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Hydrochemical and Isotopic Investigation (¹⁸O, ²H, ³H, ¹⁴C) of the Surface and Groundwater Composition in Ain Bou Mourra Basin (Central Tunisia)

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Abstract: The present study concerns the aquifer system of Ain Bou Mourra basin (Central Tunisia) where a great dam and several harvesting features have been built in order to regulate stream flow and runoff during the rainy season. This basin is submitted to a semi-arid climate with rainfall ranging between 300 to 400 mm/y and marked by high spatial and temporal variability. The multi-tracing approach based on hydrochemistry of major elements, water molecule isotopes and carbon 14 has been applied in Ain Bou Mourra basin to provide basic information on the processes that control groundwater mineralization and to delineate spatial influences of natural and artificial recharge. A total of 54 surface and groundwater samples were collected from wells, boreholes, springs, river, large dam, small hill dams and hill lakes of the study area. Chemical data showed that surface and groundwaters presented a large spatial variability of chemical facies. These results revealed that the main source of salinity in the sampled waters was related to the water-rock interaction such as the dissolution of evaporitic and carbonate minerals, evaporation and ionic exchange reaction. Isotopic study was carried out using stable (18O, 2H) and radiogenic (3H, 14C) isotopes to infer the recharge sources in the studied basin. It indicated that most of the groundwater samples were originated from infiltrating modern precipitation. However, surface water samples collected from the dams and lakes storage reservoirs showed ¹⁸O and ²H enrichment, which is typical for water that has been subject to open surface evaporation in a semi arid region. The radiogenic (3H, 14C) isotopes data provided insight into the presence of significant contemporaneous recharge waters in the basin. They indicated that groundwaters were recharged from the surface runoff coming from precipitation on the local Oligocene outcrops.

Key words: Ain Bou Mourra basin • Geochemistry • Isotopes • Recharge • Evaporation process • Hill reservoirs

INTRODUCTION

The scarcity of water resources in Central Tunisia due to the low and irregular rainfall imposes strategic difficulties for economic development. Since the early 1965s, the Tunisian government has undertaken the execution of the "National Strategy of Surface Runoff Mobilization". This strategy aims at building several large dams, small hill dams and other structures for irrigation and aquifer recharge.

The Ain Bou Mourra basin is located in Central Tunisia and covered a surface of 162.3 km². This semi arid basin is drained in its northern part by Nebhana River which is considered one of the important valleys in Central Tunisia. Adjacent to this zone are the Atlasian Heights and Mountains, which at 550 m a.s.l. are the highest uplands in the region. With this combination of dramatic relief and active tectonic environment, it is not surprising that this zone hosts tremendously prolific artesian aquifers.

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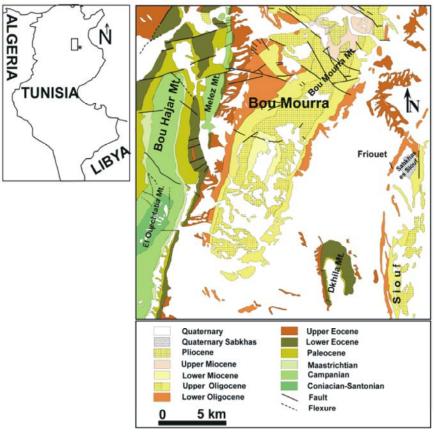


Fig. 1: Geological map of the Ain Bou Mourra basin.

In Ain Bou Mourra basin, like many other semi arid regions, water resources are limited. A large dam "Nebhana" has been built since 1966 in order to regulate stream flow and runoff during the rainy season. Additionally, several harvesting features i.e. 3 small hill dams and 7 hill lakes have been built between 1992 and 2006 for groundwater recharge and irrigation (Fig. 1).

In the studied basin, mean annual precipitation averages is less than 400mm and perennial surface water resources area are restricted to the Nebhana River.

The groundwaters of the Ain Bou Mourra basin are vital to the fresh water resources of the region. They contribute over 90% of the flow in many regional canals, which supplies the region with irrigation and potable water. Consequently, the recharge origin of these groundwaters and aquifer configurations has been the focus of several studies in the past. Besbes [1] and Beji [2] examined the geological and hydrodynamic setting of the principal aquifers through borehole information and considered the recharge area to be essentially within the Atlasian Highlands of the region.

Appropriate environmental tracers are useful for the identification of recharge sources in a groundwater system on both local and regional scales [3]. They provide valuable insights into recharge processes and are necessary for developing sustainable water resource management plans within the context of climate variability [4].

The goal of this study is (1) to characterize water chemistry at a given time, (2) to infer the recharge sources and, (3) to determine the residence time of groundwater.

Geology and Hydrogeology

Stratigraphy: The geological setting of the Ain Bou Mourra basin, described by Kassionoff [5] and Turki *et al.* [6] is dominated by a SSW-NNE synclinal structure between Bou Hajar Mountain in the west and Dkhila Mountain in the east, which is truncated to the north by the down-faulted eastern margin (Fig. 1). Geological formations, recognized in the syncline, have been developed during the Tertiary, which were intensely folded by Atlasian tectonic movements resulting in rock layers dipping steeply SW to nearly vertical.

The Cretaceous deposits represent the oldest outcrops in the syncline and consist of marine limestone which appeared in Ouechtatia, Melez and Bou Hajar Mountains. The Paleocene formation is represented mainly by clayey sand with some intercalations of sandy limestone, gypsum and Glauconeous clays [7,8]. It outcrops on more than 390 m at the foot of the western highlands. The Lower Eocene limestone and the Upper Eocene marl deposits are found in the boundaries of the basin. The Oligocene deposits outcrops largely and covers more than 70 km² of the syncline [1]. This formation is overlayed partially by recent Quaternary sediments. The Mio-Pliocene formation outcrops and includes detrital sediments of sandy and sandy clays [7].

Tectonic Setting: Generally, the geological and structural contexts of the study area draw their origin from early tectonic events which characterized central Tunisia during the geological history [7,9]. The present architecture of the study area is defined by a general SW-NE Atlas geological structure. Flexure folding and faulting associated with uplift along the margins of the highlands bounding the Ain Bou Mourra syncline have produced additional discontinuities in the stratigraphy which affect the hydrogeological environment.

Hydrogeology: The hydrogeological study reveals that the aquifer system consists of three principal hydrostratigraphic series. The first is formed by Lower Oligocene deposits thick of 300 m and comprising inter-bedded fine sandstone, sands and clay. This unit outcrops locally in the borders of the syncline, but it is not a consistently viable aquifer due to salinity and depth constraints. This formation underlies the detrital deposits of Upper Oligocene-Lower Miocene age which represent the second productive and the most regionally extensive aquifer with a thickness of 300 m. These deposits outcrop largely and constitute an unconfined aquifer layer in the central part of the basin.

The Upper Oligocene formation can be divided into two groups: the first is attributed to the "Lower Houaria" of Aquitanian age. It is formed by deposits of sandstones that are interstratified with clayey sandstones and clays and the second is only formed by highly permeable sandstones, sands and gravel sediments. It is attributed to Burdigalian age. The Upper Eocene marl deposits represent the substratum in the syncline.

The boreholes of Ain Bou Mourra basin, drilled to 250~m depth to explore the groundwater potential, yielded a flow with a total discharge varying from 3.7~to~34~l/s~[10].

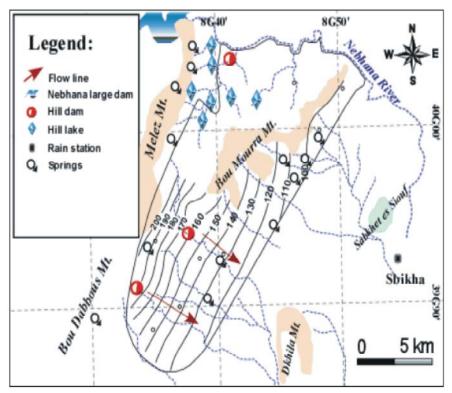


Fig. 2: Piezometric map.

Between 1966 and 2009, many fields of forty boreholes were drilled near Oligocene outcrops. The groundwaters discharge from the three hydrostratigraphic units.

The regional potentiometric surface reveals high levels in the north western highlands, a general decline towards the southeast (Fig. 2). The general flow is from North West to South East. In the boundaries of the basin, the groundwater overflows as springs and emerge along the faults several km to the east of the basin. They signify discharge of deeply circulating groundwaters. The spring's waters are used for domestic and agricultural purposes. For this reason, the discharge of the springs has varied largely between the periods of 1960-2009.

A continuous decrease in static water levels recorded in piezometers between 1960 and 2009. The drawdown produced in the water levels of Oligocene aquifer by the intensive abstraction over the past 51yr has caused a significant decline in groundwater flow.

Sampling and Analytical Procedure: Sampling of groundwaters and surface waters within the study area was carried out during September 2008, April 2009 and June 2009 to observe temporal as well spatial variations in geochemical and isotopic parameters. Monthly water samples from precipitation from the Sbikha rainfall station (Fig. 1) were also collected.

A total of 54 samples were collected from the Ain Bou Mourra basin. Samples are distributed as follows (Fig. 3):

- 13 samples were taken from the shallow wells;
- 13 samples were taken from the boreholes;
- 4 samples were taken from artisan springs;
- 2 sample was taken from the Nebhana river;
- 2 sample was taken from the Nebhana large dam;
- 6 samples were collected from the hill dams and
- 14 samples were taken intermittently from the hill lakes;

The measurements of pH, temperature and electrical conductivity (EC) were performed in the field. Water samples were collected in 1000 ml polyethylene bottles with poly-seal caps for major elements. Chemical analyses and isotopic measurements were determined in the Radio-Analysis and Environment Laboratory of the National Engineering School of Sfax (Tunisia).

Major elements (Cl $^{-}$, SO $_4^{2-}$, NO $_3^{-}$, HCO $_3^{-}$, Na $^{+}$, Mg $^{2+}$, K $^{+}$ and Ca $^{2+}$) were analyzed by ion liquid chromatography.

Stable isotope ratio (¹⁸O/¹⁶O and ²H/¹H) analyses were performed by using the Laser Absorption Spectrometry measurements LGR DLT 100 [11]. Analyses are reported in ‰ versus VSMOW standard (Vienna-Standard Mean Oceanic Water).

10 groundwater samples were selected to be analyzed for Carbon-14 dating activities. Precipitation of $BaCO_3$ from groundwater samples was done in the field. ^{14}C activities were determined by scintillation counting on C_6H_6 [12].

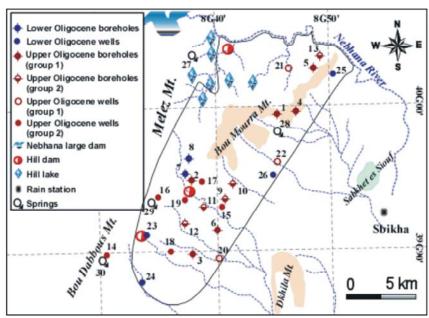


Fig. 3: Sampling map.

28 samples were selected to be analyzed for Tritium content using electrolytic enrichment and liquid scintillation spectrometry [13] 3H concentration is expressed in Tritium Units (TU). One TU is defined as the isotope ratio $^3H^{\text{/}}H=10^{18}$.

Results of 14 C abundances are reported as percent of modern Carbon (pmC). Precision of measurement for stable isotope and radioactive analysis was \pm 0.1% for the δ^{18} O, \pm 1% for the δ^{2} H and \pm 0.3% for 3 H.

RESULTS AND DISCUSSION

Geochemical Data: The EC values of the shallow groundwater samples vary between 0.7 and 5.3 mS/cm. The highest value is recorded in well No. 25 (Fig. 3) located near the evaporitic marls, whilst, the lower values are revealed in the Upper Oligocene aquifer (group 2).

The EC values of the hill dams range from 0.4 mS/cm to 5 mS/cm. However, the EC values of the hill lakes show higher values and vary between 1.8 and 10 mS/cm.

Chemical compositions of the analyzed samples are plotted on the Piper trilinear equivalence diagrams shown in Fig. 4. The surface and groundwater exhibit a large spatial variability of hydrochemical facies.

Upper Oligocene groundwaters reveal an evolution between Ca-HCO₃ and Cl-SO₄-Ca-Mg type, whilst the lower Oligocene groundwaters fall predominantly in the category of Cl-SO₄-Ca-Mg type to mixed ionic type.

Surface waters of hill dams show an evolution between Ca-HCO₃ and Ca-SO₄ types, while the geochemical facies of hill lakes is dominated by Ca and SO₄. This water is sulfate enriched as a result of the dissolution of evaporitic material present in the gypsiferous marl deposits of Upper Eocene outcrops rich in SO₄ (Fig. 4).

To identify the origin and the processes of groundwater contributing to groundwater mineralization, plots of Na versus Cl, Ca versus SO₄ and Ca versus HCO₃ are established. The Na-Cl relationship (Fig. 5a) shows a parallel enrichment in both ions and demonstrates that the majority of points cluster along the halite dissolution line. Conversely, if Na was only derived from dissolution of evaporitic minerals, then Na should balance Cl. Accordingly, the depletion in Cl⁻ contents relative to Na⁺ concentrations, observed in some samples of Upper Oligocene aquifer (group 1) and those of hill reservoirs is probably due to cation exchange reactions leading to Na⁺ adsorption on clay minerals and simultaneous releasing of Ca²⁺ ions.

On the other hand, the Ca²⁺ versus SO₄²⁻ plot (Fig. 5b) reveals 3 clusters. The first illustrates the points representing Nebhana dam water and the Upper Oligocene (group 1) groundwaters which are plotted on/ just above the gypsum dissolution line. This result could be explained by a compound effect of gypsum/anhydrite dissolution and evaporation processes. The second cluster is formed by Lower Oligocene groundwaters and surface lake waters and shows sulfate-rich waters. The third cluster is formed by Upper Oligocene groundwaters (group 2) and exhibits a more pronounced loss of SO₄²⁻ relative to Ca²⁺. This excess of Ca²⁺ is believed to originate from the probable dissolution of carbonate minerals. As confirmed by Fig. 5c, the points representing the Upper Oligocene groundwaters fall either on, or just above 1:1 line (calcite dissolution line). All other surface water samples and Lower Oligocene groundwaters are plotted above the line, indicating another source of Ca which may possibly be present from weathering and erosion of gypsum and/or clay minerals. Therefore, the chemistry of the surface and groundwater samples appears to be dominantly controlled by the dissolution of minerals in the catchment's host lithologies.

Isotope data

Stable isotopes $\delta^{18}O$ and $\delta^{2}H$: Oxygen-18 and deuterium values of the dam storage reservoirs range respectively from -5.95 to 2.65 % and from -35.15 to 2.17 %. Data from the hill lakes varies between -5.71 and 4.17 % for Oxygen-18 and between -33.59 and 11.77 % for deuterium.

Oxygen-18 and deuterium values of the Lower Oligocene samples range, respectively, from -5.98 to -2.08 ‰ and from -36.07 to -16.96 ‰. Those of Upper Oligocene samples range from -5.68 to -4.10 ‰ and from -35.93 to -24.04 ‰. The isotope content of the springs varies between -5.21 and -5.92 for oxygen-18 and between -30.22 and -32.51 ‰ for deuterium.

Values of $\delta^{18}O$ and $\delta^{2}H$ from surface and groundwater samples are plotted in Fig. 6. The majority of groundwater samples fall on the Global Meteoric Water Line (GMWL) ($^{62}H = 8 \ \delta^{18}O + 10$ as reported by Craig, 1961) and the Local Meteoric Water Line (LMWL) ($^{62}H = 8 \ \delta^{18}O + 11$ as reported by Celle, [14] Celle Jeanton *et al.* [15] Gay, [16] for the Western Mediterranean, indicating that the groundwaters have been recharged under climatic conditions which are similar to those which prevail today in the regio2n [17]. This recharge is considered to have taken place in the outcrop areas of the Oligocene sandstone aquifers in the side wadis area.

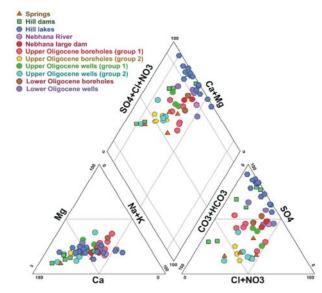


Fig. 4: Piper diagram of the analyzed water samples.

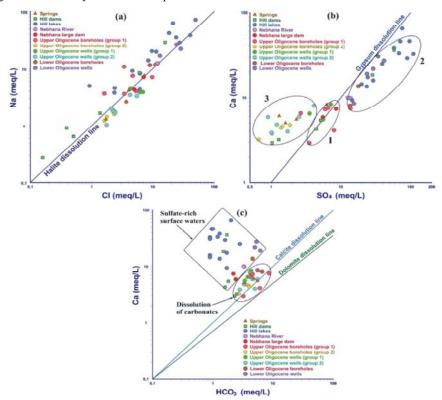


Fig. 5: Relationships between major elements in the analyzed sampled water: Na/Cl (a), Ca/SO₄ (b) and Ca/HCO₃ ©

The mean isotopic composition of the sampled groundwaters from the aquifer system is similar to local precipitation recorded in the Sbikha station (Fig. 1) which is -5.27 ‰ vs. SMOW. This similarity in isotopic composition between most groundwater and local precipitation supports the mechanism of rapid infiltration

of runoff water before significant evaporation at the soil surface can take place. However, some data from the Lower and the Upper Oligocene groundwaters lie widely below the GMWL and reveal enriched isotopic compositions due to the evaporation process. In fact, slower infiltration or seepage of the surface water through

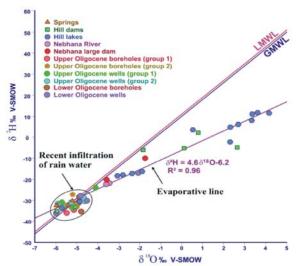


Fig. 6: Relationship $\delta^{18}O/\delta^{2}H$ of surface and groundwater samples in the Ain Bou Mourra basin

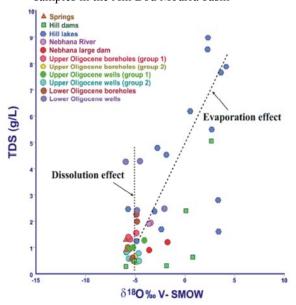


Fig. 7: Relationship δ^{18} O/TDS of surface and groundwater samples in the Ain Bou Mourra basin

the clayey sandstone of the unsaturated zone would have exposed much of the water to evaporation, resulting in an enriched composition of the groundwater.

Surface water samples are noticeably enriched in H and O isotopic composition. The evaporative enrichment line (δ^2 H = 4.6 δ^{18} O - 6.2, R² = 0.98) for the reservoir waters has a slope of nearly 4.4, indicative of evaporation from an open water body under conditions of low relative humidity in semi arid region [18]. These data reveal also distinct seasonal variability. Likewise, these enriched values are relatively correlative with the TDS values and,

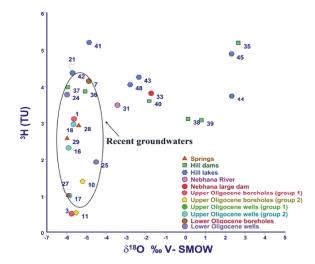


Fig. 8: Relationship δ^{18} O/3H of surface and groundwater samples in the Ain Bou Mourra basin

indeed, provide evidence that water loss by evaporation is an important process in the open surface reservoirs (Fig. 7). This supports strongly that the evaporation process may be a major control on the chemical and isotopic compositions of the reservoir waters. However, no relation between these two parameters in groundwater samples can be observed. This supports the hypothesis that the salinity of these groundwaters is mainly governed by a dissolution process previously highlighted by hydrochemical analyses.

Tritium Isotope:

- ³H isotope is an important tracer for water flow and it can give indication of the relative age of waters varying on time scale of 50 years before present.
- The ³H content of the surface waters vary from 3.07 to 5.19 TU (Fig. 8). These concentrations are quite similar to ³H content of local rainfall which was measured (4.53 TU) in Sbikha rain station (Fig. 1).
- The diagram δ¹⁸O/³H (Fig. 8) illustrates that the majority of sampled groundwaters exhibit values higher than 1 TU and suggest clearly the occurrence of recent recharge in the Ain Bou Mourra basin probably during the last two decades.
- The measured ³H concentrations of the Oligocene samples are quite variable. The ³H activities range from 0.54 (borehole No. 3) to 4.14 TU (borehole No. 7). The ³H data from spring's water shows that ³H concentrations range from 1.02 to 2.92 TU.

This indicates that these waters are recharged by the direct infiltration of meteoric water through the local Oligocene outcrops of the study area.

 Additionally, the combination of ³H and δ¹⁸O values (Fig. 8) suggests that the isotopic signature of surface water samples collected from the dams and lakes storage reservoirs differs clearly from that of Oligocene groundwaters.

Carbon -14 Contents: To provide additional information on the age and to support evidence of the recharge process inferred from the stable isotopes and tritium data, carbon isotopes of DIC (Dissolved Inorganic Carbon) in groundwater have been used in Ain Bou Mourra basin.

Radiocarbon activity of Oligocene aquifer varies between 23.5 pmC in borehole No. 5 tapping the Upper Oligocene (group 1) aquifer and 83.3 pmC in borehole No. 10 drilled in the second group of this formation. This difference could be explained by the the existence of the clayey levels which contribute to delay the infiltration of meteoric water in the unsaturated zone and to increase the groundwater residence time.

In general, the spatial distribution of the radiocarbon reveals that all measured Oligocene groundwaters have high ¹⁴C activities (more than 50% of modern C) exception for sample (No. 5). These values confirm that Oligocene aquifer receives a modern recharge which is assumed by rainfall infiltration on the local Oligocene outcrops of the region. These data give evidence at least of a present day direct infiltration towards the water table in the basin.

CONCLUSION

Major element concentrations, stable (δ^{18} O, δ^{2} H) and radiogenic (3 H, 14 C) isotopes are used to provide basic information about the processes that control the groundwater chemistry and to understand the recharge mechanisms in the Ain Bou Mourra basin (central Tunisia).

The principal changes in chemical composition of surface and groundwater are caused by chemical reactions such us dissolution of evaporitic and carbonate minerals and ionic exchange.

Isotopic data indicate that all groundwaters are characterized by a modern stable isotope signature. This suggests that the sampled groundwaters receive a recent recharge which is facilitated by the high permeability characterizing Oligocene sandstones. However, surface water samples reveal ¹⁸O and ²H

enrichment, which is typical for water that has been subject to open surface evaporation in semi arid region and provide evidence that water loss by evaporation is an important process in hill reservoirs.

The radiogenic (³H, ¹⁴C) isotopes data confirm the occurrence of recent recharge which is assumed by rainfall infiltration on the local Oligocene outcrops of the study area.

The resources in the Oligocene aquifer represent a significant reserve of good quality water which needs to be properly managed as high quality resources and as part of integrated plans for the basin's future supplies.

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