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Use of geochemical, isotopic, and age tracer data to develop models of groundwater flow: A case study of Gafsa mining basin-Southern Tunisia

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ABSTRACT Hydro-(major and trace elements: Cd, F and Sr), isotope (^{18}O , ^2H , ^3H and ^{13}C) geochemistry and radiogenic carbon (^{14}C) of dissolved inorganic carbon (DIC) were used to investigate the sources of groundwater contamination and the hydrodynamic functioning of the multilayer aquifer system in the mining Gafsa basin (Southwestern Tunisia). The groundwater of the study area is subject to intense exploitation to accommodate all the water demands of this arid area. The Gafsa basin contains a multi-layered aquifer with four principal levels: Upper Zebbag (Cenomanian–Turonian), Abiod (Campanien–Maastrichian), Beglia (Miocene) and Segui (Plio–Quaternary) Formations. The hydrogeology of this system is largely affected by tectonics (Gafsa–Tebessa, Sehib, Negrine–Tozeur, Tabeddit and Metlaoui faults...). The groundwater of these aquifers undergoes a significant decline in water level ($\approx 0.5 \text{ m y}^{-1}$), increasing salinity (TDS increase from 400 to 800–6,000 mg l^{-1} : generally, TDS increases from the mountainous regions towards the discharge area) due to a long time of aridity, irregular rainfall and overexploitation (irrigation and industrial activities). Groundwater pumped from the semi-confined Complex Terminal (C.T) aquifers (Cretaceous and Mio-Plio-Quaternary: MPQ) and from the confined Continental Intercalaire (C.I) aquifers is an important production factor in irrigated oases agriculture and phosphate washing in Southwestern Tunisia. A rise in the groundwater salinity has been observed as a consequence of increasing abstraction from the aquifer during the last few decades. The salinization phenomena in the region are complex. Several possible causes for salinization exist: (1) the upwelling of saline and “fossil” water from the underlying, confined “C.I” aquifer; (2) as well as the backflow of agricultural drainage water; (3) phosphate and domestic wastewater; (4) brine intrusion from the salt lake (Sebkha/Garaat); (5) evaporate meteoric water dams (El Khangua and El Oudeï); (6) reduced rainfall and (7) land and air alterations. The isotopic study of waters establishes that the deep groundwater is “fossil” water (6,000–37,000 years) recharged probably during the late Pleistocene and the early Holocene periods. The relatively

recent water in the MPQ aquifer is composed of mixed waters resulting presumably from upward leakage from the deeper groundwater.

Keywords Tunisia; Mining basin; Multi-layered aquifer; Groundwater salinity; Phosphate wastewater.

1. Introduction

Geochemical indicators constitute effective tools for solving various problems in hydrology, in particular in the arid and semi-arid regions (Fontes, 1980; Clark and Fritz, 1997; Cook and Herczeg, 2000; Etcheverry, 2002). About 30% of land area on the Earth is arid or semi-arid where potential evapotranspiration exceeds rainfall (McKnight and Hess, 2000). These areas, collectively called “the arid and/or semi-arid zone“, constitute much of the Earth’s land between latitudes 18 and 40° north and south of the equator and include most of northern and southern Africa, the Middle East, western USA and the southern areas of South America, most of Australia, and large parts of central Asia and even parts of Europe (NOAA, 2010). In arid/semi-arid countries, issues related to water resources are of growing concern due to different environmental, economic and social factors. Continuously increasing abstraction of groundwater resources to meet rising industrial, agricultural, domestic and touristic needs, coupled with severe drought periods during the past decades leads to growing deficit of water. The drawdown of piezometric levels, progressing degradation of water quality, extinction of the artesianism (drying of spring and disappear of the Foggara “Mkayel, traditional system of irrigation”) are the main consequences of such intensive exploitation of MPQ aquifer ($2,500 \text{ l s}^{-1}$) (Hamed et al., 2010b, 2013a,b,c). But after 2011 the number of illegal wells has been increased; the quantity of water discharge by exploitation is about 3,200

1 s^{-1} . Due to extensive pumping, agricultural and industrial activities, aquifers are at risk of being contaminated (Choura, 2010; Hamed et al., 2012a, 2013a). Intensive application of pesticides and fertilisers, discharge of wastewater, and industrial effluent and excessive groundwater abstraction are just a few examples of activities that lead to groundwater contamination. These activities have resulted in the deterioration of water resources in various regions around the world (Pandey et al., 1999; Al Gamal, 2011; Hamed et al., 2012a,b). Aquifers are valuable sources for water in the mining basin of Gafsa. Therefore, a quick action should be taken to prevent aquifers from contamination and to reduce the risk of contamination impact. Groundwater contamination risk mapping can help planners and decision-makers on proper land use and water resources management. This will enable incorporation of groundwater protection and health impact assessment in the analysis. Risk mapping is not only a preventative measure but it also assist with mitigation processes of groundwater contamination. In groundwater context, risk can be defined as the probability that groundwater at a drinking well becomes contaminated to an unacceptable level by activities on the land surface (Morris and Foster, 1998). Risk can be reduced by implementing a mitigation strategy with best management practice. Best practice avoids high-risk areas when locating a site of possible pollution potential. In this study, hydrogeologic, hydrochemical and isotopic data from the aquifer system will be integrated and used to determine the main factors and mechanisms controlling the chemistry of groundwaters in the study area (southwestern Tunisia) and to identify the origins of water bodies and their migration pathways. The main issues that will be addressed by this study include: (1) the relative importance of geologic and hydrogeologic factors in controlling the groundwater circulation within the aquifer system; (2) the geochemical effects and age of leakage influencing groundwaters and (3) the appraisal of the value of chemical and isotopic (^2H , ^{18}O , ^3H , ^{13}C and ^{14}C) approaches to delineate flowpaths and evaluate evolutionary processes.

2. Location and climate

From a geomorphologic point of view, Tunisia is characterized by an absence of high mountains and a relatively limited geographic extension, allowing the integration of Saharan air streams into the atmospheric circulation (Celle-Jeanton et al., 2001a). However, due to its position in the western Mediterranean, it represents a climatic transition zone open to Atlantic and Mediterranean influences (Kallel et al., 1997a, 2000; Jedoui et al., 2001; Zouari et al., 2003; Hamed, 2004; Dassi, 2009; Ben Moussa et al., 2010a,b; Hamed et al., 2012a). Indeed, regional hydrometeorological studies (Celle, 2000; Celle-Jeanton et al., 2001b) mention the existence of two major trajectories for dominant air masses (Fig. 1). These are : (i) the North Atlantic warm air masses that circulate from the west over the Northern Africa and (ii) the Mediterranean cool air masses that derive from the north. Quantitatively, Mediterranean precipitation represents 66% of the total rain amount. The main part of the regional aquifer recharge is supplied by the Mediterranean events. The study area, which is located in south western Tunisia, covers an area of 2,500 km² and lies between the longitudes 6°30'–7°00'E and the latitudes 34°00'–34°30'N (Fig. 1). It corresponds to a synclinal structure limited in the North and in the East by the Gafsa Mountains, in the South by the Northern Chott Range and in the West by the Algerian territory.

According to UNESCO/FAO (1963), the study area has a temperate Mediterranean climate, with moderately hot summers and cold winters. It shows a mean annual rainfall of about 350 mm year⁻¹ (data based on observations from 1964 to 2008, Hamed, 2009a) with a maximum amount of rainfall from November to January. The maximum rainfall amounts are associated with the highest elevations (Jebel Bouramli ≈1,140 m) of the study area (Fig. 1).

Hamed (2009a) estimated an average annual precipitation of about 150–250 mm year⁻¹ and a potential evapotranspiration of about 1,680 mm year⁻¹ (Yermani et al., 2002; Mokadem, 2012). The annual average temperature for the study area is about 19°C (data from 1984 to 2013), with a maximum from July to August (29°C) and a minimum between December and January (~10°C). The drainage network is subdendritic to dendritic. It is composed of the El Oudeï, El Khangua, El Karma, Zallez, Douaher, Berka, Jabbaria, Louza, Nabech, Tfal, Magroun, El Maleh and Bayeich non-perennial rivers (locally known as wadis) which collect surface runoff from the surrounding hills of Gafsa, the Metlaoui ranges and the Algerian territories and the Tabeddit perennial wadi by the phosphate and the domestic wastewater. The surface water of these wadis is carried to the large continental depression (locally known as “Sebkha/Garaat” or “Chott”) of Chott Djerid, south of the mining Gafsa basin (Fig. 1).

3. Geology and Hydrogeology

The study area takes part in the Southern Tunisian Atlas consisting of fault-related fold belts caused by the Miocene and Quaternary compressive stress due to Eurasian and African craton collision (Outtani et al., 1995; Ahmadi, 2006). The study area represents a transitional zone between two structurally different regions: in the South, the simple and monotonous Saharan Platform, and, in the North, the Tunisian Atlas Mountain belt with its major thrust faults, diapirs and old compression structures (Zargouni, 1985; Outtani et al., 1995; Ahmadi et al., 2006, 2013). The zone of subsidence between the Atlas and the Saharan bloc have given rise to the alignment of the Sebkhas and Chotts where Holocene evaporitic deposits, such as gypsum and calcrete, accumulate. Adjacent to the Chotts and elsewhere, fine-grained loess deposits have accumulated to form dune-like landforms referred to as lunettes; these are late Quaternary/Holocene in age (Coque, 1962).

The hydrostratigraphic units in the Gafsa region are shown in Figs. 2 (a, b and c). These units consist of three main aquifer systems, namely, from the bottom to the top, the Continental Intercalaire (C.I), the Complex Terminal (C.T: Cretaceous and Mio-Plio-Quaternary) and the shallow aquifers.

The Continental Intercalaire (C.I) aquifer

The C.I is present beneath an area of about 1,100,000 Km² and constitutes one of the largest groundwater systems in the world. The geological formations which host the C.I aquifer are composed by fluvio-deltaic continental deposits (Cornet, 1964; Castany, 1982; M'Rabet, 1987; Mamou, 1990) producing intercalations of detrial levels with horizons of clay silts and frequent gypsum layers. The C.I aquifer is located within a succession of clastic sediment of Mesozoic age, the thickness and lithology of which vary laterally (UNESCO, 1972). The aquifer is continuous from north to south from the Saharan Atlas to the Tassilis of the Hoggar (Algeria) and west to east from western Algeria to the Libyan Desert through southern Tunisia (Edmunds et al., 1997; Moulla et al., 2012; Petersen et al., 2013). It can be found at depths of 800–2,500 m with a thickness of around 300–1,200 m. Most of the wells tapping the C.I show strong artesian conditions (OSS, 2008). The groundwater of the C.I is mainly paleogroundwater which dates back to the Pleistocene and early Holocene under a cooler and humid climatic regime (UNESCO, 1972). The C.I has its recharge source in the Algerian and Tunisian Atlas Mountains (270 mm³ year⁻¹) (Appelgren, 2002). It is mainly confined and discharges in the Chotts (Fejej, Djerid, El Gharssa, Garaat Douza and El Guettar) of Tunisia and in the Gabes Gulf (Mediterranean Sea, Fig. 1) (Guendouz et al., 2003; OSS, 2003; Abidi, 2007; Bouri, 2008; Hamed et al., 2010b; Kamel, 2012; Hamed et al., 2013a,b). Recent recharge is observed at the periphery of the Sahara basin (Edmunds et al., 1997). The water is geothermal with temperatures between 45 and 70°C. This geothermal

water is utilized mainly: in agriculture; to help irrigate oases, to heat and irrigate greenhouses, for bathing purposes and in some cases for watering of animals (El Guedri, 1999; Kamel, 2012; Jamel et al., 2012). In the Gafsa region, the continental formations extend from the Neocomian at the base to the Albian. The Lower Cretaceous may be divided into five main formations (Sidi Khalif, Melloussi, Boudinar, Bouhedma and Sidi Aïch). Sidi Aïch Formation constitutes the principal productive levels of the C.I aquifer in the study area. The C.I is a very important water resource in Algeria, Tunisia and Libya. Most of the water contained in the North-West Sahara Aquifer System (NWSAS) is non and/or low-renewable. Increasing water extraction has resulted in a decrease in the groundwater pressure in many places and a termination of natural oasis systems (OSS, 2003, 2008; Hamed et al., 2008, 2012b, 2013a; Mokadem, 2012; Mokadem et al., 2012, 2014; Henchiri, 2014).

The Complex Terminal (C.T) aquifer

The aquifer system of C.T covers the major part of South Tunisia and the northern Sahara in Algeria, Tunisia and Libya (approximately 250,000 Km², UNESCO, 1972). The term Complex Terminal describes a multi-layer aquifer which consists of the Upper Cretaceous formations in the northern Saharan basin, i.e. the Upper and Lower Senonian and sandy formations of the Eocene and the Mio-Pliocene. The C.T formations are relatively heterogeneous and are composed of three main aquifer horizons separated by semi-permeable to impermeable strata. The main productive levels are located either in the carbonates levels of the Upper Cenomanian Zebbag Formation and Upper Senonian Abiod/Berda Formation in the mining region.

* Zebbag Formation (Cenomanian–Turonian): represented by two distinct members: to the bottom, dolomite and chalky dolomite with a thickness varying between 100 and 250 m and to

the top by intercalations of marls, clays, gypsum and thin levels of limestone. The thickness of the superior member of this formation varies between 200 and 400 m.

* Abiod/Berda Formation (Campanian–Maastrichtian): the Upper Senonian is formed by a white fissured limestone, reaching a thickness of 100 to 400 m. The lower Senonian starts by an intercalation of limestone and gypsum and can reach a thickness of 500 m in the North of the basin. The Upper Cretaceous aquifer is confined. It is mainly drained through several springs near or in the ranges with a flow varying between 0.5 and 15 l s⁻¹. This reservoir is characterized by fractured limestone locally suffering dissolution and grading to karstic system, which is frequent in Gafsa basin (Henchiri and S'Himi, 2006; Ahmadi, 2006; Hamed et al., 2012a). Karst aquifers are known to be highly heterogeneous, formed by a complex conduit system that is generally impossible to locate. Moreover, the resources are very hard to exploit, with permeability coefficients ranging from 10⁻⁸ to 10⁻¹ m s⁻¹, and flow velocities ranging from a few centimeters a day to hundreds of meters an hour (Redouania et al., 2012; Hamed et al., 2012b; Inoubli, 2014). Note, however, that karst aquifers can be particularly favorable for very high exploitation rates when adequate wells are located close to springs, as is the case, for instance, at the karst spring in Tunisia (Shimi, 2000; Hamed et Dhahri, 2013; Hamed et al., 2013c; Inoubli, 2014). Karstic rocks outcrop of Gafsa mountainous areas contribute to the increase of biological richness because they contain many local and microhabitats. In these lands especially depressions are also the refuge areas of some endemic and relict plants and their communities.

* Metlaoui Group (Eocene): The Eocene corresponds to a prolific period for the development of nummulite carbonate platforms along the continental margins of the Tethyan Ocean (Tlig et al., 2011). In the Mediterranean basin, these carbonates compose important reservoirs of:

hydrocarbon (offshore Gabes Gulf of Tunisia), phosphate (El Kef, Maknassy and Gafsa basins), gypsum (Maknassy basin) and marle rock (Beja and kairouan basins). Concerning the hydrogeological potentiality, it formed a good reservoir of groundwater (quantity and quality) in NW Tunisia (Hamed, 2004, 2012; Hamed et Dhahri, 2013; Inoubli, 2014). But in the SW Tunisia this potentiality is not good (Hamed, 2009a). This is due to the effect of several factors (tectonic, climatic, sedimentological...).

The Mio–Plio–Quaternary (MPQ) aquifers

* The Miocene aquifer (Beglia Formation): formed by the continental material coarse sand with thin levels of red clays and sands, which indicate clearly a humid paleoclimate and a paleogeography dominated by perennial fluvial system. The thickness of sand ranges from 50 to 400 m, the maximum thickness is observed in the Berka region located in the south of Moulares region. The discharge from the aquifer occurs by vertical percolation at the Sebkhia surfaces, upwelling at natural springs and spring mounds, and upwelling from water wells. Most of this discharge is concentrated on southern Tunisia around Chott Djerid in the South, where natural upwelling occurs at a relatively constant rate throughout the year (Coque, 1962; ERESS, 1972). The principal areas of recharge are located in (i) Meridional Tunisian Atlas Mountains, (ii) in Dahar uplands (Tunisia) and Tunisian Atlas strongly tectonized where the Senonien fractured calcareous formations are outcropping (due to the presence of both primary and secondary porosity and permeability of the carbonate rocks), by infiltration (iii) from *wadies* (recent and fossil) flood waters downstream of the southern Atlas and (iv) from the sub-vertical faults (Bed dip $\approx 80^\circ$) where we can observe the maximum of the compression (example of Negrine-Tozeur fault in the Chebika area) (Fig. 2a).

* The Pliocene–Quaternary aquifer (Segui Formation): formed by the heterogeneous material “clay, sand, conglomerates and pebbles”. This formation is considered as the footwall of

quaternary sequence and has been reached by several wells. Quaternary formation is much thicker than 400 m at northern part of the basin (Sidi Boubaker region) and formed by alternation of sands, clay sands and sandy clays with two major gypsum intercalations to the base and to the top of this series (Hamed, 2011; Hamed et al., 2013a,b). This facies is interpreted as the result of important periods of aridification, probably interspersed with other humid periods. These results were confirmed in SE Tunisia (J. Haidoudi; belonging to the continuity of the northern Chott ranges). In this last area, the effect of tectonic “70°<Bed dip<85°”, geothermal “± 90°C” and climate are very important. The climate change was confirmed in terrestrial and in marine environment (Kallel et al., 1997a, 2000; Jedoui et al., 2001; Hamed et al, 2013c).

* The MPQ deposits contain a shallow aquifer, which is exploited especially in irrigation use in mining Gafsa basin. This aquifer is essentially recharged by the excess of irrigation water coming from C.I and C.T deep aquifers, in oases area. Out of these agricultural zones; the MPQ aquifers are recharged during the rare rainfall events. The transmissivity of the Miocene aquifers (Beglia Formation) ranges from $18.7 \cdot 10^{-4}$ to $54 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$ and $0.33 \cdot 10^{-4}$ to $53 \cdot 10^{-4} \text{ m}^2 \text{ s}^{-1}$ concerning the PQ aquifer (Segui Formation). The permeability varies between $2 \cdot 10^{-4}$ and $6 \cdot 10^{-4} \text{ m s}^{-1}$ in Beglia Formation and it is between $8.5 \cdot 10^{-6}$ and $13 \cdot 10^{-5} \text{ m s}^{-1}$ in Segui Formation (Kachouri, 1988; Coba, 1994; Mamou and Hlaimi, 1999b; Abidi, 2007; Hamed, 2009a; DGRE, 2010; Mokadem et al., 2012, 2014). Probably, the increase of soil organic matter content can improve soil structure and texture, which increases soil porosity (especially macro and micropores: bacteriological activity) and permeability.

In the riverbeds, the C.T (Cretaceous and MPQ aquifers) gets recharged by direct infiltration through floods descending from the Gafsa and Metlaoui mountain ranges. In the

central basin, water ages dated by radiocarbon (^{14}C) indicate paleogroundwater of Pleistocene and early Holocene age (6,000–37,000 years), whereas younger water ages, at the fringes of the basin where C.T formations outcrop, are an indication of modern recharge (Edmunds et al., 1997). However, present recharge is low due to the arid to hyperarid conditions within the catchment and depends mostly on infrequent storm events. The shallow aquifers are found in the MPQ sediments and the alluvial fillings of the wadis, i.e. the beds of ephemeral wadies. They are recharged by vertical percolation from the confined C.T and by infiltration of excess irrigation water, as well as water from flood events that descend in the wadis from the surrounding mountains to the Chott Djerid (discharge area). The flow direction of the shallow groundwater is generally towards the Chott Djerid (N–S) (Hamed, 2009a). But, in the Sidi Ahmed Zaroug (east part of study area), an inversion of piezometric is observed caused by overexploitation of groundwater to the industrial sector of the complex CPG-GCT (Fig. 2c). In this part of basin, a “fossil, geothermal and mediocre” groundwater and an enrichment of H_2S , ^2H and Fluorure of C.I groundwater are detected (CPG-GCT, 2009; Hamed et al., 2012a,b). Groundwater abstraction from wells causes modifications in the piezometric head distribution and increased the hydraulic gradients towards the abstraction zone and so to let the aquifer supply the amount of water pumped. In the same way, that may cause or accelerate vertical migration of poor quality water from deeper aquifers and/or may cause also, an inversion of piezometric (Hamed et al., 2012a). The effect of pumping on the head distribution spreads in all directions and not only in the direction of the flow as it would be expected when comparing to surface water where with drawal affects only the downstream section of the wady (Ben Dhia, 1987, 1990; Hamed et al., 2013c). But, after the Tunisian revolution (2011-2014), the stopping of washing the phosphate caused the return of the initial stage like 1920 to 1980: upwelling of the geothermal water, increasing of the artesianism of groundwater in Sidi Ahmed Zaroug and the increasing of the number of

springs. Among the damage observed actually on 2014 in this region is the destruction of houses (increasing of the C.I. piezometric level) near J. Ben Younes affected by Tebessa-Gafsa faults.

The hydrodynamics of these aquifer systems are closely influenced by tectonics (Zargouni, 1985; Dlala and Hfaiedh, 1993; Ahmadi et al., 2006; Zouaghi et al., 2009; Hamed et al., 2010a,b). Thus, the basin is controlled by the major NW–SE trending fault system such as the Gafsa–Tebessa, Sehib, Negrine–Tozeur faults (Bésbés, 1978; Zargouni, 1985; Ben Ayed, 1986; Ben Dhia, 1990; Boukadi et al., 1991; Chalbaoui and Ben Dhia, 2004) and Tabeddit faults (Gouasmia, 2008; Hamed, 2009a) as well as the East–West fault system such as the Metlaoui faults (Addoum, 1995) (Fig. 1). The groundwater flow directions of the MPQ aquifers follow generally the surface water flowing. In fact, they are discharged into Chott El Gharsa salt lakes (Hamed, 2009a). Concerning the C.I aquifer, the Carbon-14 dating shows low activities to the south of the basin and high activities to the north, which suggest a general groundwater flow North-South toward Chott El Gharsa (620 km²) and Chott Djerid (10,000 Km²) depressions. These continental depressions formed during Late Miocene–Early Pleistocene time as a result of compression between the African and European lithospheric plates (Swezey, 2003). The center of the Chott El Gharsa lies at –20 to –30 m below sea level, whereas altitude of Chott Djerid is 10–20 m above sea level (Swezey, 2003). Chotts are considered to function as evaporation pumps. The special surface distribution of evaporites and the distribution of subsurface sediments are often related to artesian sources in the centers or at the edges of the basins and to the climate impact on groundwater (Pouget, 1968; Schulz et al., 2002).

Tectonic activity, changes in facies and in thickness of sedimentary deposits seem to play an important role in groundwater flow and hydraulic continuity. Lithologic variability in the aquifer may affect water chemistry and groundwater age distributions because of its effect on rock/water interactions and directions of groundwater movement (Mamou, 1990; Edmunds et al., 1997). This is visible in the Sidi Ahmed Zaroug region (estern part of the study area), where thickening of the units and lithological changes had an important influence on piezometry levels and chemical composition of groundwater (Fig. 2c).

4. Hydrochemistry study

4.1. Materials and methods

Sampling sites and sample collecting

Water samples for laboratory analyses were collected at the humid season (December 2006). A total of 56 groundwater samples were collected from the (Cretaceous and MPQ) wells with depths ranging between 20 and 800 m, 2 water samples were collected from the dams (El Khangua and El Oudeï) and 3 groundwater samples from phosphate lavatories (Moulares, Redayef and Metlaoui) (Fig. 1) (Yermani, 2000; Yermani et al., 2002; Abidi, 2007; Hamed, 2009a; Hamed et al., 2010a). Prior to sampling, all wells were purged in order to remove the stagnant portion and collect representative water samples. Temperature, pH, and electrical conductivity (EC) of the discharge water were measured *in situ* using a Consort C535 multi-parameter analyzer. After that, sample bottles were filled and kept in a refrigerator (4°C) upon collection. Cation and anion analyses were performed at the laboratory of “Water, Energy and Environmental: L3E” of the National Engineers College of Sfax (Tunisia), using a Dionex DX 100 ion chromatograph equipped with a CS12 and an AS14A-SC Ion Pac

columns and an AS-40 auto-sampler. The total alkalinity (as HCO_3^-) was determined by titration with 0.01 or 0.1 M HCl against methyl orange and bromocresol green indicators (APHA, 1998). Strontium ion was analysed using an inductively coupled plasma-atomic emission spectrometer (ICP-AES), Liberty 200AX-Varian on samples that had been filtered through 0.45- μm filters and acidified to pH 2 using 16 N pure HNO_3 . Samples revealing relatively high salinity (exceeding 3 g l^{-1}) were diluted before analysis. The ionic balance for all samples is within $\pm 7\%$. Ten water samples were taken for bacterial analysis and water quality parameter tests. These water samples were taken in sterilized bottles for analysis at the University Hospital of Sfax (UHS, 2011).

A limited number of water samples (35 boreholes) were selected for carbon isotope analysis (^{14}C and $\delta^{13}\text{C}$). Radiocarbon analyses were carried out at the laboratory of the National Engineering College of Sfax (Radio-analysis and Environmental of Sfax), Tunisia (Hamed, 2009a), by scintillation counting on C_6H_6 synthesised from BaCO_3 stripped in the field from 150 l of water samples. Results of ^{13}C analyses are reported in ‰ versus PDB (American Belemnite from Pee Dee Belemnite, North California, USA) (Coplen, 1996) standard and ^{14}C abundances are expressed as percent modern carbon (pmC) (Stuiver and Polach, 1977). The $\delta^{13}\text{C}$ was measured at the laboratory of the IAEA, by converting the DIC to CO_2 with 100% phosphoric acid (H_3PO_4). Analytical uncertainties are in the range of ± 0.3 for $\delta^{13}\text{C}$ and between 1 and 1.5 pmc for ^{14}C . Hydrogen and oxygen isotope analyses were performed in the laboratory of the International Agency of Atomic Energy (IAEA) in Vienna, by employing, respectively the standard CO_2 equilibration (Epstein and Meyada, 1953) and the zinc reduction techniques (Coleman et al., 1982), followed by analysis on a mass spectrometer. Oxygen and hydrogen isotopes analyses were reported to δ notation relative to Vienna-Standard Mean Oceanic Water (VSMOW), where $\delta = [(R_S/R_{\text{SMOW}}) - 1] \times 1,000$; R_S

represents either the $^{18}\text{O}/^{16}\text{O}$ or the $^2\text{H}/^1\text{H}$ ratio of the sample, and RSMOW is $^{18}\text{O}/^{16}\text{O}$ or the $^2\text{H}/^1\text{H}$ ratio of the SMOW. Typical precisions are ± 0.1 and $\pm 1.0\%$ for oxygen-18 and deuterium, respectively. Tritium (^3H) analyses were performed in the laboratory of the IAEA by electrolytic enrichment and liquid scintillation counting method (Thatcher et al., 1977). Tritium contents were reported in Tritium Unit (TU), in which one TU equals one tritium atom per 10^{18} hydrogen atoms.

4.2. Results and discussion

In situ measurements interpretation

In situ parameters such as pH, temperature, electric conductivity (EC) and total dissolved solids (TDS) together with analytical data of the major ions in groundwater samples are represented in Table 1. The groundwater pH values range from 5.52 to 8.1 and the temperature varies within a wide range of 15.8–39.1°C, indicating the combination effects of numerous factors, i.e. the depth to groundwater, the residence time in the flow system and/or the groundwater flow time from the recharge area. The EC and the TDS range from 0.37 to 11.2 mS cm^{-1} and from 0.47 to 6.85 g l^{-1} , respectively. Higher values of these parameters characterize wells located in the southern parts of the basin (discharge zones), especially in the Aguila, Berka and Tamerza, suggesting both the insufficiency of recharge in these parts and the relatively long-term water-rock interaction and the evaporation effect of El Khangua and El Oudeï dams (Tamerza zone); also, the anthropogenic activities (agricultural and industrial). Generally, TDS increases from the mountainous regions (the piedmont zone of the Gafsa chain in the North of the study area) towards the discharge area (southern part) (Fig. 3).

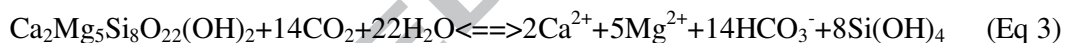
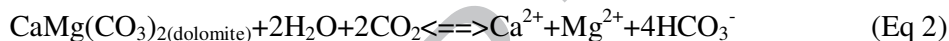
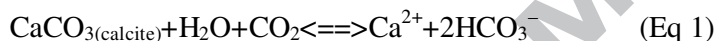
4.3. Factors controlling hydrochemical facies

Based on the contents of major cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (Cl^- , HCO_3^- , NO_3^- and SO_4^{2-}), three hydrochemical facies could be identified including facies 1: Ca–Mg– HCO_3 (predominant water type in the carbonate-rock aquifers because calcite and dolomite are abundant in these aquifers), facies 2: Ca–Mg– SO_4 and facies 3: Na–Cl– NO_3 . Water types were defined by use of the trilinear plotting technique (Piper, 1944); the trilinear diagrams are shown in figure 4.

To study the saturation state of the waters with respect to halite (NaCl), gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$), anhydrite (CaSO_4), calcite (CaCO_3) and dolomite $\text{CaMg}(\text{CO}_3)_2$ were performed using WATEQP (Plummer et al., 1976; Appelo et al., 1993). Most of the water sampled (85%) are saturated/undersaturated with respect to calcite and dolomite ($-0.2 \leq \text{SI}_{(\text{calcite})} \leq 1$ and $-0.6 \leq \text{SI}_{(\text{dolomite})} \leq 1$, Table 1). Carbonate dissolution may occur systematically for the majority of groundwater samples. For groundwater samples, there is an undersaturation state with halite ($-7.4 \leq \text{SI}_{\text{halite}} \leq -0.6$), gypsum and anhydrite (100%: $-5.8 \leq \text{SI} \leq 0.6$) (Table 1), indicating possible dissolution of these minerals. These eventual dissolutions were confirmed by strong positive relationships of Na versus Cl and Ca versus SO_4 as well as by the positive correlations between the SI of the referred dissolved minerals and some of ions resulting from each dissolution (Figs. 5 and 6). The plot of Ca versus SO_4 shows that most groundwater samples indicating obvious excess calcium (Fig. 6a). This excess can be attributed to the release of the Ca cation through the weathering of ancient silicate minerals such as plagioclase within the aquifer. In this region, plagioclase minerals are represented mainly by anorthite ($\text{CaAlSi}_2\text{O}_8$), which can release calcium through weathering (Hem, 1989). Another process that can account for the excess of Ca is the reverse cation exchange, occurring between

groundwater and Ca-clay minerals, such as illite, sepiolite and montmorillonite, which are relatively abundant in the MPQ aquifers. In fact, reverse cation-exchange process is confirmed through the plot of (Na+K-Cl) versus [(Ca+Mg) - (HCO₃+SO₄)], in which the two members vary in inverse proportions (especially for 95% of MPQ wells) (Fig. 7) (Mc Lean et al., 2000; Garcia et al., 2001; Hamed et al., 2008). The geochemical and hydrologic processes responsible for the various water types in the study area are discussed in the following sections:

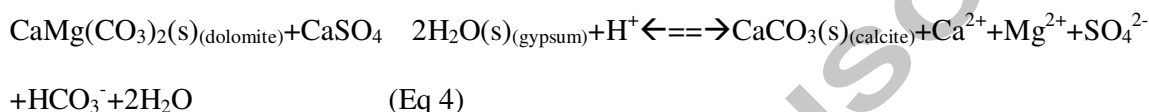
* Ca-Mg-HCO₃ WATER: this water type is predominant in the carbonate-rock aquifers (Lower and Upper Createcous), is generally produced by dissolution of the carbonate minerals (calcite and dolomite). The reaction of these minerals with water and carbon dioxide can be written as follows:



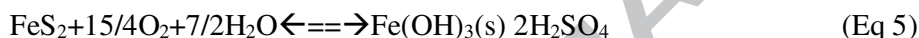
Bicarbonate is the dominant anion and represented greater than 65 percent of the anion composition of the samples (Fig. 4). Calcium and magnesium are the dominant cations, relative to sodium and potassium, and represented greater than 60 percent of the cation composition of these samples. The major ion composition of the water in these samples can be classified as calcium-magnesium-bicarbonate.

* Ca-Mg-SO₄ WATER: the predominant water type in the center part (Berka zone) of the study area is Ca-Mg-SO₄. The predominance of sulfate over bicarbonate and the lack of agreement of the Ca-Mg-SO₄ water with the simple dolomite dissolution model indicate that

other processes are controlling the chemistry of this water type. Two reactions can produce this type of water: (1) dedolomitization, which involves dissolution reactions with carbonate minerals and gypsum, and (2) sulfuric acid neutralization, which involves dissolution of carbonate minerals with sulfuric acid generated by the oxidation of pyrite which comes from the phosphate rock (Chaabani, 1995; Ounis et al., 2006; Felhi et al., 2008; Felhi, 2010; Aloui et al., 2012; Tlili et al., 2012). Dissolution of dolomite causes increases in the concentration of magnesium in the water. The overall reaction can be written as:



Dedolomitization is not the only process. An alternative model involves dissolution of dolomite by sulfuric acid (H_2SO_4) produced by the oxidation of pyrite (FeS_2):



The sulfuric acid reacts with dolomite:



Calcium and magnesium are the dominant cations, relative to sodium and potassium, and represented greater than 70 percent of the cation composition. The sulfate is the dominant anion for water samples of this type and represents 49 to 88 percent of the major anion composition. The major ion composition of the MPQ samples can be classified as calcium–magnesium–sulfate water.

* Na–Cl–NO₃ WATER: this water type predominates in the discharge zones (El Guettar, Aguila-El Jar, Garaat Douza and Berka) reflects the dominance of sodium and chloride; and the influence of land use activities (excess of NO₃) on groundwater mineralization (agricultural regions, where flood irrigation is applied). However, this water type is rare in other parts of the study area.

4.4. Sources of the groundwater degradation

4.4.1. Agricultural activity

Agriculture can have a significant impact on the quality of groundwater. Nitrate pollution of surface water is of high concern as it may have negative impacts on water supply and ecosystems (Rouabhia et al., 2004, 2008a; Hamed, 2009a; Ben Moussa et al., 2010a; Darwish et al., 2011; Diédhiou, 2012; Hamed et al., 2013a). Nitrate (NO_3^-) is a familiar pollutant in groundwater. Large amounts of nitrate in drinking water are a cause of fatigue, nephropathy, circulatory problems, damage to the eyes, methemoglobinemia (also known as blue baby syndrome) and a blood disorder primarily affecting infants under 6 months of age (Bengtson and Annadotter, 1989; Avery, 1999; Atabey, 2005a). As nitrate contamination is related to human, animal, or industrial waste practices, excessive levels of nitrate in drinking water may indicate the presence of other types of contaminants, which may cause health problems. Therefore, nitrate concentration is an important criterion of groundwater quality. Furthermore, nitrate is one of the important parameters that can be traced easily and used for assessment of contamination risks due to its low degree of attenuation of the contaminant load in the soil matrix and water (Purves, 1985; Pontius, 1993). In the mining Gafsa basin unconfined aquifer, about 65% of samples have nitrate concentration that exceeds the drinking water standards of 50 mg l^{-1} for the adults and 25 mg l^{-1} for the children (WHO, 2006). The average value of nitrate in the whole groundwater samples is 120 mg l^{-1} . These high nitrate concentrations provide evidence for the significance of the return flow waters contribution in the recharge of the unconfined aquifer. Hamed (2009a) found that nitrate concentrations in groundwater were highest in areas where wastewaters were present in a Berka zone (perennial Tabeddit wady: $16.5 \text{ Mm}^3 \text{ year}^{-1}$) and in Aguila-El Jar oasis. Indeed, ammonium nitrate, liquid fertilizer and other commercial complex nitrogen fertilizers are used in large scale in the

agricultural regions to enhance productivity due to rapid population increase and development of technology, where flood irrigation is applied. In these regions, NO_3^- contents are up to 300 mg l^{-1} (Figs. 2b and 2c). The excessive use of $\text{Ca}(\text{NO}_3)_2$ fertilizers is verified through the well-defined relationship between NO_3^- and Ca^{2+} (Fig. 8a). Similarly, the well-defined relationships in the plots of NO_3^- versus SO_4^{2-} and Mg^{2+} versus SO_4^{2-} suggest that N and S are used in the study area in the form of $(\text{NH}_4)_2\text{SO}_4$, MgSO_4 and superphosphate: $\text{Ca}(\text{H}_2\text{PO}_4)_2 \cdot \text{H}_2\text{O} + \text{CaSO}_4$ fertilizers (Figs. 8b and 8c), pesticides (atrazine “ $\text{C}_8\text{H}_{14}\text{ClN}_5$ ”, deethylatrazine, simazine, metolachlor, and prometon were detected more frequently in the areas); and also from organic matter of phosphate rock (Gi-Tak, et al., 2004; Bohike et al., 2007; Hamed, 2009a; Hamed et al., 2013a,b).

Aguila, El Jar-Lalla and Berka (discharge area: Figs. 2b and 2c) are the regions that suggest the infiltration of effluents from septic tank, wastewater and open dumping site. Even though ammonium is not found in groundwater; bacterial population strongly suggests the source of ammonium from surface contamination sources. In addition, as per the reaction kinetics, NH_4^+ undergoes rapid oxidation to NO_3^- in the presence of oxygen; hence, NH_4^+ seems to be below detection limit in this aquifer. Under oxic conditions, ammonium is readily oxidized to nitrate by the nitrification process ($\text{NH}_4^+ + 2\text{O}_2 \rightarrow \text{NO}_3^- + 2\text{H}^+ + \text{H}_2\text{O}$) (Eq 7). Nitrate also can be generated by aerobic decomposition of organic matter “phosphate sediments” ($\text{C}_{106}\text{H}_{263}\text{O}_{110}\text{N}_{16}\text{P} + 138\text{O}_2 \rightarrow 106\text{CO}_2 + 16\text{NO}_3^- + \text{HPO}_4^{2-} + 122\text{H}_2\text{O} + 18\text{H}^+$) (Eq 8) (Belayouni, 1983; Felhi et al., 2008). Groundwater affected by nitrification and decomposition organic matter will show negative relationship between pH and NO_3^- (Tables 2 and 3) due to acidic protons that originate in these reactions (Hamed et al., 2013a).

4.4.2. Industrial activity

In the Gafsa mining basin, soil contamination by metals and dust has become a widespread serious problem in many area of this basin, including M'Dilla, Moulares, Redayef and Metlaoui cities. Among these, phosphate mine activity is considered as one of the most famous and dangerous anthropogenic activities in Tunisia (contamination of soil, air, water, and degradation of land resources) (Hamed, 2009a, 2011). Dental fluorosis is an irreversible condition caused by excessive ingestion of fluoride during the tooth forming years (drinkable water, tea and alcohol consumption "70% of the population in the study area", proteins deficiency, climatic conditions, etc.). It is the first visible sign that a child has been overexposed to fluoride. Fluorosis is a considerable health problem worldwide, which is afflicting millions of people in many areas of the world, for example, East Africa (Nanyaro et al., 1984; Gaciri and Davies, 1993; Gizaw, 1996), Turkey (Oruc, 2003), India (Subba Rao and John Devadas, 2003; Gupta et al., 2005; Jacks et al., 2005), southeastern Korea (Kim and Jeong, 2005) and Morocco (Msefer and Hamza, 1999). According to World Health Organization (WHO, 2006), the limit value for fluoride is 1.5 mg l^{-1} . Similarly, the high fluoride concentration in groundwater has now become one of the important toxicological and geo-environmental issues in the most part of the arid and semi-arid areas in the North of Africa and especially in Southern Tunisia (mining Gafsa basin: El Guettar, M'Dilla, Metlaoui, Moulares, Redayef and Djerid regions). The occurrence of the high-fluoride groundwater seriously threatens the drinking water safety of the local inhabitants, and is one of the important reasons for the scarcity of the fresh groundwater in the region. Due to the threat to human health, a series of studies in high-fluoride groundwater have been conducted to indicate the high concentration of fluoride in groundwater, to improve the management of the water resources, and to reduce the risk of the fluorosis hazards in the some arid areas in Tunisia (Kamel et al., 2008; Hamed, 2009a; Tarki et al., 2010; Ben Moussa et al., 2010a,b; Mokadem et al., 2012, 2014). In the study area, the fluoride concentration (2.10^{-2} – $10^{-1} \text{ mg l}^{-1}$)

was detected in 75% of the drinking-water samples (Hamed and Ben Sâad, 2010; Ben Sâad, 2012) and especially in M'Dilla-Moulares-Metlaoui zones (mining regions).

In the study area, cadmium ($10^{-2} - 2.10^{-2}$ mg l⁻¹) was detected in 45% of the drinking-water samples located in the South of study area and especially in M'Dilla-Moulares-Metlaoui zones (mining regions). The high Cd concentration was observed in relatively shallow boreholes near the discharge zones. Contamination of drinking-water may occur as a result of the presence of cadmium in phosphate sediments (apatite) (Friberg et al., 1986; Chaabani, 1995; Felhi, 2010; Tlili et al., 2012). Caused effects on fertility, DNA degradation (mutation: decreased fidelity of DNA synthesis), increased tumour of the prostate (cancer especially as the CPG-GCT employee), resorption function of the proximal tubules, the first symptom being an increase in the urinary excretion of low-molecular-weight proteins, known as tubular proteinuria. Other possible effects include aminoaciduria, glucosuria, osteomalacia and phosphaturia (especially for the women after monopooses: 65%), haematopoietic system and immune, respiratory, and nervous systems (Sittig, 1985; Hamed and Ben Sâad, 2010). Cadmium is present also in ambient air (atmospheric pollution), soil (polluted soil “this may be due to strong adsorption of Cd by the surface soils which have higher organic matter content” or irrigated with polluted water “recycling water: phosphate wastewater and/or wastewater treatment”) and food in the form of particles in which cadmium oxide is probably an important constituent. Use of contaminated water in food preparation can result in contaminated food, because high cooking temperatures do not affect the toxicity of most chemical contaminants (Howari et al., 2001; Banat et al., 2005; Ben Sâad, 2012). This contamination by Cd has also observed in marine area in Gabes Gulf “Gabes and Sfax basins” (industrial coast, eastern border of the mining Gafsa basin) with different degrees, and caused many health problem (Barhoumi et al., 2009).

Strontium (Sr), is especially dangerous to humans because it tends to accumulate in calcium dependent bone marrow tissues. This element is generally used as a tracer due to its geochemical characteristics. Calcium (Ca) is readily absorbed by the body for the building of bones. Since calcium and strontium are in the same atomic group ($A.R_{Ca} = 0.197 \text{ nm}$; $A.R_{Sr} = 0.215 \text{ nm}$), they have similar physical and chemical properties. The body, therefore, has a hard time distinguishing between the two and strontium is absorbed just as though it were calcium. The Sr values range from $1.4 \cdot 10^{-2}$ to $6.1 \cdot 10^{-2} \text{ mg l}^{-1}$ with an average $3.7 \cdot 10^{-2} \text{ mg l}^{-1}$. These high concentrations provide evidence for the significance of the phosphate contamination (interaction water-host rock: recycling water in phosphate lavatories $\approx 0.2 \text{ mg l}^{-1}$). Groundwaters acquire Sr because of their interaction with Sr-bearing minerals such as celestite (SrSO_4) associated with gypsum, carbonate and clay minerals through adsorption and ion exchange reactions accompanying calcium (Ca) ion (Morgan-Jones and Eggboro, 1981). Enrichment of Sr in some waters could be related to the time of residence of MPQ groundwater (0.2 to 0.6 m year^{-1} : “piston flow” type transfer) (Hamed et al., 2008, 2010a), so that the ion is a good environmental tracer (Brondi et al., 1983). The correlation of SO_4 versus Sr (Fig. 9) shows a positive relationship with the MPQ groundwater and not with the Cretaceous groundwater, which indicates some Sr contribution from dissolution celestite (SrSO_4) associated with gypsum, and anhydrite (Faye et al., 2005). The mobility of these trace elements depends not only on the total concentration in the soil, but also on soil properties (texture and structure). This mobility is controlled by many others factors: chemical and biochemical processes, such as precipitation, dissolution, adsorption, oxidation-reduction, soil pH, exchange with organic matter and mainly by the climate effect.

4.5. Microbial pollution

The table 3 shows the results of the microbiological analyses arranged from the most contaminated wells to the least contaminated. Total coliforms, *E. coli*, enterococci, and *C. perfringens* were monitored as evidence of fecal contamination. Nine wells were positive for total coliforms and eight wells were positive for *E. coli* by the membrane filtration method. All wells were positive for both total coliform and *E. coli* by the Colilert Presence/Absence test kit. Seven wells tested positive for enterococci. *C. perfringens* was not detected in any well. The high permeability of Miocene Formation (sands), the alluvial deposits of phreatic aquifers and the low depth of wells (under 5 m) would have allowed for the transport of microorganism throughout the subsurface. Many existing on-site septic systems (Gafsa, Metlaoui, Moulares and Redayef regions) were installed in areas of thin to absent soils (recharge zone) (Figs. 2b and 2c). This study showed that microbial contamination affects wells in the surrounding rural area of mining Gafsa basin (Ben Sâad, 2012; Mokadem et al., 2012; Hamed et al., 2013a).

Tunisia is one of the largest phosphate producers in the world (more than 10 million tons per year since the early nineties). In the mining Gafsa basin, the phosphorites formed during the Paleocene/Eocene were found to be composed of apatite, calcite, dolomite, clay minerals (illite, smectite, sepiolite and kaolinite), quartz, opal-CT, and gypsum (occasionally) (Sassi, 1974; Chaabani, 1978; Tlig et al., 1987; Boujlel et al., 2008; Tlili et al., 2012). In Tunisia, phosphorite deposits occur in several areas, such as the North-South Axis (Nosa) and in the Gafsa-Metlaoui region. Gafsa basin is one of the most geologically investigated areas in southern Tunisia. Pollution of shallow aquifers by anthropogenic contaminants is becoming one of the central problems in the management of water resources. Figure 10 shows the characteristic anthropogenic contaminants (nitrate, sulfate, chloride, phosphate wastewater of CPG) in Quaternary and Tertiary aquifer systems in the area of Southwestern Tunisia,

(Hamed, 2009a). The substantial contamination observed in the Quaternary aquifers of this region is typical not only for highly industrialized regions, but is becoming apparent also in developing countries. Perhaps the high pollution is the one caused by nitrate originating from agriculture and wastewater from phosphate sector.

5. Isotopic study investigation

5.1. Oxygen-18 and deuterium data

The use of oxygen-18 and deuterium isotopes in hydrogeology offers information on the origin and movement of groundwater. It can offer an evaluation of physical processes that affect water masses, such as evaporation and mixing (Geyh, 2000). Although, the major constraint in the use of these isotopes is the availability of long-term stable isotope records of local rainfall that is fundamental for understanding the relationship between isotopic compositions of groundwater and precipitation input function. A general estimate, however, can be derived from data and study results from nearby areas. Data from the nearest Global Network for Isotopes in Precipitation (GNIP) station number 7622500, located at Sfax city, were used to establish the Local Meteoric Water Line, that follows the linear regression and the Regional Precipitation Mean Value for $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (-4.59 and -23.30% , respectively) (IAEA/WMO, 1999).

A representative set of groundwater samples was collected during February 2005 (Hamed, 2009a). Nine samples of isotopic analysis refer to the studies of Yermani, 2000 (North Gafsa basin) and Abidi, 2007 (Tamerza basin) (Table 2). A total of 37 samples were collected from boreholes tapping the MPQ and Cretaceous aquifers (70–800 m depth), shallow dug wells (5–50 m depth) and 2 samples were also collected but from water dams

(Fig. 1 and Table 2). The observed variation in stable isotope content in deep Cretaceous wells ranges from -7.43 to -5.46‰ for $\delta^{18}\text{O}$ and from -52.5 to -35.45‰ for $\delta^2\text{H}$. The stable isotope composition of MPQ aquifers is represented by 26 samples and ranges from -8.29 to -6.36‰ for the $\delta^{18}\text{O}$ and from -55.3 to -41.3‰ for $\delta^2\text{H}$ (Table 2). This isotopically difference attests to the heterogeneity of recharge modes and probably longer residence time in the aquifer (Gonfiantini et al., 1974; Fontes et al., 1983; Zouari et al., 2003; Zuppi and Sacchi, 2004).

In Fig. 11, the $\delta^{18}\text{O}$ and $\delta^2\text{H}$ data of all groundwater samples were plotted together with the Global Meteoric Water Line “defined by the annual average isotope compositions of precipitation at locations around the globe” (GMWL: $\delta^2\text{H}=8 \delta^{18}\text{O}+10$) (Craig, 1961; Rozanski et al., 1993) and the regional Meteoric Line of the Sfax city SMWL (SMWL: $\delta^2\text{H}=8 \delta^{18}\text{O}+13.5$) (Maliki, 2000; Celle et al., 2001), located at a distance of 150 Km in Mediterranean coastal eastern study area (Fig. 1). Some MPQ samples (64.16%), which plot mainly between the GMWL and the SMWL, indicating that these aquifers have been recharged by rainfall derived from a mixture of Oceanic and Mediterranean vapour masses (Fig. 1). The MPQ groundwater group (Group A: about 33.3%), characterized by the most $\delta^{18}\text{O}/\delta^2\text{H}$ -depleted contents. This indicated the old origin of the CT groundwaters in relation to their recharge during the paleoclimatic cooler regimes. Indeed, paleowater stable isotope signatures in the mining Gafsa basin, like all low-latitude semi-arid regions, are likely to be controlled more by precipitation amount and intensity than temperatures as in higher-latitude temperate regions (Clark and Fritz, 1997). These paleowaters are characterized by an excess of deuterium of 10‰ in contrast to the modern rainfall with a ^2H excess of 15‰ representing the lower humidity caused by primary evaporation in the vapor source as it moves from the Atlantic region (Sadek and Abd El-Samie, 2001; Edmunds et al., 2003; Andreo et al., 2004).

Moreover, the fact that the CT groundwater lies well below the meteoric water lines also indicates that the evolution of air masses was different to the present-day with little or no primary evaporation and probably little upcoming from its Atlantic Ocean source region which was isotopically enriched as a result of ice-cap formation (Andreo et al., 2004). On the other hand, the stable isotope results are also consistent with the those of carbon-14 (ERESS, 1972; Gonfiantini et al., 1974; Fontes et al., 1983; Mamou, 1990; Daoud, 1995; Guendouz and Moulla, 1996; Guendouz et al., 1997; Zouari and Mamou, 1997; Jedoui et al., 2001; Yermani et al., 2002; OSS, 2003; Edmunds et al., 2003; Zouari et al., 2005; Kamel et al., 2006; Hamed et al., 2008; Hamed, 2009a; Mokadem et al., 2012; Hamed et al., 2012b), which indicate that the main recharge of the C.T in Southern Tunisia and Algeria occurred during the Late Pleistocene and the Early Holocene periods. In North Africa, three major humid phases have been identified: (1)- the Early Würm pluvial (MIS 3) “70 to 40 ka before present”, (2)- the Middle Würm pluvial (MIS 3) “32 to about 22 ka before present” and (3)- the Late Würm pluvial (MIS 2) “18 to 11 ka before present” (Zuppi and Sacchi, 2004).

The second group (Group B: about 12.8%), constituted by the deepest Cretaceous boreholes and by those located near the major fault (Gafsa–Tebessa fault), was characterized by the more depleted contents of $\delta^{18}\text{O}$ and $\delta^2\text{H}$. Unusually, these samples (3 boreholes) are displaced to the left of both the GMWL and the SMWL and two boreholes are located between the two lines, which signify an enrichment of deuterium. Probably, that is due to an exchange with the organic matter of the marine formation (Metlaoui Group: phosphate sediment deposits during the Eocene period) “OM+Water \Rightarrow $^2\text{H}+\text{H}_2\text{S}$ ” (Eq 9). This groundwater is interpreted as contemporaneous recharge at the high-altitude surrounding mountains (Hamed, 2009a; Hamed et al., 2010a). Also, sulphate reduction can affect the isotopic composition of dissolved sulfate in groundwater. Sulphate reduction is mediated by

bacteria, which reduce sulfate to sulfide and oxidize organic carbon to CO₂ under anaerobic conditions. The sulphate-reduction reaction can be written as “SO₄²⁻+C_{organic}+2H₂O <==> H₂S+2HCO₃” (Eq 10). If the pH is greater than 7, HS⁻ will predominate over H₂S as the sulfide product. Bacterial sulphate reduction preferentially incorporates ³²S into the sulphide product, causing the residual sulfate to be enriched in the heavier isotope, ³⁴S. Thus, as sulphate reduction progresses, δ³⁴S of sulfide will be less than that of sulphate, and δ³⁴S_(sulfate) will increase relative to the original composition (Garrels and Christ, 1990; Boujlel et al., 2008; Tlig et al., 2011; Hamed et al., 2012b).

Between these two groups, we can be distinguished another group (Group C: about 48.8%). These points representing groundwaters of these aquifers are located almost parallel to the GMWL towards the paleoclimatic waters of the C.T aquifer suggesting an existence of mixing of two different end-members or a direct infiltration of recent precipitation through the faults and/or fractures. Southward of the Gafsa fault, the Miocene groundwater tends to be more enriched in δ¹⁸O and δ²H and this suggests an evaporation effect during recharge processes. This strongly supports the hypothesis about a vertical leakage of C.I deeper groundwater to the C.T aquifers (Fig. 2c). This process has been mentioned also by the geophysical studies in the Gafsa basin especially in Sidi Ahmed Zaroug basin (Zouaghi et al., 2009). Concerning the water dams (5.1%), the stable isotope composition of these waters is represented by 2 samples and ranges from -2.22 to + 1.64‰ for the δ¹⁸O and from -15.91 to + 0.56‰ for δ²H (Table 2). These waters are characterized by more enriched stable isotope contents, which could be explained by an evaporation effect. In these zones, the water that largely fractionates in the surface and/or subsurface (low depth) due to their long exposure to the atmosphere (recycling by evaporation), especially after siltation with mud (clogging of soil) and even the impact of arid climate in the study area (Abidi, 2007; Yermani, 2000;

Yermani et al., 2002; Hamed, 2009a; Hamed et al., 2010a, 2013c; Hamed et Dhahri, 2013). The localization of these two dams in the Tamerza basin and the others dams in the Bir El Ater basin (Algerian territory in the west) has improved the quantity of groundwater but the quality has deteriorated. This has influenced even the quality and the rentability of the palms "*Phoenix dactylifera*" and the Olive "*Olea europea L.*" in the Tamerza region (downstream of dams). But, it is not the case in the upstream portion of the dams. Currently there is a scientific project during realization (Khlifi, 2014), referred to find solutions to these problems in Tamerza basin.

5.2. Radiogenic isotope of water molecule

Tritium (^3H) is the only natural radioactive isotope of hydrogen. ^3H , a short-lived isotope of hydrogen with a half-life of 12.32 years, is a commonly used tracer for determining the age of groundwater less than 50 years old (Lucas and Unterweger, 2000). Most of tritium that was present in the atmosphere prior to thermonuclear testing in the 1950s and 1960s was the result of natural production in the stratosphere by the bombardment of nitrogen (^{14}N) by neutrons in cosmic radiation in the upper atmosphere (Clark and Fritz 1997; Solomon 2000). Most of tritium is produced in the high atmosphere (from 10 to 30 km of altitude) by the action of cosmic particles (protons and neutrons) on ^{14}N and ^{16}O (Le Goff et al., 2014). Incorporated directly into the water molecule in the global hydrological system, tritium is the only direct tracer for groundwater dating (Cartwright and Morgenstern, 2012; Morgenstern and Daughney, 2012). The natural background activity of ^3H in precipitation and surface water prior to 1951 varied between 2 and 10 TU (Von Buttlar and Libby, 1955; Thatcher, 1962; Roether, 1967; Plummer, 2005). The presence of tritium in water samples is a reliable indicator of samples that contain at least a fraction of post-1950s water (Plummer, 2005). From 1986 the Chernobyl nuclear disaster, also known as the nuclear accident at Chernobyl

nuclear accident is rated at Level 7, the highest on the International Nuclear Event Scale (INES) which took place April 26, 1986 in Central Lenin, located at the time in the Ukrainian (anthropogenic activities); Until today, due to the radioactive decay, groundwater derived from meteoric water that fell before the onset of atmospheric testing of nuclear weapons would have contained less than 0.75 TU. More recently tritium is increasingly being applied to calibrate and validate three-dimensional groundwater flow and solute transport models of aquifer systems at the regional scale (Orban et al., 2010; Zuber et al., 2011). Thus, if we consider the data of the tritium contents in precipitation collected in the Tunisian GNIP stations (Tunis-Carthage, no 6071500 and Sfax city, no 7622500) between 1968 and 2006 (IAEA/WMO, 2006), the ^3H contents in water from the study area, which vary from 0 to 8.23 TU (Table 3), suggest two recharge periods (Fig. 12) and of course this amount of ^3H will subsequently be detected on groundwater in the study area. Waters with ^3H contents below 2 TU likely represent pre-nuclear recharge (during the periods 1950s and 1960s). However, waters with ^3H contents between 2 and 6 TU originate either from post-nuclear recharge, that infiltrated before nuclear weapon tests, or from recharge occurring during the last two decades. Waters with ^3H contents under 6 TU represent the modern recharge. These results are also confirmed in the Northeastern of Tunisia, in Cap Bon basin (Ben Moussa et al., 2010b; Ben Hamouda et al., 2011) and by other scientific researches in North Africa and in the world.

5.3. Radiogenic isotope of DIC

In the hydrologic cycle, the natural source of carbon-14 is the atmosphere. The DIC in recharge water is assumed to be in equilibrium with the atmospheric reservoir of carbon-14 of approximately 100 percent modern carbon (pmC) or greater, and to have a stable carbon isotopic composition in equilibrium with carbon dioxide from soil zone respiration of plants

and oxidation of organic matter of approximately -21 to -25 per mil. Carbon-14 (^{14}C) is a naturally-occurring radioactive isotope of carbon, and was also produced by atmospheric thermo-nuclear testing during the mid-twentieth century, similar to tritium (Thatcher, 1962; Zuppi and Sacchi, 2004). ^{14}C radioactivity is used for the study of old hydrological systems in which groundwater residence times extend to ca. 30 ka (Clark and Fritz, 1997). The interpretation of radiocarbon data to obtain groundwater absolute ages is, however, largely complicated by the potential mixing with younger and older sources of carbon (carbon-14 originating from widespread nuclear testing and from interaction of groundwater with carbonate mineral, respectively) (Clark and Fritz, 1997; Edmunds and Smedley, 2000). As water flows from the recharge area into the confined groundwater system and becomes isolated from the atmospheric source of carbon-14, the concentration of carbon-14, which has a half-life of 5,730 years, decreases in the confined groundwater flow system by radioactive decay as a function of time. Therefore, carbon-14 concentration is partially an indication of the residence time of groundwater in an aquifer. The carbon-14 concentration of groundwater, however, can also be diluted with “radioactively dead” carbon derived from the dissolution of carbonate minerals and reduction of organic carbon in the aquifer, which complicates the calculation of age and the speed of groundwater and the results will be inefficient.

The ^{14}C activities vary widely from 3.00 to 75.3 pmC. 21% analysed samples show carbon-14 activities greater than 50 pmC. These relatively high activities lend support to the existence of an important fraction of organic ^{14}C , likely in relation with the infiltration of return flow waters, which largely affects the initial ^{14}C contents. However, they corroborate the recent origin of the shallow groundwaters in the study area. This evolution could be explained by a larger participation of a depleted source of carbon which could be organic matter in the deeper part of the aquifer system (Le Gal La Salle et al., 1996), or by different

recharge regimes (paleo-recharge). The available chemical and isotopic data allow construction of the conceptual models of groundwater migration within the C.T aquifers. Such a models are presented in Figs. 2 (a, b and c). In the mining Gafsa region the C.T groundwater is mixed with the C.I water ascending/upwelling through the fault system. This phenomenon is accelerating by the overexploitation of the industrial sector of the complex CPG-GCT. Stratigraphic, tectonic, hydraulic, climatic and anthropogenic conditions seem to be important factors controlling the geochemical evolution and the hydrodynamic of groundwater in the study area.

6. Conclusions

The decline of groundwater table was affected by extraction of groundwater in mining Gafsa basin may be due to the changes in the direction of groundwater flow in the basin that was caused by overexploitation. Human activities in the basin played a key role in the hydrological change of study area. Besides precipitation in the basin decreased between 1950 and 2014, which was another factor that led to water resources deficit and the decrease of groundwater water level and the decrease of spring outflow or even disappearance of springs/Foggara in the Southwestren Tunisia.

Based on the stable isotopes of water molecule ($\delta^{18}\text{O}$, $\delta^2\text{H}$ and $\delta^3\text{H}$) and radiogenic carbon activities in the DIC and $\delta^{13}\text{C}$, it was possible to identify various types of groundwater and mixing process in the system: (i) an old palaeoclimatic groundwater. This groundwater was likely recharged during the Late Pleistocene and Early Holocene periods under a cooler climatic regime; (ii) a relatively recent groundwater, that indicates the presence or the influence of modern water (less than 50 years) or possible contamination of a groundwater sample with modern atmospheric water vapor during sampling. This groundwater is

interpreted as contemporaneous recharge at the high-altitude surrounding mountains; (iii) a mixing groundwater resulting from the dominant upward leakage from the deep C.I artesian water table. Tritium contents in these groundwaters provide evidence to the presence of pre-1950 and post-1960 recharge periods. The homogeneity of the isotopic composition of large aquifers may reflect either very stable recharge conditions in time or very long residence time of water during which diffusion processes occurred and smoothed any past fluctuations, as is the case in the great regional North African aquifer "C.I" (Gonfiantini et al., 1974; Hamed et al., 2012a,b). The recharge of these aquifers in SW Tunisia generally occurs through three major mechanisms: (i) direct infiltration of rain and mining pollution (phosphate waste water); (ii) lateral and/or vertical percolation from (wadies, faults, fractures and dams) and (iii) upwelling from surrounding aquifers (C.I/C.T) (Hamed et al., 2013b,c).

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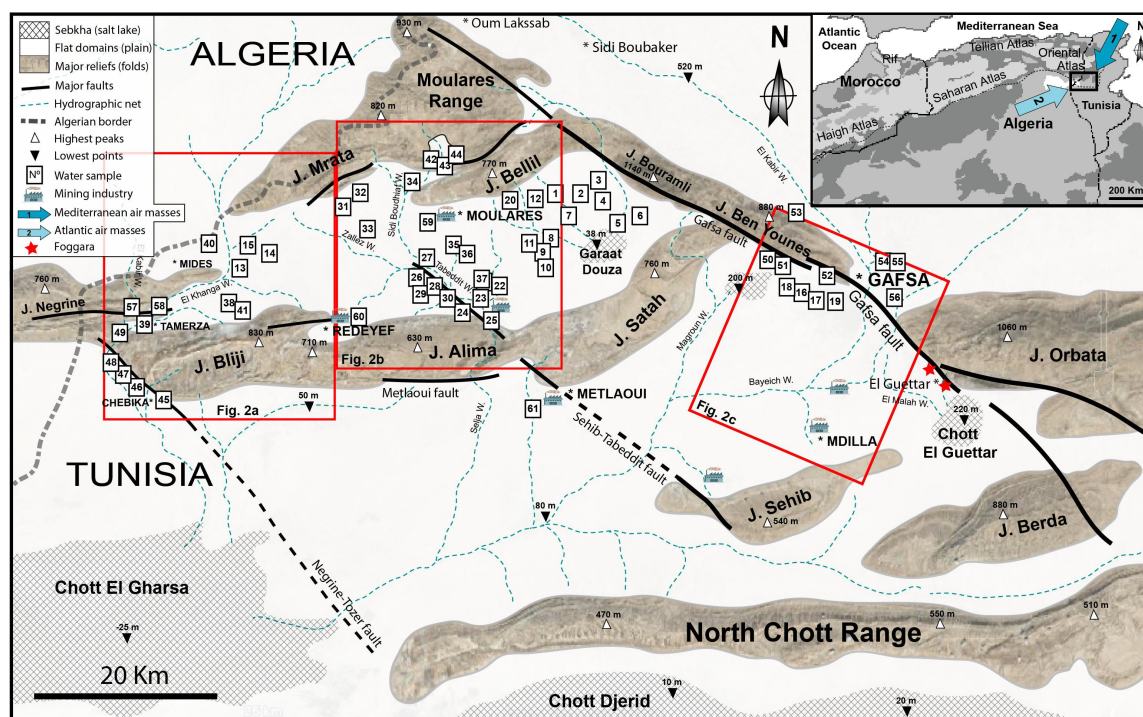


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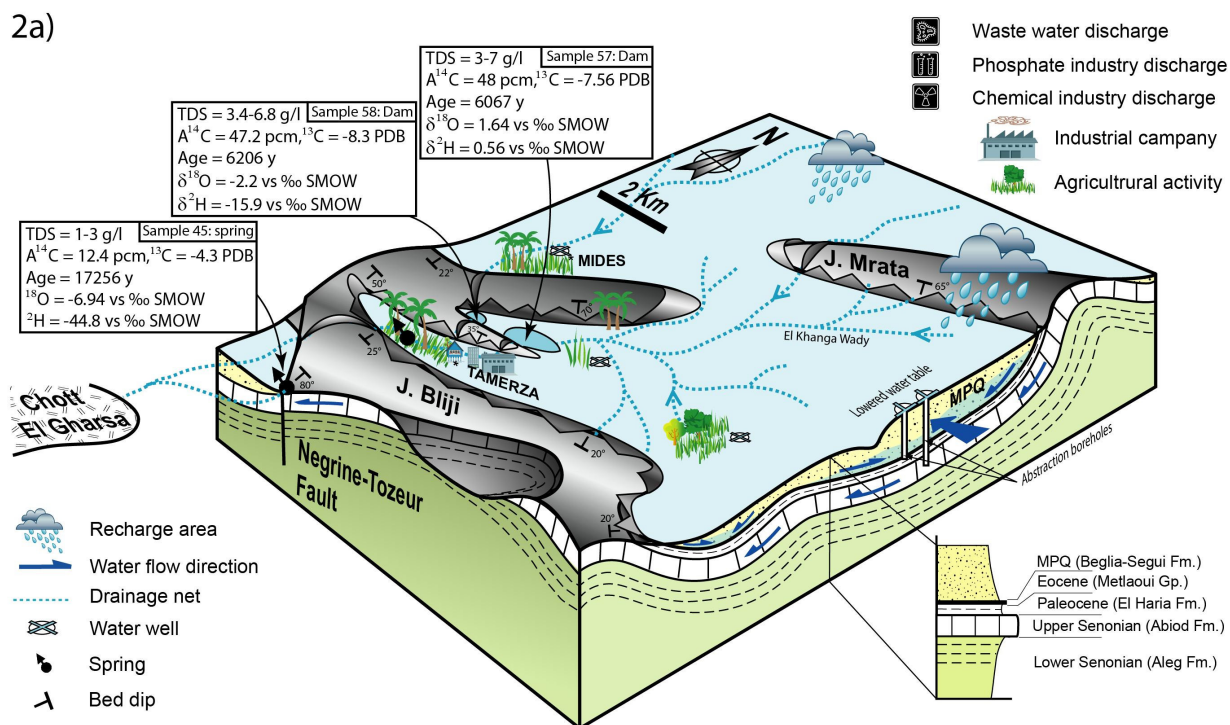


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2b)

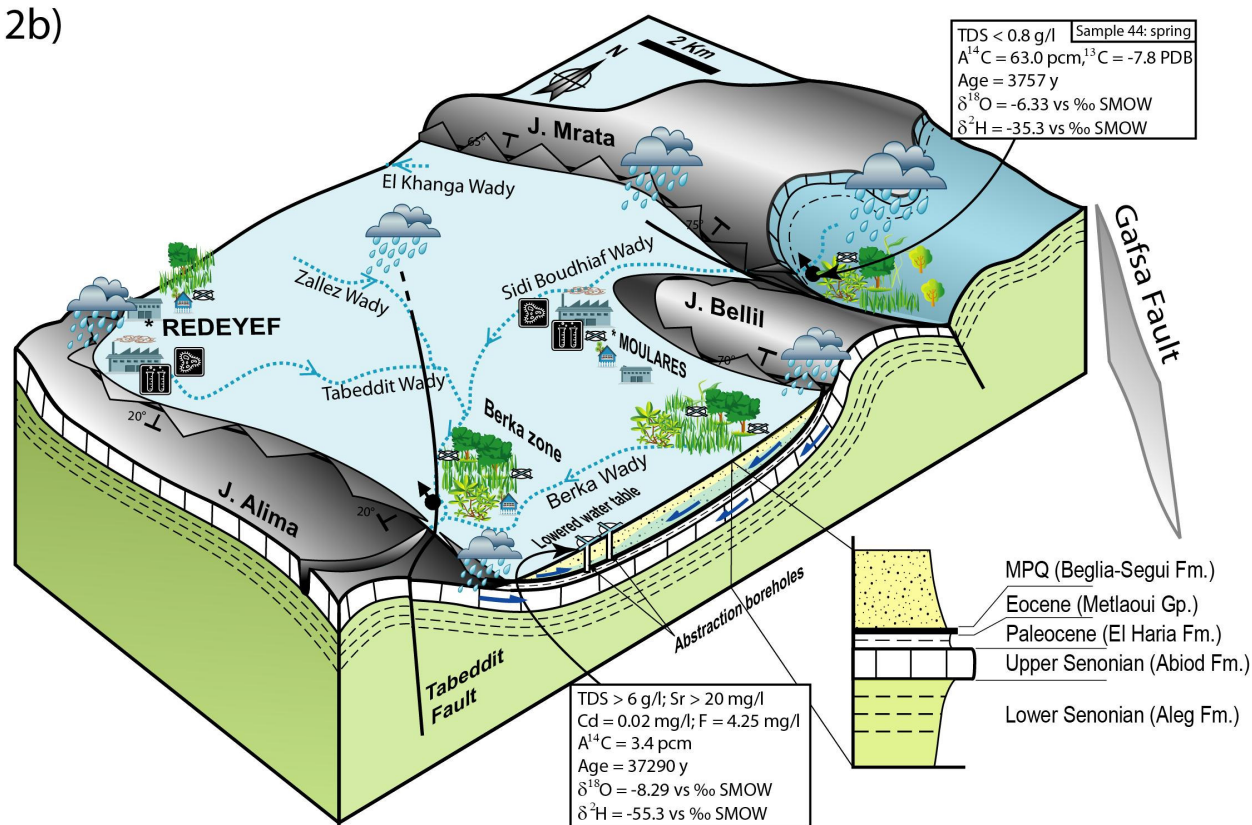
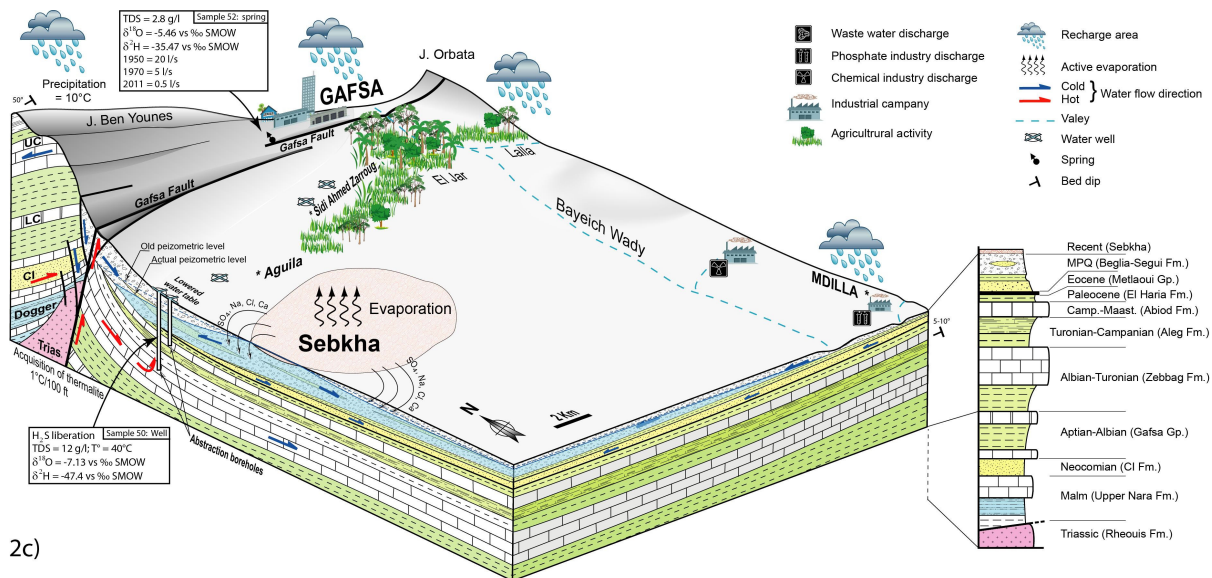


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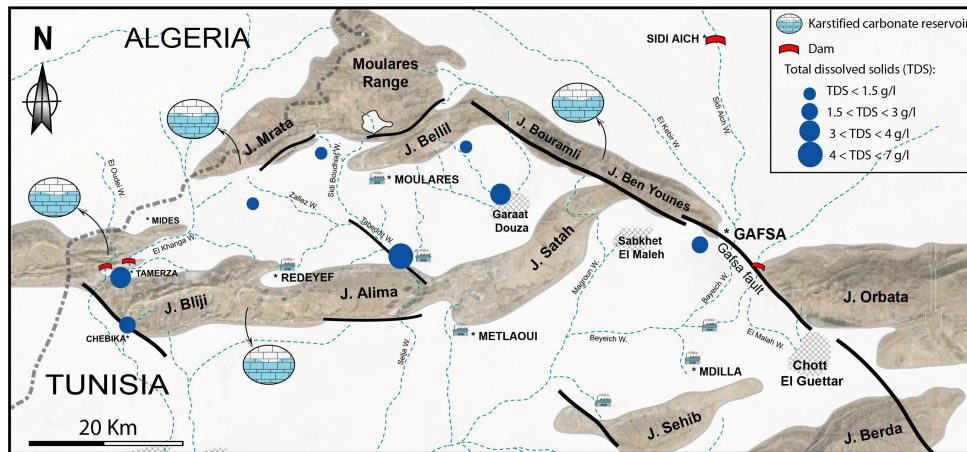


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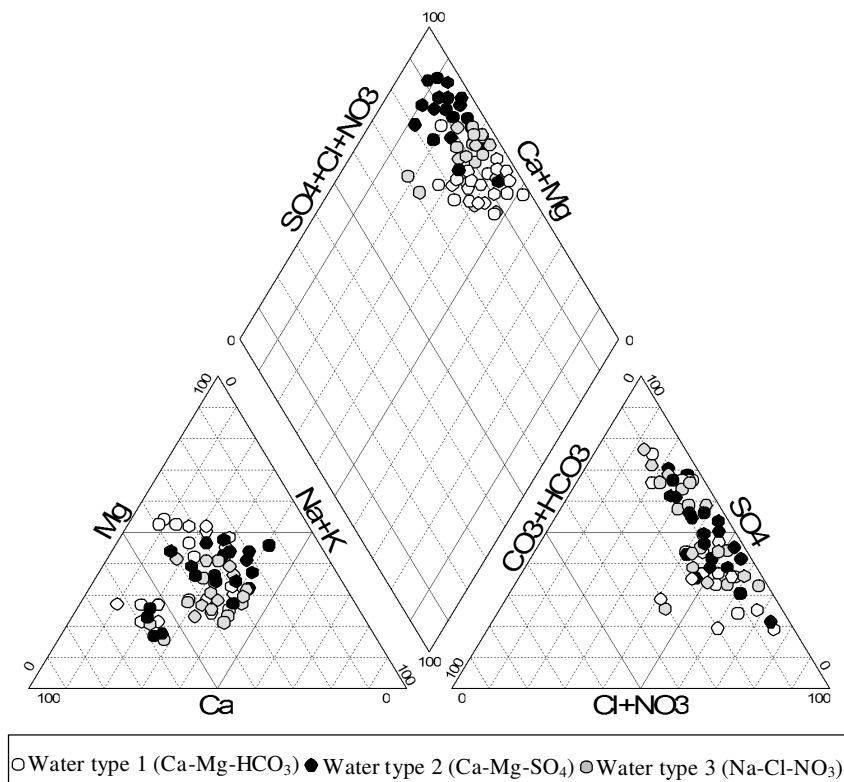


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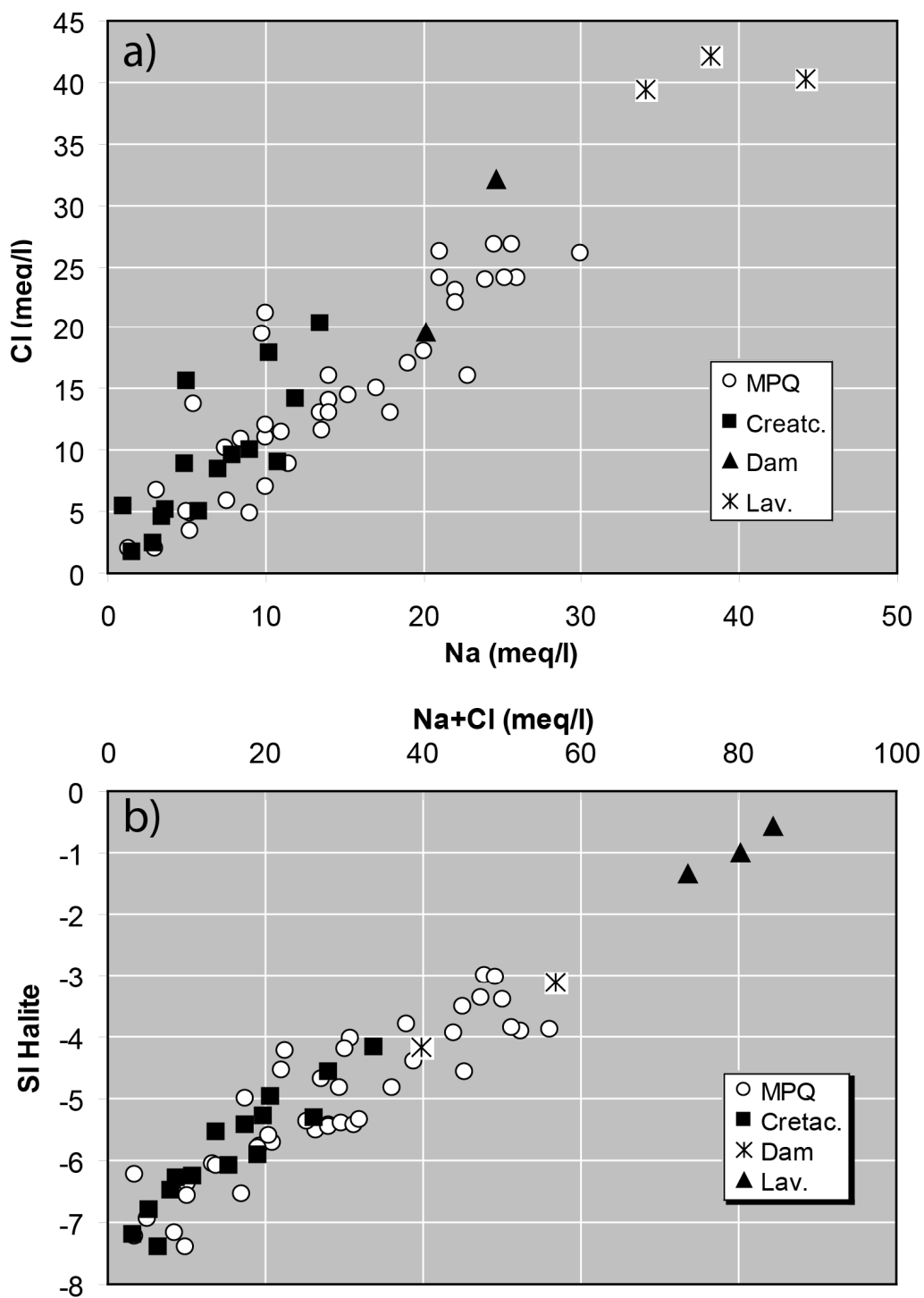


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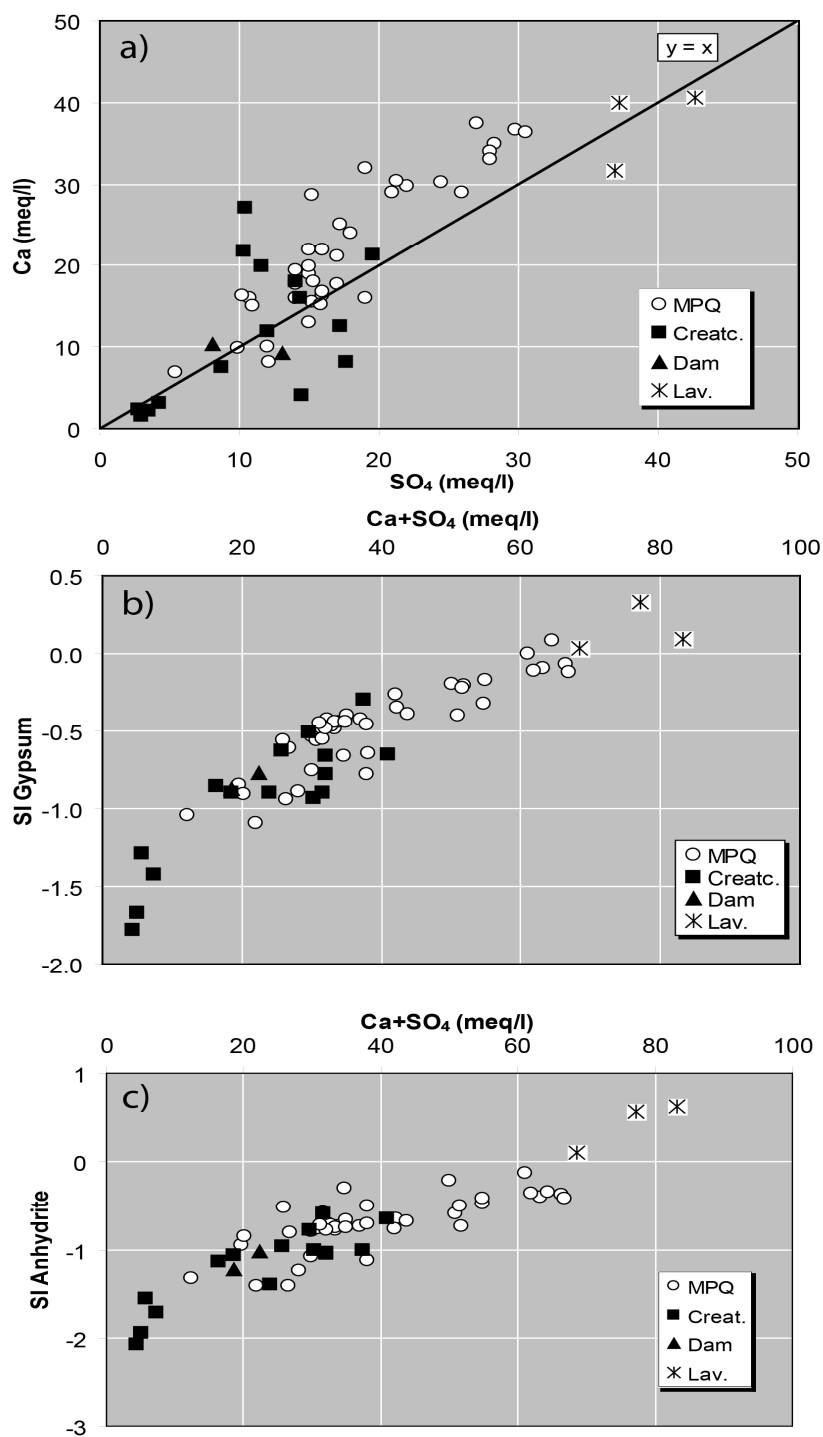


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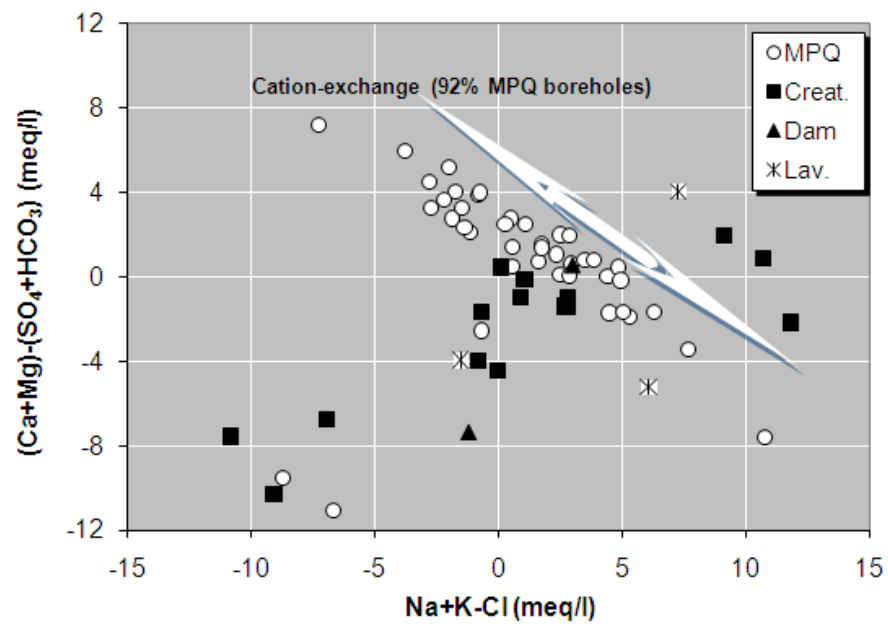


Fig. 7. Plot of $(Na^+ + K^+ - Cl^-)$ versus $[(Ca^{2+} + Mg^{2+}) - (HCO_3^- + SO_4^{2-})]$ showing reverse cation exchange process.

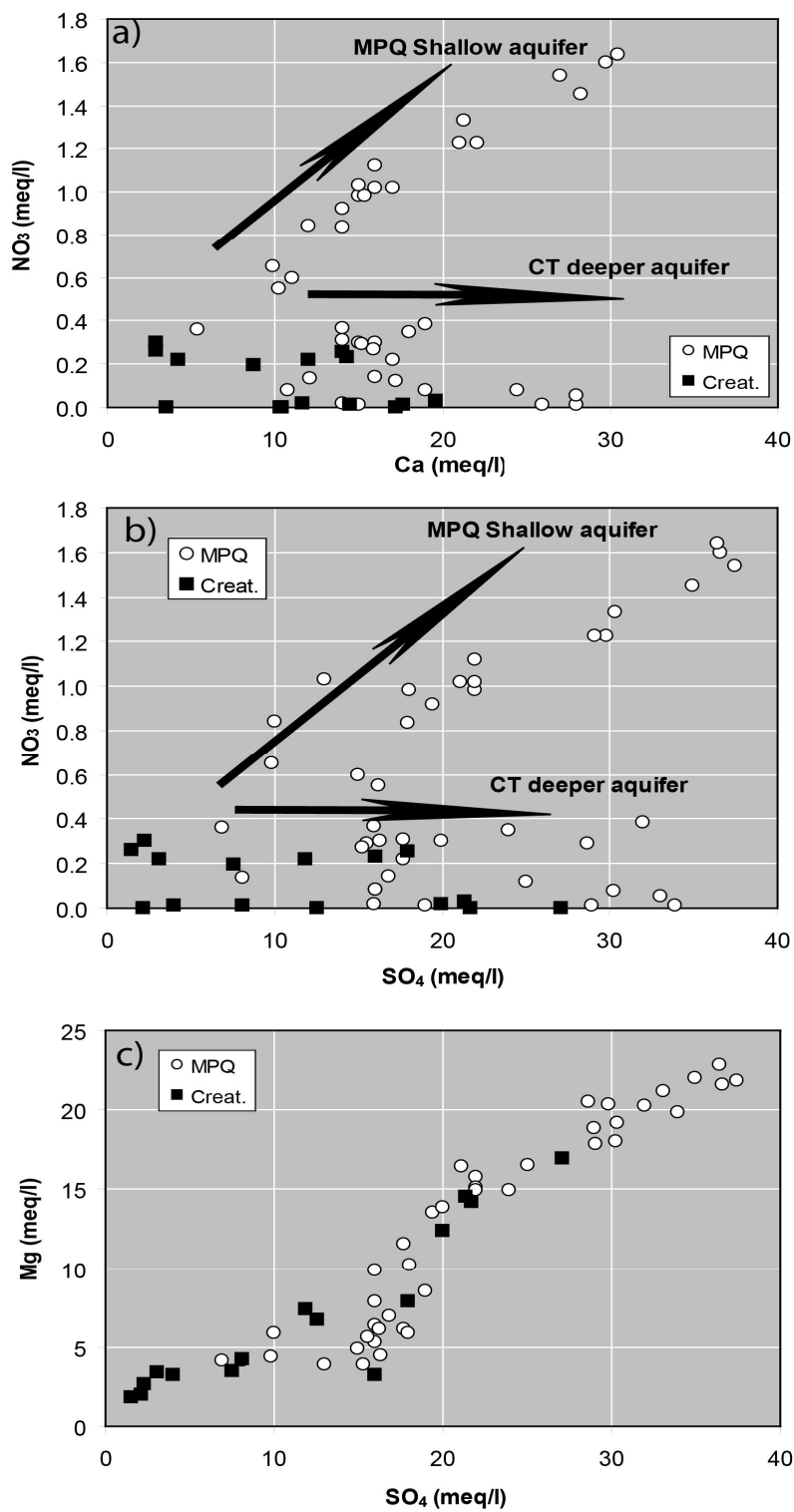


Fig. 8. Plots of Ca^{2+} versus NO_3^- (a), SO_4^{2-} versus NO_3^- (b) and Mg^{2+} versus SO_4^{2-} (c).

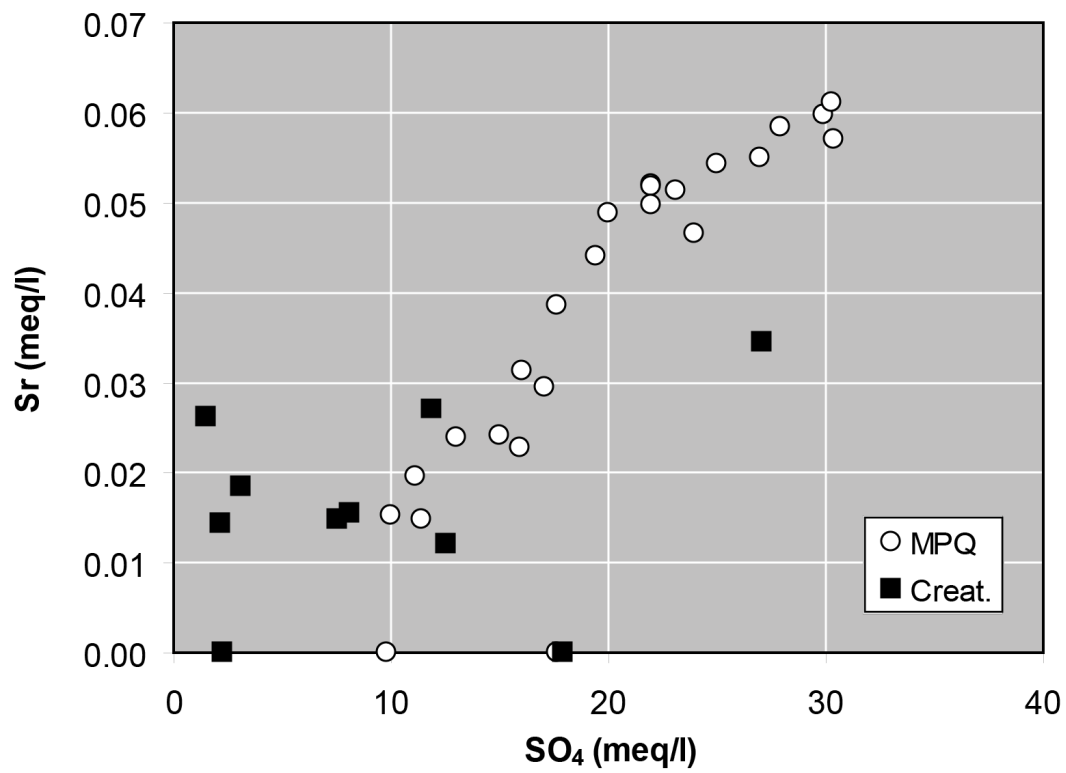


Fig. 9. Plot of Sr versus SO₄.

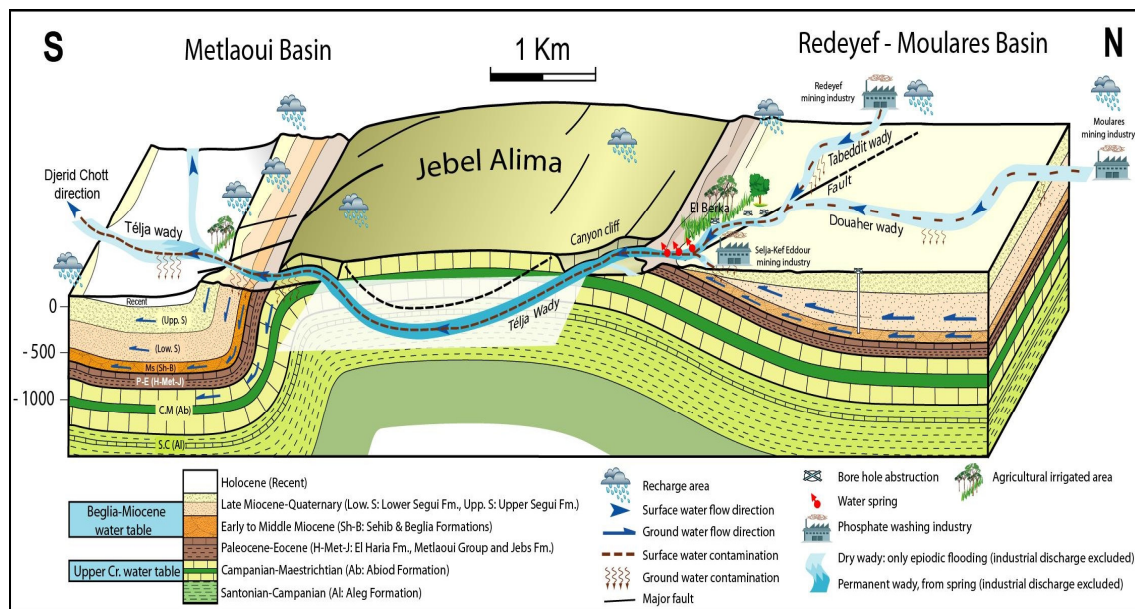


Fig. 10. Simplified diagram showing the anthropogenic impact on groundwater quality in the mining Gafsa basin.

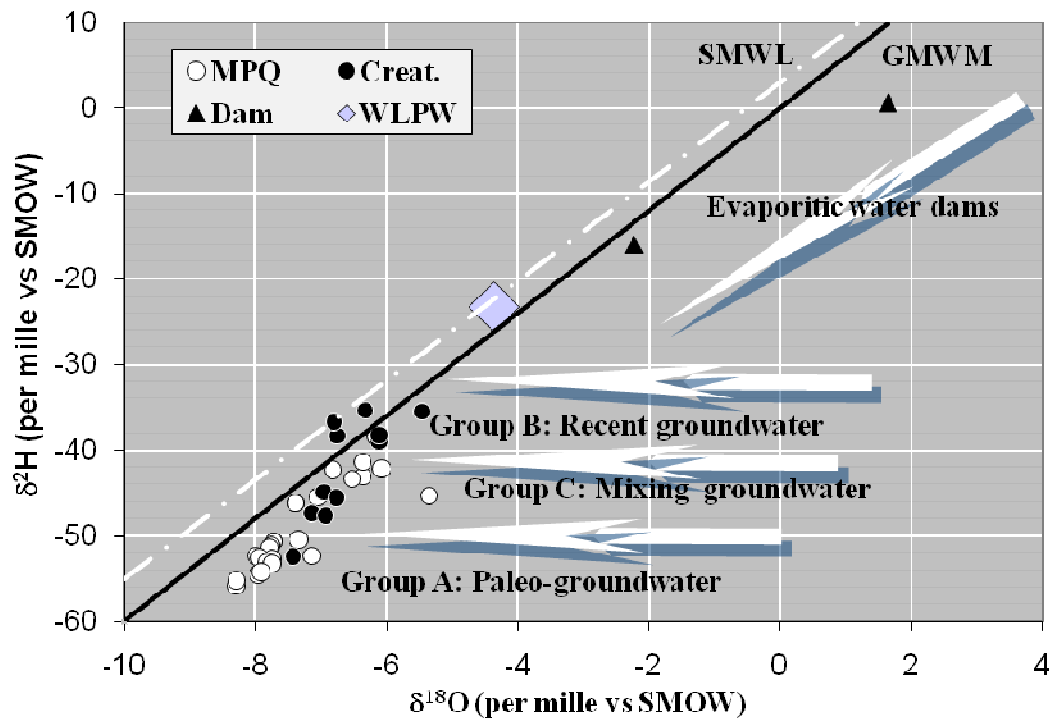


Fig. 11. $\delta^{18}\text{O}/\delta^2\text{H}$ diagram.

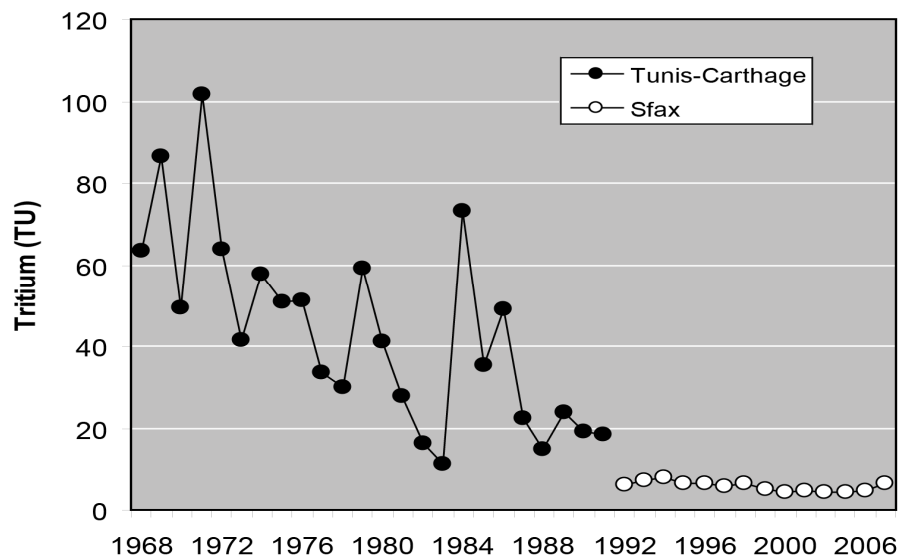


Fig. 12. Tritium contents in precipitation in Tunisian GNIP stations.

Table 1- *In situ* measurements and Saturation indexes of groundwater.

N°	aquifer	T (°C)	pH	EC (µS/cm)	TDS (mg/L)	Saturation Indexes (SI)				
						Halite	Gypsum	Anhydrite	Calcite	Dolomite
1	MPQ	19	7.75	2,35	2,35	-5.77	-0.48	-0.77	0.66	1.4
2	MPQ	17	7.33	3,51	2,6	-5.70	-0.42	-0.74	0.31	0.7
3	MPQ	18	7.56	4,2	3,85	-5.50	-0.35	-0.65	0.65	1.26
4	MPQ	18	7.80	4,99	3,84	-3.51	-0.17	-0.47	0.92	1.6
5	MPQ	18	7.84	2,94	2,28	-5.44	-0.44	-0.74	0.42	0.66
6	MPQ	17	8.10	5,25	6,85	-3.00	-0.09	-0.40	1.24	2.3
7	MPQ	18	6.20	1,585	1,56	-3.90	-0.07	-0.37	1.15	2.1
8	MPQ	20	8.01	1,95	2,01	-6.36	-0.42	-0.70	1.01	1.6
9	MPQ	22	8.03	7,2	5,38	-3.89	-0.11	-0.36	1.22	2.3
10	MPQ	21	8.04	3,23	2,4	-5.45	-0.53	-0.79	0.96	1.78
11	MPQ	21	8.00	2,95	2,4	-5.80	-0.40	-0.66	1.08	1.71
12	MPQ	22.3	8.01	2,8	2,3	-5.40	-0.47	-0.72	1.04	1.84
13	MPQ	21.2	7.45	2,458	2,45	-5.36	-0.56	-0.76	0.97	1.04
14	MPQ	22.6	6.10	2,35	1,479	-5.59	-0.85	-0.95	0.88	1.44
15	MPQ	23	7.90	1,825	1,152	-6.07	-0.91	-0.85	0.96	1.67
16	MPQ	22.2	6.87	1,785	2,254	-5.01	-0.44	-0.75	1.04	0.98
17	MPQ	21.4	7.01	1,94	2,15	-4.22	-0.64	-0.71	1.23	1.03
18	MPQ	19	7.11	2,53	2,14	-5.42	-0.20	-0.91	1.03	1.23
19	MPQ	20	7.00	1,94	2,25	-4.84	0.09	-0.84	0.98	1.02
20	MPQ	18.5	6.52	3,25	1,56	-4.04	-0.61	-0.80	-0.21	0.57
21	MPQ	20	7.04	370	3,8	-4.84	-0.44	-0.75	0.01	0.2
22	MPQ	19	8.20	889	3,53	-3.39	-0.40	-2.09	1.01	1.13
23	MPQ	19.4	5.80	1,23	4,76	-3.37	-0.32	-1.60	0.98	1.12
24	MPQ	18.7	5.52	783	3,49	-3.79	-0.78	-1.97	0.99	1.09
25	MPQ	21.8	5.90	1,17	2,67	-6.58	-0.89	-1.55	1.42	1
26	MPQ	22	7.72	1,59	1,34	-6.94	-0.56	-0.31	0.46	0.7
27	MPQ	18.4	7.90	599	2,3	-7.17	-0.55	-2.38	0.78	0.98
28	MPQ	16	7.30	1,71	1,12	-4.19	-1.09	-1.41	0.56	0.79
29	MPQ	20.8	5.90	1,5	1,04	-3.95	-0.20	-1.41	0.98	1.02
30	MPQ	19	7.80	1,18	2,78	-6.54	-0.26	-1.61	0.14	1.15
31	MPQ	17.2	6.00	591	3,47	-4.69	-0.46	-2.39	1.02	1.32
32	MPQ	20.9	6.10	5,65	4,85	-4.56	-0.22	-0.50	1.18	2.1
33	MPQ	19.2	7.42	3,55	2,6	-5.33	-0.48	-0.77	0.37	0.44
34	MPQ	18.7	6.30	660	512	-7.39	-0.66	-2.20	0.68	0.98
35	MPQ	20	7.50	11,2	1,6	-3.02	0.00	-1.13	0.96	1.03
36	MPQ	22	6.80	953	645	-4.54	-0.75	-1.67	0.78	1.01
37	MPQ	19	7.20	1,28	4,25	-3.86	-0.12	-0.41	0.70	1.21
38	MPQ	21.4	7.75	4,27	3,25	-4.41	-0.39	-0.68	0.68	1.59
39	MPQ	21.6	6.82	2,1	1,76	-6.09	-0.45	-0.72	0.80	1.09
40	MPQ	19.5	8.00	1,6	1,8	-7.24	-1.04	-1.32	0.49	0.95
41	MPQ	20	7.02	1,89	1,4	-6.23	-0.94	-1.41	0.78	1.45
42	Cret.	20.3	5.80	900	586	-7.40	-1.29	-1.56	1.76	1.67
43	Cret.	18.9	7.50	1,62	1,07	-6.09	-0.90	-1.40	0.96	0.99
44	Cret.	19.8	5.90	2,43	1,6	-5.90	-0.78	-1.06	1.06	1.07
45	Cret.	18.4	7.90	702	473	-7.20	-1.78	-2.07	1.03	1
46	Cret.	19.4	7.10	1,22	592	-6.80	-1.67	-1.95	1.74	0.87
47	Cret.	19.1	7.10	2,18	1,25	-6.30	-0.86	-1.14	0.76	1.01
48	Cret.	18.3	7.10	2,51	1,84	-6.47	-1.42	-1.71	1.06	1.04
49	Cret.	19	7.01	2,13	1,43	-5.54	-0.93	-1.65	1.32	1.08
50	Cret.	20	7.02	3,21	1,67	-5.32	-0.90	-3.77	0.89	1.32
51	Cret.	20.9	6.30	4,09	2,88	-4.98	-0.30	-5.85	1.29	1.41
52	Cret.	39.1	6.10	1,77	553	-5.28	-0.51	-0.77	1.32	0.92
53	Cret.	16.6	6.50	2,81	1,77	-6.27	-0.63	-0.97	0.95	1
54	Cret.	18	7.21	1,33	1,5	-5.43	-0.65	-0.64	0.81	1.22
55	Cret.	21	6.98	2,44	1,98	-4.57	-0.66	-1.04	1.03	0.78
56	Cret.	21	6.86	1,3	1,96	-4.17	-0.90	-0.99	0.90	1.02
57	Dam	15.8	6.80	1,28	1,82	-3.11	-0.87	-1.22	0.78	0.98
58	Dam	18.5	7.90	1,66	1,33	-4.17	-0.77	-1.02	0.69	1.01
59	Lav.	23.2	6.40	1,64	6,78	-0.57	0.03	0.10	1.54	1.01
60	Lav.	21	5.78	1,65	8,76	-1.34	0.09	0.13	1.68	1
61	Lav.	23	6.50	1,45	7,5	-1.00	0.33	0.57	1.89	1.22

Table 3- Microbial analysis of some groundwater (Aguila and Berka regions).

Number wells	Region	Total coliform	E.coli	Enterococci	C.perfringens
15	Aguila	±	+	-	-
16	Aguila	+	+	+	-
17	Aguila	+	±	+	-
18	Aguila	+	±	+	-
19	Aguila	+	+	-	-
21	Berka	+	+	+	-
22	Berka	+	+	+	-
35	Berka	+	+	+	-
36	Berka	+	+	+	-
37	Berka	+	+	-	-

Highlights

Hydro and isotope geochemistry were used in this study:

- to investigate the sources of groundwater contamination in the semi-arid southwestern Tunisia;
- to identify the hydrodynamic functioning of the multilayer aquifer system;
- to identify inter-aquifer mixing;