Journal of African Earth Sciences 78 (2013) 16–27

Contents lists available at SciVerse ScienceDirect

Journal of African Earth Sciences

journal homepage: www.elsevier.com/locate/jafrearsci

# Hydrogeochemical investigation of surface and groundwater composition in an irrigated land in Central Tunisia

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ARTICLE INFO

*Article history:*
Received 18 April 2012
Received in revised form 26 September 2012
Accepted 2 October 2012
Available online 13 October 2012

*Keywords:*
Cherichira basin
Geochemistry
Isotopes
Recharge
Evaporation process hill reservoirs

ABSTRACT

Major element concentrations, stable ($\delta^{18}O$ and $\delta^{2}H$) and radiogenic ($^{3}H$, $^{14}C$) isotopes determined in groundwater provided useful initial tracers for understanding the processes that control groundwater mineralization and identifying recharge sources in semi-arid Cherichira basin (central Tunisia).

Chemical data based on the chemistry of several major ions has revealed that the main sources of salinity in the groundwaters are related to the water–rock interaction such as the dissolution of evaporitic and carbonate minerals and some reactions with silicate and feldspar minerals.

The stable isotope compositions provide evidence that groundwaters are derived from recent recharge. The $\delta^{18}O$ and $\delta^{2}H$ relationships implied rapid infiltration during recharge to both the Oligocene and Quaternary aquifers, with only limited evaporation occurring in the Quaternary aquifer.

Chemical and isotopic signatures of the reservoir waters show large seasonal evolution and differ clearly from those of groundwaters.

Tritium data support the existence of recent recharge in Quaternary groundwaters. But, the low tritium values in Oligocene groundwaters are justified by the existence of clay lenses which limit the infiltration of meteoric water in the unsaturated zone and prolong the groundwater residence time.

Carbon-14 activities confirm that groundwaters are recharged from the surface runoff coming from precipitation.

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## 1. Introduction

In semi arid areas, the scarcity of water due to the low and irregular rainfall is a perennial problem. The ever growing population and changing climate have seriously increased the pressure on water resources in the world and has required new approaches for water planning and management (Ma et al., 2009).

In Tunisia (North Africa), the government has undertaken the implementation of the "National Strategy of Surface Runoff Mobilization" since the early 1990s. This strategy aims at building several large dams, small hill dams, and other structures for irrigation and aquifer recharge. More than 800 hill reservoirs have already been constructed in the central and northern parts of the Tunisian country within the semi arid climate (DG/ACTA, 2005; Montoroi et al., 2002; Talineau et al., 1994).

Many investigations, based on hydrogeological and geochemical data, have dealt with the influence of hill reservoir construction on groundwater flow and chemistry in the Mediterranean basin (Armengol et al., 1994; Marc et al., 1996; Prinz, 1999; Stigter et al., 1998), but only a few studies in Tunisia (Grünberger et al., 2004; Montoroi et al., 2002) have been carried out on this topic using isotope hydrology.

In Cherichira basin (central Tunisia), like many other semi arid regions, water resources are mainly limited to groundwater. Since 1993, a hill reservoir has been built for water storage and irrigation. Furthermore, numerous water and soil conservation projects have been planned.

Identification of recharge sources in semi arid areas provides insights into recharge processes and is necessary for developing sustainable water resource management plans within the context of climate variability (Scanlon et al., 2006). Hence, stable and radiogenic isotopes combined with chemistry can provide helpful tracers for groundwater recharge in a groundwater system on both local and regional scales (Edmunds and Tyler, 2002).

The objectives of this study are (1) to characterize water chemistry at a given time, (2) to infer the recharge sources and (3) to determine the residence time of groundwater under the natural conditions.

## 2. General setting

The Cherichira basin is located 40 km West of Kairouan City in central Tunisia between latitudes 39G 58′ and 39G 70′N, and longi-

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http://dx.doi.org/10.1016/j.jafrearsci.2012.10.001

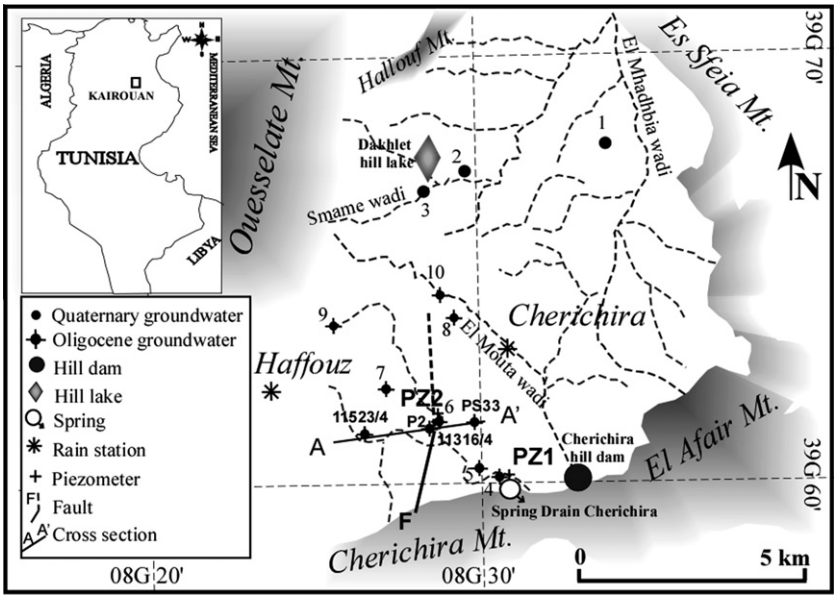


**Fig. 1.** Sample's map of surface and groundwaters in the Cherichira basin.

tudes 8G 20′ and 8G 35′E (Fig. 1). The semi arid climate is marked by distinct summer (warm and dry) and winter (cool and humid) seasons. The mean annual precipitation is 278.3 mm. The mean annual air temperature is 19 °C. The mean annual minimum temperature occurs in January (13.6 °C) and the mean annual maximum in August (33.4 °C). Most of the precipitation occurs in autumn. The driest months are July and August. In Cherichira basin, potential evapotranspiration far exceeds the annual rainfall and is 1736 mm/year (Riou, 1980).

The Cherichira basin is supplied by several intermittent rivers (locally named wadis) which originate from mountains and discharge to the spring "Drain Cherichira" (Fig. 1). These wadis are characterized by a seasonal flow.

In fact, the El Mouta wadi drains the southern part of the basin, and is controlled by a hill dam "the Cherichira" built in 1993 and used to manage and stabilize water flow for recharge and irrigation systems. It is constructed of earth materials and has a maximum capacity of 0.870 $hm^3$ with an annual input of 0.350 $hm^3$ (DG/ACTA, 2005).

The Smame wadi drains the northern part of the basin, and it is controlled by a hill lake "the Dakhlet" built in 2002. It has a maximum capacity of 520,000 $m^3$ (DG/ACTA, 2005).

The reservoir water is used for irrigation and development of agriculture. The pumping of the water from reservoirs is ensured either by motor-driven pumps or by tanks (DG/ACTA, 2005).

Several physiographic features have been developed according to North East–South West and North–South extensions (Abbes, 2004). The most important ones are Atlas structures and the major North–South structural feature in central Tunisia. The study area is located around the west boundary of the SW–NE oriented Ouesselat Mountain. It is limited in the south by Cherichira Mountain, in the east by Es Sfeia Mountain and in the North West by Hallouf Mountain (Fig. 1). The regional geology has been discussed by several authors (Abbes, 2004; Castany, 1952; Jauzein, 1967; Rigane, 1991). Geological formations have been developed during the Triassic and the Tertiary sedimentary units, which were intensely folded by Atlasian tectonic movements resulting in rock layers dipping steeply SW to nearly vertical in the eastern part of the basin.

The geological map of the study area (Fig. 2) shows that Cretaceous-age carbonates form many outcrops in Cherichira and El Afair mountains. The Early Eocene age that begins with a thick

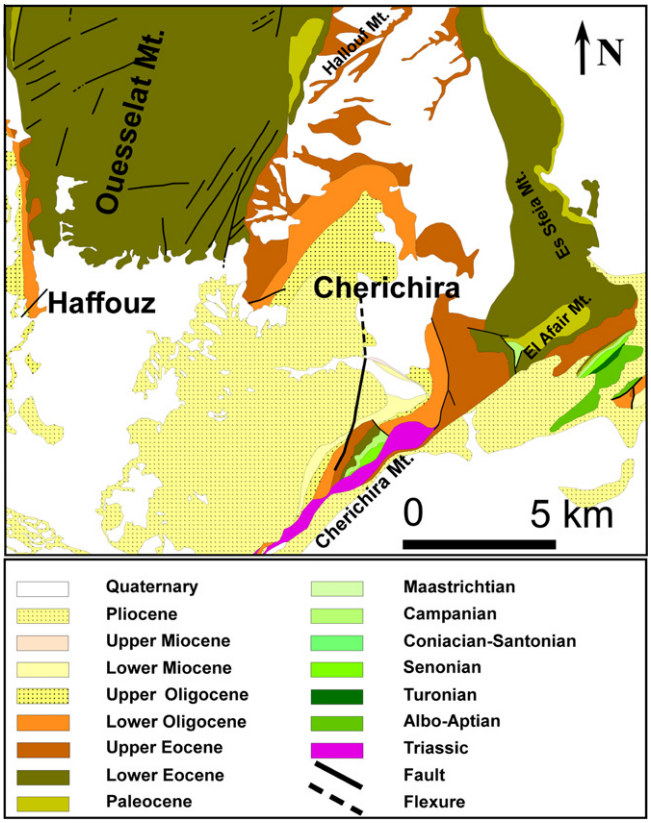


**Fig. 2.** Geological map of the study area.

Ypresian limestone unit (Rigane, 1991) appears in most geological features of the investigated zone (Ouesselate and Sfeia mountains) and shows significant facies and thickness variations. This carbonate formation represents an important feature of the Atlas morphology in Central Tunisia (Rigane, 1991). Additionally, The Paleocene formation is represented mainly by clayey sand with some intercalations of sandy limestone, gypsum and Glauconeous clays (Abbes, 2004). The Upper Eocene-age marls are found in the

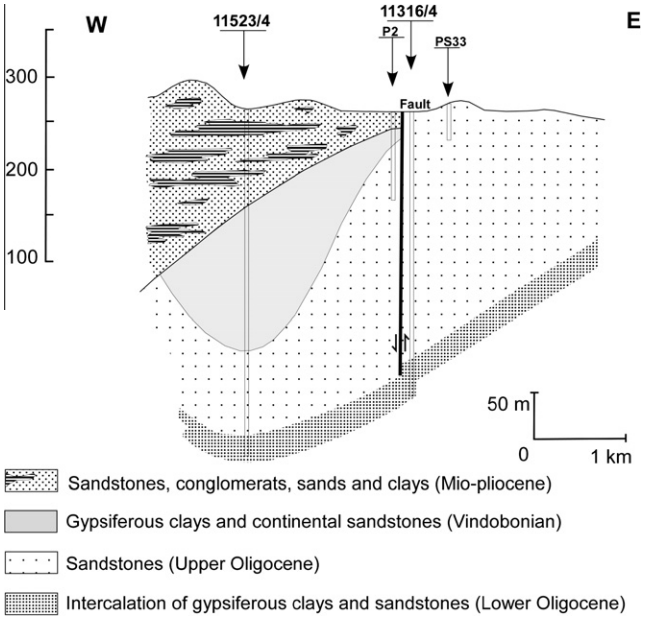


**Fig. 3.** Hydrogeological cross section AA′.

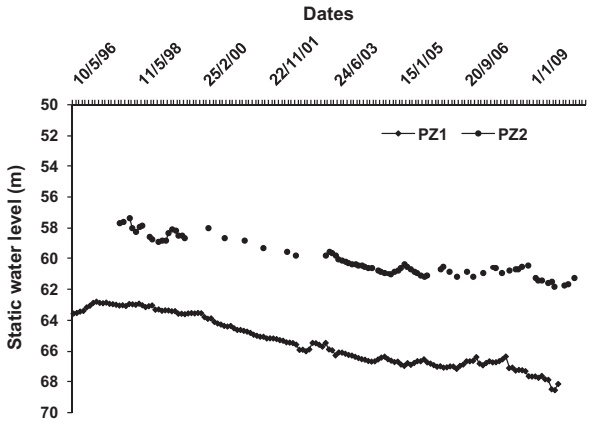


**Fig. 4.** Evolution of static water level recorded by piezometers PZ1 and PZ2 in Oligocene aquifer with time.

northern and southern parts of the basin. This formation is formed by marl series, gray clays and gypsum. Its thickness exceeds 800 m in the northern part of the basin (Abbes, 2004). The Oligocene unit is principally made up of coarse to medium-grained sandstone outcrops largely in the Cherichira syncline (Abbes, 2004). In the southern part of the syncline, the Mio-Pliocene formation outcrops and includes detrital sediments of sandy and sandy clays (Abbes, 2004). The surface geology within the study zone is represented by recent Quaternary soil and terraces that partially cover the Eocene formations. They result from an old alluvial basin.

As shown in the representative W–E cross section AA′ (Fig. 3), the Cherichira hydrogeological basin is featured by a NNE–SSW synclinal structure which is geometrically crossed by a normal fault known as wadi El Kharrouba fault (Kingumbi, 2006). Fig. 3 shows that deposits of Lower Oligocene comprising inter-bedded fine sandstone and clay underlie the sandstones of Upper Oligocene which represent the deep and the productive aquifer. It is mainly formed of highly permeable sandstones and some beds of sands, clayey sandy, sandy clays, gravel sediments and fine clayey lenses with a thickness of 200–350 m. These deposits constitute an unconfined aquifer layer in the eastern part of the basin, whilst it becomes confined and dips SW under Mio-Pliocene and Vindobonian deposits in the western part (Haffouz region). This structure is controlled by the Wadi El Kharrouba fault which results in a complex groundwater hydraulic circulation (Kingumbi, 2006).

Presently, static water levels vary between 67 and 70 m below surface in the deep Oligocene aquifer. The permeability is about $5 \times 10^{-5}$ m s$^{-1}$. The specific capacity is about 13.9–122.7 l s$^{-1}$. The storage coefficient is $4 \times 10^{-3}$. The dynamic resources are 120 l s$^{-1}$. This allows a large amount of surface runoff in the piedmont fan to seep down and recharge the aquifer (Hamza, 1976).

The regional potentiometric surface reveals high levels in the north western part, a general decline towards the southeast. The general flow is from North West to South East. In the southern part of the basin, the groundwater overflows as springs and re-emergences as streams.

Fig. 4 shows a continuous decrease in static water levels recorded in piezometers PZ1 and PZ2 between 1996 and 2009. The drawdown produced in the water levels of Oligocene aquifer by the intensive abstraction over the past 13 years has caused a significant decline in groundwater flow.

The Quaternary deposits outcrop locally at the northern part and form an unconfined aquifer with very limited spatial extension. Most wells in this aquifer are logged in clayey sands, sand and gravel lenses that are interstratified with clays and silt clays with a thickness between 15 and 20 m (Abbes, 2004).

## 3. Sampling and analytical procedure

Few groundwater wells and boreholes exist in the study area because population is sparse and the spatial extension of the aquifers is very limited. Regarding the Oligocene aquifer, the water table is deep, and specific yields are low.

A sampling campaign for the geochemical and isotopic analyses was performed during August 2008, March and April 2009. A total of 22 samples were collected from the Cherichira basin (Table 1). Samples are distributed as follows (Fig. 1):

- three samples were taken from the shallow wells (Quaternary aquifer) with a total depth ranging from 7.1 to 18.8 m;
- seven samples were taken from the boreholes (Oligocene aquifer) with a total depth varying between 58 and 306 m;
- one sample was taken from artisan spring "Drain Cherichira";
- nine samples were collected intermittently from the Cherichira hill dam between August 2008 and January 2010 and
- two samples were taken from the Dakhlet hill lake.

The pumping method is used for collection of water samples. The measurements of pH, temperature and electrical conductivity (EC) were performed in the field (Table 1). Water samples were collected in 1000 ml polyethylene bottles with poly-seal caps for major elements after the stabilization of pH, electrical conductivity and temperature.

Chemical analyses and isotopic measurements were determined in the Radio-Analysis and Environment Laboratory of the National School of Engineers of Sfax (Tunisia).

Major elements ($Cl^-$, $SO_4^{2-}$, $NO_3^-$, $Na^+$, $Mg^{2+}$, $Ca^{2+}$ and $K^+$) were analyzed using ion liquid chromatography (ILC) equipped with columns IC-Pak TM CM/D for cations, using EDTA and nitric acid as eluent, and on a Metrohm chromatograph equipped with columns CI SUPER-SEP for anions using phthalic acid and acetonitrile as eluent. The overall detection limit for ions was 0.04 mg l$^{-1}$. The $CO_3^{2-}$ and $HCO_3^-$ concentrations were analyzed by titration using 0.1 N HCl acid. The ionic balance for all samples is within ±5%. The total dissolved solids (TDS) are measured in the laboratory by evaporating of 100 ml of water sample during 24 h at 105 °C.

**Table 1**
In situ measurement, geochemical and isotopic data of surface and groundwater samples in the Cherichira basin.

| No. | Sample's type | $T$ (°C) | pH | EC (µS/cm) | TDS (mg/l) | $Ca^{2+}$ (mg/l) | $Mg^{2+}$ (mg/l) | $Na^{+}$ (mg/l) | $K^{+}$ (mg/l) | $HCO_3^{-}$ (mg/l) | $Cl^{-}$ (mg/l) | $SO_4^{2-}$ (mg/l) | $NO_3^{-}$ (mg/l) | $^{18}O$ (‰ versus SMOW) | $^{2}H$ (‰ versus SMOW) | $^{3}H$ (TU) | $^{14}C$ (pmC) |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| 1 | Quaternary aquifer | 21.00 | 7.05 | 2830 | 1942 | 205.94 | 78.34 | 258.98 | 5.88 | 402.60 | 430.30 | 370.54 | 42.20 | −4.00 | −30.40 | 1.08 | 40.50 |
| 2 | Quaternary aquifer | 18.80 | 7.50 | 3160 | 2385 | 194.03 | 100.23 | 413.35 | 11.03 | 280.60 | 596.13 | 782.15 | 4.10 | −3.75 | −32.50 | 1.47 | |
| 3 | Quaternary aquifer | 19.50 | 7.04 | 5270 | 4314 | 437.60 | 195.60 | 650.32 | 10.08 | 347.70 | 772.08 | 1803.16 | 3.08 | −4.04 | −28.72 | 2.23 | 58.30 |
| 4 | Upper Oligocene aquifer | 24.10 | 7.40 | 1823 | 1194 | 93.59 | 38.79 | 187.05 | 9.30 | 262.30 | 239.25 | 292.08 | 11.42 | −6.21 | −37.00 | | |
| 5 | Upper Oligocene aquifer | 23.30 | 7.52 | 949 | 761 | 88.98 | 30.78 | 87.22 | 5.24 | 305.00 | 103.89 | 117.59 | 3.01 | −5.24 | −34.28 | 0.17 | 33.40 |
| 6 | Upper Oligocene aquifer | 23.80 | 7.45 | 917 | 560 | 68.07 | 25.08 | 67.63 | 3.05 | 231.80 | 98.26 | 81.32 | 12.77 | −5.12 | −32.58 | 0.85 | 46.70 |
| 7 | Upper Oligocene aquifer | 22.70 | 7.56 | 635 | 431 | 51.15 | 15.17 | 47.59 | 1.61 | 219.60 | 49.72 | 32.35 | 12.55 | −5.03 | −32.46 | 0.00 | |
| 8 | Upper Oligocene aquifer | 23.10 | 7.46 | 1308 | 795 | 98.30 | 35.46 | 93.89 | 4.38 | 237.90 | 187.52 | 124.85 | 24.23 | −6.15 | −35.43 | 0.18 | 55.60 |
| 9 | Upper Oligocene aquifer | 22.90 | 7.59 | 634 | 450 | 69.29 | 15.64 | 30.53 | 2.55 | 207.40 | 36.89 | 81.53 | 9.55 | −5.25 | −32.91 | 0.32 | 54.80 |
| 10 | Upper Oligocene aquifer | 27.70 | 7.49 | 1143 | 723 | 119.33 | 28.65 | 64.47 | 3.63 | 250.10 | 102.54 | 187.72 | 27.98 | −5.04 | −32.86 | | |
| 11 | Spring | 17.90 | 7.77 | 889 | 592 | 101.26 | 23.91 | 49.88 | 2.20 | 250.10 | 66.70 | 129.93 | 11.96 | −3.89 | −29.28 | 0.59 | |
| 13 | Hill lake (08/2008) | 30.70 | 7.66 | 1730 | 1210 | 151.45 | 30.23 | 95.81 | 11.67 | 420.90 | 139.72 | 210.02 | 0.00 | 0.12 | −12.54 | 6.94 | |
| 12 | Hill lake (03/2009) | 22.40 | 7.56 | 2450 | 1657 | 236.02 | 62.12 | 184.36 | 10.62 | 219.60 | 305.66 | 627.18 | 6.08 | −2.82 | −17.14 | 3.46 | |
| 14 | Hill dam (08/2008) | | 9.21 | 1250 | 870 | 135.74 | 23.64 | 72.84 | 20.45 | 134.20 | 120.20 | 337.22 | 0.00 | 10.71 | 39.85 | 5.95 | |
| 15 | Hill dam (03/2009) | | 7.22 | 360 | 217 | 44.93 | 4.09 | 5.79 | 1.89 | 97.60 | 5.24 | 56.51 | 0.00 | −3.57 | −23.28 | 3.52 | |
| 16 | Hill dam (04/2009) | | 9.19 | 305 | 248 | 53.12 | 7.54 | 12.01 | 2.69 | 61.00 | 23.24 | 89.57 | 1.79 | −1.65 | −13.02 | | |
| 17 | Hill dam (05/2009) | | 7.47 | 322 | 223 | 45.29 | 4.76 | 8.83 | 1.46 | 67.10 | 11.80 | 83.59 | 3.17 | −0.14 | −11.60 | | |
| 18 | Hill dam (06/2009) | | 7.32 | 268 | 185 | 30.64 | 5.38 | 10.28 | 2.16 | 36.60 | 12.89 | 69.90 | 1.33 | 2.57 | 1.72 | | |
| 19 | Hill dam (10/2009) | | 6.97 | 373 | 259 | 62.03 | 6.08 | 12.12 | 3.09 | 52.46 | 11.01 | 128.93 | 2.25 | −3.55 | −23.04 | | |
| 20 | Hill dam (11/2009) | | 7.02 | 365 | 254 | 51.70 | 5.91 | 8.40 | 4.47 | 61.00 | 9.73 | 102.16 | 0.00 | −1.13 | −10.89 | | |
| 21 | Hill dam (12/2009) | | 7.18 | 451 | 300 | 59.62 | 8.07 | 9.14 | 2.82 | 54.90 | 12.02 | 118.44 | 1.33 | 0.94 | −1.87 | | |
| 22 | Hill dam (01/2010) | | 7.38 | 590 | 430 | 85.31 | 10.69 | 18.50 | 3.38 | 128.10 | 24.34 | 137.86 | 0.00 | 3.08 | 9.58 | | |
| 23 | Rain water (04/2009) | | | | 138.3 | 10.15 | 1.23 | 4.68 | 6.52 | 65.55 | 9.81 | 13.37 | 7.78 | −4.92 | −36.5 | 3.24 | |

Stable isotope ratio ($^{18}O/^{16}O$ and $^{2}H/^{1}H$) analyses were performed by using the Laser Absorption Spectrometry measurements LGR DLT 100 (Penna et al., 2010). Analyses are reported in ‰ versus VSMOW standard (Vienna-Standard Mean Oceanic Water).

Six 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 $C_6H_6$ (Fontes, 1971; Stuiver and Polach, 1977).

14 samples were selected to be analyzed for Tritium content using electrolytic enrichment and liquid scintillation spectrometry (Taylor, 1976). $^{3}H$ concentration is expressed in Tritium Units (TU). One TU is defined as the isotope ratio $^{3}H/^{1}H = 10^{-18}$.

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

## 4. Results and discussion

### 4.1. Physico-chemical data

The physico-chemical parameters (temperature, pH and EC) of the analyzed samples are presented in Table 1. Groundwater samples in Cherichira basin show heterogeneous values of temperature, varying between 18.8 and 27.7 °C. The temperature values of the Quaternary shallow aquifer are influenced by the surface air temperatures since the water table is close to the surface. But, regarding the Oligocene deep aquifer, the groundwater temperatures are influenced by the structural and the geochemical features of the aquifer (i.e. the geothermal gradient, and the regional $CO_2$ degassing process) (Edmunds et al., 2003).

The groundwater samples are circum-neutral. The pH values of the groundwaters are very homogenous and vary between 7.05 and 7.59. However, the pH values of the surface waters ranges from 6.97 to 9.21.

The EC values of Quaternary groundwater samples vary between 2830 and 5270 µS/cm. The higher values are recorded in well No. 3 (Fig. 1) located near the evaporitic marls of the Hallouf Mountain (Fig. 2). The lower values are revealed in the deep aquifer (springs and boreholes) with an average of 1019 µS/cm.

The total dissolved solids (TDS) values of Cherichira hill dam range from 185 mg/l (sample collected during June 2009) to 870 mg/l (sample collected during August 2008). Generally, waters of hill reservoirs reveal low values due to the direct alimentation by rainwater. The TDS values of the Dakhlet hill lake vary between 1210 (sample collected during August 2008) and 1657 mg/l (sample collected during March 2009).

Chemical compositions of the analyzed samples are plotted on the Piper trilinear equivalence diagrams shown in Fig. 5. The surface and groundwater exhibit a large spatial variability of hydrochemical facies.

Quaternary groundwaters (Nos. 1, 2 and 3) reveal a Ca–Mg–Cl–$SO_4$ type, whilst the Oligocene groundwaters (Nos. 5, 6, 7 and 9) collected from the north western part with high water level fall predominantly in the category of $Ca^{2+}$—$HCO_3^-$ to mixed ionic type (Ca–Mg–Cl–$SO_4$) in the eastern part of the basin (Nos. 4, 8 and 10).

Surface waters of Dakhlet hill lake show an evolution between Ca–$HCO_3$ and Ca–$SO_4$ types, while the geochemical facies of Cherichira hill dam is dominated by $Ca^{2+}$ and $SO_4^{2-}$. 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 $SO_4^{2-}$ (Fig. 5).

To identify the origin and the processes contributing to groundwater mineralization, plots of $Na^+$ versus $Cl^-$, $Ca^{2+}$ versus $SO_4^{2-}$ and $Ca^{2+}$ versus $HCO_3^-$ are established. The $Na^+$–$Cl^-$ relationship (Fig. 6a), which has frequently been used to specify mechanisms for acquiring salinity in semi-arid regions, shows a parallel enrichment in both ions and demonstrates that the majority of points

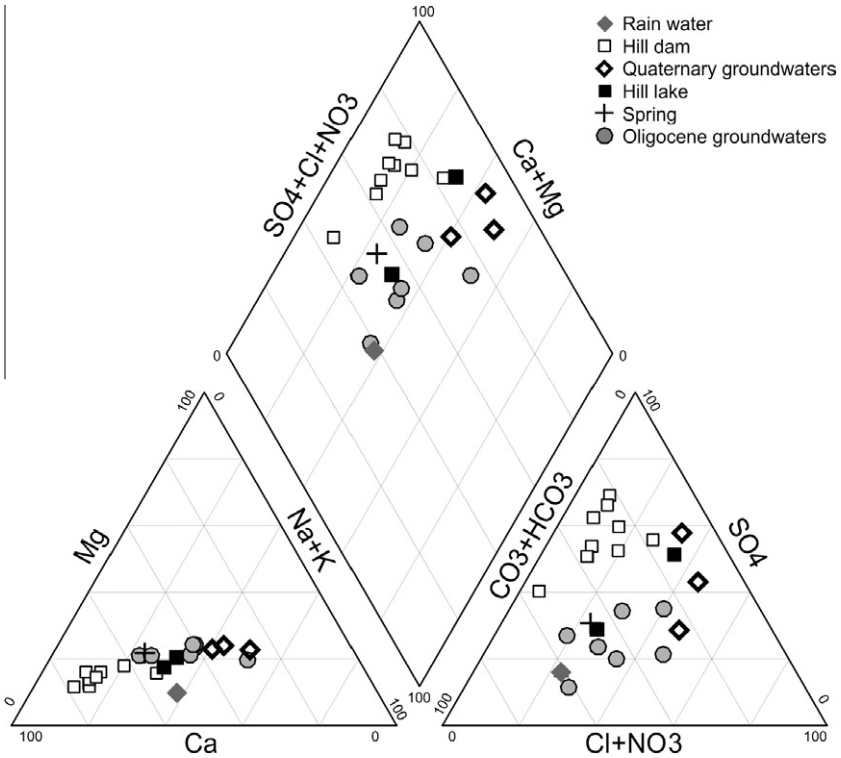


**Fig. 5.** Trilinear diagram showing some major chemical compositions of the surface and groundwater samples in the Cherichira basin.

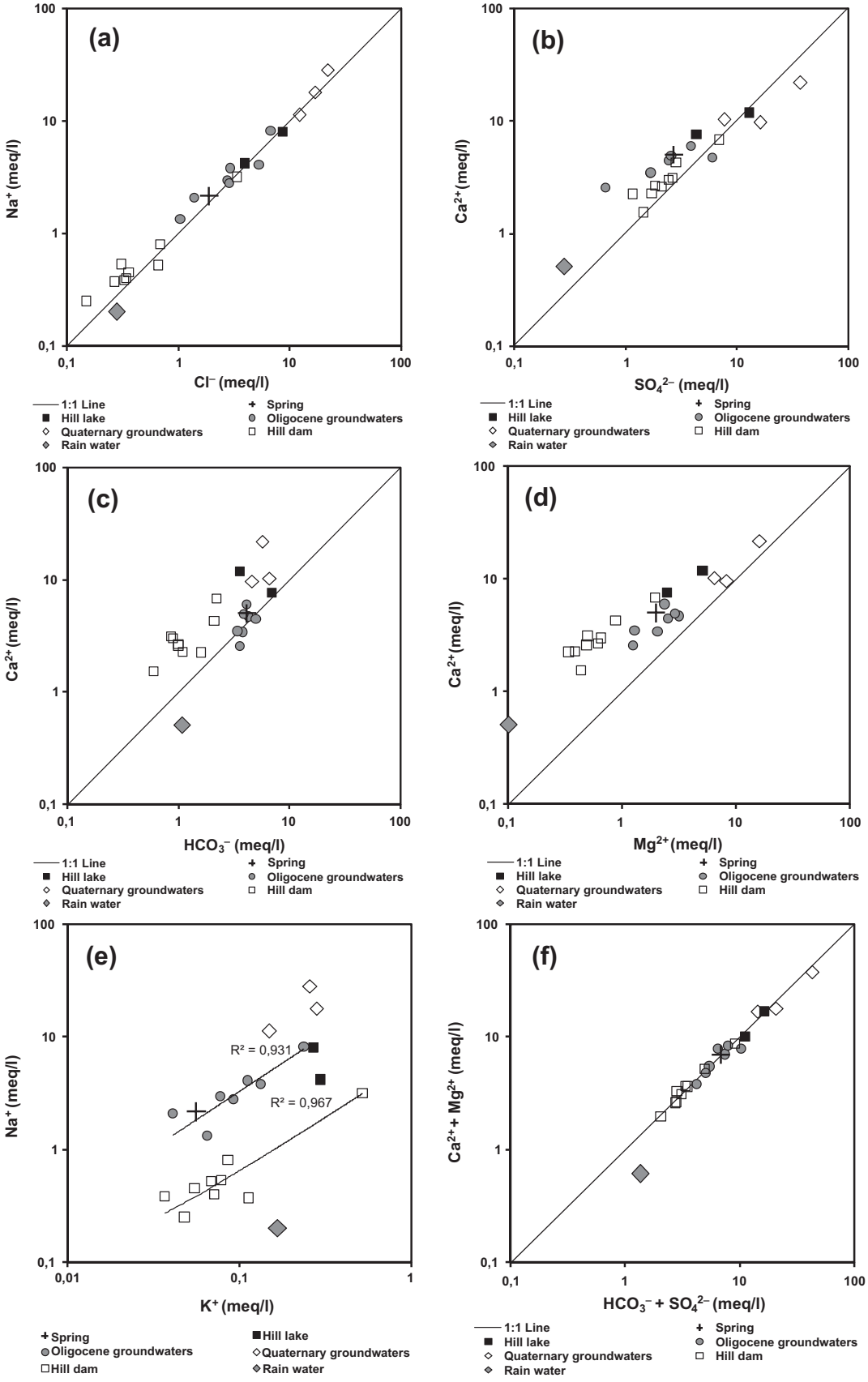


**Fig. 6.** Relationships between major elements in the analyzed sampled water: $Na^+/Cl^-$ (a), $Ca^{2+}/SO_4^{2-}$ (b), $Ca^{2+}/HCO_3^-$ (c), $Ca^{2+}/Mg^{2+}$ (d), $Na^+/K^+$ (e) and $Ca^{2+} + Mg^{2+}/HCO_3^- + SO_4^{2-}$ (f).

**Table 2**
Some ionic ratios and mineral saturation indices of surface and groundwater samples in the Cherichira basin.

| No. | Sample's type | $Na^+/Ca^{2+}$ | $Mg^{2+}/Ca^{2+}$ | $K^+/Na^+$ | Saturation indices | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | | | | Halite | Gypsum | Anhydrite | Dolomite | Calcite |
| 1 | Quaternary aquifer | 1.10 | 0.63 | 0.01 | −5.59 | −0.92 | −1.15 | −0.24 | 0.22 |
| 2 | Quaternary aquifer | 1.86 | 0.85 | 0.02 | −5.26 | −0.7 | −0.94 | 0.17 | 0.38 |
| 3 | Quaternary aquifer | 1.30 | 0.74 | 0.01 | −4.99 | −0.2 | −0.44 | −0.15 | 0.25 |
| 4 | Upper Oligocene aquifer | 1.74 | 0.68 | 0.03 | −5.97 | −1.22 | −1.44 | −0.3 | 0.15 |
| 5 | Upper Oligocene aquifer | 0.85 | 0.57 | 0.04 | −6.64 | −1.54 | −1.76 | 0.07 | 0.38 |
| 6 | Upper Oligocene aquifer | 0.86 | 0.61 | 0.03 | −6.76 | −1.76 | −1.98 | −0.43 | 0.11 |
| 7 | Upper Oligocene aquifer | 0.81 | 0.49 | 0.02 | −7.19 | −2.2 | −2.43 | −0.55 | 0.11 |
| 8 | Upper Oligocene aquifer | 0.83 | 0.59 | 0.03 | −6.35 | −1.49 | −1.72 | −0.19 | 0.24 |
| 9 | Upper Oligocene aquifer | 0.38 | 0.37 | 0.05 | −7.52 | −1.7 | −1.93 | −0.44 | 0.22 |
| 10 | Upper Oligocene aquifer | 0.47 | 0.40 | 0.03 | −6.79 | −1.25 | −1.46 | 0.07 | 0.43 |
| 11 | Spring | 0.43 | 0.39 | 0.03 | −7.05 | −1.41 | −1.65 | 0.11 | 0.53 |
| 12 | Hill lake (08/2008) | 0.55 | 0.33 | 0.07 | −6.5 | −1.16 | −1.36 | 1.02 | 0.92 |
| 13 | Hill lake (03/2009) | 0.68 | 0.43 | 0.03 | −5.89 | −0.64 | −0.87 | 0.21 | 0.52 |
| 14 | Hill dam (08/2008) | 0.47 | 0.29 | 0.16 | −6.67 | −0.99 | −1.21 | 2.29 | 1.62 |
| 15 | Hill dam (03/2009) | 0.11 | 0.15 | 0.19 | −9.07 | −1.93 | −2.15 | −2.38 | −0.57 |
| 16 | Hill dam (04/2009) | 0.20 | 0.23 | 0.13 | −8.12 | −1.72 | −1.94 | 1.11 | 1.08 |
| 17 | Hill dam (05/2009) | 0.17 | 0.17 | 0.10 | −8.54 | −1.78 | −2 | −2.17 | −0.49 |
| 18 | Hill dam (06/2009) | 0.29 | 0.29 | 0.12 | −8.43 | −1.98 | −2.2 | −3.06 | −1.05 |
| 19 | Hill dam (10/2009) | 0.17 | 0.16 | 0.15 | −8.44 | −1.51 | −1.73 | −3.2 | −0.99 |
| 20 | Hill dam (11/2009) | 0.14 | 0.19 | 0.31 | −8.65 | −1.66 | −1.88 | −3.02 | −0.94 |
| 21 | Hill dam (12/2009) | 0.13 | 0.22 | 0.18 | −8.53 | −1.56 | −1.78 | −2.63 | −0.78 |
| 22 | Hill dam (01/2010) | 0.19 | 0.21 | 0.11 | −7.93 | −1.4 | −1.62 | −1.28 | −0.09 |
| 23 | Rain water (04/2009) | 0.39 | 0.20 | 0.84 | −8.87 | −3.06 | −3.28 | −4.18 | −1.53 |

cluster along the halite dissolution line. Conversely, if $Na^+$ was only derived from dissolution of evaporitic minerals, then $Na^+$ should balance $Cl^-$. Accordingly, the increase of the $Na^+/Cl^-$ ratio above 1 in some samples of Oligocene deep aquifer (Nos. 4, 5, 7 and 9) and those of hill reservoir would suggest some reaction of silicate minerals (Montoroi et al., 2002; Edmunds et al., 2003). The molar $Na^+/Ca^{2+}$ ratio has an increasing trend along the groundwater flow from 0.38 (sample No. 9) to 1.74 (sample No. 4) (Table 2), which also indicates the dominance of reaction of silicate minerals derived mainly from weathering of sandstones (Montoroi et al., 2002).

The $Ca^{2+}$ versus $SO_4^{2-}$ plot (Fig. 6b) illustrates that most points representing hill reservoirs are plotted on or just above the gypsum dissolution line. This result could be explained by a compound effect of gypsum or anhydrite dissolution and evaporation processes. Nevertheless, Oligocene groundwaters exhibit a more pronounced loss of $SO_4^{2-}$ relative to $Ca^{2+}$. This excess of $Ca^{2+}$ is believed to originate from the probable dissolution of carbonate mineral (probably the dolomite). As confirmed by Fig. 6c, the points representing the Oligocene groundwaters fall either on, or just above 1:1 stoihiometric equilibrium line. All other samples including Quaternary groundwaters and surface water samples are above the line, indicating another source of $Ca^{2+}$ which may possibly be present from weathering and erosion of gypsum and/or clay minerals. Dissolution of evaporite is also justified by the saturation indices calculated with the aid of PHREEQC program (Parkhurst and Appelo, 1999) (Table 2). They show that almost all samples are undersaturated with respect to halite, gypsum and anhydrite (Fig. 7a–c).

The $Mg^{2+}$ versus $Ca^{2+}$ plot reveals an excess of $Ca^{2+}$ ions (Fig. 6d). The abundance of carbonate rocks and the erosion rates in the study area suggest that the dissolution of carbonate minerals (probably the dolomite) may potentially add significant amounts of $Ca^{2+}$ and $Mg^{2+}$ to the groundwaters of the Oligocene aquifer. The $Mg^{2+}/Ca^{2+}$ ratio in groundwater samples is maintained at around 0.4 over much which is consistent with an equilibrium control although slightly lower than that expected if both calcite and dolomite minerals are the controls (Appelo and Postma, 1993) (Table 2). There is a decrease in $Mg^{2+}/Ca^{2+}$ ratio in hill dam samples (0.15–0.29), which coincide with the $Na^+/Ca^{2+}$ decrease, indicating the effect of dissolution of both carbonate and sulfate minerals.

The relationship between saturation indices (SI) with respect to calcite and dolomite of the analyzed water samples is presented in Fig. 7d and e. The saturation indices of the hill dam samples cover the range between −0.09 and 1.62 for calcite and from −3.06 to 2.99 for dolomite. Regarding the groundwater samples, the calcite SI are close or above equilibrium (SI = 0) and the dolomite SI show saturation to undersaturation state. In fact, the saturation of the groundwater samples is explained by the fact that outgassing of $CO_2$ is the primary process responsible for supersaturation of the studied groundwaters with respect to calcite mineral (Edmunds et al., 2003). The central assumption of the open-system model is that infiltrating waters is in permanent contact with an infinite reservoir of $CO_2$ and the solid phase being dissolved under saturation conditions are reached (Edmunds et al., 2003).

The dissolution of gypsum in the Quaternary groundwater samples and hill lakes should also tend to maintain saturation or oversaturation with respect to carbonate minerals.

Potassium shows a steady increase with sodium according to the flow direction (Fig. 6e). The $K^+$ increase is likely to reflect progressive reactions with feldspars or clay minerals and may be used as an indicator of residence time along the flow line (Edmunds et al., 2003). One significant characteristic of the Oligocene groundwaters is the very low molar $K^+/Na^+$ ratio of 0.01–0.05 (Table 2), which would suggest the dominance of feldspar in the study area (Ma et al., 2009). This mineral is most likely derived from erosion of sandstones and reservoir sediments, as evidenced by the mineralogical data investigated on the El Gouazine watershed located at 10 km from the study area (Montoroi et al. 2002).

The plot of $Ca^{2+} + Mg^{2+}$ versus $SO_4^{2-} + HCO_3^-$ (Fig. 6f) in all analyzed samples display a good linear relationship with a 1:1 linear stoichiometry ratio, indicating that $Ca^{2+}$, $Mg^{2+}$, $SO_4^{2-}$ and $HCO_3^-$ were most probably derived from simple dissolution of calcite, dolomite and gypsum. 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.

Representative major ionic compositions and TDS of waters from repeatedly sampled Cherichira hill reservoir are listed in Fig. 8. These results are used to characterize the current surface water quality and chemical variations in time.

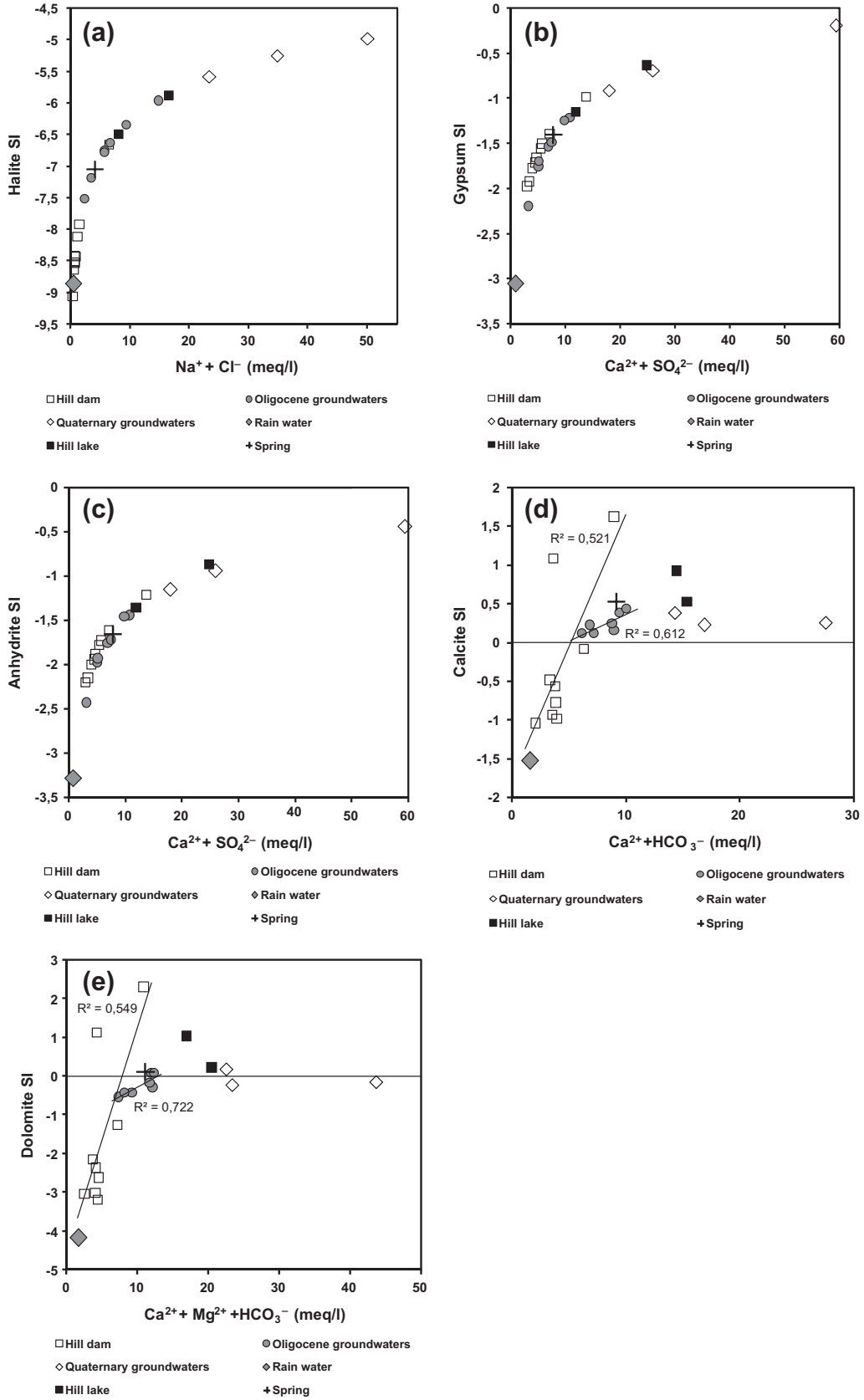


**Fig. 7.** Halite SI versus $Na^+ + Cl^-$ (a), gypsum SI versus $Ca^{2+} + SO_4^{2-}$ (b), anhydrite SI versus $Ca^{2+} + SO_4^{2-}$ (c), calcite SI versus $Ca^{2+} + HCO_3^-$ (d) and dolomite SI versus $Ca^{2+} + Mg^{2+} + HCO_3^-$ (e) relationships of the analyzed water samples.

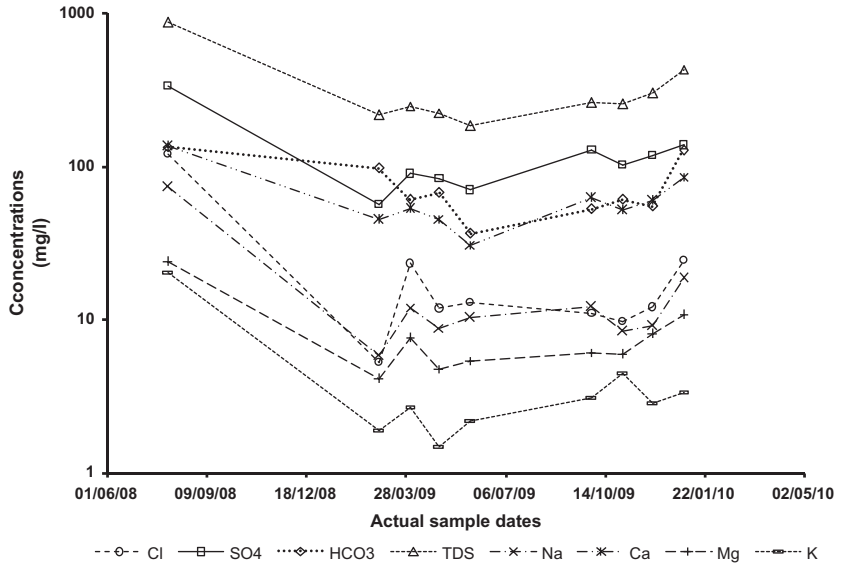


**Fig. 8.** Variations of major ionic compositions and TDS of waters from Cherichira hill reservoir with actual sample dates.

The chemical signature of the hill reservoir water reveals clear variations with actual sample dates. In fact, the increase in TDS and major elements concentrations can be seen in August 2008 which is characterized by a severe drought in central Tunisia. The $SO_4^{2-}$ concentration of the water increases to over 330 mg/l in the same period. The observed pattern could be explained by the intensive evaporation process, whereas the low values result in a dilution effect by rainwater. It is noticed that the surface samples reveal seasonal composition differences that are attributed mainly to variations in evaporation rates and rainfall inputs (Gay, 2004).

### 4.2. Isotope data

Isotope study is an important complementary tool in the evaluation of hydrogeological and hydrochemical processes that affect water masses, such as evaporation and mixing in any groundwater system (Tijani et al., 1996). In this way, isotopic tracers have been investigated to shed further light on the origins of water and residence times, augmenting evidence provided by the major ions (Geyh, 2000).

#### 4.2.1. Stable isotopes $\delta^{18}O$ and $\delta^{2}H$

The stable isotopes $\delta^{18}O$ and $\delta^{2}H$ can be used to distinguish between waters from different sources. Hence, they can improve the knowledge of groundwater balance between lake or reservoir and aquifer (Gay, 2004; Gonfiantini, 1986).

Oxygen-18 and deuterium values of Cherichira hill dam range respectively from −3.57‰ to 10.71‰ and from −23.28‰ to 39.85‰. Data from the Dakhlet hill lake varies between −2.82‰ and 0.12‰ for Oxygen-18 and between −17.14‰ and −12.54‰ for deuterium (Table 1).

Oxygen-18 and deuterium values of the Quaternary samples range, respectively, from −3.75‰ to −4.04‰ and from −28.72‰ to −32.50‰. Those of Oligocene samples range from −6.21‰ to −5.03‰ and from −32.46‰ to −37‰. The isotope content of the spring (Drain Cherichira) is −3.89 for oxygen−18 and 29.28‰ for deuterium (Table 1).

Fig. 9 illustrates the variations in the $\delta^{18}O$ content of Cherichira hill reservoir with time. In fact, the most enriched values are measured in August 2008 (10.71‰ for $\delta^{18}O$ and 39.85‰ for $\delta^{2}H$). Additionally, the $\delta^{18}O$ contents show obvious trends to enrichment

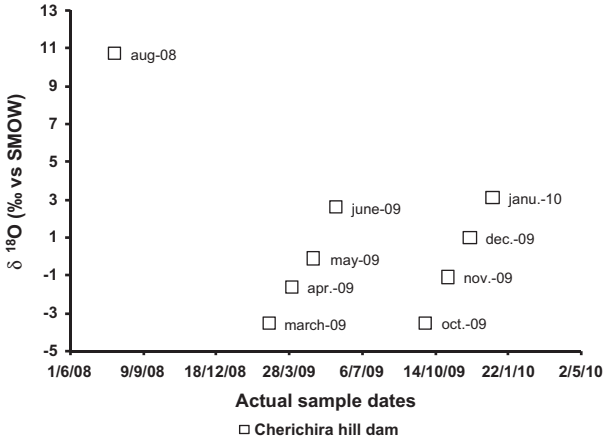


**Fig. 9.** Variations of the $\delta^{18}O$ content of Cherichira hill reservoir water with actual sample dates.

from March 2009 to June 2009 and also from October 2009 to January 2010. This pattern is in agreement with chemical data previously observed in Fig. 8. Hence, it is important to note here that the isotopic signature of the reservoir waters is strongly influenced by seasonality and shows significant seasonal evolution. It is largely controlled by the atmospheric exchanges (precipitations, evaporation, etc.) and the fluctuations of water level in the reservoir.

Values of $\delta^{18}O$ and $\delta^{2}H$ for surface and groundwater samples are plotted in Fig. 8. Oligocene groundwater samples fall on the Global Meteoric Water Line (GMWL) ($\delta^{2}H = 8\ \delta^{18}O + 10$ as reported by Craig, 1961) and the Local Meteoric Water Line (LMWL) ($\delta^{2}H = 8\ \delta^{18}O + 11$ as reported by Celle, 2000; Celle-Jeanton et al., 2001; Gay, 2004) for the Western Mediterranean, indicating that they originated from modern precipitation infiltration that was not subject to surface or subsurface alteration of its isotopic composition (Grünberger et al., 2004; Montoroi et al., 2002).

The 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, data from Quaternary groundwaters lie widely below the GMWL and reveal enriched isotopic compositions due to the evaporation process. In fact, slower infiltration

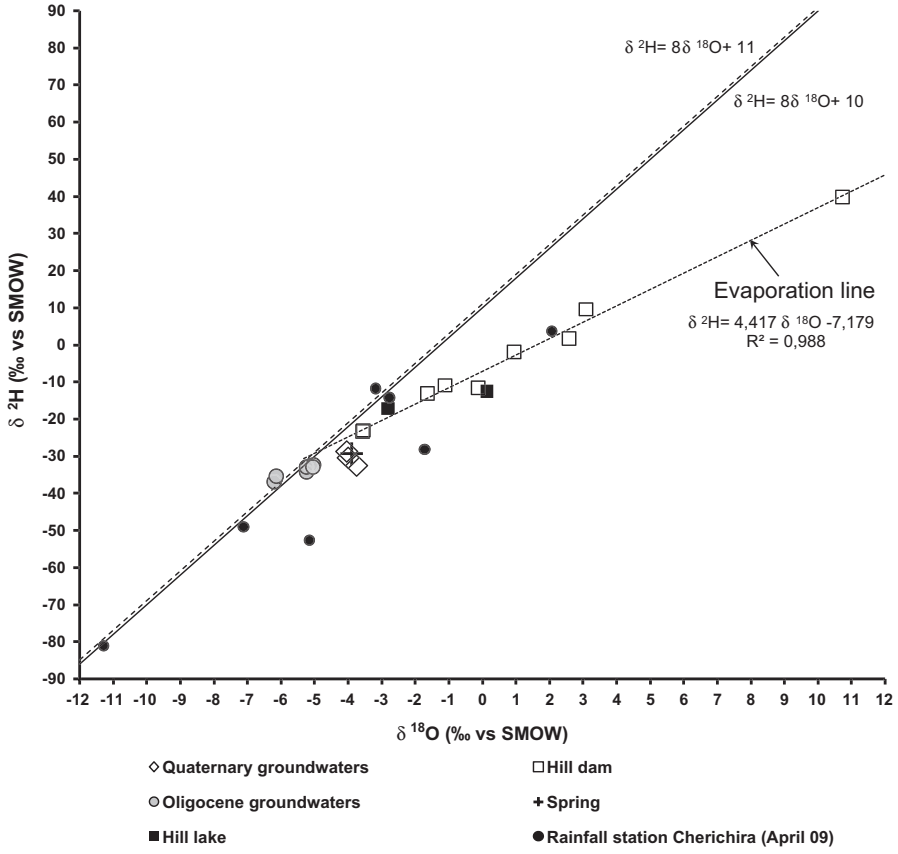


**Fig. 10.** Relationship $\delta^{18}O/\delta^{2}H$ of surface and groundwater samples in the Cherichira basin.

or seepage of the surface water through the clayey sands of the unsaturated zone of the Quaternary aquifer whose depth does not exceed 20 m would have exposed much of the water to evaporation, resulting in an enriched composition of the groundwater.

Surface water samples of Dakhlet hill lake, collected during the two seasons (August 2008 and March 2009), are noticeably enriched in $^{2}H$ and $^{18}O$ isotopic composition. Besides, samples of Cherichira hill dam reveal $^{18}O$ and $^{2}H$ enrichment (Fig. 10). The evaporative enrichment line ($\delta^{2}H = 4.4\ \delta^{18}O - 7.17$, $R^{2} = 0.98$) for the reservoir water 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 (Clark and Fritz, 1997). The intersection of the evaporative line and the LMWL define the initial composition of rain water ($-5.05$ for $\delta^{18}O/-30.05‰$ for $\delta^{2}H$) which contributes to the recharge of the Cherichira hill reservoir.

Likewise, these enriched values display a well-defined relationship when they are correlated with the TDS values and, indeed, provide evidence that water loss by evaporation is an important process in Cherichira hill dam (Fig. 11). The relative high TDS (870 mg/l) recorded in August 2008 has been attributed to intensive evaporation from the open surface hill reservoir. 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.

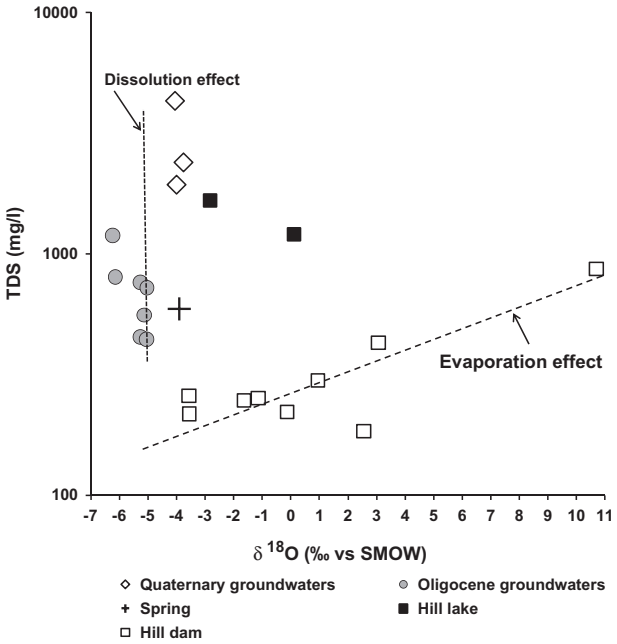


**Fig. 11.** Relationship $\delta^{18}O$/TDS of surface and groundwater samples in the Cherichira basin.

*4.2.2. Tritium isotope*

The $^{3}H$ content in the groundwater system depend primarily on the original atmospheric concentration at the recharge time and the radioactive decay that has occurred since infiltration. This requires that the initial precipitation $^{3}H$ input record be identified in order to semi-quantitatively interpret the groundwater age from the pattern of $^{3}H$ contents along the groundwater flow path (Ma et al., 2009).

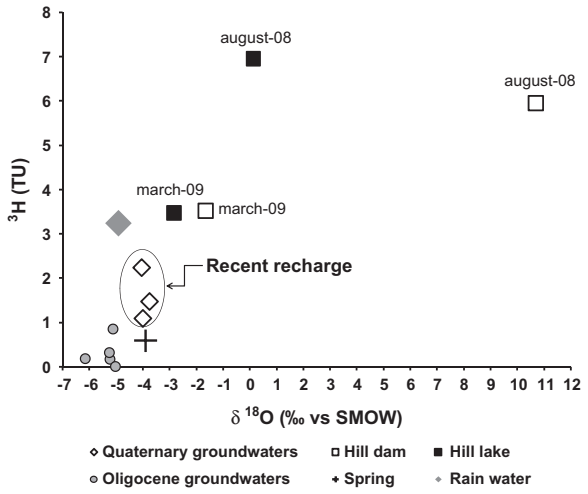


**Fig. 12.** Relationship $\delta^{18}O/^3H$ of surface and groundwater samples in the Cherichira basin.

The $^3H$ content of the surface waters were measured during two seasons (Table 1). In fact, in August 2008, the $^3H$ content was 5.95 TU, whilst during March 2009, it was 3.52 TU. The same process was observed in the Dakhlet hill lake: the $^3H$ content was 6.94 TU in August 2008, but 3.46 TU during March 2009. These concentrations analyzed in March 2009 are quite similar to $^3H$ content of local rainfall which was measured (3.24 TU) in Cherichira rain station (Fig. 1) during April 2009. These data suggest that surface flows which arrive to reservoirs present similar isotopic signal as local precipitations and are subject to a seasonal variation of $^3H$ activities.

The measured $^3H$ concentrations of the Quaternary samples are quite variable. The $^3H$ activities range from 1.08 (well No. 1) to 2.23 TU (well No. 3) (Table 1), clearly suggesting the occurrence of recent recharge in Quaternary aquifer probably during the last two decades. In contrast, groundwaters from the Oligocene deep aquifer have lower or undetected $^3H$ concentrations with the $^3H$ values ranging from 0 (borehole No. 7) to 0.85 TU (borehole No. 6). No significant tritium content could be detected in most boreholes due to high depth and low transmissivity of the clayey levels which are interbedded with sandstones contributing to delay the water infiltration in the unsaturated zone and to increase the groundwater residence time. The combination of $^3H$ and $\delta^{18}O$ values (Fig. 12) suggests that the isotopic signature of reservoir waters differs clearly from that of groundwaters.

*4.2.3. Carbon-14 contents*

Radiocarbon data are required to provide additional information on the age and to support evidence of recharge process inferred from the stable isotopes and tritium data. Carbon isotopes of Dissolved Inorganic Carbon DIC in groundwaters have been used in Cherichira basin. However, only two wells drilled in Quaternary aquifer were dated using $^{14}C$. Radiocarbon activity is 40.5 pmC in well No. 1 and 58.3 pmC in well No. 3 (Table 1). Regarding Oligocene aquifer, the $^{14}C$ activities range from 33.4 (borehole No. 5) to 55.6 pmC (borehole No. 9). The spatial distribution of the radiocarbon is in accordance with the general flow path (NW–SE) in the study area. These values confirm that Oligocene deep aquifer receives a modern recharge which is assumed by rainfall infiltration on the local outcrops of the region. These data give evidence at least of a present day direct infiltration towards the water table in the basin. Unfortunately, age calculations have not been made in this study due to the lack of $^{13}C$ data since corrections must be made to account for water–rock interactions.

## 5. Conclusion

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

The principal changes in chemical composition of surface and groundwater are caused by chemical reactions with feldspars, silicate, and especially the dissolution of evaporitic and carbonate minerals.

The stable isotopes signatures show that Oligocene groundwaters are non-evaporated and controlled by the rapidly moving mass of unevaporated recharging water, whilst Quaternary groundwaters are more enriched in $^{18}O$ and $^2H$ due to evaporation from shallow depth. Surface water samples reveal $^{18}O$ and $^2H$ enrichment, which is typical for water that has been subject to open surface evaporation in semi arid regions. This is confirmed by the well defined relationship between the TDS and the $^{18}O$ values. Isotopic signature of the reservoir waters shows significant seasonal evolution. It is largely controlled by the atmospheric exchanges (precipitations, evaporation, etc.) and by the fluctuations of water level in the reservoir.

The geochemical information is comparable to the isotopic results and illustrates that the chemical and isotopic signatures of reservoirs waters differ clearly from those of groundwaters. Tritium contents provide evidence of the presence of modern recharge in the Quaternary aquifer. But, the deeper Oligocene groundwaters show low to undetected tritium contents due to the high depth and the low transmissivity of the confined layers which contribute to delay the groundwater residence time. Carbon-14 data confirm the occurrence of recent recharge assumed by rainfall infiltration on the local outcrops of the study area. The resources in the deep 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. It is apparent that Cherichira hill reservoir has no impact on the groundwater recharge system. The scientific results of this study have important implications for groundwater management in the Cherichira basin under this Development Strategy. The results of such a study could be extended to explain the catchment chemistry and dynamics of similar reservoirs. It is advised to seriously consider conserving water by harvesting and managing this natural resource by artificially recharging the system. Hence, a strategy to implement the groundwater recharge, in a major way need to be launched with concerted efforts by various Governmental and Non-Governmental Agencies and Public at large to build up the water table and make the groundwater resource, a reliable and sustainable source for supplementing water supply needs of the dwellers.

## Acknowledgements

The authors gratefully acknowledge the contributions of the staff members of Kairouan Water Resources Division/Agriculture Ministry, for their help during field-work. We also thank the technical staff at the Laboratory of Radio-Analyses and Environment of the National Engineering School of Sfax (ENIS) for their constant help and assistance during laboratory analyses. We wish to thank the editors and the anonymous reviewers. Their comments helped to improve significantly the manuscript.

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