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Evaluation of geo-hydrochemical and biological contamination of Massah spring water, Massah city, NE Libya

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ABSTRACT

This work attempts to characterize the chemical and biological characteristics of Massah spring water, NE Libya, with especial emphases on the environmental status of this water. The pH, major ions and TH values are below the permissible limit, while the values of TDS and heavy metals (except for Cu and Zn) are over the acceptable limit of WHO (2011). The MI values indicate that the water is very pure with Cu and Zn (class I) and seriously affected by Pb and Cd (class VI). Important parameters such as RSC, Na%, SAR, MAR, KR and PI, reveal good quality water for irrigation purposes. However, some signs of bacterial contamination of *Escherichia coli* (*E. coli*) have been detected when tested in different laboratories. The type of water that predominates in the study area is $CaHCO_3$-type.

1. Introduction

Massah spring water has been utilized for potable use since the Greek and Roman times and is still used for the water supply to Massah town. The spring is located along the Massah-Hanniah road on the second plateau near the water divide between the first plateau and the Wadi Al Kuf. It is 1.5km due south of the second main escarpment and 1km due northwest of Massah town (ACSAD, 1983). The spring is coordinated by 020º 37' 09" E and 32º 45' 22.5" N (Fig. 1). The spring outlet is at an elevation 458 m.a.m.s.l., and falls on the right side of Wadi Massah. The explored part of the gallery is found at 355m E-NE of the entrance and the elevation of the gallery bottom at this end is +7 m higher than at the entrance (Hydrogeo, 1982). Recently, new neighborhood properties have been built on the plateau above the Massah spring. These building, which dug their sewage waste into underground septic tanks, they raised preliminary warning that the waste from the tanks might reached the spring water and put the safety of this water into risk of contamination. World Health Organization (WHO) guidelines have been used in this study for comparison.

2. Objectives

The present work is done to achieve the following:

I. To verify the safety of the Massah spring water with respect to WHO guidelines.
II. To verify the chemical and biological contamination of this water.
III. To determine the irrigation water quality at Massah spring water.

3. Geological Setting

Al Jabal Al Akhdar region has an extraordinary position within the geotectonic scheme of northeastern Libya (Röhlich, 1974). A direct evidence of this tectonic movement is the folding, faulting, and deformation that started from Upper Cretaceous to Middle Miocene. The structural conditions are characterized by an intense network of fractures. These fractures subdivided the study area into blocks that gently tilted toward different directions, following the NNW-SEE, NE-SW trends. Röhlich (1974) divided these tectonics into lower, middle, and upper structural stages. The latter stage is further subdivided into five single sedimentation cycles responsible for the deposition of the Eocene (Apollonia and Darnah formations), Lower Oligocene (Al Bayda Formation), Middle to Upper Oligocene (Al Abraq Formation), Lower Miocene (Al Faidiyah Formation), Middle Miocene (Benghazi Formation), and Middle to Upper Miocene (Wadi Al Qattarah Formation).

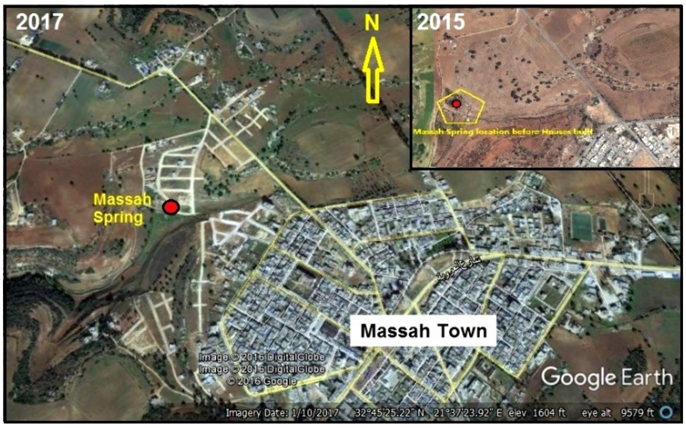

Fig. 1: Landsat image showing the location map of Massah spring before (2015 inset map) and after (2017) the construction of the houses. *Note*: the lithostratigraphic section is 20 m. east and is concise with the spring outlet (Black-red dot).

A part from interfingering relation between Darnah and Apollonia formations, the other formations are separated by disconformities. The areal distribution of Darnah, Al Bayda, and Al

Abraq formations is given in the Al Bayda Geological Map in scale 1: 250,000 (Fig. 2). However, they are exposed at the base of Wadi Massah and continue to the top of the plateau crossing the Massah spring. Al Bayda Formation is further subdivided into Shahhat Marl Member overlain by Algal Limestone Member (Fig. 3, Röhlich, 1974). Several researchers believe that the contact between the Shahhat Marl and Algal Limestone Members is gradational whereas others (Muftah, Pers. Comm. 2017) indicated that this contact is a disconformity surface. Figs. 3 and 4 show the sharp contact nature of the surface, indicating sudden change in lithology. Additionally, the age difference between the two rock units; Shahhat Marl Member (Late Eocene) (Muftah and Boukhary, 2016) and Algal Limestone Member (Early Oligocene), supporting the presence of disconformity surface. However, the existence of the disconformity is still under study (Muftah, *in press*). The Shahhat Marl Member is composed of limestone, yellowish to orangey, thinly-bedded, medium hard, pelecypod shells are frequently present, and overlain by fine-grained, greenish-yellow, thinly-bedded soft maryl limestone. The Algal Limestone Member is composed of thickly-bedded limestone, yellowish-white with echinoid at the lower part and nummulites, and algae in the upper part (Fig. 4). This study has confirmed that the Massah spring is a contact spring and its water is flowing through the surface between Shahhat Marl and Algal Limestone members. The ground water body in the Al Bayda and Darnah regions is mainly producing from the Darnah Formation (partly extending into the Apollonia Formation). There are many aquifers producing from this main water body and they are; Al Faidiyah, Al Abraq and Al Bayda Formations.

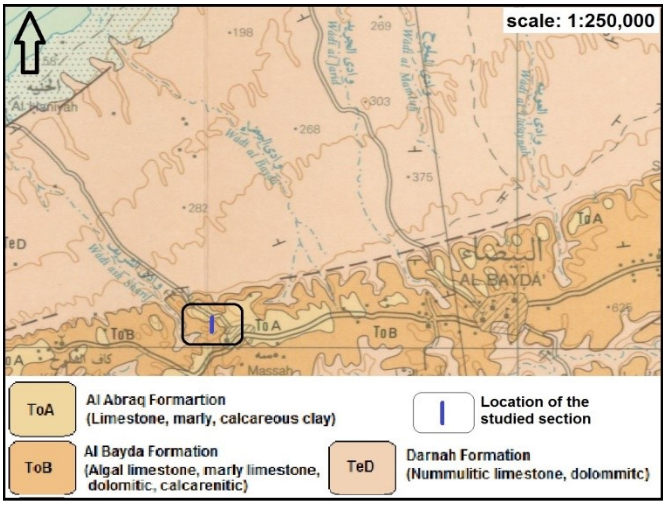

Fig. 2: Geological map of the Al Bayda–Massah area (modified from Röhlich, 1974).

Fig. 3: General view of the Wadi Massah outcrop showing sharp contact between Shahhat Marl and Algal Limestone Members of the Al Bayda Formation.

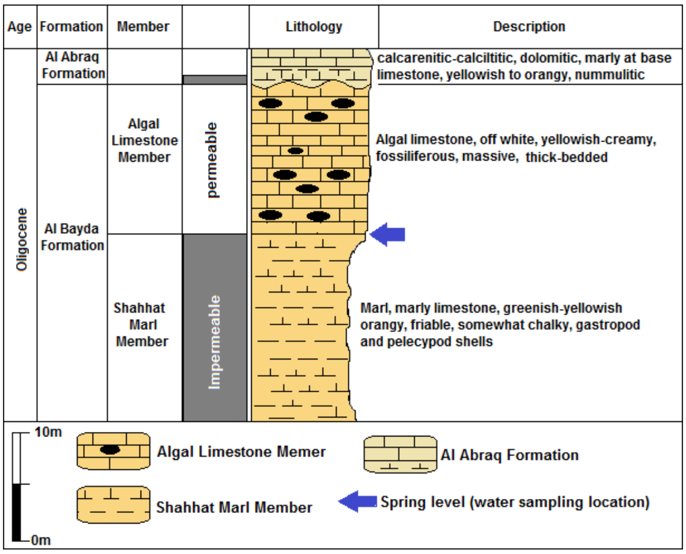

Fig. 4: Lithostratigraphic composite columnar section of the Massah spring site. The location of the outcrop is ~20 m east of the spring outlet.

4. Hydrogeology

The known aquifers in the area of study relative to the geologic formations from older to recent are Darnah, Al Bayda, Al Abraq and Al Faidiyah. However, the main aquifer is represented by Darnah Formation, which is composed of highly fractured nummulitic limestone. It is widely spread all over Al Jabal Al Akhdar and founded through drilled water wells at 250 to 450m deep with a static water level ranging between 190 to 220m (Hydrogeo, 1982). Fig. 5 illustrates the groundwater potential lines with flowlines directed to the north and north western. On the contrary, Al Bayda, Al Abraq, and Al Faidiyah aquifers are local and limited as a water source due to their limited thicknesses and areal extent as can be seen in the geology map on Fig. 2. Lithologically, the Algal Limestone Member is anisotropicly heterogeneous. This characteristic controls the distribution of the openings and pathways of water flow in the basin (G.E.F.Li, 1972). In addition, the karstic features within this formation improve the permeability and consequently the discharge of springs during and after rainy season, particularly in the central and northern areas of Al Jabal Al Akhdar (Hydroprojecat, 1968). Unfortunately, this karstic phenomenon is simultaneously acting as a transporting media of the contaminants to the same basin in the same time. In general, all producing springs outlets located to the north of the main Al Bayda highway are contact-type springs flowing through the disconformity surface between the two members as well, which are practically dipping about 2° WSW.

Since the beds of the Al Bayda Formation are dipping WSW indicates that the groundwater basin extends eastward, which is discharging into Massah spring (Fig. 5). Although, there are many other springs flowing from the algal limestone aquifer in the same area; however, they are not of high importance due to their low discharge despite their high-quality values. The layout and cross section of the gallery presented in Fig. 6. The second aquiclude is represented by a thin layer of calcarenitic, marly limestone of the Al Abraq Formation. In the vicinity of Massah town, there are no springs related to this formation.

According to GWA (1976-2016), in their files, there are several difficulties to monitor accurate water levels in order to construct proper hydrogeological maps. The prospecting groundwater contamination in addition to what is mentioned above, caused by constructing uncased wells that penetrated the Oligocene Shahhat marl aquiclude, accordingly, water of this aquifer percolates into the Darnah reservoir below. It is well documented that the improper water wells design and construction (uncased wells) are considered as one of the ways where physical, chemical, and biological contamination takes place. Given to this fact, all authorities related to the waste and water resource management should undertake serious measures to correct any environmental damages caused by the uncontrolled contaminations.

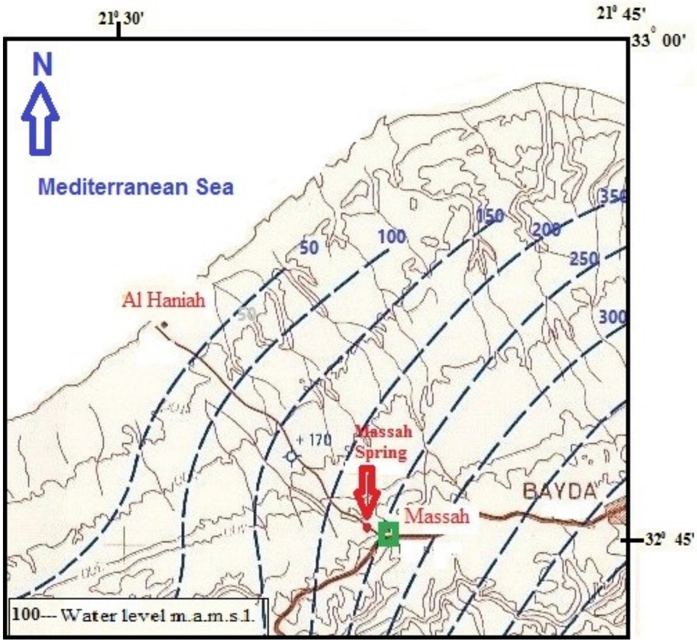

Fig. 5: Hydrogeological map, presenting the main aquifer in the region, including the study area (after Hydrogeo, 1982).

The explored part of the gallery (Fig. 6) is at 355 m ENE of the entrance and the elevation of the gallery bottom at this end is +7 m higher than at the entrance (Hydrogeo, 1982). According to (Marchetti, 1938) the spring outlet was previously flowing inside the ruins of an ancient Greek town; unfortunately, these ruins have been removed at the present time. As shown in Figs. 6 and 7, a covered concrete ditch with 0.5m in height runs all along the gallery outlet and carries the water to its outlet. The spring discharges into a small concrete reservoir of about $1m^3$ capacities. A 4" pipe outlet from where the water flows thoroughly into a big cistern with 100 m^3 capacity (Hydrogeo, 1992). This is equipped with a pumping station that pushes the water from the cistern into a distribution system for the public supply to Massah Town.

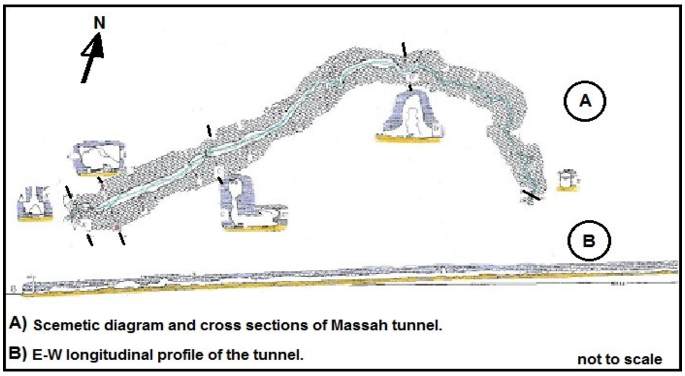

Fig. 6: scheme displays the explored part of the Massah spring gallery.

According to Hydrogeo (1982), the water discharged within the stream channel (Table 1) is in the order of 10 liters per second (l/s) or $35m^3$/hour. Measurements started on May 1981 continued to April 1984 indicate that stream flow with high discharge values ranging from 6.5 to 15 l/s between Januarys to Aprils every year. Peaks of discharge were observed during February to March 1982 during heavy rains. This is in agreement with the periodical observations of spring discharge values measured at Massah spring. The early moderate rainfall effect on the spring discharge as a good part of the infiltration is spent to restore the moisture of the superficial layer.

Fig. 7: View of the spring location (left) and an inside view (right).

Table 1: Monthly discharge measurements of Massah spring (l/s).

Month	Year			
	1981	1982	1983	1984
January	-	6.5	12.0	10.0
February	-	15.0	9.0	10.0
March	-	12.0	10.0	9.7
April	-	9.0	6.2	8.7
May	8.0	7.0	5.8	-
June	7.2	6.0	5.3	-
July	5.7	5.5	4.7	-
August	5.4	4.5	2.3	-
September	5.0	4.0	3.0	-
October	4.5	4.0	4.8	-
November	5.0	4.5	5.2	-
December	6.8	5.5	5.5	-

5. Methodology

The study was started with field geology in order to confirm the stratigraphic and sedimentologic setting of the water-bearing formations of the Massah spring. Two surface water samples were collected from the spring water during January 2017. The samples were taken from a depth of 15 cm below the surface. The major ions, heavy elements and Total Dissolved Solids (TDS) were determined by spectrophotometry technique. The analysis was done in the Al-Alamia Center for Chemical Physical Microbiology Analysis, Benghazi, Libya. The microbiological samples were cultured on the MacConkey agar media using a direct count method, technique

6. Results and Discussions

6.1 Chemical characteristics

From May 1981 to May 1984, Hydrogeo (1992) has collected and measured water samples for Electrical Conductivity and temperature in site while the chemical analyses had been performed at the General Water Authority laboratory in Benghazi. Regarding the chemical potability, this water would be acceptable except for the high Nitrate content (± 804 ppm), which not detected during the recent sampling in 2017.

The hydrochemical characteristics performed on the spring water samples collected in June 1981 to 1983, November 1982, and February 2017 show very similar values. The chemical analysis of the Massah spring samples collected in February 2017, includes a group of major ions such as Ca^{2+}, Na^{+}, K^{+}, Fe^{2+}, Mg^{2+}, Cl^{-}, HCO_3^{-}, and SO_4^{2-} and heavy metals such as Pb, Cd, Cu, and Zn are presented in Table 2. In this table, data from previous study in 1981 have been recorded for comparison as shown below.

Table 2: Comparison between the chemical analysis collected data of Massah spring water in 1981 and 2017 with the permissible limits of WHO (2011) in Drinking water.

Major ions and heavy metals	Year		WHO
	1981	2017	
pH	6.2	7.45	8
K	2	5	100
Ca	164	130	200
Na	81	84	200
Mg	12	43	150
Cl	150	218	250
HCO_3	405	390	600
SO_4	46	48	600
TDS	746	718	500
TH	459.2	500	500
Pb	N.A	0.13	0.01
Cd	N.A	0.02	0.002
Cu	N.A	0.09	2
Zn	N.A	0.09	3

6.2 Rock-water interaction

The Cl/Na ratio is more than average seawater ratio (1.17) in all water samples. According to Shaltami (2014), waters with a Cl/Na ratio larger than 1.17, may have not only marine and terrigenic but also anthropogenic origins. The molar Na/Na+Cl and $Ca/Ca+SO_4$ ratios are imperative to relate the genetic relationship (Hounslow, 1995).

According to El-Fiky (2010), the average HCO_3/Cl ratio is valuable to discriminate either seawater intrusion or rock weathering. The HCO_3/Cl ratio of the study area is much higher than the average seawater ratio (0.004). Probably the high ratio is due to the weathering of rocks. Based on the above information, the data of the studied samples signify a field of evaporation (Fig. 8). This is supported by m the mutual relationship of $Cl/Cl+HCO_3$ vs. log TDS in form of Gibbs (1970) diagram that signifies dominance of rock and evaporation in the water samples (Fig. 9).

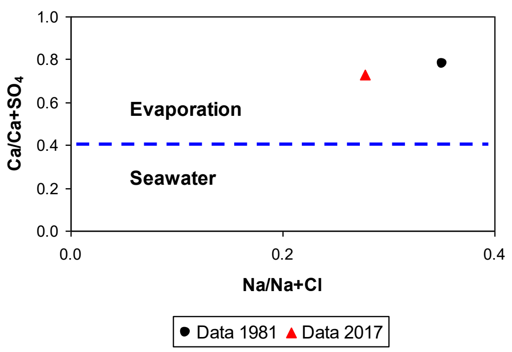

Fig. 8: Molar Na/Na+Cl and $Ca/Ca+SO_4$ to differentiate water of different origin (fields after Hounslow, 1995).

The variations in the composition of water can be used to distinguish limestone, dolomite, and silicate rock sources of ions (Han and Liu, 2004). Accordingly, the studied samples fell in between the terra rossa soil and limestone fields (Fig. 10).

6.3 Composition

Major ions and their ratios are significant to infer impact of rock chemistry on the composition of water. The samples of 1981 and 2017 show approximately the same signature in mg/l in terms of cations (Ca>Na>Mg>K) and anions ($HCO_3>Cl>SO_4>CO_3$) (Fig. 11). The shape analysis of stiff diagram signifies dominance of $Ca\text{-}HCO_3+CO_3$.

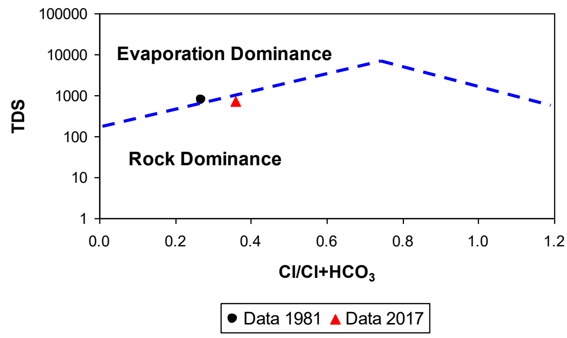

Fig. 9: Dominance of rock and evaporation on $Cl/Cl+HCO_3$ vs. log TDS of the study area (fields after Gibbs, 1970).

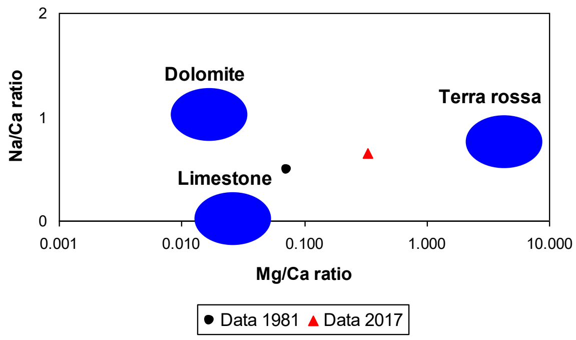

Fig. 10: Plots of Mg/Ca vs. Na/Ca ratios of the studied water samples (modified from Han and Liu, 2004).

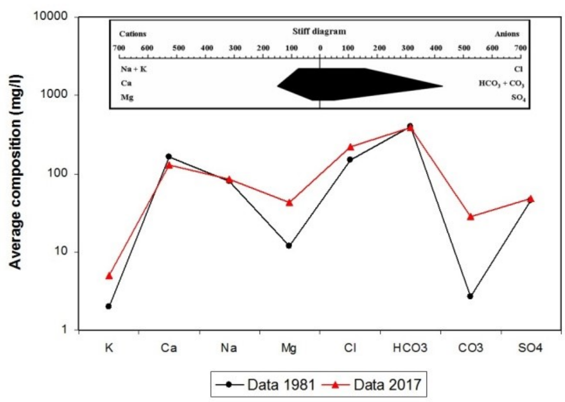

Fig. 11: Schoeller diagram showing average composition in mg/l of the studied water samples (Schoeller, 1977). Stiff diagram is shown in the inset.

6.4 Drinking Water Quality

In the present study, the values of pH, major ions and TH are within the permissible limit (Table 2), while the values of TDS and heavy metals (except for Cu and Zn) are over the acceptable limit of WHO (2011). The TH is calculated as: TH (mg/l $CaCO_3$) = 2.5 Ca (mg/l) + 4.1 Mg (mg/l). According to Caerio et al. (2005), the metal index (MI) is calculated as: 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 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 MI values suggest that the studied samples are very pure with Cu and Zn (class I) and seriously affected by Pb and Cd (class VI).

6.5 Irrigation Water Quality

6.5.1 Residue Sodium Carbonate (RSC)

In the present study, the RSC is calculated as:

$$RSC = [HCO_3 + CO_3)]-[Ca+Mg]$$

(All concentrations are expressed in meq/l)

According to Nishanthiny, et al. (2010), when the RSC value <1.25 meq/l, the water is considered good quality, while if the RSC value > 2.5 meq/l, the water is considered harmful. The RSC in the samples of 2017 is -2.76, indicating good quality water for irrigation purpose.

6.5.2 Sodium Percent (Na %) and Electrical Conductivity (EC)

According to Prasad et al. (2009), the Na% is calculated as:

$$Na\% = (Na^{+} * 100) / (Ca^{2+} + Mg^{2+} + Na^{+} + K^{+})$$

(all concentrations are expressed in meq/l)

The Na% equals 26.34% in the samples of 2017. According to Hakim et al., (2009), irrigation water with Na% >60% may result in Na accumulation and possibly a deterioration of soil structure, infiltration, and aeration. Fig. 12 shows that the water of Massah spring is classified as good for irrigation.

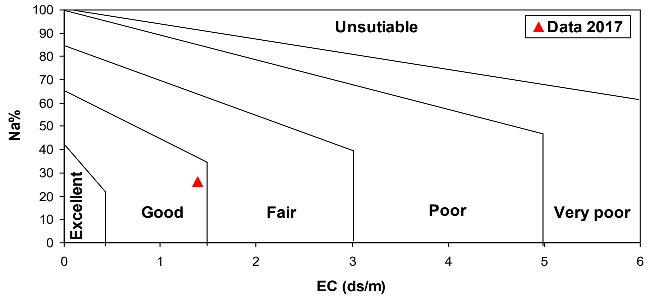

Fig. 12: Classification of irrigation water on EC vs. Na% and its suitability for agriculture (fields after Johnson and Zhang, 1990).

6.5.3 Sodium Adsorption Ratio (SAR)

SAR can be determined from the following expression:

$$SAR = Na / \sqrt{(Ca+Mg)/2}$$

(all concentrations are expressed in meq/l)

SAR values <10 is classified as excellent for irrigation. Values in between 10-18 are good, 18-26 are moderate, and >26 are hazardous. In the samples of 2017, the SAR equals 1.62, indicating that the water of Massah spring is classified as excellent for irrigation.

6.5.4 Magnesium Adsorption Ratio (MAR)

According to Raghunath (1987), the MAR is calculated as:

$$MAR = [Mg^{2+} / (Mg^{2+} + Ca^{2+})]100$$

(all concentrations are expressed in meq/l)

MAR values >50 is considered harmful and unsuitable for irrigation use and may causes infiltration problem (Ayers and Westcot, 1985). The samples of 2017 display MAR values <50 (35.54) which also indicates that the studied water is suitable for irrigation.

6.5.5 Kelley's Ratio (KR)

According to Paliwal (1967), the KR is based on the level of Na measured against Ca and Mg. Water with KR<1 is suitable for irrigation. In the samples of 2017 the KR equals 0.36, indicating their suitability for irrigational uses.

6.5.6 Permeability Index (PI)

According to Doneen (1962), the PI can be determined from the following expression:

$$PI = [(Na^{+} + HCO_3^{-}) / (Ca^{2+} + Mg^{2+} + Na^{+})] 100$$

(all concentrations are expressed in meq/l)

Irrigation water with high permeability (>75%) is classified as class I; class II has permeability between 50-75%; while class III has permeability <25% and unsuitable for irrigation purpose (Nagaraju et al., 2006). The water of Ain Massah spring belongs to class II (PI equals 73.14).

6.5.7 Corrosivity Ratio (CR)

According to Tripathi et. al., (2012) the CR is expressed as:

$$CR = [135.5\ Cl + 2(SO_4/96)] / 2[(HCO_3 + CO_3)/100]$$

(all concentrations are expressed in meq/l)

In the samples of 2017 the CR equals 1.15. According to Raman (1985), the water with CR<1 is considered to be safe for transport of water in any type of pipes, whereas >1 indicate corrosive nature and hence not to be transported through metal pipes.

6.6 Classification of water

Fetter (1994), classifies the water based on TDS as shown in Table 3. Therefore, Massah spring water, which has a TDS value of 746 ppm (1981) and 718 ppm (2017), it is classed as a fresh water type.

Table 3: Classification of water based on Total Dissolved Solids (TDS) (after Fetter, 1994).

Class	TDS (mg/l)
Fresh	0 - 1,000
Brackish	1,000 - 10,000
Saline	10,000 - 100,000
Brine	>100,000

As water flows through an aquifer, it assumes a diagnostic chemical composition as a result of interaction with the lithologic framework. The term hydrochemical facies is used to describe the bodies of groundwater in an aquifer that differ in their chemical composition. The facies are a function of the lithology, solution kinetics and flow patterns of the aquifer (Back, 1960, 1966; in: Fitter, 1994). The major source of carbonate and bicarbonate in natural waters is dissolved limestone (calcium carbonate and other carbonate minerals, such as dolomite.

Fig. 13 shows that the water of Massah spring has influence of Ca-type water on Piper diagram (Piper, 1944). Among the major anions, the water samples are plotted towards CO_3+HCO_3-type. Majority of the samples are plotted in the $CaHCO_3$-type (Type II) of water.

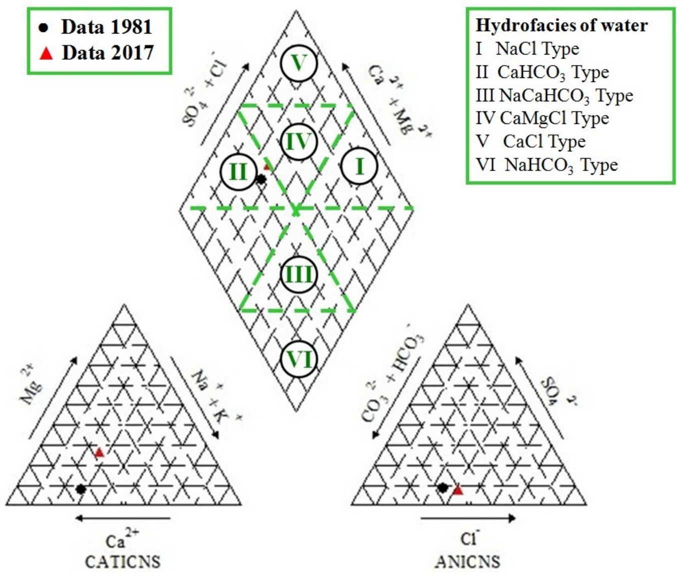

Fig. 13: Piper diagram of water chemistry in the study area (fields after Tweed et al., 2005).

6.7 Isotopic Characteristics

The General Water Authority through their consultants Hydrogeo (1992) has conducted several special missions on isotopes studies using stable isotopes ($\delta^{18}O$ and δD) and Tritium content. Samples of Massah spring water were collected and processed in three different seasons within the periods; (1981 to 1983). The amounts of $\delta^{18}O$ and δD are virtually constant in the Oligocene springs. This is confirmed for Massah spring in the three samples, (Table 4).

Table 4: Isotopes analysis during different seasons in 1981 to 1983 for Massah Spring water (Hydrogeo, 1992).

Period		Season	Isotopes		
Month	Year		$\delta^{18}O$	δD	Tritium
July-August	1981	Dry season	5.0–4.99	21.5–22.10	19.4 T.U.
October-November	1982	End of dry season			15.3 T.U.
February-March	1983	Beginning of rainy season			13.6 T.U.

7. Microbiology

The microbial hazard of Massah spring water was assessed using the MacConkey Agar medium (an agrarian medium designed to grow gram-negative bacteria and dye them through fermentation) (Forbes, 2007). It also used the EMB medium (an optional dye for gram-On a toxic dye of Gram positive bacteria and toxic yellow salts of Gram-negative bacteria other than *Escherichia coli* (*E. coli*)). To identify the risk of *E. coli* bacteria to human health, the spring water was probably contaminated with the nearby sewage caused by the expansion of the recent constructed buildings. Recalling the satellite image of Fig. 1 shows the area around the spring basin before and after the construction. In addition to this, the greatest danger is the lack of awareness of local people and authorities who are using this water for drinking, irrigation, and watering animals.

Drinking water containing *E. coli* bacteria beyond the WHO limit, may cause inflammation of the colon accompanied by hemorrhage with acute abdominal contractions, bloody diarrhea, meningitis, vomiting, nausea, and may have developed into kidney injury causing renal failure, especially the toxin type. Symptoms of the infection are severe in the case of the elderly and children due to incomplete or weak immune system as well as persons with HIV/AIDS and may lead to death (Suleiman and Al Tahir, 2008).

The sample was transplanted onto the MacConkey Agar and Iosin two-color Blu-ray to detect any growth of *E. coli* bacteria on them and confirm the contamination of this water. Concerning the counting of the bacterial colonies in the samples, two replicates have been made using counting device. The results are shown in Table 5.

Table 5: The count of bacterial colonies per/ml.

Sample Source	Number of Bacterial Colonies.	Colony per/ml.
Massah spring	35×10^4	40×10^2

Researchers at the University of Humboldt, Germany in 2008, have come to know how colorectal cancer sometimes causes hemorrhage. It was found in 2011 that this bleeding caused the death of 53 people who were unable to get help. Researchers in Berlin found that *E. coli* produce a di-GMPP to cause an adhesive network on the intestinal wall, leading to inflammation.

The tested Massah spring water has shown a type of algae called Spirogyra or Spirigyra (Spirigyra). This is a species of green algae that follows the large-scale Zyggenium species, which grow on the surface of seeping or stagnant fresh water in ponds or marshes. *Navicula moss* is a large group of single-celled siliceous diatomite algae. These diatomites possess a silicon oxide (SiO_2) envelope with a hydrous silicic acid (H_4O_4Si), which called the frustule. Diatomites are an important tool for monitoring past and present environmental conditions and are generally used to verify water quality. Many algae and fungi are of great economic values, while others are harmful.

8. Conclusions

The historic Massah spring is the most important water source in the town of Massah. Recently it was subjected to many questions concerning its safety of use for humans and irrigation purposes. Therefore, several field trips been conducted and water samples were collected in 2017 for chemical and biological evaluation, comparing with samples collected in the 1980s. Massah spring considered a contact spring producing from the surface between the Shahhat Marl Member and the overlain Algal Limestone Member of Al Bayda Formation. The values of pH, major ions and TH are below the permissible limit, while the values of TDS and heavy metals (except for Cu and Zn) are over the acceptable limit of WHO (2011). The MI values show that the water is seriously affected by Pb and Cd. The irrigation parameters like RSC, Na%, SAR, MAR, KR and PI indicate that the studied water is suitability for irrigational uses. The $CaHCO_3$-type (Type II) is the dominant hydrochemical facies in the studied water. The sources of contamination, which detected by the presence of *E. coli*, are either directly or indirect from the recent sewage or from the surface water runoff through the karstic features in the spring basin or both. For the time being, no signs of harmful algal and fungi were detected from the tested samples.

9. Recommendations

Heavy metal contamination in drinking water has become an ecotoxicological hazard of prime interest. Conventional treatment technologies such as coagulation, ion exchange, adsorption and usage of activated alumina should be regularly operated for the removal of heavy metals from drinking water. Alert action and attention to related authorities should be given to better control and protect the spring from any contact with the surrounding sewers or non-sealed septic tanks. Therefore, regular spring water testing throughout the year should be established in order to confirm confidence in its safety.

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