alkalinity, calcium, potassium, magnesium, sodium, chloride, sulphate, nitrate, sulfide, aluminum, copper, iron, manganese & nickel) showed spatio-temporal variation. Three main Varimax-rotated factors counted for 82.53 % of the total variance of the quality variables significant loads alkalinity, calcium, pH & sulfide, aluminum, copper, iron, manganese & nickel followed by chloride, hardness &TDSin decreasing order were identified. The spatial-temporal variation in pollutants originated from

the dissolution of calcite through water-rock interaction, cation exchange of both meteoric water affected by calcite, limestone, and cement dust (containing CO₂, nitrogen and sulfur), reduction of sulphate by SRB, salinization factor, and leaching of trace element from combustible waste in cement plant (tire rubber, raw materials & fly ash), crustal elements & corrosion product of well casing materials. Chlorine demand, conventional aeration and draft aeration were suggested to get rid of from rotten egg odor. Also, the ionic ratios indicated that, the groundwater samples have a mixed mineralization that is possibly pure marine water affected by leaching, dissolution and cation exchange of both meteoric water and terrestrial salts. Saturation indices of calcite, dolomite, and aragonite are higher than one, indicating the super saturation of water via those minerals. Groundwater wells aren't suitable for direct drinking and irrigation (based on TDS, SAR and KI) but it can be used for coarse textured or organic soil with good permeability under certain condition. For industrial uses these water need a few remedies to be appropriate for all industries. The study concludes to somehow useful information to decision makers and investors on groundwater quality and trends in Minya Governorate, Upper Egypt. Based on the outcome of the study, proper well design is recommended to reduce water treatment costs. Further studies on water treatment technology as desalinization are required.

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ARABIC SUMMARY

تقييم نوعية المياه الجوفية للإستخدامات المختلفة: حالة دراسية : محافظة المنيا – مصر

حسين عبد الحليم الجمال لبنى عبد العزيز إبراهيم المركز القومي لبحوث المياه- مصر

تتمثل الأهداف الرئيسية لهذه الدراسة في تقييم إتجاهات (تباين) تركيزات نوعية المياه الجوفيه لإستخدامات الشرب، الزراعة، والصناعة. أجريت هذه الدراسة على ثلاث آبار تم إنشاؤها في منطقة المنيا، مصر. حيث لايوجد دراسة سابقة أجريت على هذه الأبار. حيث تم رصد مؤشرات نوعية المياه (الرقم الهيدروجيني، القلوية، الأملاح الكلية الذائبة، العسر الكلي، ايونات كلاً من الصوديوم، البوتاسيوم، الماغنسيوم، الكالسيوم، الكلور، الكبريتات، النترات، الكبريتيد، الألومنيوم، الماغنسيوم، الكالسيوم، الكلور، الكبريتات، النترات، الكبريتيد، الألومنيوم، الماغربيوم، الماغنسيوم، الكالسيوم، الكلور، الكبريتات، النترات، الكبريتيد، الألومنيوم، الموناس الحديد، المنجنيز، والنيكل) لمدة أربع سنوات (٢٠١١، ٢٠١٣، ٢٠١٢، ٢٠١٤، و ٢٠١٥). واستناداً إلى النتائج فان المياه الجوفية صنفت بأنها مياه معوس. كما أوضحت النتائج أن الرقم الهيدروجيني، وأيونات كلاً من: الكالسيوم، الكالسيوم، الكور، الكبريتات، النترات، الكبريتيد، النتائج فان المياه الجوفية صنفت بأنها مياه معوس. كما أوضحت النتائج أن الرقم الهيدروجيني، وأيونات كلاً من: الكالسيوم، الكبريتات، النترات، الكبريتيد، الألومنيوم، النحاس، الحديد، المنجنيز، والنيكل المان الجوفية مع منعات كلاً من: الكالسيوم، الكبريتات، النترات، الكبريتيد، الألومنيوم، النحاس، الحديد، المنجنيز، والنيكل ارتفع تركيزها على مدى سنوات الرصد. وتبين من إجراء طريقة التدوير المتعامد للعوامل (كمدينز و عية المياه تكشف كيف أن عملية التفاعل بين المياه والصخور، والتملح، والتلوث الصناعي تؤثر على نوعية المياه الجوفية. ويعتبر الاحتمال الأكبر لمصدر المياه الجوفية هو والصخور، والتملح، والتلوث الصناعي تؤثر على نوعية المياه الجوفية. ويعتبر الاحتمال الكبر لمصدر المياه الجوفية هو رالصخور، والتملح، والتلوث الصناعي تؤثر على نوعية المياه الجوفية. ويعتبر الاحتمال الأكبر لمياه الجوفية ويعتبر الاحتمال الأكبر لمصدر المياه الجوفية هو والصخور، والتملح، والتلوث الصناعي تؤثر على نوعية المياه الجوفية. ويعتبر الاحتمال الأكبر لمصدر المياه الجوفية هو والصخور، والتملح، والتلوث الصناعي تؤثر على نوعية المياه الجوفية. ويعتبر الحتمال الأكبر لمصدر المياه الجوفية هو والصخور، والملح، والتبلام التي تحتوي على غبر الإسمنت) والأملاح الأرضية. الرضيوة الأملام الأيونيي الماء ويوني الماملول الأرضية.