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HYDROCHEMISTRY REVIEW OF AL DABOSIA, MASSAH, APOLLO AND AL HUFARA SPRINGS, AL JABAL AL KHDAR, NE LIBYA

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ABSTRACT

The water springs are the main sources for drinking and irrigation in Al Jabal Al Khdar, NE Libya. This study will be reviewed the hydrochemistry characterization of Al Dabosia, Massah, Apollo and Al Hufara springs. The results showed the Al Dabosia , Apollo and Al Hufara springs are characterized by moderate fresh water whereas Massah spring is characterized by hard fresh water. The piper diagram is classified the water springs as Ca HCO3 (II Type) except Apollo spring is contained CaMgCl (IV Type). Plot of Mg/Ca vs. Na/Ca ratio of water springs revealed the source of major ions were originated from limestone and terra rossa soil weathering. According to WHO (2018) the water springs in study areas should be treated for drinking water.

Introduction

Al Jabal Al Khdar is a high mountain area covered with forests in northeastern Libya, which is distinguished by its height over most areas of Libya and is characterized by its high rates of rainfall and many springs that are a source of drinking and irrigation for local people, in addition to the availability of fertile lands suitable for agriculture. In this work will review four water springs are located in Al Jabal Al Khdar, NE Libya (Fig.1); namely as the following:

- 1- Al Dabosia spring is considered one of the largest springs in the Al Jabal Al Akhdar and used to supply the drinking water and irrigation to Al Qubbah city.
- 2- Massah spring is used supply to the drinking water and irrigation to Massah city.
- 3- Apollo and Al Hufara springs are used to supply the drinking water and irrigation to Shahhat city.

Aims of the work

- 1- To review the hydrochemistry characterization of Al Dabosia, Massah, Apollo and Al Hufara springs for drinking and irrigation proposes.
- 2- To verify the safety of the water springs with the international quality standards of WHO (2018) guideline.

3- To aware the local people on the health risk of drinking water and irrigation.

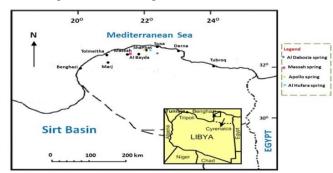


Fig.1: Location map of the studied water springs (Shaltami *et al.*,2020).

Methodology

Seven samples were collected from water springs by Shaltami *et al.*, (2017a, 2019) and El-Shawaihdi *et al.*, (2107); these samples were taken average depth 15cm below the water surface. The samples were subjected to the following techniques:

Major ions of Al Dabosia, Massah and Al Hufara water springs were measured by using a Flame photometer. Total dissolved solid (TDS) and alkalinity (Alk) were determined by gravimetric method and acid-base titration. The heavy metals were analyzed by using AAS Hitachi-5000.

Major ions of Apollo water spring measured by AAS Hitachi-5000. Heavy metals were analyzed by using Inductively Coupled Plasma-Mass Spectrometry technique (ICP-MS) technique. The chemical analyzes of Al Dabosia and Al Hufara springs were done in the Chemistry Department, Faculty of Science, Benghazi University, The chemical analyzes of Massah water spring was done in the Al-Alamia Center for chemical physical and microbiology analysis, Benghazi, Libya and the chemical analysis of Apollo water spring was done in the Nuclear Materials Authority of Egypt.

Table 1: Chemical analysis data (major ions and trace elements in mg/l, EC in ds/m) of the studied water springs

Parameters	Al Dabosia spring		Massah spring	Apollo spring		Al Hufara spring	
Ph	7.6	7.3	7.5	6.8	6.91	7.6	7.5
EC	0.87	0.86	1.1	1.5	1.44	0.82	0.8
Alk	248	252	91	57.66	58.13	208	188
CI	84	80	218	74.4	74.76	80	92
TH	304	320	501	348	352.5	284	232
Ca	96	99	130	100	100.6	98	92
Mg	15.4	17.3	43	24	25.14	9.6	0.5
Na	55	46.9	86	49.55	50.13	53.1	63.6
Fe	0.1	0	_	5.6	6	0.1	0.1
K	0.3	4.2	5	8.11	8	3.3	3.5
SO ₄	26	29	48	101	100.89	10	10
HCO ₃	201	195	405	164	164	171	180
TDS	340	338	718	877	883	350	344
Cu	0.05	0.02	0.09	1.6	1.43	0.02	0.03
Pb	0.02	0.01	0.13	0.04	0.03	0.01	0.02
Zn	_	_	0.09	1.4	1.56	_	_
Hg	-	_	_	0.02	0.03	_	_
As	-	_	_	0.05	0.07	-	_
Cd	_	_	_	0.05	0.06	_	_
Cr			_	0.06	0.06	_	_

Results and discussion

Hydrochemistry of water springs

The major ions analysis of surface water samples were evaluated by using Schoeller, Stiff and Piper diagrams. Schoeller (1977) diagram provides a convenient way to present chemical composition of water of a region. In the present study, the relative tendency of ions in mg/l shows Ca > Na > Mg > K and HCO₃+CO₃ > Cl > SO₄ (Fig.2).. A piper (Piper, 1953) diagram of cations Na, K, Ca, and Mg and anions HCO₃, CO₃, Cl , and SO₄ was used to determine water types for water springs in the study areas. The results showed Al Dabosia, Massah and Al Hufara springs are characterized by Ca HCO₃ (II Type) whereas Apollo spring is characterized by CaMgCl (IV Type)(Fig. 3).

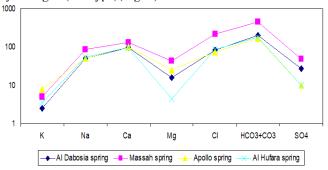


Fig. 2: Schoeller diagram showing the average composition of the studied water springs.

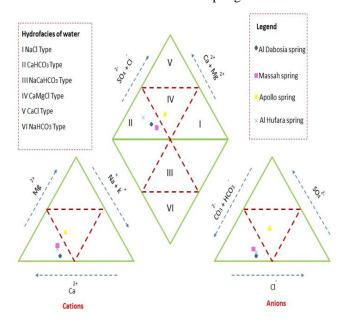


Fig. 3: Piper diagram of water chemistry in the study area (fields after Tweed *et al.*, 2005).

Seawater mixing index

The seawater-mixing index for surface water is evaluation to identify seawater-mixing base on four major ions such as Mg, Na, SO₄, Cl which is highly employed in research investigation of saline water mixing with surface or groundwater (Kumar 2014; Kanagaraj and Elango, 2016). (Figs.5-6) showed the studied water springs were not affected by seawater intrusions; in addition, the water springs are characterized by soft fresh water except Massah spring belongs as hard fresh water.

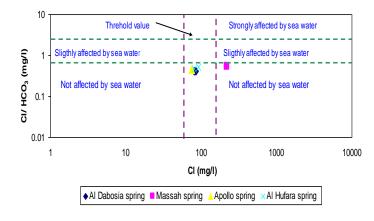


Fig.4: Molar ratio Cl vs. Cl/HCO₃ in the water samples (fields after Todd D., 1989).

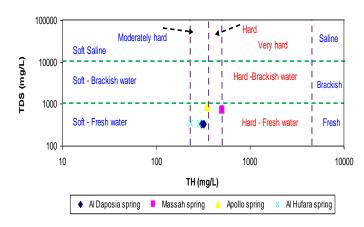


Fig.5: Plot of total dissolved solids (TDS) versus total hardness (TH) of the water springs (fields after Todd D., 1989).

Rock - water interaction

A Gibbs plot (Gibbs, 1970) was used to classify the hydrogeochemical data of water based on precipitation rock, and evaporation dominance. Major interference of the studied water springs were originated from rock dominance (Figs.7-8). Han and Liu (2004) have used the variations in the composition of water (Mg/Ca vs. Na/Ca) to distinguish limestone, dolomite and silicate rock sources of ions. The source of major ions were came from Limestone and terra rossa soil weathering (Fig.9).

The saturation index (SI) can help to identify the precipitation and dissolved minerals in the water samples (e.g., Shaltami *et al.*, 2017 b). The SI values of relevant minerals were calculated using the following equations:

Log SI halite = $\log a_{\rm Na} + \log a_{\rm Cl} + \log Ks$ halite **Log SI gypsum** = $\log a_{\rm Ca} + \log a_{\rm SO4} + \log Ks$ gypsum **Log SI calcite** = $\log a_{\rm Ca} + \log a_{\rm HCO3} + \log Ks$ calcite **Log SI dolomite** = $\log a_{\rm Ca} + \log a_{\rm Mg} + \log a_{\rm HCO3} + \log Ks$ dolomite

The log SI is more than zero in all minerals indicating the super saturation with calcite, dolomite, gypsum and halite.

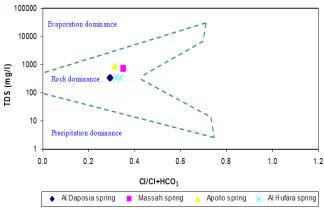


Fig. 6: Dominance of precipitation, rock and evaporation on Cl/Cl+HCO₃ vs. TDS of the study area (fields after Gibbs, 1970).

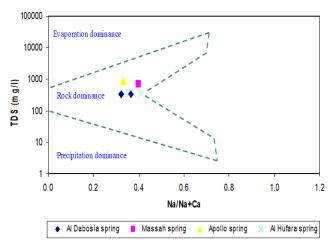


Fig. 7: Dominance of precipitation, rock and evaporation on Na/Na+Ca vs. TDS of the study area (fields after Gibbs, 1970).

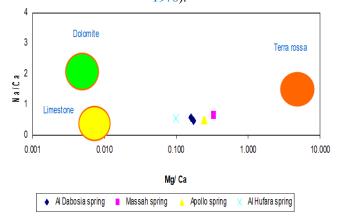


Fig. 8: Plot of Mg/Ca vs. Na/Ca ratios of the studied water samples (modified after Han and Liu, 2004).

Drinking water quality

Table (1) shows the values of different parameters for analyzed water samples compared to WHO (2018) for drinking water. The values of the analyzed parameters of Al Dabosia and Al Hufara springs such as Alk and Pb are over the permissible limit, the values of the analyzed parameters of Massah spring such as TDS, Pb and Cd are over the permissible limit and the values of the analyzed parameters of Apollo spring such as TDS, Fe, Pd, Hg, Cr,Cd and Ni are over the permissible limit. According to Caerio et al., (2005) the studied water samples in the present study determined the level of heavy metal contamination for drinking. The metal index (MI) is calculated as:

(Metal index) MI = C / MAC

Where, C is the metal concentration (mg/l) in water sample and MAC (mg/l) is the maximum allowable concentration (WHO, 2011). MI is classified into six (6) classes: class 1, very pure <0.3; class II, pure 0.3-1; class III, slightly affected 1-2; class IV, moderately affected 2-4; class V, strongly affected 4-6 and class VI, seriously affected >6 (Caerio et al., 2005). The Pd is slightly affected (class III) in Al Dabosia and Al Hufara springs, Pb and Cd are seriously affected (class VI) in Massah spring, Fe, Cd and Hg are seriously affected (class VI), Pb and Ni are moderately affected (class IV) in Apollo spring.

Irrigation water quality

Total salt concentration (EC), sodium adsorption ratio (SAR), percentage sodium (Na %), residual sodium carbonate (RSC), permeability index (PI), Kelley's ratio (KR) and magnesium adsorption ratio (MAR) are the important parameters used in assessing the suitability of water for irrigation uses. These parameters are defined as:

Na% = (Na*100)/(Ca+Mg+Na+K) $SAR = Na / \sqrt{(Ca+Mg)/2}$ MAR = [Mg/(Mg+Ca)]100 KR = Na/(Ca+Mg) $PI = [(Na+HCO_3)/(Ca+Mg+Na)]100$

(All concentrations are expressed in meq/l)

The plot of EC versus Na % shows that the water springs of the Al Dabosia, Massah and Al Hufara springs are characterized as good quality while Apollo spring is characterized as fair quality for irrigation (Fig.9). Table (2) shows the irrigation parameters are suitable for irrigation uses as well.

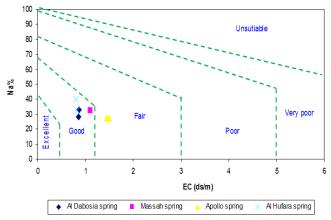


Fig. 9: Plot of EC vs. Na % showing the classification of irrigation water (fields after Johnson and Zhang, 1990).

Table 2: Irrigation parameters of the studied water springs

	Parameters							
Locations	Na%	SAR	MAR	KR	Pl			
Al Dabosia spring	30	10.5	32.4	0.5	51.6			
Massah spring	28	1.62	35.5	0.36	73.5			
Apollo spring	31	1.64	29	0.31	53			
Al Hufara spring	31	10.5	32	0.4	50.9			

Conclusions and recommendation

- 1- The hydrochemistry of water springs display Ca > Na > Mg > K and HCO₃+CO₃ > Cl > SO₄ trend.
- 2- The plots of studied samples on Gibbs diagram supports

influence of rock weathering.

- 3- The saturation index (SI) is over than zero indicating the super saturation with calcite, dolomite, gypsum and halite.
- 4- The water springs were classified as moderate to hard fresh waters and were not affected by seawater intrusion.
- 5- In general Al Dabosia and Al Hufara spring are suitable for drinking water but should be noted for the slight increase in lead (Pb) and alkalinity (Alk) values may be due to pesticides.
- 6- Apollo and Massah springs are not suitable for drinking waters due to contained high levels of contamination such as Pb, Cd, Hg, Fe and Ni, which indicating strongly affected by sewage water and local industrial wastes.
- 7- Importance parameters of water springs such as Na %, SAR, MAR, KR and PI revealed the studied water samples are fitting for irrigation proposes.
- 8- We recommend the government and other responsible authorities to take appropriate corrective measures. The common techniques that use to removal of heavy metals (contamination) from drinking water including reverse osmosis, Nano filtration, adsorption (e.g., iron-coated limestone) and usage of activated alumina.

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