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# Ground water quality in Wadi Shati (Libya): Physicochemical analysis and environmental implications

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Abstract: This study aimed at evaluating water quality of groundwater wells (GWWs) in Wadi Shati, Libya, and assessing its suitability for drinking. Water samples were collected from 17 GWWs and subjected to laboratory testing for 24 physical and chemical water quality parameters (WQPs). Analysis uncovered that the recorded values of 11 WQPs were consistent with the Libyan drinking water quality standard (DWQS). These parameters were pH, temperature (*T*), acidity, alkalinity, electrical conductivity (*EC*), sodium, potassium, calcium, magnesium, zinc, and cadmium. However, values of colour and turbidity exceeded the maximum levels set by the Libyan DWQS at five out of the 17 study wells. Likewise, concentrations of chloride (Cl<sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), and ammonia (NH<sub>3</sub>) violated the local DWQS in three locations, each. Additionally, concentrations of phosphate (PO<sub>4</sub><sup>3-</sup>), iron, manganese, chromium, and nickel exceeded their maximum allowable concentrations according to the Libyan DWQS. The levels of these five parameters are alarming. Overall, the 17 studied GWWs suffer from varying levels of pollution that, mostly, arise from domestic and agricultural sources, e.g., septic tank seepage and agricultural drainage of agro-chemicals like fertilisers and pesticides. The results of this study emphasise that routine monitoring of groundwater resources plays a vital role in their sustainable management and stresses that water quality data are critical for characterisation of pollution, if any, and for protection of human health and ecosystem safety. Our results serve as guideline for sustainable management of water quality in the Wadi Shati District.

Keywords: drinking water quality, groundwater, physicochemical parameters, Wadi Shati

# INTRODUCTION

Groundwater is the primary source of water for human use in the arid and semi-arid regions [ACKAH *et al.* 2011], in general, and in Libya, in particular [JUMMA *et al.* 2012; SHOAYWI *et al.* 2016]. Actually, it is the only source of water supply for drinking, agricultural, and other purposes in Libya, where about 90.0% of the water supply in the country comes from groundwater [JUMMA *et al.* 2012].

Libya is one of countries in Africa that suffer from shortage of water resources and limited water availability. Most of the country includes either arid or semi-arid areas. In Libya, the yearly average rainfall ranges from 10 to 500 mm. Only about 5.0–7.0% of the country receives more than 100 mm of rain annually [ABDELRHEM *et al.* 2008; IBEDA *et al.* 2014]. Moreover, evaporation rates are very high. They range from almost 1,700 mm in the northern parts of the country to nearly 6,000 mm in the southern areas [ABDELRHEM *et al.* 2008]. Because of this, and the growing population and urbanization rates, there is a growing demand for safe water for drinking, irrigation, and other domestic uses, with a concomitant pressure on the groundwater supplies [AHMIDA *et al.* 2016].

A number of factors influence the quality of ground water, mainly geology, atmospheric conditions, rock weathering, and soil properties. In addition to the natural factors influencing water quality, human activities, especially urban development and agricultural practices, have negative bearings on groundwater quality [ACKAH *et al.* 2011; AHMIDA *et al.* 2016]. In light of this, quality of groundwater is steadily changing in response to climatic and land use factors. Therefore, continuous monitoring of surface and ground water quality is highly critical considering that changes in water quality have far reaching impacts on humans and biota.

In Libya, groundwater resources are under escalating pressure as a result of limited fresh water supplies and rapid population and urbanisation growth. Particularly in the Wadi Shati District, groundwater is the only source of water for drinking and other domestic uses [SALEM, ALSHERGAWI 2013]. Water quality data are critical for characterisation of pollution, if any, and for the protection of human health and ecosystem safety. Therefore, routine monitoring of groundwater resources plays a vital role in sustainable management of the surface and ground water resources. Bearing in mind that periodic water quality evaluations are vital for human health protection and environmental safety, this study was conducted with the objective of assessing the water quality in 17 groundwater wells (GWWs) in

the Marzouk Basin in Wadi Shati (Ash Shati Valley), south west of Libya, with particular emphasis on potential pollution of these wells and their suitability for domestic purposes.

# MATERIALS AND METHODS

### STUDY AREA

Libya is an arid African country with average yearly rainfall depth of less than 100 mm over about 93.0% of its land area. The country has four major aquifers, including the Marzuq-Djado Basin, over which the study area, Wadi Shati (Ash Shati Valley), is located (Fig. 1). This basin is shared between Libya and Algeria IBEDA *et al.* [2014]. Estimates of its area and the volume of water it holds vary; while AMHIMMID *et al.* [2020] reported that it has an area of nearly 450,000 km<sup>2</sup> and that it incubates about 4,800 km<sup>3</sup> of water, IBEDA *et al.* [2014] estimate that it has an area of 350,000 km<sup>2</sup> and that it holds 7,700 km<sup>3</sup> of water.



Fig. 1. Study area location in map of Libya; source: UN [2012]

The Marzuq-Djado Basin comprises two main groundwater reservoirs [IBEDA *et al.* 2014]:

- the lower groundwater reservoir, which is made up of Cambro Ordovician and Siluro-Devonian sandstone (Acacus sandstone and Tadrart sandstone); this reservoir includes the districts of Al Awaynat, Ghat, Wadi Aril, Wadi Shati, and Wadi Tanezzuft;
- the upper groundwater reservoir, which is made up of continental formations of Jurassic, Lower Cretaceous, and Triassic sandstone (known as the post-Tassilian and Nubian series); the districts located in this reservoir include Marzuq district, Sabha, Samnü-Azzighan, Tamanhant, Wadi Ajal, Wadi Barjij, and Wadi Irawan.

Wadi Shati is one of six districts of the Fezzan governorate. The district lies in the central west part of Libya. It is located between the longitudes of 9°49'59" E and 15°53'38" and the latitudes of 26°13'03" N and 29° 34'03", thus extending for 150 km, with a width that ranges from 15 to 20 km. Moreover, it varies in elevation from 262 to 412 m a.s.l., with a gradient that is predominantly toward the south. It has an area of 97,160 km<sup>2</sup> [SALEM, ALSHERGAWI 2013]. According to the Bureau of Statistics and Census, Libya [BSCL 2021], Wadi Shati had a population of 95,294 in 2020.

#### WATER SAMPLING AND ANALYSIS

Water samples were collected from 17 ground water wells in 17 locations in Wadi Shati: 1) Ashkadah, 2) Dabdab, 3) Gairah Assareerah 2, 4) Agar (Eastern Well), 5) Faculty of Engineering Well, 6) Brak Almosallah, 7) Tamzawah Assareerah, 8) Mahroogah (Eastern Well), 9) Algardhah (Western Well), 10) Addeesah (Eastern Well), 11) Taroot Algadeemah, 12) Bargan (Eastern Well), 13) Bargan (Western Well), 14) Azzahra', 15) Wanzareek Alkhadra', 16) Almansoorah, and 17) Tamsan (Eastern Well).

Samples were collected in 500-cm<sup>3</sup> polyethylene bottles that were washed well several times with double-distilled water and rinsed with the water to be sampled. One cm<sup>3</sup> of 5.0% nitric acid (HNO<sub>3</sub>) solution was then added to each bottle to harness the microbial activity, if any. At each location, water was allowed to run at full capacity for five minutes before the samples were collected. Then, the bottles were filled with water to the rim and covered immediately. Right after collection, the water samples were stored in ice boxes and transported to the laboratory, where they were stored in refrigerators at 4°C until analysis. Sample analysis was performed by the technical staff of the Environmental Chemistry Laboratory in the Department of Environmental Sciences at the Faculty of Engineering and Technology in the Sebha University.

The priority water quality parameters to be assessed included 25 physicochemical parameters, comprising 18 common parameters and seven heavy metals (Tab. 1). These 25 parameters are pH, temperature (*T*), acidity (Acid), alkalinity (Alk), electrical conductivity (*EC*), colour (Clr), turbidity (Turb), the total dissolved solids (*TDS*), total hardness (*TH*), and the concentrations of sodium (Na), potassium (K), calcium (Ca), magnesium (Mg), chloride (Cl<sup>-</sup>), sulphate (SO<sub>4</sub><sup>2-</sup>), ammonia (NH<sub>3</sub>), nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>), phosphate (PO<sub>4</sub><sup>3-</sup>), iron (Fe), manganese (Mn), zinc (Zn), cadmium (Cd), chromium (Cr), and nickel (Ni). These parameters were analysed according to standard methods of the American Public Health Association [APHA 2017] as illustrated in Table 1. To ensure that the assessments were accurate and precise, the samples were analysed in triplicates. In addition, standard solutions, whenever applicable, and blanks were incorporated with each batch of samples. Afterwards,

Table 1. Methods of analysis of the water quality parameters

Parameter	Unit	Analytical method
рН	_	4500-H <sup>+</sup> B. Electrometric method
Temperature (T)	°C	thermometer
Acidity (Acid)	mg·dm <sup>-3</sup>	2310 B. Titration method
Alkalinity (Alk)	mg·dm <sup>-3</sup>	2320 B. Titration method
Electric conductivity ( <i>EC</i> )	µS·cm <sup>−1</sup>	2510 B. Laboratory method
Colour (Clr)	Pt-Co unit	2120 B. Visual comparison method
Turbidity (Turb)	NTU	2130 B. Nephelometric method
Total dissolved solids ( <i>TDS</i> )	mg∙dm <sup>-3</sup>	2540 C. Total dissolved solids dried at 180°C
Total hardness ( <i>TH</i> )	mg·dm <sup>−3</sup>	2340 C. EDTA titrimetric method
Na	mg∙dm <sup>-3</sup>	3500-Na B. Flame emission photometric method
К	mg∙dm <sup>-3</sup>	3500-K B. Flame emission photometric method
Ca	mg∙dm <sup>-3</sup>	3111B,D. Flame atomic absorp- tion spectrometry
Mg	mg∙dm <sup>-3</sup>	3111B. Flame atomic absorp- tion spectrometry
Cl⁻	mg∙dm <sup>-3</sup>	4500-Cl <sup>−</sup> B. Argentometric method
SO4 <sup>2-</sup>	mg∙dm <sup>-3</sup>	4500-SO <sub>4</sub> <sup>2–</sup> E. Turbidimetric method
NH <sub>3</sub>	mg∙dm <sup>-3</sup>	4500-NH <sub>3</sub> C. Titrimetric method
NO <sub>2</sub> <sup>-</sup>	mg∙dm <sup>-3</sup>	4500-NO <sub>2</sub> <sup>-</sup> B. Colorimetric method
NO <sub>3</sub> <sup>-</sup>	mg∙dm <sup>-3</sup>	4500-NO <sub>3</sub> <sup>-</sup> B. Ultraviolet spec- trophotometric screening method
PO4 <sup>3-</sup>	mg∙dm <sup>-3</sup>	4500-P C. Vanadomolybdo- phosphoric acid colorimetric method
Fe	mg∙dm <sup>-3</sup>	3111B. Flame atomic absorp- tion spectrometry
Mn	mg·dm <sup>−3</sup>	3111B. Flame atomic absorp- tion spectrometry
Zn	mg∙dm <sup>-3</sup>	3111B. Flame atomic absorp- tion spectrometry
Cd	mg·dm <sup>−3</sup>	3111B. Flame atomic absorp- tion spectrometry
Cr	mg·dm <sup>−3</sup>	3111B. Flame atomic absorp- tion spectrometry
Ni	mg·dm <sup>−3</sup>	3111B. Flame atomic absorp- tion spectrometry

Source: own elaboration.

descriptive statistics were determined for each measured WQP using version 24.0 of the Statistical Package for Social Sciences (SPSS). The various descriptive statistics (minimum, maximum, range, mean, and standard deviation) were pooled over the 17 study ground water wells.

Groundwater in Wadi Shati is found in the geological formations of the Paleozoic Era (Cimbro-Ordovician), consisting of hard sandstones, alluvial stones, and mud with thickness ranging from 50 to 75 m. The area consists of interchanges of sandstones and alluvial mudstones that are very rich in Iron-Oolitic and characterised by severe cracks and fractures (joints and faults). The subterranean reservoirs in Wadi Shati are considered as one hydraulic unit, especially in the absence of a solid stratum in the upper part of the Ordovician period, which separates the upper and lower reservoirs.

The groundwater was formed in the study area 20,000–48,000 years ago. This supported the formation of underground reservoirs in an ancient era.

# **RESULTS AND DISCUSSION**

The water samples were analysed in triplicates. Therefore, the values of the WQPs reported in Table 2 are averages of three readings, each. The obtained values of the WQPs were then compared with the Libyan Drinking Water Quality Standard (DWQS). In the cases when a WQP has no value stipulated for it in the standard (i.e., *T*, Acid, *EC*, and  $PO_4^{3-}$ ), the corresponding value in the DWQS of the World Health Organization [WHO 2017b] was used in the evaluation as an alternative.

The water pH values ranged from 6.6 to 7.3, with a mean of 6.96  $\pm 0.250$  (Tab. 2). The variation between the sample GWWs is thus small. These values, which indicate slightly acidic (pH = 6.6) to almost neutral (pH = 7.3) water, agree with the ranges of values stipulated for pH in the Libyan and WHO DWQSs (Tab. 2). This finding compares with that of SHOAYWI et al. [2016]. These researchers examined water quality in five ground water wells in Qavrat Al Shati in the Wadi Shati District and found that, with the exception of one well whose mean pH value was 6.22, the range of pH values was 6.63-7.11. To some extent, these results compare with results of the local of study by SALEM and ALSHERGAWI [2013] who investigated the quality of 50 ground water wells in Wadi Shati and found that, on average, pH values of water in sample wells ranged from 6.32 to 7.67. As well, AMHIMMID et al. [2020] assessed quality of water in 10 GWWs in the Marzuq Basin and found that water pH values ranged in these wells from 6.5-7.73, with an average of 7.2. However, higher pH values (6.70-8.90) were reported for the district of Wadi Shati. Moreover, IBEDA et al. [2014] investigated water quality of 13 ground water wells in the Sabha District, which is adjacent to Wadi Shati and also located in the Fezzan Basin, and found that pH values ranged in these wells from 6.7 to 8.9 with a mean of 7.54 ±0.75. Furthermore, higher pH values (7.5-7.7) were reported for five GWWs. Higher pH values (7.5-7.7) were reported by HAMED [2019] for five GWWs in the Marzug District, a nearby district located in the same basin (Fezzan Basin).

The lithological characteristics of geological formations are among primary factors that control the quality and quantity of dissolved salts in waters of the lower and upper layers of reservoirs, especially during periods they were interspersed between soluble rocks or saline layers and limestone of the marine environment. They represent water dissolved elements in the region that are arranged according to their concentration, with positive ions (sodium, calcium, magnesium) and negative ions (chlorine, sulphate, and bicarbonate), the origin of which goes back to their original sources, namely sodium, chloride, and gypsum.

Temperature varied noticeably from one location to another in the present study. The mean water temperature ranged from 22.1 to 29.3°C, with a pooled mean of 25.14 ±0.25°C (Tab. 2). These temperature values are very close to the temperatures reported in earlier local studies of wells in the Wadi Shati District, including the study by SALEM and ALSHERGAWI [2013] which found that the temperature of water in their 50 sample wells fell in the range of 19.4–30.8°C. These temperature values are slightly different from those reported in the study by IBEDA *et al.* [2014]; 26.30–26.50°C, with a mean of 26.40 ±0.041°C. However, it is noticed that the mean water temperature values are almost the same in these three studies. The differences can be ascribed to the time and date of sample collection.

Acidity of water ranged in the sample GWWs from 9 to 28 mg·dm<sup>-3</sup>, with an overall mean of 15.65  $\pm$ 6.17 mg·dm<sup>-3</sup> (Tab. 2). It should be highlighted that there exists no standard, or recommended, reference value for this WQV, neither in the Libyan DWQS, nor in that of the WHO. Interestingly, the researchers could not find previous local studies of groundwater quality anywhere in Libya that included water acidity in the water quality assessment. While this hinders comparison of acidity levels between the present study and previous local studies, it means that the water acidity reported here would be a reference value for similar future investigations.

Alkalinity ranged in the 17 sample GWWs from 25 to 180 mg·dm<sup>-3</sup>, with a pooled average of 86.94 ±46.04 mg·dm<sup>-3</sup> (Tab. 2). However, the standard deviation of 46.04 is high, indicating wide variations in alkalinity between the sample GWWs. The highest alkalinity concentrations were recorded in five areas: Almansoorah (180 mg·dm<sup>-3</sup>), Wanzareek Alkhadra' (142 mg·dm<sup>-3</sup>), Azzahra' (135 mg·dm<sup>-3</sup>), Addeesah, Eastern Well (130 mg·dm<sup>-3</sup>), and the Faculty of Engineering Well (118 mg·dm<sup>-3</sup>). The Libyan DWQS does not set a threshold value for alkalinity. Therefore, the researchers compare the foregoing alkalinity values with the DWQS of the WHO, which sets the acceptable alkalinity concentration at 50 mg·dm<sup>-3</sup>. Considering the above, the researchers find that only six of the 17 study GWWs meet alkalinity values abided by the WHO standard: Bargan, Western Well (25 mg·dm<sup>-3</sup>); Bargan, Eastern Well (30 mg·dm<sup>-3</sup>); Gairah Assareerah 2 (35 mg·dm<sup>-3</sup>); Ashkadah (40 mg·dm<sup>-3</sup>), Taroot Algadeemah (40 mg·dm<sup>-3</sup>), and Dabdab (45 mg·dm<sup>-3</sup>). However, it seems that these alkalinity values are not uncommon. SALEM and ALSHERGAWI [2013] obtained comparable results. They found that alkalinity ranged in 50 GWWs in Wadi Shati from 64 to 142 mg·dm<sup>-3</sup>. However, it is interesting that IBEDA et al. [2014] reported an average alkalinity value of 36.810 mg·dm<sup>-3</sup> for 13 GWWs in the Sabha District, which is a nearby district that is also part of the Fezzan Basin. Much higher alkalinity values have been reported for other parts of Libya. For instance, NAIR et al. [2006] reported an alkalinity range of 213-270 mg·dm<sup>-3</sup> (a mean of 243 ±19.35 mg·dm<sup>-3</sup> for six areas north east of Libya. As well, AHMIDA et al. [2016] found that alkalinity

Demonstern (consist)		Value in groundwater well location														NC	Mar	D	Aver-	(D	Libyan	wно		
Parameter (unit)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	Min.	Max.	Range	age	SD	DWQS	DWQS
рН	7.2	7.1	6.7	6.7	6.9	7.3	6.8	6.9	7.1	7	7.2	6.7	7.3	7.3	6.6	7	6.6	6.6	7.3	7	6.965	0.25	6.5-8.5	6 - 9
T (°C)	24.2	25.5	29.3	26.5	28.7	26.6	26	24.9	24.3	23.8	25.8	22.2	22.1	24.5	24.5	25.3	23.1	22.1	29.3	7.2	25.135	0.25	-	-
Acid (mg·dm <sup>-3</sup> )	9	10	10	9	22	24	18	19	15	14	17	10	11	10	25	15	28	9	28	19	15.65	6.174	-	-
Alk (mg·dm <sup>-3</sup> )	40	45	35	75	118	104	100	90	80	130	40	25	30	135	142	180	109	25	180	155	86.94	46.037	200	50
$EC \ (\mu S \cdot cm^{-1})$	729	42	788	42	248	-	290	96	208	329	284	105	654	682	221	522	326	42	788	746	347.88	250.078	-	2500
Colour (Pt-Co unit)	10	10	10	70	15	15	10	5	15	10	40	15	70	5	20	5	70	5	70	65	23.24	23.713	15	15
Turb (NTU)	0.162	-	-	0.564	0.208	0.212	-	0.194	0.852	0.712	0.92	0.224	0.18	-	0.2	-	0.656	0.162	0.92	0.758	0.424	0.294	5 JTU	0.2
TDS (mg·dm <sup>-3</sup> )	740.7	41	270.2	40.7	279.2	116.8	284.2	415.4	252.5	402.7	336.3	110.9	691.9	688.8	267.4	633.7	403.6	40.7	740.7	700	351.529	224.948	1000	600
$TH (mg \cdot dm^{-3})$	136	168	176	156	60	52	64	48	56	84	102	106	108	84	70	102	76	48	176	128	96.94	40.781	500	200
Na (mg·dm <sup>-3</sup> )	35.5	44.37	35.5	29.58	43.75	42.44	43.42	40.48	39.83	52.89	55.18	38.46	32.54	54.85	66.93	64	61.38	29.58	66.93	37.35	45.947	11.27	200	200
K (mg·dm <sup>−3</sup> )	20.43	19.78	20	18.61	17.96	18.28	18.12	17.17	16.94	16.62	14.73	18.97	18.61	8.98	24.27	12.21	20.4	8.98	24.27	15.29	17.769	3.431	40	-
Ca (mg·dm <sup>-3</sup> )	24	32	25.6	21.6	20.8	16	17.6	12.8	12	9.6	12	20.8	17.6	28	18.4	33.6	19.2	9.6	33.6	24	20.094	6.904	200	
Mg (mg·dm <sup>-3</sup> )	18.24	21.12	26.88	24.48	1.92	2.88	4.8	3.84	6.24	14.4	17.28	12.96	15.36	3.36	5.76	4.32	6.72	1.92	26.88	24.96	11.209	8.183	150	-
Cl <sup>−</sup> (mg·dm <sup>-3</sup> )	195.66	187.67	165.7	152.73	177.69	143.75	155.73	139.75	135.76	233.59	244.57	168.7	165.71	228.6	398.31	323.44	336.42	135.76	398.31	262.55	209.046	76.987	250	250
$SO_4^{2-}$ (mg·dm <sup>-3</sup> )	141	303.4	239	282.1	137.3	171.8	170.1	177.5	303.4	878.1	1100	225.8	203.4	574.7	172.9	574.7	235.6	137.3	1100	962.7	346.518	276.993	400	250
$NH_3^-$ (mg·dm <sup>-3</sup> )	0.924	0.32	0.085	0.48	0.36	0.036	0.024	0.024	0.48	0.36	0.121	0.607	0.024	0.24	0.24	0.36	0.6	0.024	0.924	0.9	0.311	0.254	0.5	0.5
$NO_3^-$ (mg·dm <sup>-3</sup> )	0.79	17.27	2.43	0.35	nd	nd	0.841	0.708	nd	0.08	nd	nd	nd	41.62	nd	30.56	1.63	0.08	41.62	41.54	9.628	15.085	45	10
$PO_4^{3-} (mg \cdot dm^{-3})$	5.66	5.84	5.19	6.72	5.3	4.24	1.76	1.41	2.47	4.24	7.43	6.01	6.19	2.65	2.83	4.48	1.59	1.41	7.43	6.02	4.354	1.913	-	0.2
Fe (mg·dm <sup>-3</sup> )	2.69	0.53	0.45	5.76	3.9	4.85	0.5	4.53	8.36	5.85	5	4.21	9.66	0.44	5.97	1.43	10.02	0.44	10.02	9.58	4.362	3.116	0.3	0.3
Mn (mg·dm <sup>-3</sup> )	0.36	0.37	1.12	0.29	0.47	0.2	1.32	0.24	0.67	0.43	0.68	0.61	0.2	0.02	0.36	0.26	0.5	0.02	1.32	1.3	0.476	0.332	0.1	0.1
Zn (mg·dm <sup>-3</sup> )	4.26	0.1	0.05	8.3	1.84	0.85	0.05	1.66	0.05	1.21	0.09	0.11	0.63	0.32	0.06	0.38	0.2	0.05	8.3	8.25	1.186	2.124	15	4
Cd (mg·dm <sup>-3</sup> )	0.0038	0.0076	0.0026	0.0006	0.0096	0.0247	0.0172	0.0015	0.0043	0.002	0.0023	0.0043	0.0008	0.0072	0.0009	0.0062	0.0006	0.0006	0.0247	0.0241	0.00566	0.006	0.005	0.01
Cr (mg·dm <sup>-3</sup> )	0.0905	0.086	0.0957	0.0895	0.0938	0.0894	0.0785	0.0772	0.0929	0.083	0.0906	0.0928	0.0877	0.0962	0.0934	0.0955	0.0945	0.0772	0.0962	0.019	0.08988	0.00576	0.05	0.05
Ni (mg·dm <sup>-3</sup> )	0.075	0.089	0.079	0.088	0.08	0.102	0.091	0.087	0.077	0.095	0.096	0.094	0.076	0.079	0.075	0.089	0.086	0.075	0.102	0.027	0.0858	0.0088	0.02	0.02

Table 2. Mean values of water quality parameters in the 17 study groundwater wells in Wadi Shati, Libya

Explanations: 1 = Ashkadah, 2 = Dabdab, 3 = Gairah Assareerah 2, 4 = Agar (Eastern Well), 5 = Faculty of Engineering Well, 6 = Brak Almosallah, 7 = Tamzawah Assareerah, 8 = Mahroogah (Eastern Well), 9 = Algardhah (Western Well), 10 = Addeesah (Eastern Well), 11 = Taroot Algadeemah, 12 = Bargan (Eastern Well), 13 = Bargan (Western Well), 14 = Azzahra', 15 = Wanzareek Alkhadra', 16 = Almansoorah, 17 = Tamsan (Eastern Well), SD = standard deviation, DWQS = drinking water quality standards, T = temperature, Acid = acidity, Alk = alkalinity, EC = electrical conductivity, Turb = turbidity, TDS = total dissolved solids, TH = total hardness, SD = standard deviation, nd = not detected.

Source: own study.

ranged from 176 to 400  $\text{mg}\cdot\text{dm}^{-3}$  in 20 GWWs in the Benghazi city, Shebna District.

In the 17 study GWWs, electric conductivity (EC) ranged from 42 to 788 µS·cm<sup>-1</sup>, with a pooled mean of 347.88 µS·cm<sup>-1</sup> and a standard deviation of 250.08. No threshold EC value has been set in the Libyan DWQS. As to the WHO, to researchers' best of knowledge, no threshold EC value has been stipulated or recommended by the WHO. However, in the revision of Annex I Council Directive 98/83/EC on the Quality of Water Intended for Human Consumption (Drinking Water Directive), the WHO [2017b] recommended the EC value of 2500 µS·cm<sup>-1</sup> at 20°C as a permissible value for drinking water. In the light of this, the researchers conclude that the EC values of water in the sample GWWs did not deviate from the WHO permissible EC value. Indeed, they are much lower than this recommended EC value. These EC values (Tab. 2) to some extent compare with the findings of SHOAYWI et al. [2016] who examined water quality in five GWWs in Qayrat Al Shati in the Wadi Shati District and found that the EC values lied in the range of 975–1310  $\mu$ S·cm<sup>-1</sup>. Still, the aforementioned EC values correspond to lower salinity levels than what has been reported for nearby sites in the Fezzan Basin, in general, and in Wadi Shati, in particular. For instance, SALEM and ALSHERGAWI [2013] found that the EC values ranged in 50 GWWs in Wadi Shati from 117 to 2214 µS·cm<sup>-1</sup>. In other studies, HAMED [2019] found that EC of water ranged in 36 GWWs in the Marzuq District from 319 to 2488 µS·cm<sup>-1</sup>, whereas AMHIMMID et al. [2020] reported an EC range of values of 85-2970  $\mu$ S·cm<sup>-1</sup>, also in the Marzuq Basin, corresponding to a mean EC value of 733 µS·cm<sup>-1</sup>. IBEDA et al. [2014] even reported much higher EC values (198–4390  $\mu$ S·cm<sup>-1</sup>, with an average EC of 1152  $\mu$ S·cm<sup>-1</sup>) for 13 GWWs in the neighbouring district of Sabha.

Colour of the water samples drawn from the 17 study GWWs ranged from 5 to 70 Pt-Co units, with an average of 23.24 Co-Pt units and a standard deviation of 23.71. According to the Libyan DWQS, water colour must not exceed 15 Pt-Co units. The review of Table 2 shows that the majority of the sample wells met the colour standard. However, while four GWWs had borderline colour values (Faculty of Engineering Well, Brak Almosallah, Algardhah, Western Well, and Bargan, Western Well (15 Pt-Co units)), water colour departed from the threshold value of 15 Pt-Co units in five wells: Agar, Eastern Well (70 Pt-Co units), Bargan, Eastern Well (70 Pt-Co units), Tamsan, Eastern Well (70 Pt-Co units), Taroot Algadeemah (40 Pt-Co units), and Wanzareek Alkhadra' (20 Pt-Co units). We could not find local or international water quality assessment study that included water colour in the analysis, which prevented any comparisons in water colour between this study and other studies.

Turbidity ranged in the sample GWWs from 0.162 to 0.920 NTU. The average turbidity pooled over all these wells was 0.424 NTU and the standard deviation was 0.294. These findings (Tab. 2) are compared with the WHO DWQS (0.20 NTU) because the turbidity threshold in the Libyan DWQS is based on the Jackson, rather than the nephleometric method. Analysis outcomes show that five of the 17 GWWs had missing turbidity values. Of the remainder 12 wells, only four wells complied with the WHO DWQS threshold. These are Ashkadah (0.162 NTU), Mahroogah, Eastern Well (0.194 NTU), Bargan, Eastern Well (0.180 NTU), and Wanzareek Alkhadra' (0.200 NTU). Meanwhile, turbidity values of the remaining wells were high, ranging from 0.208 to 0.920 NTU. These high levels of turbidity are,

mostly, due to suspended and dissolved non-organic substances, such as mud and fine sand, that may be ascribed to overpumping of the wells.

We had no information about a published assessment of water quality in the Fezzan Basin that included turbidity analysis. Therefore, we paid an effort to review published assessments of groundwater quality in other parts of Libya and found one study only that took turbidity evaluation into account, which is the study by HAMAD et al. [2021]. These researchers examined quality of water in 11 GWWs in the city of Al-Marj, which is a city located in the north east part of Libya. They found that turbidity in those wells ranged from 0.2 to 1.2 NTU, with a pooled average of 0.53 and a standard deviation of 0.30. This suggests that high groundwater turbidity values may not be uncommon in Libya. Since turbidity refers to cloudiness of water caused by suspended solids like sediments and clay, it may be concluded that the turbid GWWs are subject to over-pumping. We also link turbidity with the high Fe and Mn concentrations in the study wells as will be discussed in sequent paragraphs. When ground water with high Fe and Mn concentrations is pumped to the surface, the Fe<sup>2+</sup> reacts with atmospheric oxygen, thus resulting in oxidation of Fe<sup>2+</sup> to Fe<sup>3+</sup> and formation of rust-coloured iron minerals. The dissolved Mn may form blackish particulates and produce similar coloured stains in water.

Total dissolved solids (TDS) concentration was another WQV that we took into consideration in the present study. As Table 2 shows, the TDS concentration fell in the range of 40.7 -740.7 mg·dm<sup>-3</sup>, with a mean concentration of nearly 351.53 mg·dm<sup>-3</sup> and a standard deviation of 224.95. The standard TDS value in the Libyan DWQS is 1000 mg·dm<sup>-3</sup>. Thus, the TDS concentrations in all sample GWWs comply with this value. Two GWWs had very low TDS values of about 41 mg·dm<sup>-3</sup>: Dabdab (41.0 mg·dm<sup>-3</sup>) and Agar, Eastern Well (40.7 mg·dm<sup>-3</sup>). With the exception of the lowest two TDS concentrations reported here (about 41 mg·dm<sup>-3</sup>), the results of this study are consistent with findings of previous studies of GWWs in the Fezzan Basin, e.g. Амнимид et al. [2020] (54–1901 mg·dm<sup>-3</sup>), Намед [2019] (502  $-1372.8 \text{ mg} \cdot \text{dm}^{-3}$ ), IBEDA et al. [2014] (240-2897.4 mg \cdot \text{dm}^{-3}), SALEM and ALSHERGAWI [2013] (354–1411 mg·dm<sup>-3</sup>), and SHOAYWI et al. [2016] (624-838.4 mg·dm<sup>-3</sup>).

The total hardness (TH) analysis disclosed that none of the 17 study GWWs had hard water. The minimum and maximum TH values were 48 and 176 mg·dm<sup>-3</sup>, respectively, and the pooled average TH was 96.9 mg·dm<sup>-3</sup>. According to the Libyan DWQS, total hardness must not exceed 500 mg·dm<sup>-3</sup>. Thereupon, the researchers conclude than the TH concentrations in all study wells abide by the standards. In other words, water of none of these wells is hard, rather, it is soft. Based on findings of the current study and those of earlier studies in the Marzuq Basin, the researchers highlight that water in most of the GWWs in the basin is soft water. The minimum and maximum TH values in the study of Shoaywi et al. [2016] were 114 and 150 mg·dm<sup>-3</sup>, respectively. SALEM and ALSHERGAWI [2013] obtained slightly higher results since the TH concentrations in their sample wells lied in the range of 88-309 mg·dm<sup>-3</sup>. Similarly, the study by HAMED [2019] reported a TH range of 41-389.3 mg·dm<sup>-3</sup>. Other studies in the same basin reported somehow higher TH values, with some wells violating the TH threshold of the Libyan DWQS. For instance, IBEDA et al. [2014] found that TH ranged in the GWWs they studied from 72.0 to 520.0 mg·dm<sup>-3</sup>. AMHIMMID et al. [2020], however, reported a wider range (20–992 mg·dm<sup>-3</sup>). But when the GWW having the highest *TH* concentration is excluded, then the range narrows to 20–522 mg·dm<sup>-3</sup>, which is not much wider than the *TH* values reported in other studies of the same basin.

Sodium concentration was in general low in all the study GWWs. It ranged from 29.58 to 66.93 mg·dm<sup>-3</sup>, with a pooled mean of 45.95  $\text{mg}\cdot\text{dm}^{-3}$  and a standard deviation of 11.27. These values are compliant with the Libyan DWQS, which sets the maximum allowable sodium concentration at 200 mg·dm<sup>-3</sup>. Comparative review of results of previous local studies of GWWs in Fezzan Basin reveal somewhat comparable sodium concentrations. As an example, SALEM and ALSHERGAWI [2013] found that the minimum and maximum concentrations of sodium were 57.39 and 126.86 mg·dm<sup>-3</sup>, respectively. The sample GWWs in the study by SHOAYWI et al. [2016] had a narrow sodium concentration range of 70.46 to 73.25 mg·dm<sup>-3</sup>. However, AMHIMMID et al. [2020] reported a higher range of sodium concentrations (4-183 mg·dm<sup>-3</sup>). Comparable concentrations were reported by IBEDA et al. [2014] (6-284 mg·dm<sup>-3</sup>) and HAMED [2019] (15.2-259 mg·dm<sup>-3</sup>). We, thereupon, conclude that sodium concentrations in the GWWs in the Fezzan Basin are in general low and that they do, in most of the cases, fall below the threshold concentration of 200 mg  $\cdot$  dm<sup>-3</sup>.

The potassium (K) concentration was generally low in the sample GWWs. It varied from 8.98 to 24.27 mg·dm<sup>-3</sup> (Tab. 2). The average K concentration, pooled over these 17 GWWs, was 17.77 mg·dm<sup>-3</sup>. All recorded concentrations lie well below the maximum allowable K concentration (40 mg·dm<sup>-3</sup>) according to the Libyan DWQS. Review of the studies evaluating quality of GWWs in the Fezzan Basin unveils that the K concentrations reported in this study are common. AMHIMMID et al. [2020] reported a close range of K concentrations (6-39 mg·dm<sup>-3</sup>). Likewise, SHOAYWI et al. [2016] found that potassium concentrations in five GWWs in Geerah (Fezzan Basin) varied from 23.02 to 24.58 mg·dm<sup>-3</sup>. These findings coincide with findings of SALEM and Alshergawi [2013] who reported a range of K concentrations of 10.29-34.29 mg·dm<sup>-3</sup> in 51 GWWs in the Al Shati District. Though, higher K concentrations in certain parts of the Fezzan Basin were reported by HAMED [2019] (15.2-315 mg·dm<sup>-3</sup>) and IBEDA et al. [2014] (4.3-362 mg·dm<sup>-3</sup>). These variations may be related to differences between wells in the Fezzan Basin in age, depth of the water table, and the pumping rate.

Calcium (Ca) concentrations in all 17 GWWs were low and well below the maximum allowable concentration (MAC) according to the Libyan DWQS, which is 200 mg·dm<sup>-3</sup>. Furthermore, only slight differences between these wells in Ca concentrations were observed since the concentrations ranged from 9.6 to 33.6 mg·dm<sup>-3</sup> (Tab. 2). To some extent, these concentrations are close to the corresponding concentrations reported earlier for other GWWs in Fezzan Basin, e.g., 22.4–30.4 mg·dm<sup>-3</sup> [SHOAYWI *et al.* 2016]. However, these concentrations differ from concentrations reported for other GWWs in the Fezzan Basin, e.g., 8.3–54.6 mg·dm<sup>-3</sup> [HAMED 2019], 8.64–104 mg·dm<sup>-3</sup> [IBEDA *et al.* 2014], 6–306 mg·dm<sup>-3</sup> [AMHIMMID *et al.* 2020], and 11.2–332.8 mg·dm<sup>-3</sup> [SALEM, ALSHERGAWI 2013].

Magnesium (Mg) concentrations in the 17 studied GWWs are in general low, ranging from 1.92 to 26.88  $mg \cdot dm^{-3}$  (Tab. 2). The pooled mean Mg concentration was 11.21  $mg \cdot dm^{-3}$  and the standard deviation was 8.18. This standard deviation value points

to noticeable differences between the wells in Mg concentrations as can be seen in Table 2. However, the Mg concentrations are all low. Contrary to the foregoing WQPs, in which differences are noticed between various local studies, there is high level of agreement about Mg concentrations between the present study and previous studies of GWWs in the Fezzan Basin. More precisely, reported ranges of Mg concentration were 5–17.2 mg·dm<sup>-3</sup> [HAMED 2019], 9.12–22.08 mg·dm<sup>-3</sup> [SHOAYWI *et al.* 2016], 2–55 mg·dm<sup>-3</sup> [AMHIMMID *et al.* 2020], and 3.36–57.6 mg·dm<sup>-3</sup> [SALEM, ALSHERGAWI 2013]. An exception is the study by IBEDA *et al.* [2014] which reported a Mg concentration range of 14.40–93.28 mg·dm<sup>-3</sup> for 13 GWWs in Sabha District.

Chloride (Cl<sup>-</sup>) concentration is another WQP that meet the Libyan DWQS. Its concentration ranged in the 17 sample GWWs from 135.76 to 398.31 mg·dm<sup>-3</sup> (Tab. 2). Three exceptions were detected, where the concentrations of Cl<sup>-</sup> exceeded the standard threshold of 250 mg·dm<sup>-3</sup>: Wanzareek Alkhadra' (398.31 mg·dm<sup>-3</sup>), Almansoorah (323.44 mg·dm<sup>-3</sup>), and Tamsan, Eastern Well (336.42 mg·dm<sup>-3</sup>). If we exclude these three wells, then chloride concentrations range from 135.76 to 244.57 mg·dm<sup>-3</sup>, with a pooled average of 178.26 mg·dm<sup>-3</sup>, which fall below the maximum Cl<sup>-</sup> concentration of 250 mg·dm<sup>-3</sup>. Close results were reported earlier for this basin. For example, HAMED [2019] found that Cl<sup>-</sup> concentration ranged from 17.6 to 193.3 mg·dm<sup>-3</sup>. AMHIMMID et al. [2020], however, reported close, but somewhat wider range of (10-349 mg·dm<sup>-3</sup>) in the Marzuq Bain. Nevertheless, higher Cl<sup>-</sup> concentrations have been reported for some GWWs in this basin by few previous studies, including SALEM and Alshergawi [2013] (143–648.9 mg·dm<sup>-3</sup>) and Ibeda et al. [2014]  $(16.97-568 \text{ mg} \cdot \text{dm}^{-3}).$ 

Sulphate (SO<sub>4</sub><sup>2-</sup>) concentrations in the 17 study GWWs were in general below the maximum allowable SO4<sup>2-</sup> concentration of 400 mg dm $^{-3}$ , according to the Libyan DWQS, except for three cases: Azzahra', Taroot Algadeemah, and Addeesah, Eastern Well, where the  $SO_4^{2-}$  concentrations were 574.7, 878.1, and 1100 mg·dm<sup>-3</sup>, respectively (Tab. 2). These three wells also had somehow high Cl<sup>-</sup> concentrations (228.60, 233.59, and 244.57 mg·dm<sup>-3</sup>, respectively). A comparison of these findings with those of previous studies in the same basin show that the  $SO_4^{2-}$ concentrations reported here are common. For instance, IBEDA et al. [2014] found that  $SO_4^{2-}$  concentrations ranged from 22.14 to 220.00 mg·dm<sup>-3</sup>, though SALEM and ALSHERGAWI [2013] reported slightly broader range (19.12-440.12 mg·dm<sup>-3</sup>). However, the range was narrower (262–385 mg·dm<sup>-3</sup>) in the study by SHOAYWI et al. [2016]. A much narrower range (16–87 mg·dm<sup>-3</sup>) was reported for this basin by HAMED [2019]. These differences indicate variations within the Marzuq Basin in SO4<sup>2-</sup> concentrations that may be the result of variations in aquifer mineralogy, well age, and land uses around each well.

Ammonia (NH<sub>3</sub>) concentrations were generally acceptable ( $<0.5 \text{ mg}\cdot\text{dm}^{-3}$ ). They varied from a minimum of 0.024 mg·dm<sup>-3</sup> to a maximum of 0.924 mg·dm<sup>-3</sup>. Its average concentration, pooled over all 17 GWWs, was 0.311 mg·dm<sup>-3</sup> (Tab. 2). Three GWWs had higher concentrations than the maximum NH<sub>3</sub> concentration allowed by the Libyan DWQS: Ashkadah (0.924 mg·dm<sup>-3</sup>), Bargan, Western Well (0.607 mg·dm<sup>-3</sup>); and Tamsan, Eastern Well (0.600 mg·dm<sup>-3</sup>). These three GWWs in particular might be located close to urban settlements, and thus, subject to domestic wastewater pollution originating from septic tanks. Of the previous local water quality assessments in the Marzuq Basin,

which we knew about, only the study by IBEDA et al. [2014] assessed the NH3 concentrations. These researchers found that NH<sub>3</sub> concentrations ranged from 0.061 to 0.122 mg·dm<sup>-3</sup>, which corresponded to lower NH<sub>3</sub> concentrations than what we obtained. It is possible that the 17 GWWs investigated in this study receive domestic wastewater from septic tanks located in the nearby urban areas. These high levels of NH<sub>3</sub> in the study GWWs may be attributed to geologic depositions of peat and lignite beds in these wells. They may also be ascribed to anthropogenic sources of pollution like seepage from septic tanks in the urban areas around these wells that are not served by municipal wastewater collection systems. Another potential anthropogenic source is synthetic agricultural fertilisers.

Nitrate (NO<sub>3</sub><sup>-</sup>) concentrations met the maximum NO<sub>3</sub><sup>-</sup> concentration limit set by the Libyan DWQS, which is 45.0  $mg \cdot dm^{-3}$ . They varied from 0.08 to 41.62  $mg \cdot dm^{-3}$  (Tab. 2). The overall average NO<sub>3</sub><sup>-</sup> concentration was 9.63 mg·dm<sup>-3</sup>. However, while HAMED [2019] reported lower  $NO_3^-$  concentrations (4.0–9.4 mg·dm<sup>-3</sup>) elsewhere in the Marzuq Basin, there are a few instances of NO<sub>3</sub><sup>-</sup> concentrations exceeding the threshold of 45.0  $mg \cdot dm^{-3}$ , e.g. IBEDA et al. [2014] (0.0-63.0 mg \cdot dm^{-3}) and SALEM and AlsherGawi [2013] (0.01-97.97 mg·dm<sup>-3</sup>). The high NO<sub>3</sub><sup>-</sup> concentrations may be ascribed to nitrogen fertiliser leaching to agricultural drainage.

Phosphate (PO<sub>4</sub><sup>3-</sup>) concentrations were high in the 17 study GWWs. They ranged from 1.41 to 7.43 mg·dm<sup>-3</sup>. Since the Libyan DWQS does not set a threshold value for PO<sub>4</sub><sup>3-</sup> concentration, these concentrations (Tab. 2) are compared with the WHO DWQS, which specifies the maximum allowable  $PO_4^{3-}$ concentration as  $0.20 \text{ mg} \cdot \text{dm}^{-3}$ . Accordingly, it is concluded that the  $PO_4^{3-}$  concentrations in the 17 study GWWs far exceed the threshold of 0.2 mg·dm<sup>-3</sup>. These high concentrations can be ascribed to leaching of phosphate fertilisers from agricultural lands. Comparable PO<sub>4</sub><sup>3-</sup> concentrations were reported earlier for the Marzuq Basin by IBEDA et al. [2014] (0-2.78 mg·dm<sup>-3</sup>) and SALEM and ALSHERGAWI [2013] (0.01-43.31 mg·dm<sup>-3</sup>). The researchers ascribe the high  $PO_4^{3-}$  concentrations in the studied wells to long-term agricultural over-use of chemical fertilisers, especially phosphate fertilisers, and manures. It may also be inferred that the study GWWs experience reducing conditions, since these conditions facilitate dissolution of iron oxides, to which phosphorous is adsorbed, and its subsequent release into the water system.

Iron (Fe) concentrations were high in all GWWs under study. They varied from a minimum of 0.44 mg·dm<sup>-3</sup> to a maximum of 10.02 mg·dm<sup>-3</sup> (Tab. 2). As both the Libyan and the WHO DWQSs set the maximum allowable Fe concentration at 0.3 mg·dm<sup>-3</sup>, it is concluded that the levels of Fe in the study GWWs are much higher than what is acceptable. However, it seems that such levels are not uncommon in the GWWs in the Marzuq Basin because two previous studies reported close levels. For instance, IBEDA et al. [2014] found that the Fe concentrations in 13 GWWs in the Sabha District lied in the range of 0.02-2.10 mg·dm<sup>-3</sup> while SALEM and ALSHERGAWI [2013] found that the Fe concentrations in 51 wells in the Al Shati District had a range of 0.01-6.94 mg·dm<sup>-3</sup>. Hence, it can be concluded that GWWs in the Marzuq Basin commonly have high Fe concentrations.

Manganese (Mn) concentrations were in general high in the study wells, ranging from 0.02 to 1.32 mg·dm<sup>-3</sup>, and having an overall average of 0.476 mg·dm<sup>-3</sup> (Tab. 2). The maximum

allowable Mn concentration, both in the Libyan and the WHO DWQSs, is 0.10 mg·dm<sup>-3</sup>. As such, with the exception of the GWW at Azzahra', which had a mean Mn concentration of 0.02 mg·dm<sup>-3</sup>, all study GWWs have higher Mn concentrations than recommended. This finding agrees with results of previous studies on water quality in this basin, e.g. studies by IBEDA et al. [2014] (0.0–0.60 mg·dm<sup>-3</sup>, with an average of 0.262 mg·dm<sup>-3</sup>), and SALEM and ALSHERGAWI [2013] (0.01-1.83 mg·dm<sup>-3</sup>).

The most common sources of Mn and Fe in groundwater are natural sources and processes, such as weathering of Mn-, and Fe-bearing rocks, and minerals and rocks. Anthropogenic sources of these two metals in groundwater also include sewage. Furthermore, high concentrations of Fe and Mn are associated with reducing conditions in groundwater wells. Therefore, the researchers attribute the high Fe and Mn levels in the 17 study GWWs to reducing conditions, as was highlighted in the explanation of the high PO43- concentrations in the preceding paragraph. Thus, it is now concluded that the wells have a reducing environment.

Mineralogical studies indicate the presence of large quantities of sulphur ores throughout Wadi Shati if these sulphur minerals are associated with the presence of mineral ores in Ashkada, Tarout, and Dabdab members, such as gypsum (CaSO<sub>4</sub>·H<sub>2</sub>O), anhydrite (CaSO<sub>4</sub>), thenardite (Na<sub>2</sub>SO<sub>4</sub>), and pyrite (FeS) if sulphur minerals are present. In the Tarot member, the sulphur ores are combined with iron clay-stone (of pyrite origin) and oolite (goethite, limonite) combined with gypsum. Gypsum also constitutes the material for iron sandstone.

As for the Ashkadeh member, which consists of exchanges of clay, alluvial and sandstones bearing iron ores, it is interrupted by layers of gypsum. In the Murar formation, the clay layers containing salt and gypsum are revealed in successions. In the formation of the Al-Qasr well, laminate clay stones are distinguished by their content of sulphur granules mixed with muscovite minerals and sulphidic quartz grains, and the clay sediments are clearly mixed with sulphides in this member. From geological studies of the Adrei plate, it has been found that the majority of salt deposits in the region contain large amounts of gypsum, anhydrite, and thenardite, which are components of the Ordovician-carbon water reservoir rocks.

Zinc (Zn) concentrations were in general low and much below the maximum allowable Zn concentration of 15.0 mg·dm<sup>-3</sup> according to the Libyan DWQS (Tab. 2). They varied from 0.05 to 8.30 mg·dm<sup>-3</sup>. Two sites had relatively high Zn concentrations: Ashkadah (4.26 mg·dm<sup>-3</sup>) and Agar, Eastern Well (8.30 mg·dm<sup>-3</sup>). Once these two sites are excluded, the minimum, maximum, and mean Zn concentrations become 0.05, 1.84, and 0.51 mg·dm<sup>-3</sup>, respectively. To our best of knowledge, no earlier investigations of water quality in the Marzuq Basin included the assessment of Zn, which prevents us from reaching a conclusion on whether or not such concentrations are popular in this area.

Cadmium (Cd) concentrations in the study wells are in general very low, indicating limited abundance of this heavy metal in the Marzuq Basin. They varied from a minimum of 0.0006 to a maximum of 0.0247 mg·dm<sup>-3</sup> (Tab. 2), with a polled average of 0.00566 mg·dm<sup>-3</sup>. These concentrations comply with the maximum allowable Cd concentration of 0.005 mg·dm<sup>-3</sup> according to the Libyan DWQS, except Brak Almosallah, where the concentration was higher (0.0247 mg·dm<sup>-3</sup>) than recommended. Review of the literature which we could access disclosed that no previous evaluations of water quality in the Marzuq Basin included Cd in the analysis. Therefore, it is not clear whether the Cd levels reported here are common or not to this basin.

Chromium (Cr) concentrations in the study wells exceed the maximum allowable Cr concentration of  $0.05 \text{ mg} \cdot \text{dm}^{-3}$  according to the Libyan DWQS. They ranged from 0.0772 to  $0.0962 \text{ mg} \cdot \text{dm}^{-3}$ , with a pooled average of about  $0.09 \text{ mg} \cdot \text{dm}^{-3}$  (Tab. 2). The same applies to nickel (Ni) concentrations, which too were higher than the maximum concentration of  $0.02 \text{ mg} \cdot \text{dm}^{-3}$  that is allowed by the Libyan DWQS. The values recorded in the 17 study GWWs had a range of  $0.075-0.102 \text{ mg} \cdot \text{dm}^{-3}$  and an overall mean of  $0.0858 \text{ mg} \cdot \text{dm}^{-3}$ . The researchers could not find any previous evaluation of water quality in the Marzuq Basin that included Cr or Ni in the analysis. Consequently, it is not clear whether the herein reported Cr and Ni levels are prevalent or not in this basin. In other respects, cadmium, Cr, and Ni in the studied GWWs can find roots in the use of pesticides containing heavy metal salts, besides natural sources.

The Murzuq Basin, located in western Libya, includes areas of Wadi al-Shati and the northern outskirts of the Qarqif Heights, where ancient rocks (such as granite, granodiorite, gneiss (metamorphic rocks), schist and amphibolite) are found at the edges of these heights, while the middle of the basin is formed mostly of sedimentary rocks such as sandstone, clay, alluvial and limestone. Dolmens and sand dunes cover depressions and valleys.

The age of the geological formations in Wadi Shati dates back to the Paleozoic era (Cambrian era) to the Carboniferous era. The Devonian and Carboniferous periods unfold along the central extension of Wadi Shati.

## CONCLUSIONS

This study aimed at evaluating water quality of groundwater wells (GWWs) in Wadi Shati, Libya, and assessing its suitability for drinking. Water samples were collected from 17 GWWs and subjected to laboratory testing for 24 physical and chemical water quality parameters (WQPs). The analysis showed that the observed values of 11 WQPs were in line with the Libyan drinking water quality standard (DWQS). These parameters included pH, temperature, acidity, alkalinity, electrical conductivity, Na, K, Ca, Mg, Zn, and Cd. However, values of colour and turbidity exceeded the maximum levels stipulated by the Libyan DWQS at five of the 17 studied wells. Similarly, the concentrations of NH<sub>3</sub>, Cl<sup>-</sup>, and SO<sub>4</sub><sup>2-</sup> violated the local DWQS in three locations, each. Additionally, concentrations of PO<sub>4</sub><sup>3-</sup>, Fe, Mn, Cr, and Ni exceeded their maximum allowable concentrations according to the Libyan DWQS. The levels of these five parameters are alarming.

Noticeable variations in the values of the 24 studied WQPs are observed among GWWs in the Marzuq Basin. These variations can be ascribed to land covers and land use activities around each of the 17 study wells. The generally high values of several examined WQPs are signs of water quality deterioration in the Wadi Shati District. In general, the 17 studied GWWs suffer from varying levels of pollution that, mostly, arise from domestic and agricultural sources, e.g. septic tank seepage and agricultural drainage of agro-chemicals like fertilisers and pesticides. Accordingly, our results point to some level of groundwater pollution. In consequence, water in the GWWs is in general not much suitable for human consumption unless it is subjected to pre-treatment.

In view of the high  $NH_3$  and  $PO_4^{3-}$  concentrations, the researchers conclude that the 17 GWWs experience anthropogenic pollution of domestic (septic tank seepage, mainly) and agricultural origins (agro-chemicals, especially synthetic fertilisers and, presumably, pesticides). Based on the high heavy metal concentrations, particularly Fe and Mn, the researchers conclude that the wells have a reducing environment; these wells most probably exist in a confined aquifer.

The results of the study emphasise that routine monitoring of groundwater resources plays a vital role in their sustainable management and stress that water quality data are critical for characterisation of pollution, if any, and for the protection of human health and ecosystem safety. Our results serve as a guideline for a sustainable management of water quality in the Wadi Shati District.

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