

Assessment of Some Heavy Metals in Groundwater: Case Study Around an Archaeological Site, Abydos, Sohag, Egypt

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Abstract: Water is extremely essential for existence of the human life, livestock and plants. With growth of world population rapidly and increasing reclamation extension, their needs for water increased dramatically. However, the increase of water discharge and lack of the sewage treatment and system in the study area and adequate industrial disposal system increase the contamination. In the current study, analysis of heavy metals contamination has been studied around the Osireion Lake. The quality index of the collected groundwater samples indicated that the water is of poor to unsuitable water class for domestic use. Some heavy metals such as B-1, Al+3, Fe+3, Mn+2, Ni+2, Ba+2, Cu+2, Pb+2, and Sr+2 were measured in the present study to assess the risk factor. The heavy metals contamination has been reported as a potential risk in the groundwater in the study area. Iron and Manganese show some values higher than the maximum permissible of WHO. Iron might have resulted from the interaction of oxidized Fe minerals and organic matter. Strontium and Barium reveal higher values, therefore the higher concentrations of Sr⁺² and Ba⁺² indicating that the source could be a result of anthropogenic through fertilizer in agricultural activity causes an input of Sr⁺² and Ba⁺². It is believed that the mixing of groundwater with agricultural return flow and sewage waste, increase the concentration levels of pollutants.

Keywords: Quality Index, Heavy Metals, Osireion Lake, Abydos, Egypt

1. Introduction

Sohag Governorate located in the Upper Egypt at about 465 km distance south to Cairo, however, Sohag occupying about 125 km long from the Nile Valley the average width ranging from 16 to 20 km. Abydos area located in El-Balyana city in the southwestern part of the Sohag Governorate, some of 70 kilometers from Sohag and about 13 Km. west of the Nile River, it is considered as one of the most important tourist sites in the county due to the importance of the presence of the temple of King Seti I and the Temple of Ramses II [1]. The area located between longitude 31° 53' and 31° 57' E and latitude 26° 10' and 26° 15' N. Climatologically, Egypt belongs to arid belt; as a result of location Sohag to the south of Egypt, which characterized by hot summer, cold winter, and

scarce rainfall with occasional storms. The recorded average value of precipitation was 2.25 mm/y [2]. Several researchers have studied the chosen study area [3-6].

The aim of this study was to understand the source of some heavy metals around Osireion Lake. Heavy metals such as; Fe⁺³, Mn⁺², Cu⁺², Zn⁺², Co⁺³, Ni⁺² etc. are of importance for the functioning of the biological system and their deficiency or excess in the human system can lead number of disorders, other heavy metals such as Pb+2, As+3, Hg+2 are not only biologically non-essential but even with low concentration levels could be toxic. Due to weathering, leaching and water interaction, soils normally have low background levels of heavy metals. In the area where the flooded irrigation has applied and industrial fertilizers have been used, the concentrations of specific heavy metals could

be much higher. It's for sure that the higher concentration of heavy metals would be hazardous to human, animals, and plants. In this study, we shall report the heavy metals B^{-1} , Al^{+3} , Fe^{+3} , Mn^{+2} , Ni^{+2} , Ba^{+2} , Cu^{+2} , Pb^{+2} , and Sr^{+2} concentration levels in groundwater around Osireion lake and the water of Osireion. Groundwater in the area west to this area normally used for land irrigation and to some extent for domestic use. Therefore, the groundwater within the Quaternary aquifer in the study area located under inhabitants, and reclaimed lands especially from the south of the Osireion Sacred Lake.

2. Physiography of the Study Area

2.1. Geological Setting

The area of study is a part of the Nile Valley that has been geologically investigated by many authors such as [7-10]. The area of the Osireion is located 70 km south of Sohag on the west side of the Nile valley, at the border with Desert to the west. The plateau assumes an average elevation of 300 m above sea level, whereas the pediment surface has an average altitude of 100 m above sea level. The plateau runs in a very irregular course, including many promontories. The most conspicuous promontory is the one just 3 km due southwest (local west) of the Osireion. The exposed rock units in the study area are represented by Eocene shales and limestone and Quaternary sediments [7, 10]. The thick hard limestone section (Thebes Formation) forming the top of the scarp and plateau surface. The limestone has a residual thickness average + 80 meters and constantly increases in thickness westward, (Figure 1) the Thebes belong to the Early Eocene. The pediment surface is covered by Quaternary sands and gravel getting to be muddy towards the East i.e., toward the cultivated part of the valley. The mud section (+ 5 m) overlooking the Osireion is known as the Dandara Formation, which represents the first Ethiopian sediment brought by the Nile from Ethiopia [10].

2.2. Hydrological Setting

Many authors such as [6, 12-14] have dealt with the hydrogeologic setting of the Sohag area. In the floodplain of the River Nile, the Quaternary aquifer system consists of fluvial sands with minor conglomerate and clay (Prenile, Qena Formation). It is capped with the Neonile silt and fine-grained sands that constitutes the base of the cultivated lands. Along the eastern and western fringes, the Neonile silty layer is replaced by the recent sediments. Therefore, the aquifer system in the floodplain is under semi-confined condition (silty cap), but in the desert fringes it is under unconfined condition. The Qena sands are the main water bearing formation in the area and the formation thins out to the west abutting against the Paleocene to the Lower Eocene shales and limestones of the western Limestone Plateau. The groundwater level became higher than that of the Nile and consequently seepage from the aquifer to the Nile (return flow) created in the Nile Valley except in the upstream of

barrages [14].

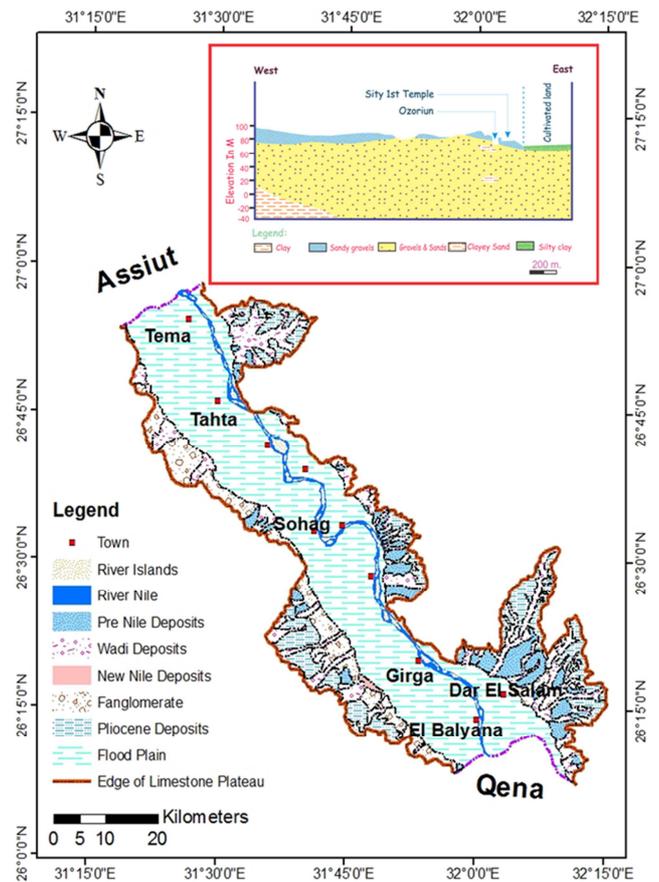


Figure 1. Geology of the study area (modified after, [11]).

The water level in the Osireion is about 13.30 m below around land surface, and the average water level in the Osireion is around 64 m amsl. Six drilled holes in year 2010 were submitted during this study around the Osireion in depth from 67 m. to 104 m to investigate the water table. The water level in the drilled wells was recorded to be from 25 m to 29 m below the around ground surface. The aquifer thickness in the area of study ranging from 50 to 70 m with some clay intercalation [1]. Figure 1 show the geology of Sohag area and the cross section at Abydos site from west-east (Modified after, [6]).

3. Materials and Methods

Seven groundwater samples from the aquifer in and around the Osireion were collected in 1 L polyethylene bottles and acidified in the field by HNO_3 . Wells were pumping before collecting water, to remove stagnant water if found from the well pipe. Osireion water samples collected from the Osireion Lake, which is currently open as water accumulation. The pH meter kit was used to measure the pH values of collected water in the field. Portable kit with electrodes were used to get the values of electrical conductivity (EC) in the site. The heavy metals such as; B^{-1} , Al^{+3} , Ba^{+2} , Cu^{+2} , Fe^{+3} , Mn^{+2} , Ni^{+2} , Pb^{+2} , and Sr^{+2} , were carried out in Geochemistry Laboratory, Sohag Univ., Sohag,

Egypt, summary of statistics are shown (Table 1).

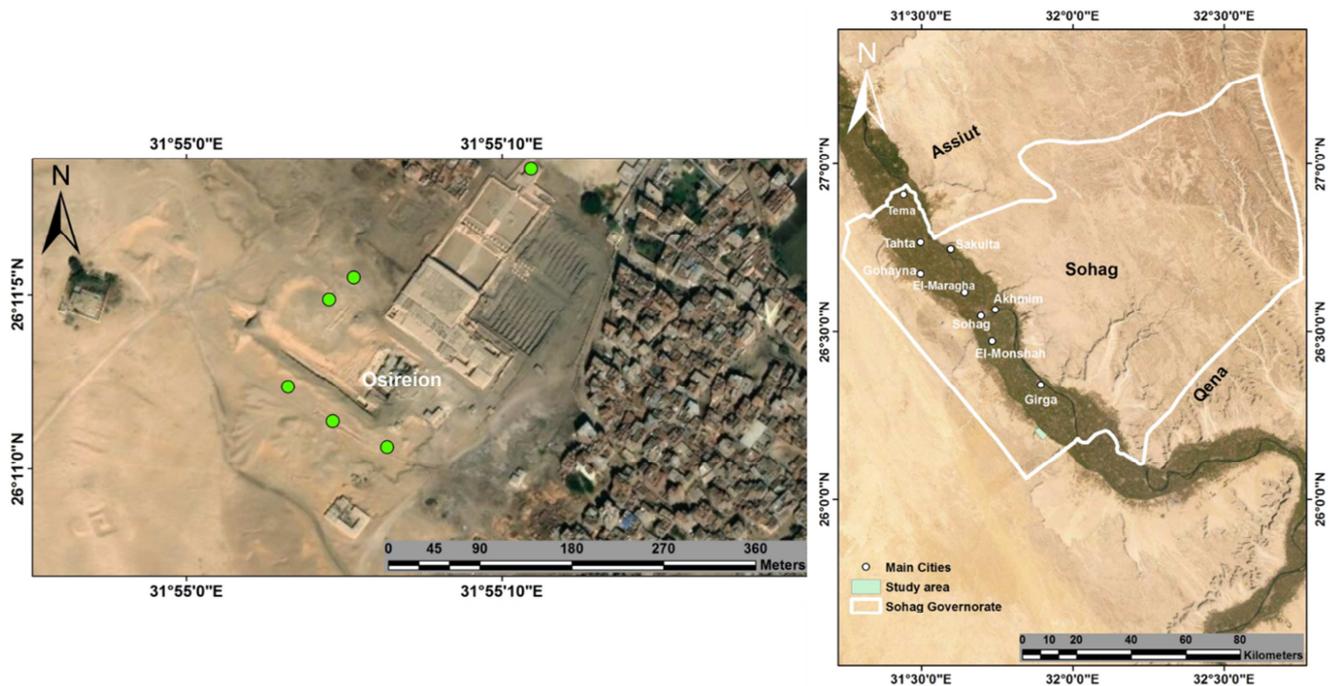


Figure 2. Location map of the study area.

Table 1. Physio-Chemical results of groundwater samples.

	Range	Minimum	Maximum	Mean	Std. Deviation	Skewness	Kurtosis
pH	1.06	7.48	8.54	7.76	0.35	2.29	5.68
Ec	3992.00	1438.00	5430.00	2958.00	1736.59	0.97	-1.04
TDS	2542.00	920.00	3462.00	1619.86	865.45	1.99	4.58
Ca ⁺²	134.60	74.90	209.50	134.71	51.12	0.57	-1.11
K ⁺¹	74.70	26.30	101.00	52.13	25.41	1.29	1.73
Mg ⁺²	28.40	29.80	58.20	39.11	12.68	1.16	-0.87
Na ⁺¹	348.00	150.00	498.00	321.86	134.20	0.41	-1.18
HCO ₃ ⁻¹	289.16	219.60	508.76	404.89	100.23	-1.09	1.02
Cl ⁻¹	380.00	160.00	540.00	388.57	134.96	-0.57	-0.13
NO ₃ ⁻¹	10.62	0.18	10.80	4.51	4.26	0.43	-1.67
SO ₄ ⁻²	500.00	160.00	660.00	330.00	218.25	1.02	-0.99
Al ⁺³	13.41	0.99	14.40	3.36	4.89	2.60	6.81
Fe ⁺³	8.76	0.05	8.81	1.66	3.18	2.56	6.64
Mn ⁺²	4.14	0.22	4.36	1.23	1.43	2.27	5.50
Cu ⁺²	0.09	0.00	0.09	0.03	0.03	0.83	-0.05
Ni ⁺²	0.04	0.01	0.04	0.02	0.01	1.61	2.23
Pb ⁺²	0.04	0.01	0.05	0.02	0.02	0.92	-1.26
Sr ⁺²	1.17	0.13	1.30	0.66	0.46	0.38	-1.99

* All concentrations mentioned above are given in (mg/l).

4. Results and Discussion

The pH was measured at the sample collection site using kid tools of electrodes, to avoid pH changes caused by escape of CO₂⁻² and it ranges between 7.48 and 8.54. Electrical Conductivity values ranged between 1.45 to 5.43 mmhos in the study area. The results of chemical analysis of groundwater samples show that the concentrations of major anions SO₄⁻², HCO₃⁻¹, Cl⁻¹, and NO₃⁻¹ were in the ranges of 160 to 660, 219.60 to 508.76, 160 to 540 and less than 0.2 to 10.80 mg/l, respectively. Where phosphate it was reported as less than 0.2 mg/l. Major cations, Na⁺¹, K⁺¹, Ca⁺² and

Mg⁺² had concentration levels in the range of 150 to 498, 26.30 to 101, 74.9 to 196 and 29.80 to 58 mg/l, respectively. Two major groups of groundwater, characterized by distinct chemical compositions, had been identified, which were, Na-HCO₃ type and Na-Cl type. The hydrochemical results displays some of heavy metals are above the permissible limits, the results are presented in the (Table 1).

4.1. Spatial Distribution of Data

In 2014 Abdalla, et al. [15] study the heavy metals in Nag Hammadi area, located to the south of our present study. He concluded that the detection levels of heavy metals in Nag

Hammadi of Zn^{+2} , Cu^{+2} and Pb^{+2} in sediment and surface water samples were of high concentration than those of groundwater samples of the study area. Moreover, comparing of the concentration levels of some heavy metals in the study area with those of groundwater at Nag Hammadi, indicating the concentration levels in the study area were higher than those of Nag Hammadi for Fe^{+3} , Mn^{+2} , Cu^{+2} , and Pb^{+2} (Table 2). The correlation matrix of chemical data Osireion and around groundwater samples are represented in (Table 3).

High correlation (> 0.75) which observed between Fe^{+3} and Pb^{+2} , Ba^{+2} and Pb^{+2} , Ba^{+2} and Pb^{+2} as well as Al^{+3} and Ba^{+2} , Al^{+3} and Fe^{+3} , and Ba^{+2} with Pb^{+2} . High correlation values are observed between Cl^{-1} and NO_3^{-1} , Na^{+1} with Cl^{-1} , NO_3^{-1} , and SO_4^{-2} , which above 0.75. Mg^{+2} shows high correlation values with Na^{+1} , Cl^{-1} , and SO_4^{-2} as well as Ca^{+2} shows the high correlation values with Mg^{+2} and Na^{+1} . The high correlation values in the study area may be contributed to the uses of pesticides as well as the fertilizers.

Table 2. Concentration levels of the study area and the Nag Hammadi area.

$\mu g/l$		Fe^{+3}	Mn^{+2}	Zn^{+2}	Cu^{+2}	Pb^{+2}
Study Area	Mini.	0.050	0.220	--	0.000	0.005
	Max.	8.810	4.360	--	0.090	0.050
Nag Hamaadi	Mini.	0.041	0.003	0.004	0.002	0.004
	Max.	0.241	0.011	0.026	0.003	0.045

Table 3. Correlation matrix of the chemical data of the study area.

Element	B^{-1}	Ca^{+2}	K^{+1}	Mg^{+2}	Na^{+1}	Cl^{-1}	NO_3^{-1}	SO_4^{-2}
B^{-1}	1							
Ca^{+2}	0.39	1						
K^{+1}	0.91	0.46	1					
Mg^{+2}	0.39	0.98	0.53	1				
Na^{+1}	0.21	0.79	0.49	0.87	1			
Cl^{-1}	0.18	0.60	0.49	0.70	0.96	1		
NO_3^{-1}	0.22	-0.41	-0.17	-0.56	-0.80	-0.80	1	
SO_4^{-2}	0.32	0.96	0.48	0.99	0.83	0.64	-0.59	1
Al^{+3}	-0.31	0.63	-0.24	0.56	0.55	0.45	-0.35	0.53
Ba^{+2}	-0.72	0.29	-0.54	0.30	0.47	0.43	-0.60	0.32
Cu^{+2}	-0.59	-0.44	-0.34	-0.37	-0.04	0.12	-0.34	-0.35
Fe^{+3}	-0.29	0.67	-0.21	0.60	0.56	0.45	-0.37	0.57
Mn^{+2}	0.69	0.41	0.83	0.53	0.50	0.46	-0.40	0.54
Ni^{+2}	-0.19	-0.26	0.10	-0.08	0.31	0.46	-0.62	-0.07
Pb^{+2}	-0.57	0.42	-0.38	0.42	0.56	0.53	-0.57	0.40
Sr^{+2}	0.26	-0.16	0.40	-0.03	0.26	0.41	-0.30	-0.07

Table 3. Continued.

Element	Al^{+3}	Ba^{+2}	Cu^{+2}	Fe^{+3}	Mn^{+2}	Ni^{+2}	Pb^{+2}	Sr^{+2}
B^{-1}								
Ca^{+2}								
K^{+1}								
Mg^{+2}								
Na^{+1}								
Cl^{-1}								
NO_3^{-1}								
SO_4^{-2}								
Al^{+3}	1							
Ba^{+2}	0.78	1						
Cu^{+2}	0.16	0.33	1					
Fe^{+3}	1.00	0.77	0.13	1				
Mn^{+2}	-0.38	-0.37	-0.46	-0.35	1			
Ni^{+2}	-0.34	0.19	0.25	-0.35	0.43	1		
Pb^{+2}	0.92	0.94	0.41	0.91	-0.40	0.00	1	
Sr^{+2}	-0.51	-0.16	-0.17	-0.52	0.62	0.85	-0.33	1

4.2. Water Quality Index

To evaluate the water quality in the present study, water quality index has been used. The water quality index has been introduced [16] and five water quality classes have been identified. The water quality index can be calculated as the following Equation (4).

$$q_n = 100 \frac{V_n - V_i}{S_n - V_i} \quad (1)$$

Where q_n is water quality rating for the nth parameter, V_n is measured value of the nth parameter, and S_n is the standard permissible value of nth parameter. To calculate the water quality index, weighted units (W_n) and the constant for proportionality (K) has to be calculated as follows, Equations

(2 and 3).

$$W_n = \frac{K}{S_n} \quad (2)$$

$$K = \frac{1}{\sum 1/S_n} \quad (3)$$

$$WQI = \frac{\sum q_n W_n}{\sum W_n} \quad (4)$$

Using the above mention Equations (1 to 4) to calculate the water quality index for the study area. Table 4 shows the calculated results of water quality rating, weighted unit, constant for probability, and water quality index; the above Equations. The analyzed data in the present study were compared to WHO guidelines [17-21]. The index of water quality results shows that all the samples were above 100 except W2, which was 70, indicating poor to unsuitable water for domestic use classes (Table 5).

Table 4. Water quality index (WQI) for individual element (units in mg/l).

Element	Standard Value	Measured Value	1/S _n	K	W _n	q _n	W _n *Q _n	WQI
pH	8.50	7.69	0.118		0.002	59.5	0.11	
EC	1500.00	1964.00	0.001		0.000	130.9	0.00	
TDS	1500.00	1257.00	0.001		0.000	83.8	0.00	
Ca ⁺²	200.00	114.10	0.005		0.000	57.1	0.00	
K ⁺¹	12.00	32.00	0.083		0.001	266.7	0.36	
Mg ⁺²	125.00	33.60	0.008		0.000	26.9	0.00	
Na ⁺¹	200.00	150.00	0.005		0.000	75.0	0.01	
HCO ₃ ⁻¹	350.00	405.08	0.003		0.000	115.7	0.01	
Cl ⁻¹	250.00	160.00	0.004	0.016	0.000	64.0	0.00	70.42
NO ₃ ⁻¹	50.00	8.65	0.020		0.000	17.3	0.01	
SO ₄ ⁻²	250.00	270.00	0.004		0.000	108.0	0.01	
Al ⁺³	0.20	0.99	5.000		0.082	495.5	40.56	
Fe ⁺³	0.30	0.17	3.333		0.055	55.0	3.00	
Mn ⁺²	0.50	0.90	2.000		0.033	179.4	5.87	
Cu ⁺²	2.00	0.00	0.500		0.008	0.1	0.00	
Ni ⁺²	0.02	0.01	50.000		0.819	25.0	20.46	
Sum			61.085	0.016	1.000		70.42	

Table 5. Water quality index classes of the study area.

Class	WQI	Study area
Excellent	< 50	
Good	51 - 100	W2
Poor	101 - 200	W1, W3, W6, W7
Very Poor	201 - 300	W4
Un Suitable	> 300	W5

4.3. Heavy Metals

The detected levels of heavy metals in the study area such as; Pb⁺², Sr⁺², Cu⁺², Fe⁺³, B⁻¹, Mn⁺², and Al⁺³ was compared with those values reported by WHO. The sources of lead in groundwater would come where diesel fuel consumed on farms, discarded batteries, paint and leaded gasoline. WHO, reported that the consumption in higher quantity of Pb⁺², might cause hearing loss, blood disorders, hypertension and eventually, it may prove to be fatal [17]. Concentration of Pb⁺² found in the study area ranged between less than 0.005 and 0.05 mg/l. All the collected samples analyzed, have concentration levels less than the maximum permissible limit

of 0.10 mg/l. Concentration of As⁺³ in the study area found less than 0.01 mg/l in all the collected samples and it is observed that the concentration of As under the limit of the maximum permissible level of [17]. Sr⁺² minerals can be released to the groundwater from the weathering of rocks and soils. In the study area concentration of Sr⁺² was reported more than the permissible limit of 0.07 mg/l [18], and it was observed in the range of 0.13 to 1.30 mg/l. The higher concentrations, indicating that the source could be anthropogenic through agricultural activity causes an input of Sr⁺², to some extent it depends on the content of fertilizers and carbonate additives and manure likes cattle, poultry [22].

Table 6. Strontium classes in the study area.

Category	Limits	Study area	Remarks
Fresh Water	< 1.6	0.13 - 1.3	Study area fall within fresh water
Brackish Water	1.6 - 5.0	-	
Saline Water	> 5.0	-	

Saxena et al. [23] have established that Sr⁺² content could be linked to various water types [23]. They suggested Sr⁺² values of < 1.6 mg/l for fresh groundwater, 1.6 - 5.0 mg/l for

brackish water, and > 5.0 mg/l for saline groundwater in the coastal aquifers (Table 6). The Sr⁺² values obtained indicated that the all groundwater samples fall within the freshwater

category according to the above classification.

It is known that the copper found in plants, animal and human bodies, with very small amounts. The copper comes normally into life bodies through water, soil or industrials actives. The high concentration of Cu^{+2} would be of dangerous or toxic for life. However, the WHO reported the toxic limit of Cu^{+2} and mentioned that the Cu^{+2} was an essential in metabolism of human bodies and up to 0.05 mg/l was considered to be non-toxic [21]. Meanwhile, all the samples in the study area, reveals that they were within the maximum permissible limit of 1.5 mg/l and Cu^{+2} concentration levels ranged from 0.004 to 0.091 mg/l. The higher concentrations of iron may cause toxic effect on human health. The Fe^{+3} concentration was recorded in the study area between 0.05 and 8.81 mg/l. High level of Fe^{+3} concentrations was reported in all samples in the study area than the concentration level reported in [20]. Higher Fe^{+3} concentrations in the aquifers might have resulted from the interaction of oxidized Fe^{+3} minerals and organic matter and subsequent. Boron (B^{-1}) in groundwater may have several possible human affected sources, including wastewater effluent, and laundry detergent; possible natural sources include leaching of geologic materials and mixing of groundwater, [24]. Boron usually occurs as a non-ionized form as H_3BO_3 in soils at $\text{pH} < 8.5$, but above this pH, it exists as an anion, $\text{B}(\text{OH})_4$, [25]. In the present study, Boron concentration ranged from 0.152 to 0.406 mg/l, where the maximum permissible limit of B^{-1} was 0.3 mg/l [18]. Samples record the concentration of Boron more than the permissible limit of [18] except W1 and W4 which are less than those reported by WHO. WHO reported that there is

little indication that aluminum is acutely toxic by oral exposure despite its widespread occurrence in foods, drinking water, and many antacid preparations [19]. In the study area Al^{+3} was reported to be between 0.991 to 14.4 mg/l, it is observed that all the collected samples are above the maximum permissible level [21]. In general, in term of aluminum concentration in the study area were contributed to high risks. The weathering of manganese bearing rock and menials is mostly responsible for releasing manganese; accordingly, it will be a common source of manganese in water. Local groundwater could receive the manganese from leaching of manganese from municipal and industrials activates. Mn^{+2} concentration was reported in the samples in the range of 0.22 to 4.36 mg/l. it is obvious that all the samples in the area of study, are of concentration level higher than the maximum permissible limits 0.1 mg/l reported by [18]. Concentration of Nickel (Ni^{+2}) reported to be less than the concentration levels of [21] in the present study, having Ni levels ranges from less than 0.005 to 0.04 mg/l.

5. Pollution Index

Pollution index (Pi) is defined as the ratios of the concentration of individual parameter against the baseline standard (Table 7). It provides information on the relative pollution contributed by individual samples. The critical value is 1.0, values greater than 1.0 indicates a significant degree of pollution while values less than 1.0 shows no pollution [26]. Pollution Index (Pi) is computed as:

$$\text{Pollution Index (Pi)} = (\text{Concentration/Standard}) \quad (5)$$

Table 7. Pollution Index for heavy elements in the study area.

Element	W1	W2	W3	W4	W5	W6	Osireion
Boron	0.51	1.02	1.25	0.90	0.99	1.35	1.10
Aluminum	8.90	4.96	10.90	6.50	72.00	5.05	9.40
Barium	0.03	0.09	0.06	0.14	0.18	0.06	0.06
Copper	0.06	-	0.00	0.03	0.02	-	0.04
Iron	1.27	0.17	0.58	0.05	8.81	0.29	0.49
Manganese	0.44	1.79	1.98	2.58	0.74	8.72	0.99
Lead	0.48	-	-	0.21	0.46	-	0.10
Strontium	1.91	6.54sa	13.64	18.57	4.24	16.43	4.76

The pollution Index value is presented in (Table 7), which calculated using Equation (5). The values obtained of pollution index for B, in W2, W3, W6 and Osireion are of significant degrees of pollution. Values for Al^{+3} as well as Sr^{+2} in all collected samples shows a high degree of pollution. It is observed that the Pi values for iron reported as greater than the 1 in well (1 and 5) which a significant degree of pollution. The values obtained for Mn^{+2} , in W 2, W3, W4 and W6 are of significant degrees of pollution.

6. Conclusion

Water quality index in the area reveals the most of the collected groundwater samples were located in poor to unsuitable water for municipal use. The hydrochemical analysis of collected samples in the present study reveals that

the groundwater is contaminated with some metals, such as Fe^{+3} , Mn^{+2} , Al^{+3} , B^{-1} , and Sr^{+2} . This contamination has been caused by, municipal waste disposal sites and agriculture fertilization. Moreover, high levels of Ba^{+2} in some samples are suspected to originate from fertilizers and pesticide from return flow of agricultural activities. The concentrations of some heavy metals have already exceeded the maximum limit WHO standards. Despite of municipal activity is located few meters above the layer of the aquifer; using hand-dug well for their waste disposal. The correlation relation displays that the heavy metals concentrations is not completely associated with the aquifer rock unit's interaction indicating an additional anthropogenic source. The anthropogenic contribution is sufficiently high in the effect on increasing the contamination levels; which were quite related to municipal disposal, fertilization and industrial discharges.

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