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Assessment of the groundwater quality in Sebha, Libya, for drinking purposes

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ABSTRACT

The study examined water samples from wells in Sebha, analyzing their physicochemical properties such as pH, EC, TDS, Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, NO_3^-, HCO_3^-, TH, and SO_4^{2-}. The results revealed significant increases in EC, TDS, Cl^-, Na^+, K^+, Ca^{2+}, NO_3^-, TH, and SO_4^{2-} concentrations. However, pH, Mg^{2+}, and HCO_3^- remained within permissible limits set by Libyan and World Health Organization standards. The study also noted more pronounced changes in the physicochemical properties of water from wells in Abd-Alkafi1, Abd-Alkafi2, and Aljadeed on the western side of Sebha compared to those in Alnaserayah and Hajara on the eastern side. Correlation analysis showed strong positive correlations between EC-TDS, TH-Ca^2+, and K^+-Na^+ at a significant level of $p<0.01$, and positive correlations at a significant level of $p<0.05$ between EC- Cl^-, Cl^--HCO3$^-$, Cl^-- K^+, Cl^--Na^+, SO_4^{2-} - Na^+, HCO_3^-- NO_3^-, and HCO_3^-- K^+. The strong correlation between Na+ and Cl- indicated high concentrations of these ions in most samples, likely formed from chloride salts through chemical weathering. Similarly, a positive correlation between SO4-- and Na+ suggested that some of these ions resulted from weathering of magnesium and sodium minerals. The Water Quality Index (WQI) categorized water from Alnaserayah and Hajara as suitable for drinking, while water from Abd-Alkafi2, Abd-Alkafi1, and Aljadeed was deemed poor quality. Comparing the current results to a 2001 study revealed a significant increase in the measured elements' concentrations and deterioration in water quality.

INTRODUCTION

Energy and water are among the most important elements that control the distribution of humans on Earth, as it dramatically affects life because of its multiple uses, whether domestic, industrial, or agricultural (Nassar et al., 2007, Devendra et al., 2014; Salem et al., 2024). However, the rapid growth, the significant increase in the population, and the unjust exploitation of it in the last four decades, in particular, It led to a significant depletion of natural resources (especially fossil fuels and water) and a significant decline in the ecosystem and environmental diversity (Yasser et al., 2018; Ali et al., 2021; Nassar et al., 2017, Nassar, 2006; Khaleel et al., 2023, Abdulwahab et al., 2023, Bakouri et al., 2023, Andeef et al., 2023, Iessa et al., 2022). This depletion of natural resources directly affects the salinity and decreased quality of groundwater (Tuinof, et al., 20112; Salem and Chergawi 2013). Therefore, approximately 47% of the world's population currently suffers from energy and water scarcity for at least one month per year, and more than 20% consume unsafe drinking water, as polluted water is used without adequately treating it in some developing countries (Boretti and Rosa. 2019; Salem and Chirgawi 2005). Groundwater is polluted at the source or within the distribution network by a wide range of pollutants, including chemicals, pesticides of all kinds, nitrates, and salinity, leading to deterioration in groundwater quality (Jasper et al., 2012; Ó Dochartaigh et al., 2010; Salem et al., 2022]. The deterioration of water quality in many aquifers is also becoming more severe, especially in arid and semi-arid areas in developing countries, due to the scarcity of water resources and poverty. Saltwater intrusion is one of the most critical factors that lead to water quality deterioration for drinking and agriculture. It also prohibits the exploitation of water in groundwater aquifers at risk in the future (Jia et al., 2018; Mansour et al., 2022). In areas with high population density, such as India, groundwater becomes particularly vulnerable, as industrial activities release many chemicals and waste, and high levels of heavy metals such as lead, copper, and cadmium have been recorded (Mohankumar et al., 2016; Yasser et al., 2021; Ahmed et al., 2023). Libya is located in North Africa and is considered one of the dry and semi-arid desert regions, characterized by scarcity of rain and lack of freshwater resources. Rainfall is concentrated in the northern coastal strip and ranges between 100 - 600 mm/year, while the interior and southern regions receive less than

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10 mm/year. Rainfall is rare in some areas (Wheida. 2007; Yasser et al., 2023). Groundwater sources represent 95% of the total water resources available in Libya. They are divided into renewable and non-renewable water, where non-renewable groundwater is mainly in the major sedimentary basins in Murzuq, Hamada, Kufra and Sarir areas. Fossil water is found in the deep underground layers in varying quantities, controlled by the prevailing geological situation and climatic conditions (Brika, 2008; Salem et al., 2018; Ahmed et al., 2023). The excessive exploitation of groundwater for agricultural purposes, the dumping of wastewater into agricultural areas near the coast, and the low recharge of groundwater aquifers have led to the deterioration of the quality of groundwater, the interference of seawater, and the rise of salty groundwater upward, as is the case in the Al-Jafara Plain area, as it is the most damaged. It may lead to severe problems in these areas where freshwater reservoirs are connected to the sea (Alfarrah et al., 2013; Van Camp et al., 2010; Salem. 2012) extracting groundwater in the oasis region, which is the only source of fresh water, at a rate exceeding the rate of natural replacement led to a gradual decline in the groundwater level, which endangers the aquifers, deteriorating their quality, and infiltrating salt water into them, adding to their contamination with nitrates (Alamin, 2010; Salem and Al-Ethawi 2013). Therefore, analyzing the chemical properties of groundwater is an essential factor in determining the quality of drinking water. It is also necessary to determine its hydrogeological nature, how to exploit it, manage it, and protect the environment. The Murzuq underground aquifer, which is one of the essential reservoirs in the Fezzan region, also suffers from water depletion due to intensive agriculture and lack of recharge due to scarcity of rain and an increase in its rate of depletion above the acceptable rate of depletion, which is about 515 ml3/year (El Asswad, 1995). The city of Sebha is located on the northern edge of the Murzuq Basin, one of Libya's largest groundwater reservoirs. The total water reserve in this reservoir is about 5,400 km3, and it is the only water source the city relies on for various purposes (Salem and Alwalayed 2019). However, groundwater extraction is Large and rapid, exceeding the process of renewal and recharging of water basins due to the rapid and intense increase in agricultural and economic activities during the past fifty years, which led to a decrease in water levels and a deterioration in its quality (lfarrah. et al., 2017; Abdudayem and Scott 2014; Al-Ethawi and Salem 2019). Assessing groundwater quality is an essential and effective mechanism for monitoring its suitability. Water may be a source of life and health or a source of diseases and deaths. The increase in environmental degradation in recent years resulting from development, the increase in population, and climate change have increased researchers' interest in considering its negative impact on the environment and adopting monitoring systems, especially water quality monitoring (Demetillo, et al., 2019). This study aims to:

1- Assessment of the physicochemical properties of some drinking water wells in Sebha City.

2- The extent to which the studied water properties conform to Libyan and international standards and its suitability for human consumption through calculating the water quality index.

3- Compare the physicochemical properties of well water for several neighborhoods in the city, highlighting potential variations.

MATERIALS AND WORKING METHODS

Study area

Sebha is the largest city in the Fezzan region in southwestern Libya. It covers an area of 15,330 km2 and has a population of approximately 250,000. Sebha is situated between latitude 26° 10´ to 27° 04´ north and longitude 13° 58´ to 15° 59´ east (figure. 1)

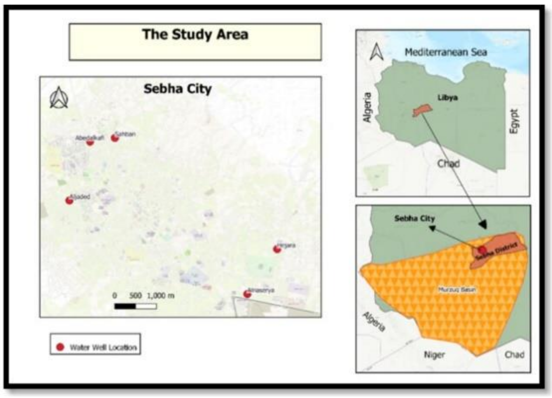

Figure 1. Study area

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Collection and analysis of water samples

In 2023, water samples were collected in clean bottles rinsed with groundwater from the same wells at the time of sampling from five artesian wells. These wells included two in the Abd-Alkafi area, one in the Aljadeed area, one in the Alnaserayah area, and one in the Hajara area. The samples were then transferred to the laboratory for analysis. The physical and chemical properties of the groundwater samples were determined, as mentioned in (APHA. 2012; Huda et al., 2024). The pH and electrical conductivity (EC) were analyzed using a multi-purpose pH device at the sampling site, total dissolved solids (TDS) were measured by evaporation, and the concentrations of calcium and magnesium ions were measured using a specific method. As reported by (Richards, 1954; Salem et al., 2020), titration with EDTA solution was used to determine the concentration of carbonates, bicarbonates, chloride, sodium, and potassium. Furthermore, the concentration of nitrates and sulphates was estimated as mentioned in (Vaughan and Byron 2000; Reda. 2016), respectively.

Calculation of water quality index.

The weighted arithmetic index method was used to calculate the water quality index (WQI) [24]. Twelve parameters were chosen based on the importance and availability of data from each well, namely, pH, EC, TDS, TH, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, NO_3^-, HCO_3^-, SO_4^{2-}. The quality evaluation metric for each parameter (qi) was calculated as follows:

$$qi = \frac{(Ci)}{(Si)} \qquad (1)$$

Where;
qi is a quality rating scale,
Ci is measured concentration ,
Si is the standard value
The relative weight was calculated through the value inversely proportional to the recommended standard value (Si).

$$wi = \frac{1}{Si} \qquad (2)$$

The overall Water Quality Index (WQI) was calculated by combining the quality rating scale (qi) with the corresponding unit weight (wi) using a linear calculation method.

$$\text{WQI} = \sum_{i=1}^{n} wi * qi \qquad (3)$$

$$over\ all\ WQI = \frac{\sum_{i=1}^{i=n} \text{wi} * \text{qi}}{\sum \text{wi}} \qquad (4)$$

Multivariate statistical analysis.

Descriptive analysis, water quality index, and water correlation coefficient were calculated using the statistical program SPSS 30, as described by (Chen, et al., 2007).

RESULTS

Physicochemical properties.

The results are presented in Table 1. The pH of the groundwater samples from the wells ranged between 7.37 and 7.67, indicating that the water samples are neutral to slightly alkaline and within permissible limits. The electrical conductivity values at 25°C ranged between 2188 and 5632 µS/cm, with lower values in the Hajar and Nasiriyah areas than in the rest of the wells. The total dissolved salts showed a considerable range, with concentrations between 1400 and 3704 mg/L. Additionally, the total hardness of the water samples varied between 600 and 810 mg/L, with potassium concentrations ranging between 232 and 1028 mg/L and calcium ion concentrations varying from 240 to 324 mg/L. These values exceeded the permissible limits mentioned in (LNCSM, 1992; WHO, 2011). The sodium concentration ranged between 48 and 552 mg/L, with concentrations exceeding the limit in the Aljadeed, Abd-Alkafi2, and Abd-Alkafi1, water samples while within permissible limits in Hajara and Alnaserayah. Chloride concentration varied

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between 45.05 and 1251.3 mg/L, with Hajar's a concentration falling within permissible limits but exceeding them in the rest of the wells. The sulfate concentration ranged between 88 and 836 mg/L, with concentrations within permissible limits in Hajara and Alnaserayah but exceeding in the other wells. The nitrate concentration ranged between 31 and 240 mg/L, with all wells except for Hajara exceeding the permissible limit. Magnesium ion concentration ranged between 43.2 and 91.2 mg/L, falling within permissible limits. The bicarbonate concentration in the water samples ranged between 30 and 90 mg/L, falling within permissible limits. (WHO, 2011; LNCSM 1992) The concentration was below the device's sensitivity in all cases.

Table 1. Summary of physical and chemical parameters of drinking water of the studied wells compared to drinking water standards.

Param.	Aljadeed	Abd-Alkafi 2	Alnaserayah	Abd-Alkafi 1	Hajara	Min.	Max.	Mean	S. D.	WHO[a]	Libyan[b]
pH	7.37	7.23	7.43	7.36	7.67	7.23	7.67	7.406	0.165	6.5-8.0	8.0 - 6.5
EC (µS/cm)	2938	3996	2188	5632	2299	2188	5632	3410.6	1434.5	400	900
TDS mg/l	1880	2557	1400	3704	1915	1400	3704	2291.2	890.4	1000	500 - 1000
TH mg/l	660	700	810	600	650	600	810	684	78.9	200 - 500	200 - 500
Na^+ mg/l	442	380	172	552	48	48	552	318.8	205.05	200	200 - 20
K^+ mg/l	736	712	548	1028	232	232	1028	651.2	291.22	200	10-40
Ca^{2+} mg/l	264	280	324	240	260	240	324	273.6	31.6	200	200 - 75
Mg^{2+} mg/l	43.2	81.6	91.2	86.4	91.2	43.2	91.2	78.72	20.3	200 - 250	150 - 30
Cl^- mg/l	655	971	325	1251.3	45.04	45.04	1251.3	649.47	483.8	250	200 - 250
NO_3^- mg/l	57.5	155	92.8	240	31	31	240	135.26	88.9	50	50
HCO_3^- mg/l	50	70	60	90	30	30	90	60	22.4	200	200
SO_4^{2-} mg/l	702	439	88	836	133	88	836	439.6	333	250	200 - 400
IWQI	115.61	113.97	99.72	123	91.72						

a = WHO (2011) b = Libyan National Center for Standardization and Metrology (LNCSM), (1992)

Water Quality Index (WQI).

The water quality index (WQI) results for several wells were analyzed, as shown in Table 2. The WQI for Hajara Well is 91.72, and for Alnaserayah., it is 99.72. These wells are located in the southeastern part of the city, and their water is considered good and suitable for drinking based on the water classification (refer to Table 2 (khudair (2013). On the other hand, the water quality index for the wells of Abd-Alkafi2, Aljadeed, and Abd-Alkafi1, located in the northwestern part of the city, are 113.97, 115.61, and 123.00 respectively, indicating that the water is not suitable for drinking according to the same classification. Additionally, the results revealed a positive correlation between WQI, EC, K^+, Na^+, Cl^-, and SO_4^{2-}.

Table 2. Water quality index of studied wells.

Site	Years tested					WQI value	classification
	1984	1994	1988	2000	2023		
Hajara	N d	N d	70.00	72.00	91.72	< 50	Excellent
Alnaserayah.	N d	N d	64.29	75.16	99.72	50 -100	Good
Abd-Alkafi 2	N d	N d	N d	N d	113.97	100 - 200	Poor
Aljadeed	N d	67.86	N d	85.82	115.61	200 - 300	Very poor
Abd-Alkafi 1	71.53	N d	N d	82.52	123.00	>300	Unsuitable for drinking

Nd= not tested

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Correlation coefficient analysis.

The Spearman correlation coefficient results in Table 3 show a positive correlation between WQI and EC, K^+, Na^+, Cl^-, and SO_4^{--}, as well as between Na+ and K^+, and Ca^{2+} and TH. There is also a correlation between Cl^- and EC, K^+ and Na^+, HCO_3^- and K^+ and NO_3^-, and SO_4^{2-} and Na^+. The correlation between Na and Cl is commonly used to determine salinity mechanisms in arid and semi-arid regions (Ganyaglo, et al., 2010).

Table 3. Spearman correlation coefficient between water quality parameters and water quality index (WQI)

	WQI	pH	EC	TDS	TH	K+	Na+	Ca++	Mg++	Cl-	NO3-	HCO3-	SO4-
WQI	1												
pH	-.684	1											
RC	.910*	-.525	1										
TDS	.830	-.378	.980**	1									
TH	-.540	-.079	-.627	-.726	1								
K+	.975**	-.766	.851	.736	-.342	1							
Na+	.980**	-.762	.822	.723	-.477	.966**	1						
Ca++	-.540	-.079	-.627	-.726	1.000**	-.342	-.477	1					
Mg++	-.301	.307	.069	.144	.219	-.274	-.459	.219	1				
Cl-	.956*	-.805	.923*	.841	-.431	.947*	.938*	-.431	-.159	1			
NO3-	.581	-.551	.649	.547	.149	.694	.492	.149	.422	.659	1		
HCO3-	.850	-.740	.861	.759	-.156	.908*	.791	-.156	.132	.909*	.912*	1	
SO4--	.940*	-.543	.796	.742	-.699	.867	.950*	-.699	-.537	.837	.277	.620	1

*Levels of significance: P<0.05. ** Levels of significance: P<0.01.

DISCUSSION

The results showed a variation in the concentration of the studied elements in the water samples, as the pH values of the water were within the permissible limits (WHO, 2011; Libyan National Center for Standardization and Metrology (LNCSM) 1992; Salem and Noralldien 2018). In contrast, the electrical conductivity values were higher than the permissible limits; thus, they were unsuitable for drinking due to the high electrical conductivity in the samples. Water is used for geochemical processes such as reversible exchange, evaporation, ion exchange, silicate weathering, rock-water interaction, human activity, sulfate reduction, and oxidation (Ramesh and Elango 2012; Salem et al., 2014; Hipkin et al., 2004). The results also showed that the concentration of total dissolved salts in the water samples exceeded the permissible limits, and they are not suitable for drinking according to the above specifications. High concentrations of dissolved solids are attributed to the filtration of salts from the groundwater tank matrix and the filtration of domestic wastewater (Prasanth et al., 2012; Hipkin et al., 1999). The results also showed that the total hardness of the water, which represents the concentration of calcium and magnesium, or both, exceeded the permissible limit for drinking water in the water samples of the wells. The high concentration of these two elements is attributed to limestone and the magnesium terrain across the water (Ben Aakame, et al., 2015; Salem and Al-Ethawi 2013). The sodium concentration in the water samples was within the permissible limits in both Hajar and Al-Nasiriyah, while its concentration was similar in the rest of the wells. The high sodium is attributed to the weathering of minerals that make up the rocks, such as Halite, in addition to human sources, such as domestic and industrial waste and animal waste (Freeze and Cherry, 1979), the results also showed a variation in the concentration of potassium in the wells, which may be due to the difference in sedimentary rocks in the region, while the concentration of potassium exceeding the permissible limits in the water is attributed to human activities and the intrusion of salt water (Ghalib, 2017; Salem and Abuhadara 2010). The calcium ion concentration also exceeded the permissible limits in all wells. The increase in calcium in Groundwater is attributed to saltwater seepage, chemical fertilizers, and various industrial activities (Prasanna, et al., 2011). The magnesium ion concentration was within the permissible limits in all wells. The main source of Mg^{2+} is likely magnesium-bearing Groundwater and human waste (Marghade et al., 2010). The results showed that the chloride concentration was within the permissible limits in the Hajar area and exceeded the permissible limit in the rest of the wells. The presence of high chloride concentrations in Groundwater is usually considered an indicator of its contamination (Loizidou and Kapetanios 1993). The high chloride in Groundwater is due to the leaching of domestic sewage and the leakage of agricultural irrigation water into the groundwater reservoir due to the region's proximity to irrigated agricultural areas (Bhatia, 2003). Nitrate also exceeded its concentration in all wells except the Hajara area.

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High nitrate concentrations may be attributed to the oxidation of nitrogenous and biological substances resulting from wastewater or industrial waste naturally produced from waste (Ghalib, 2017). From the results, we find that the bicarbonate concentration was within limits. Allowed in the studied well water, the main source of bicarbonate is the disintegration of carbonate minerals or, as a result, the dissociation of carbon dioxide through the biological decomposition of organic materials from human sources such as domestic and industrial wastewater and buried waste[39], these results are similar to what was indicated by (Bishnoi and Malik 2008; Esmaili and Moore, 2012; Toumi, et al., 2015). As for sulfate, its concentration exceeded the permissible limits in water samples. Aljadeed, Abd-Alkafi2, and Abd-Alkafi2, wells, while, in contrast, their concentration in the Alnaserayah and Hajara water samples was within the permissible limits. It is believed that the main source of sulfate is the weathering of sulfate-bearing minerals such as gypsum, anhydride, and sulfide minerals, along with industrial and mining waste (Raju, et al., 2011). The results showed that the water of the Abd-Alkafi1, Aljadeed, and Abd-Alkafi2 wells is poor and unfit for drinking according to the water quality index Table 2, and this is mainly due to the high values of the variables EC, Na^+, K^+, Cl^-, SO_4^{2-}, which exceeded the permissible limits and Which directly affects water quality, these results are similar to those reported (Salem. et al., 2022; Mansour et al., 2020). The results of comparing the water quality index for the studied wells, especially in Abd-Alkafi1, and Hajara, during the years of use showed that their water was good and over time, it became poor water due to the increase in some variables in their water during the years of use, which negatively affected its quality. The presence of a positive correlation coefficient is also due to the high concentrations of the measured ions and the fact that most of them are formed during the chemical weathering and leaching of chloride and mostly Halite salts (Esmaili and Moore, 2012). The presence of a positive correlation between SO_4 and Na is because some of these ions are derived from the weathering of magnesium minerals and sodium sulfate. The absence of a correlation between HCO3 and Ca and Mg indicates that calcite $CaCO_3$ and dolomite CaMg $(CO_3)_2$ may not be the main source of Ca and Mg (Al-hadithi 2012).

CONCLUSIONS AND RECOMMENDATIONS

The study results suggest that the physicochemical properties of the well water samples have degraded. The measured parameters exceeded the permissible limits set by the Libyan Specifications and Standards 2009 and the World Health Organization 2011. There has been a significant increase in the values of the studied parameters compared to previous years. The quality index indicates poor water quality in wells in Abd-Alkafi1, Abd-Alkafi2, and Aljadeed but good quality water in Alnaserayah and Hajara. The deterioration in water quality may be due to excessive water depletion and water leakage into the ground tank. The results also revealed a decline in water quality in the wells studied in Sebha. To maintain water quality and reduce pollution, we recommend conducting a comprehensive survey of all wells in the city to assess their suitability for human use, treating the water from wells with deteriorated quality, and establishing a method for utilizing it. Regular tests and modern studies of drinking wells are essential. Additionally, it is crucial to educate citizens about the importance of conserving water and the risks associated with its depletion for future generations.

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