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Hydrochemical and Isotope Evidence of Groundwater Contamination of Cultivated Fields of Semi-Arid Environments in Tunisia

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Hydrochemical and Isotope Evidence of Groundwater Contamination of Cultivated Fields of Semi-Arid Environments in Tunisia

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This present study, which uses geochemical and isotope hydrological approaches, attempts to provide appropriate scientific information about the dominant geochemical processes that influence groundwater chemical composition in a semi-arid region of cultivated field. Therefore, particular emphasis has been placed on (1) the evolution of solute concentrations within the hydrological system as well as in the vadose zone, (2) the contribution of anthropogenic processes to the groundwater contamination, and (3) the estimation of groundwater recharge deriving from return flow of irrigation water.

It has been demonstrated that the excess of irrigation waters has significantly influenced the rate of groundwater recharge. The annual amount of groundwater recharge related to the irrigation practices is approximately 100 mm. Modification of the geochemical characteristics of the Zeroud aquifer groundwater is caused by water-rock interaction, including both the dissolution of evaporate and the cation exchange process. However, anthropogenic processes related to the return flow of irrigation waters have led to extremely high nitrate concentrations and flushing of solutes, such as chloride, sulfate, sodium, and calcium. The isotopic signature provides evidence of groundwater contamination. Indeed, the relatively enriched stable isotope concentrations and low tritium concentrations highlight the important contribution of irrigation waters to the local groundwater recharge, particularly in the Menzel Mhiri agricultural area.

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Keywords chemical tracers, groundwater contamination, groundwater recharge, irrigation return flow, isotope tracers

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In most semi-arid regions of the southern Mediterranean, groundwater plays an increasingly important role in providing the majority of the water supply. Therefore, there is an urgent need to quantify groundwater availability, estimate the rate of recharge, and determine the quality of the groundwater and its susceptibility to degradation. Generally, water recharge originates mainly from rainwater infiltrations, which are rare and irregular. While, the recharge rate of groundwater can be modified significantly by agricultural activity and artificial recharge schemes. In the Zeroud basin, the overgrowing population, recent climate change, the expansion of irrigated agriculture, and the intensive agricultural activities are leading to severe soil degradation, generalized decrease in water levels, and groundwater pollution.

The resultant reduction in crop yield and decrease in soil productivity may eventually lead to desertification. The groundwater contamination is highlighted through high nitrate and solutes concentrations (Allaire-Leung et al., 2001; Oenema et al., 1998; Singh et al., 1995; Stigter et al., 1998). To reduce the soil contamination, water managers propose a high amount of irrigation water, more than used by plants (Appelo and Postma, 1993; Rhoades and Loveday, 1990). Nevertheless, this can provoke leaching of salts.

The major aim of this investigation that utilizes a set of hydrochemical and isotopic data is to identify the natural and anthropogenic processes controlling the groundwater mineralization as well as the origin and the rate of recharge under cultivated fields.

Study Area

The Zeroud basin, which belongs to Central Tunisia, covers an area of about 1500 Km^2 (Figure 1). The climate is semi-arid with a mean yearly rainfall of 270 mm, potential evapotranspiration of 1600 mm, and mean annual temperature of 20.4°C.

The surface network is mainly represented by the perennial Zeroud Wadi. It collects surface runoff from the bordering highlands (close to the Algerian border) toward the Sebkhet Kelbia which constitutes the discharge area (Bouzaiane and Laforgue, 1986). In 1982, the Sidi Saad dam was built on the Zeroud Wadi. The water storage reservoir of 154 Mm^3 assists this dam to protect the town of Kairouan against floods, such as the flood of 1969 that caused more than 130 deaths, and also to develop irrigation in the downstream area. Before building the dam, the major source of recharge to the aquifer was direct precipitation on intake areas. Since 1989, many artificial recharge operations from dam water have been organized in order to ensure the groundwater recharge. These dam releases were carried out during short-term recharge programs, according to water availability in the dam.

Since the 1970s, agriculture has developed on lands overlying the upper aquifers. In 1985, an irrigation system based on Zeroud Wadi water, which is collected in the Sidi Saad dam, was created. The electrical conductivity of the dam water is about 6 mS/cm. During the most recent decades, nitrate concentrations in groundwater have largely increased, which provide evidence regarding the significant effect of agricultural activities that have been dominated by over-fertilization (Ben Ammar, 2007).

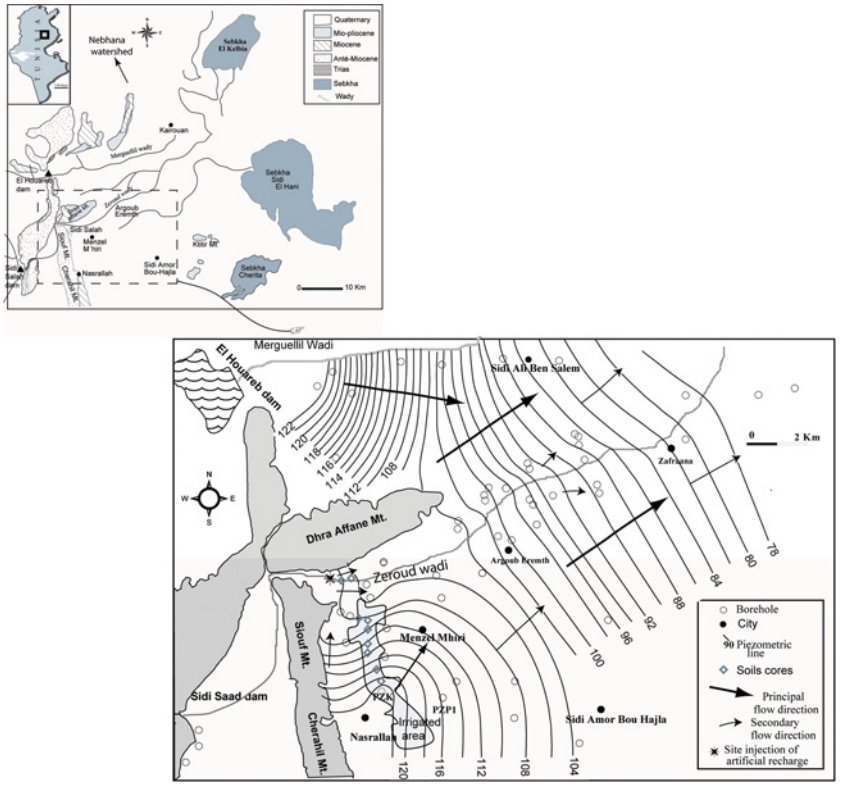

Figure 1. Location and piezometric map (March 2008). (Figure available in color online.)

Our study focused on the irrigated area of Menzel Mhiri, which is considered to be representative of areas where the vulnerability of groundwater resources to the pollution process would be more significant. It is the biggest irrigated area, which covers about 200 ha. Soils in the Kairouan Plain are composed by alluvia of coarse materials belonging to the Quaternary formation. About 45.5% of the area is represented by poorly evolved soils. The humic soils, which are brown soils with dominantly coarse texture, occupy about 33% of the Kairouan plain. The other types of soil, that is, calcic-magnesic, alluvial, saline, and those resulting from erosion activity, cover almost 10% of the plain. Saline-sodic soils are found in the depression zones, mainly in the Sebkhas such as El Kelbia and Sidi El Hani. They include alluvial materials and quaternary soils mainly composed of marls, gypsiferous clays, and sands. The altitude varies from 100 to 300 m. The dominant crops are olive trees, vegetable crops, and irrigated cereals. Both drip and pivot irrigations are largely used in the irrigation system.

Hydrologic System

The Zeroud aquifer is logged in Plio-Quaternary continental detrital deposits marked by the abundance of clayey lenticular levels. Several wells (a total of 5000 wells) in the Kairouan plain are screened in the first upper sandy layer. A total of 400 boreholes were completed in the deeper layers to 500 m of depth. The superposed

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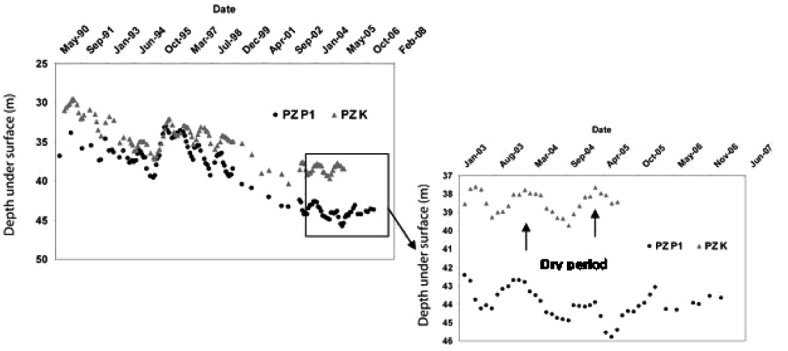

Figure 2. Changes in water levels in selected boreholes of the shallow Zeroud groundwater lens.

aquifer units are separated by semi-permeable levels with thickness increasing from west to east of the basin. Under the Wadi's bed, the depth of water table ranges from more than 60 m upstream to less than 10 m downstream. In the central and western part of the plain, communication and mixing between aquifer units seems to be possible.

The potentiometric map, established using data from 24 piezometers, shows that groundwaters flow principally SW-NE from the Cherahil and Siouf Mountains toward the Sebket Kalbia depression (Figure 1). In Menzel Mhiri area, the piezometric map shows a convex form with a converging flow that highlights a local recharge. This probably reflects either the contribution of agricultural practice to the groundwater recharge or the infiltration of rainfall at the foot of Cherahil Mountain. Several dam water release operations have been made in this basin for artificial groundwater recharge. Despite the artificial recharge operations, the aquifer level has shown a significant decrease in the whole part of the basin (Jeribi, 2004). However, in the south-western part of the basin, particularly in Menzel Mhiri district, the water table exhibits an evolution depending on agricultural activities: rise of the water table during the dry period, corresponding to the irrigation period (Figure 2).

Agricultural Activity

The water resource in the Zeroud basin, closed by dam since 1980s, is mainly collected upstream, especially in the Sidi Saad dam (Figure 1). The irrigated areas are mainly located downstream of the basin, where agricultural activity exploits about 80% of the total amount pumped per year. The long-term groundwater extraction has resulted in some dangerous problems such as a negative water-balance and a generalized decline of water-table (from 0.5 to 1 m) (Leduc, 2004; Nazoumou & Besbes, 2001).

Agricultural activity in the Kairouan plain depends largely on irrigation and the application of fertilizers to improve the conditions for crops. Most cultivators have private wells; however, others use public boreholes to irrigate their fields. On the foot of the bordering highlands, about 26% of the farmers, who exploit about 13% of the total area, cultivate rainfed cereals and olive trees. About 59% of cultivators irrigate their crop, while 50% of farmers, who use about 20% of the total surface, grew both

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rainfed and irrigated crops (Ben Massoud, 2004; Leduc, 2004). The growing season extends throughout six months of the year. The total amount of irrigation water was about 45 Mm^3/year but varies annually depending on the crop type.

Most of the farmers located downstream in the plain use about 35 Mm^3/year of groundwater to irrigate their crops; whereas, upstream in the plain, in addition to groundwater, they utilize dam water (about 25 million m^3/year) which is characterized by high salinity ranging between 3 and 4.5 g/l. In fact, the amount of irrigation water, which depends on crop types, varies between 1625 m^3ha^{-1} for barley and 7730 m^3ha^{-1} for tomatoes (Leduc, 2007; Hachicha and Soussi, 1990).

Methodology

Vadose Zone

Ten boreholes were deepened to a depth of 1–5 m in irrigated fields (P4–P9), in the Zeroud Wadi (P2–P3), and in nonirrigated soil (P1–P10). Geological formations in the cores P1–P10 (Table 1) are mainly sandy with several strata of clays. Samples were collected using a hand-auger each 10 cm interval near the surface and each 20 cm in the lower part of the profiles. When it reached the depth of 5 m, the hand-auger could not move more due to gravel at the bottom of the core. The samples were analyzed for the following: grain size distribution, soil moisture content, electrical conductivity (EC), and chemical composition of the extract water. Gravimetric water content was measured in polyethylene bagged samples protected from evaporation in air-tight containers. About 50 g from each sample was dried in an oven during 24 hours at a temperature of 105°C. The dried soil was then weighed and its moisture content (weight percent) was calculated. The extraction of waters from the porous media was carried out by elutriation method. This method requires dispersing 30 g (M_S) of dehydrated sediment in 100 mL of distilled, demineralized water (V_{lix}) in a polypropylene beaker for at least two hours, with constant stirring until a constant conductivity was attained. The supernatant was decanted and filtered through a 0.45-μm filter paper. The electrical conductivity was measured in this extract water. Water extracted was then analyzed for different chemical elements, and a correction was made for the factor of dilution to obtain ion concentrations (Edmunds and Gaye, 1994; Gargouri, 1988; Yermani et al., 2009). Indeed, the concentration of the soil water (C_i in $mg \cdot l^{-1}$) is related to the concentration of the extract, (C_{ext} in $mg \cdot l^{-1}$) that gives the soil moisture content (expressed as a percentage of the sample's dry weight), that is:

$$\%\text{moisture content} = W * 100; \quad W = \frac{m_{wet} - m_{dry}}{m_{dry}}$$

as in Equation 1:

$$C_i = \frac{V_{ext} \cdot C_{ext}}{W \cdot M_S} \tag{1}$$

Chloride Mass Balance (CMB)

This method assumes that chloride only enters the groundwater through rainfall and supposes that this later is conserved in the aquifer system. The CMB can be used for (1) estimating the moisture flux in the unsaturated zone and (2) the evaluation of

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Table 1. Unsaturated zone profiles and recharge estimates from Zeroud basin

Boring	Total depth (cm)	Elevation	No. samples	Gravel (%)	Grain size (Average for boring)		Clay (%)	Mean Cl (mg/l)	Mean annual recharge (mm/an)	Annual source water (mm)	Source water Cl concentration (mg/l)	Boring type
					Sand (%)	Silt (%)						
P1	90	168	7	10	70	13	7	1746.6	3.80	270	17.8	Not irrigated soils
P10	500	170	50	14.44	69.3	11.45	4.81	1610	2.99	270	17.8	
P2	90	166	9	4.67	72.86	15.4	7.1	1715.7	2.80	270	17.8	Zeroud wadi
P3	90	165	9	3.94	70	18.45	7.53	2046.6	2.35	270	17.8	
P4	200	152	20	21.1	60.82	14.7	3.39	1656	117.12	608	319	Irrigated soils
P5	100	164	10	1.2	57.53	34.25	7.02	1395	139.03	608	319	
P6	350	165	35	0	15	30	55	1856.9	104.45	608	319	
P7	340	171	34	4.9	70.4	20	4.6	1062.5	182.54	608	319	
P8	500	154	50	4	53.5	8	34.5	5206.7	37.25	608	319	
P9	210	153	22	11	69.87	14	5.1	7325.3	26.48	608	319	

groundwater recharge by means of a profiling technique, especially when diffuse (piston) flow is assumed (Edmunds and Gaye, 1994). For a steady state between the chloride flux at the surface and beneath an upper level, in which evapotranspiration and mixture between recharge water and extract water can take place, a moisture flux can be calculated. Given these conditions, the mean recharge (R) is determined by multiplying the mean annual input water (rainfall or irrigation water (Q)) by the ratio of the mean chloride concentration of recharge water (C_R) to the mean concentration of chloride in soil water (C_S), as expressed in the Equation 2:

$$R = Q\frac{C_R}{C_S} \tag{2}$$

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Saturated Zone

In March 2008, five boreholes were drilled into the groundwater table beneath the irrigated area of Menzel Mhiri. On the other hand, twenty-six boreholes were drilled in the remaining part of the basin. The "unpolluted wells" are those, which have low mineralization, reflecting the absence of any agricultural activity.

Chemical and Isotopic Analyses

Extracted water and groundwater samples were filtered immediately after retrieval for anions and cations analysis using 0.45 μm membrane filters. Hydrochemical analysis was carried out in the Laboratory of Radio-Analysis and Environment (LRAE) of the National School of engineers of Sfax (Tunisia). Alkalinity of filtered samples was determined by titration with HCl (0.1 M). Major cations concentrations were measured using a Waters Ion Chromatograph with IC-PakTM CM/D columns. To determine the major anions concentrations a Metrohm Ion Chromatograph was used, with CI SUPER-SEP columns. The detection limit was approximately 0.04 mg/l.

Stable isotope analyses were performed on samples collected in March 2008 from 31 wells. These analyses, which were expressed in ‰ versus the international standard VSMOW, were carried out by mass spectrometer. The measurement precision for stable isotope analysis is about of ±0.15‰ for oxygen-18 and ±2% for deuterium. Measurements of tritium were conducted from 29 wells in March 2008. Tritium concentrations, expressed in Tritium Units (TU), were performed in the Laboratory of Hydrogeology of Avignon in France and in the Laboratory of Radio-Analyses and Environment (LRAE) of the National School of Engineers in Sfax (Tunisia).

Results and Discussion

Groundwater

CO_2 Pressure

Partial pressure of carbon dioxide (pCO_2) was calculated with the PHREEQC program (Appelo and Postma, 1993) using pH measurement and total alkalinity values (TAlk). The spatial distribution of pCO2 values was visualized in March 2008 with data of 31 wells (Figure 3). The log (pCO_2) values vary between −1.7 and −2.5.

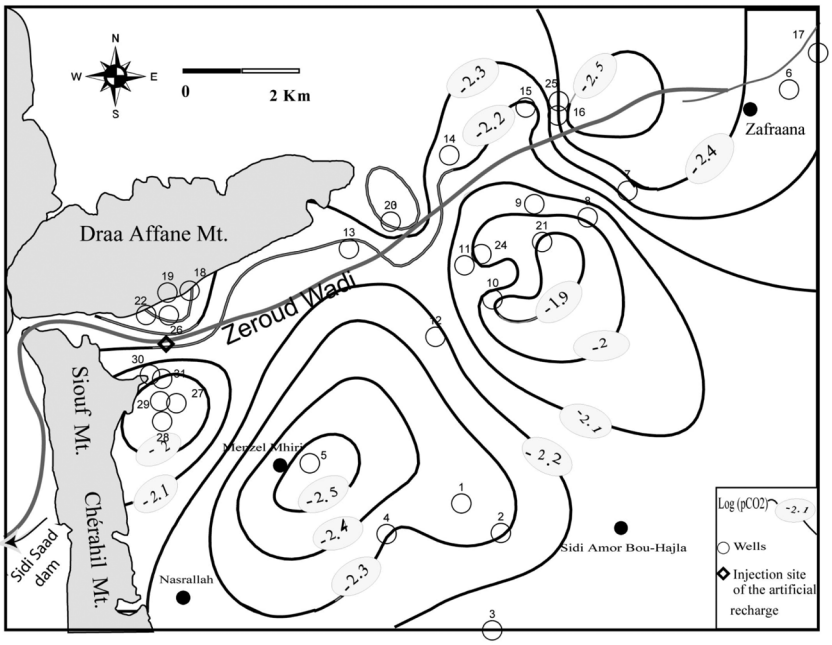

Figure 3. Spatial distribution of pCO_2 in Zeroud groundwater at March 2008.

They are lowest in the Menzel Mhiri area and near the Zeroud Wadi which represent the recharge areas. These lowest values indicate both the significant recharge by irrigation water, which is largely influenced by the atmospheric CO_2, and the infiltration of rainfall at the foot of Cherahil Mountain. The highest pCO_2 values characterize the downstream part of the basin. This may provide insight into the important effect of groundwater residence time, which permits a prolonged water-rock interaction and microbial reactions and generates a high concentration of CO_2. This latter, which increases in the same direction of groundwater flow, indicates that groundwater CO_2 is someway controlled by the residence time in the aquifer.

Major Elements Geochemistry

Groundwater salinity, which is represented by the Total Dissolved Solid values (TDS), varies largely from 1 to 4.2 g/l. The TDS increases in the same direction of groundwater flow suggesting that the mineralization is significantly influenced by the groundwater residence time. On the other hand, wells located in the vicinity of the Zeroud Wadi are characterized by low TDS values showing the important contribution of the Wadis courses to the groundwater recharge (Figure 4a). In the Menzel Mhiri area, the southern part of the basin, the high salinity contents are indicative of agricultural practices. In fact, nitrate concentrations in the studied groundwater vary largely from 0 to 150 mg/l. The majority of samples collected from wells located in the Menzel Mhiri agricultural region, showed nitrate concentrations exceeding the maximum allowable concentration for human consumption (50 mg/l).

The spatial map of NO_3 concentrations, which was established using the Kriging method, suggests that high nitrate concentrations are related to the intensive

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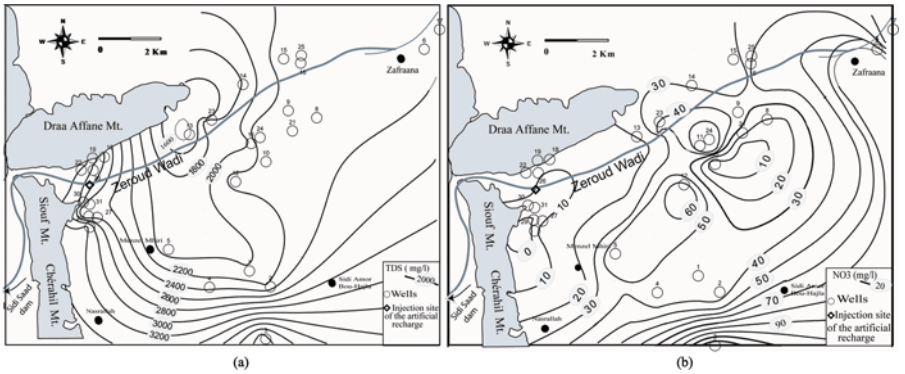

Figure 4. Spatial distributions of total dissolved solids (a) and spatial distributions of nitrates in Zeroud groundwater (b). (Figure available in color online.)

agricultural activities (Figure 4b). Indeed, the excessive application of fertilizers in the Menzel Mhiri agricultural district has resulted in groundwater contamination through soil nitrate leaching (nitrate concentrations >50 mg/l). The plot of NO_3 *vs.* Ca exhibits a positive relationship indicating that the concentrations of these two referred ions were largely modified by the application of Ca $(NO_3)_2$-fertilizers (Figure 5). This may reflect the significant component of recharge by return flow of irrigation water. Moreover, it has been demonstrated that NO_3 and TDS values display a similar spatial distribution highlighting the contribution of NO_3 as a major anthropogenic source of the groundwater salinization. Generally, there is no adsorption or precipitation of nitrate, due to its mobility in the subsurface, while it is leached and concentrated in groundwater (Hem, 1985). However, using potassium and

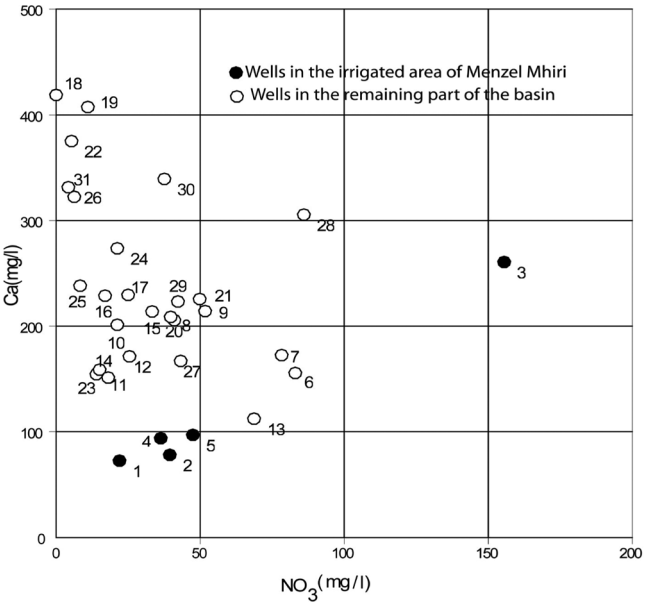

Figure 5. Relationships of Ca NO_3 in Zeroud groundwater.

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phosphorus as fertilizers has usually less effect on groundwater quality (Bohlke et al., 2002). The potassium and phosphorus concentrations in groundwater are mainly influenced by ions exchange process and plants adsorption. Therefore, these referred elements are commonly present as minor ions in groundwater. However, spatial distribution of log (pCO_2) is not consistent with the patterns of TDS and NO_3 shown in Figures 4a and 4b. Indeed, log (pCO_2) distribution illustrates different sources of recharges such as recharge by rainfall especially in the vicinity of Wadis' courses and by return flow in the irrigated lands. In fact, contrarily to rainfall recharge that causes the dilution of groundwater (low salinity near the Zeroud Wadi), return flow recharge may increase the salinization of groundwater.

When Figures 4a and 4b are compared, it is clear that TDS and NO_3 do not display the same spatial patterns, particularly in the area situated between J. Siouf and Menzel Mhiri. This can be explained by the coexistence of several sources of groundwater mineralization. In fact, in this part of the basin we have the influence of dam water (TDS between 3 and 6 g/l) which provokes the salinization of groundwater. However, in the irrigated areas the high TDS contents are likely related to the increase of nitrate concentrations that are caused by the large-scale fertilizer application.

The Na/Cl relationship shows that the majority of samples fall on the 1:1 line (Figure 6). This well-defined relationship and the relatively high concentrations of Na and Cl ions highlight the role of halite dissolution as important process contributing to the groundwater salinization in the Zeroud basin (Appelo and Postma, 1993). First, this dissolution is verified through the general increasing trend of Na and Cl concentrations along the groundwater flow direction; second, the proportional parabolic correlation between (Na+Cl) and the negative saturation indexes indicates that the studied ground waters are under-saturated with respect to NaCl. In addition, some samples, which are under-saturated with respect to gypsum, show proportional correlation between ($Ca+SO_4$) and the saturation indices of gypsum. This may reflect the contribution of eventual dissolution of gypsum to the groundwater (Figure 7). The relative excess of SO_4 with respect to Ca, suggests that there is

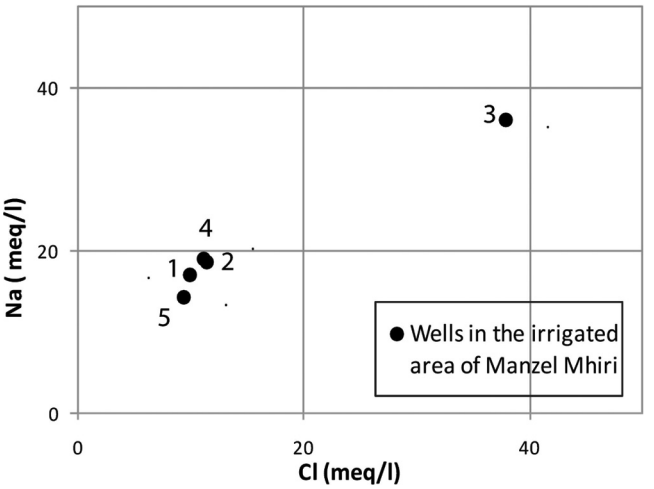

Figure 6. Relationships of Na and Cl in Zeroud groundwater.

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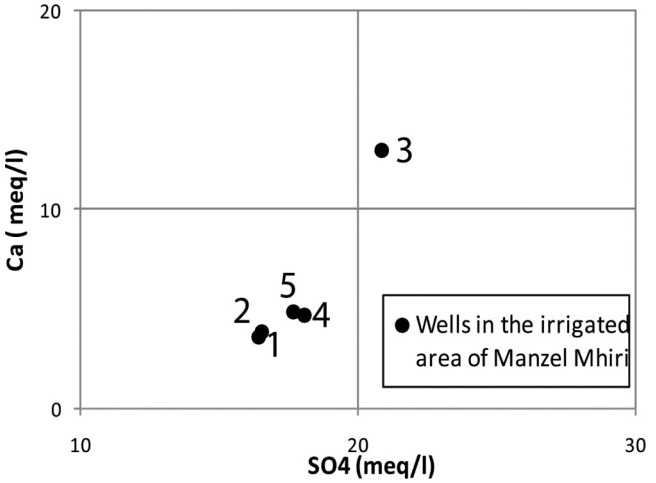

Figure 7. Relationships of Ca and SO_4 in Zeroud groundwater.

another, supplementary, source of sulfate, probably in relation with Mg-sulfate salt dissolution. The dissolution of $MgSO_4$ is highlighted by the positive correlation in the plot of Mg vs. SO_4 (Figure 8) (Adams et al., 2001). However, the irrigation by the dam waters that are characterized by high sulfate concentrations can also contribute to the increase of the concentration of this anion in groundwater.

Stable Isotopes ($\delta^{18}o$ and $\delta^{2}h$)

One of the more interesting tracer techniques is the use of the stable isotopes of water molecules, which provide reliable information about waters origins, recharge, and mixing of waters from different aquifers (Carol et al., 2009). The average values of $\delta^{18}O$ and $\delta^{2}H$ in the Zeroud groundwaters are -5.6% and -34.6%, respectively. In the $\delta^{18}O/\delta^{2}H$ conventional diagram (Figure 9), groundwater samples were plotted

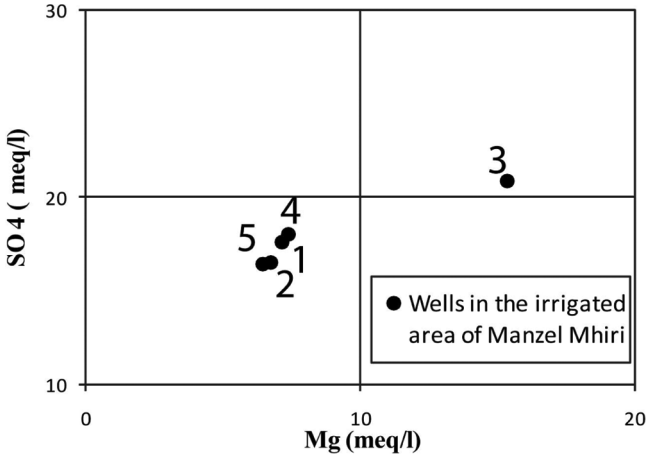

Figure 8. Relationships of Mg and SO_4 in Zeroud groundwater.

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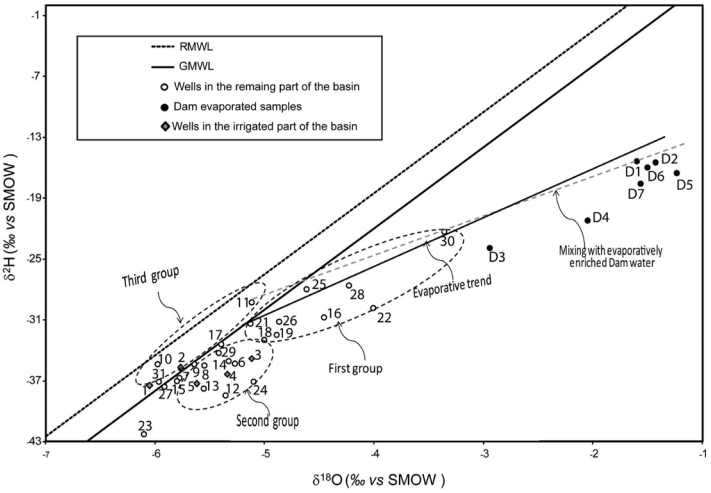

Figure 9. $\delta^{18}O/\delta^{2}H$ diagram in Zeroud groundwater.

together with the Global Meteoric Water Line (GMWL: $\delta^{2}H = 8\delta\ ^{18}O + 10$) and the Regional Meteoric Water Line (RMWL: $\delta^{2}H = 8\delta^{18}O + 11$) (Ben Ammar, 2007; Jeribi, 2004). Dam water samples show an enrichment of $\delta^{2}H$ and $\delta^{18}O$, which characterize water that has been submitted to evaporation. These samples define a linear trend with a slope of about 5 as recognized for evaporation effect. In this diagram, groundwater samples are classified into three groups. The first group encloses wells influenced by dam water, located near the injection site of artificial recharge (which transfers a flow ranging between 1 and 1.5 m^3/s from Sidi Saad dam directly to a preferential infiltration zone in the Zeroud Wadi bed to ensure the groundwater recharge). These samples are characterized by large sulfate concentrations (1000 mg/l) and the most enriched ^{18}O values. This indicates that artificial recharge has played a significant role in the groundwater recharge. The second group includes groundwater samples which are characterized by enriched $\delta^{18}O$ and $\delta^{2}H$ concentrations; and deviates from the meteoric water line. This enrichment is probably due to the infiltration of an evaporated component likely deriving from the return flow of irrigation water. However, this evaporation process is very low compared to the samples of the first group; this is probably related to the source water irrigation (groundwater or dam water). Indeed, the potential application of pivot irrigation technique, which mostly used the groundwater, ensures lower evaporation process compared to the use of the evaporated dam water. Indeed, the spatial distribution of $\delta^{18}O$ concentrations in the basin shows that the referred samples were collected from the area of potential agricultural activity of Menzel Mhiri region. In this area, where irrigation is applied at a large scale, the excess of irrigation water undergoes an excessive evaporation at the ground surface and in the vadose zone; after that, it eventually returns to the aquifer. Therefore, this low enrichment is interpreted as a small evaporative influence indicating either slow infiltration of rainfall waters in relatively low permeable zones and/or return flow of irrigation water. The third group observed in the $\delta^{18}O/\delta^{2}H$ diagram, includes the rest of groundwater samples. This sample cluster is located mostly between the GMWL and the LMWL, exhibiting depleted oxygen-18 and deuterium concentrations, which may point to the recharge

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of the Zeroud aquifer by rain waters deriving from mixing of Atlantic and Mediterranean air masses produced in high altitude.

Unsaturated Zone

Movement of Solutes Under the Unsaturated Zone

It is very important to understand factors controlling sources and water pathways in the unsaturated zone which affect largely the composition and the rate of groundwater recharge.

Figure 10 shows chloride, sulfate, and nitrate concentrations in four profiles considered to be representative of four soil types. There are natural soil, irrigated soils by dam water and by groundwater; and by Zeroud Wadi. Ions concentrations, which are expressed in mg/l, in the irrigated fields with dam water (P9) were higher than that registered in the Zeroud Wadi (P2) and the natural soil (P1). Indeed, irrigation by dam water, which is characterized by higher sulfate concentrations, provoked greater enrichment of this anion in the groundwater. The sulfate concentrations in P1 were similar in magnitude to the sulfate values in the irrigated field by groundwater (P4) but less than sulfate concentrations in P9. The electrical conductivity in the Zeroud Wadi extracted water (P2) and in the natural soil (P1) was around 500 μs/cm, whereas in the other profiles, conductivity was above 2000 μs/cm. Although P4 and P9 are located under irrigated lands, they exhibited nitrate concentrations lower than the Zeroud unsaturated profile (P2) and the natural soil (P1); this can be related to the application of a high amount of fertilizer that provokes the nitrate leaching to the aquifer groundwater and not its concentration in the vadose zone. The nonirrigated vadose zone profile (P1 and P10) showed an accumulation of nitrates in the first two meters. The accumulation in P1 can be related to low water recharge, while the higher concentration of nitrate in the deeper part (75 to 200 cm) of P10 can be linked to animal discharges (near this nonirrigated core, there is a sheep pen).

Recharge Estimation From the Chloride Mass Balance

Many studies have used chloride as a conservative tracer in recharge calculations, and CMB methods probably offer the most reliable recharge estimation approach in semi-arid and arid regions (Allison and Barnes, 1994).

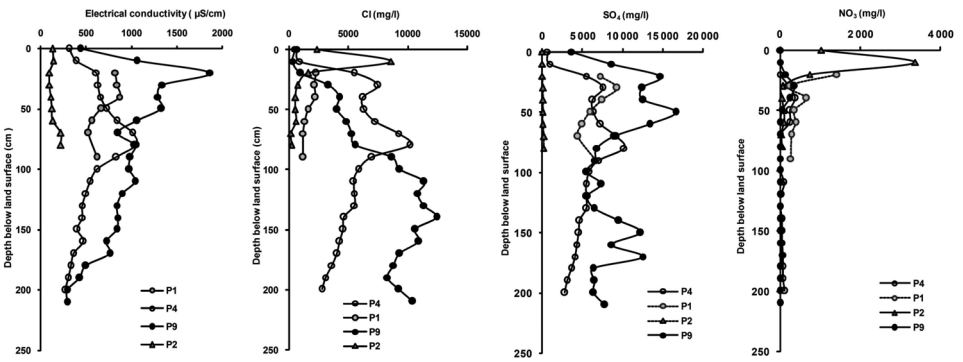

Figure 10. Vadose zone sulfates, nitrates, conductivity, and chloride concentrations in P1, P2, P4, and P9 cores.

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In this study, rainfall sampling for the determination of chemical compositions was carried out systematically since 2008 at Menzel Mhiri station, which is the nearest station from the studied area, mainly to determine the Total Chloride Deposition (TD) for groundwater recharge. The chloride concentrations in precipitation range between 4.7 mg/l and 32.1 mg/l with an average of 17.8 mg/L. The monitoring of the precipitation amounts between 1978 and 2008 allowed calculating an average annual rainfall amount of 270 mm. On the other hand, we assumed that the average amount of irrigation water was about 1.85 mm/day from February to July depending on crop types, which resulted in 338 mm/year. It was supposed that all of the pore-water and groundwater chloride in the studied area originated from recharge water. However, formations in this area contain evaporite deposits; for this reason, it is necessary to study the Cl^-/Br^- ratios in order to determine if there is a geologic source of chloride. The dissolution of rocks provokes an increase of Cl^-/Br^-; usually, this ratio exceeds 1000 if there is a geologic source. However, extracted water samples from Menzel Mhiri area had Cl^-/Br^- ratios <100 (Figure 11). Additionally, this ratio increases with depth (Heilweil et al., 2006), which indicates that there is another process in the land surface, such as plant roots that uptake Br^-. All these observations show that there are other processes that control Cl^-/Br^- rather than the geologic source.

Chloride concentrations in extracted water samples from 10 cores at Zeroud basin were used to compare possible direct recharge in the cultivated field with that in the Zeroud Wadi and in the natural soil and to investigate the evolution of groundwater quality in the studied shallow aquifer.

Assuming an average rainfall chloride concentration of 17.8 mg/l (C_R), an average annual rainfall amount of 270 mm (Q), and average soil water chloride concentrations of 1.61 to 2.05 g/l (C_S) in profiles P1, P2, P3, and P10 (Table 1), recharge rates beneath nonirrigated soils and in the Zeroud Wadi using the chloride mass balance (Eqn2) range from 2.35 to 3.8 mm/year (Table 1).

Infiltration beneath the irrigated fields is a mixture of 270 mm/year of natural precipitation having an average chloride concentration of 17.8 mg/l with

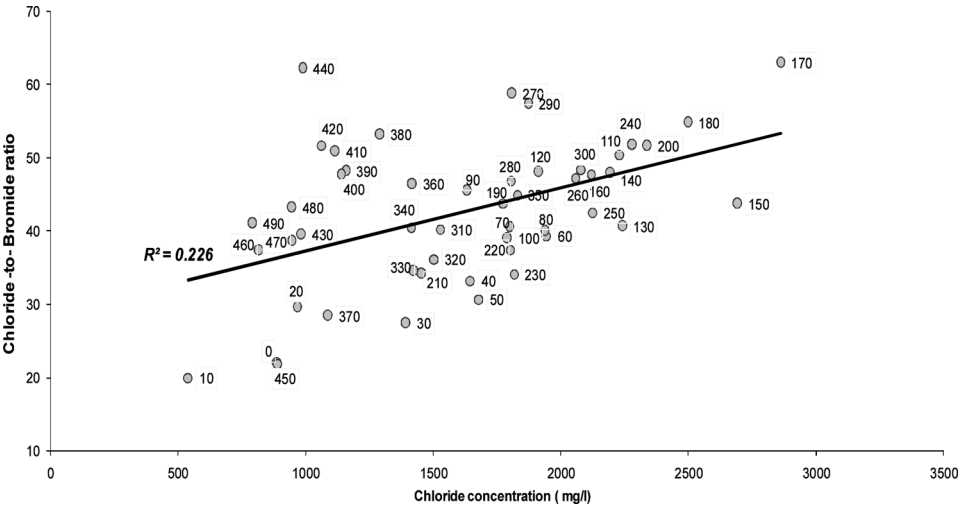

Figure 11. Relationships of Cl and Cl/Br of extract water in P10 core: depth (cm) is indicated.

338 mm/y of applied irrigation water having a mean water chloride concentration of 560 mg/l. (The mean chloride concentration of the irrigation water obtained from the long-term record at Menzel Mhiri area is representative of the 5 wells.) Thus, assuming an average water input (Q) of 608 mm/y having a weighted chloride concentration of 319 mg/l (C_R) and an average soil zone chloride concentrations ranging between 1395 to 7325 mg/l (C_S) in profiles P4-P9, estimated recharge rates beneath irrigated fields range from 26.5 to 139 mm/year (an average of 100 mm/year)

In summary, results of this work show that excessive irrigation waters in the Zeroud basin influence the quantity and the quality of groundwater recharge. Excess irrigation water contributes locally to groundwater recharge. The infiltrating water provokes an increase of the water table of the local field from June to September (Figure 2). The decline of the water table in March can be related to the reduction of irrigation water quantity and raising evapotranspiration. The dependence of the aquifer on irrigation activities shows that this is the most important recharge source to the local land (irrigated area of Menzel Mhiri). This recharge is ensured by the low water table depth in this irrigated area.

The low tritium concentrations of groundwater in the irrigated area (e.g., 0 TU in the local land) confirmed that the recharge comes essentially from irrigation water excess which derives from the groundwater source. Figure 10 shows low nitrate concentrations in irrigated soils profiles (P4 and P9) which confirm the importance of the leaching process. However, the undisturbed natural soil and Zeroud Wadi soil exhibits an enrichment of nitrate concentration. This later can be related to low water infiltration which can provoke nitrate accumulations and not leaching to the groundwater. The increase of the chloride concentrations in the first meter of

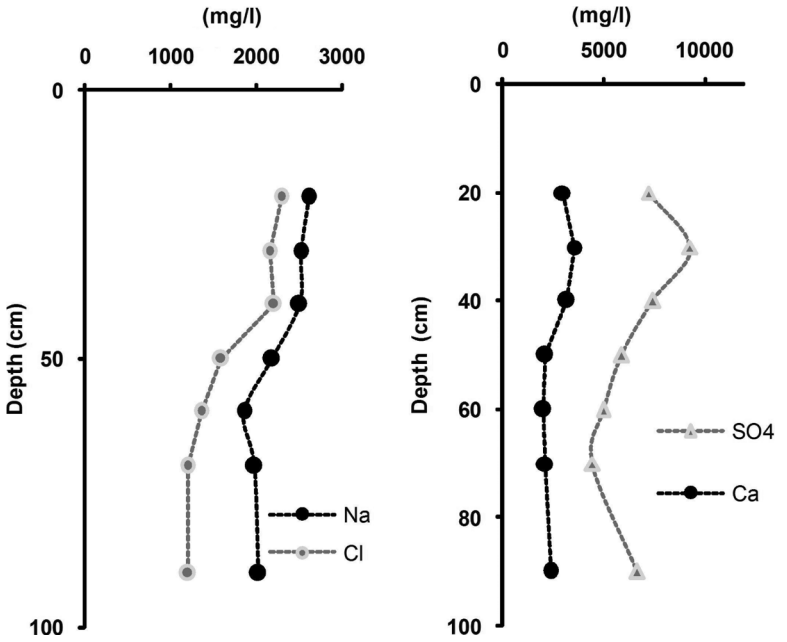

Figure 12. Vadose zone chloride, sodium, calcium, and sulfates concentrations in P1 core.

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the cultivated and irrigated profile confirms groundwater recharge by return flow irrigation.

In the natural soil, this process is negligible and, mostly, there is salt concentration process (evaporite minerals near the surface) in relation to low rain infiltration which characterizes arid and semi-arid environments. This appears in the high concentrations of Cl, Na, Ca, and SO_4 ions, especially in the two first meters (Figure 12). In fact, groundwater pollution due to excessive irrigation practices can result in two major processes: (1) contamination due to the leaching of major elements existing in irrigation water such as chloride, sulfate, magnesium, calcium, and sodium; and (2) contamination by fertilizers, which provokes an increasing concentration of nitrates and potassium. Major elements in irrigation water are usually conservative; however, nitrates and potassium are mainly taken up by plants. Potassium is affected also by cation exchange mainly if clay minerals are abundant. The K/Cl ratio of the soil water samples showed a decrease of K concentrations with depth, especially beneath the nonirrigated land and Zeroud Wadi (Figure 13). However, in the irrigated land, a lower K/Cl ratio was observed which may be related to plant absorption, as well as cation exchange. The inverse relation between the water table depth and the groundwater nitrate concentration indicates that the groundwater pollution originates mainly from the surface (Figure 14).

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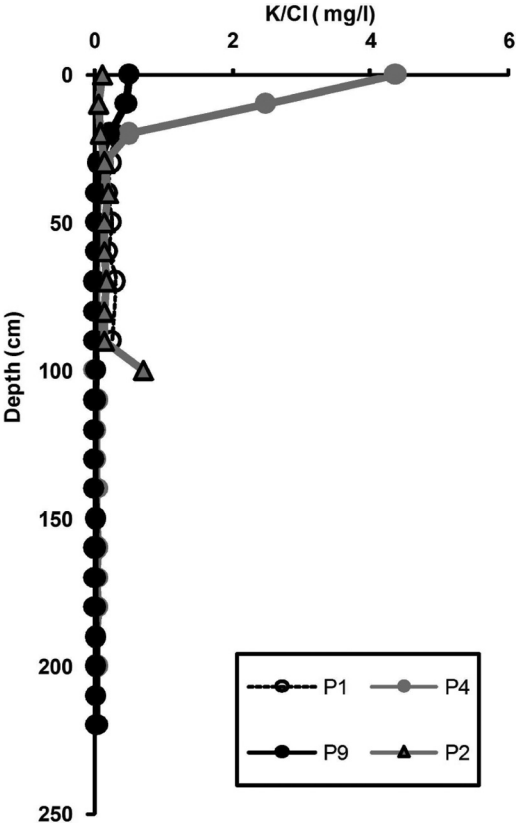

Figure 13. Vadose zone K/Cl ratio in P1, P2, P4, and P9 cores.

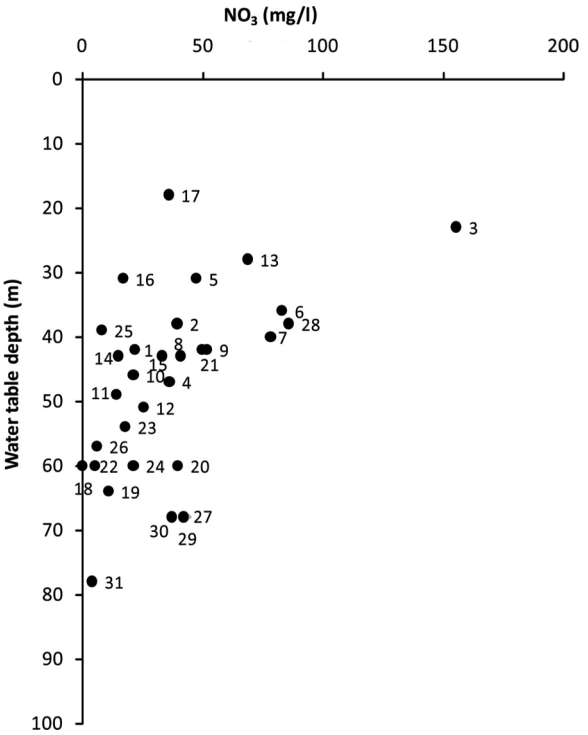

Figure 14. Variation of nitrates concentrations in groundwater according to water table depth.

Conclusions

The present paper proves that irrigation and fertilization in the semi-arid environment of the Zeroud basin influence quantitatively and qualitatively the groundwater recharge. Irrigation in the local land of Menzel Mhiri contributed approximately 100 mm/year to the hydrological system recharge as estimated by the CMB method. This recharge is local; and, the long-term exploitation from these resources in many irrigated areas of the Zeroud basin has caused a generalized decline of the water table and not its recharge. Three main groundwater contamination processes were identified: (1) contamination caused by leaching of solutes related to the return flow from irrigation waters, such as chloride, sulfate, sodium, and calcium; (2) the nitrate pollution caused by the excessive application of fertilizers; and (3) natural mineralization processes in relation with the dissolution of evaporite minerals. The isotopic signatures highlight that contaminated groundwaters, which are distinguished by relatively enriched stable isotope concentrations and low tritium concentrations, derive mainly from the return flow of irrigation waters.

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