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Underground renewal time and mixing of the main mineral waters of Tunisia : a multi-tracer study

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Abstract.

Bottled waters are increasingly popular in Tunisia. Most of them come from groundwaters, thus raising the question of the long-term availability of the mineral groundwater resources. Water collected from production springs or wells of eleven mineral waters of Tunisia among the main commercial brands were analyzed for tritium (³H), helium-3, SF₆, CFCs and carbon-14. Tracer-tracer plots indicate that all of the groundwaters of our data set are a mixture of modern rainwater with older groundwater flow waters that are beyond the time-scale of the transient tracers. ¹⁴C data suggest that the age of these old waters, which constitute the main water reservoir, is of the order of radiocarbon half-life or more. Most of the studied sites have groundwater renewal times in the range 50-150 years. For the sites where tracer concentrations are the most diluted by old waters, this value logically increase to several centuries.

Keywords: Groundwater, environmental tracers, renewal time, groundwater dating

1. Introduction

The rapid increase in bottled mineral groundwater production in Tunisia needed to meet consumer demand (110 millions bottles in 1995 and 1.04 billion bottles in 2015 – Office du thermalisme at www.thermalisme.nat.tn) raises the question of the long-term sustainability of this economic sector.

Renewal time of groundwater, which is clearly related to the ratio of the storage volume to the recharge rate, is an important notion regarding vulnerability and sustainability of groundwater resources. Numerical models of groundwater flow can describe accurately the hydrodynamic functioning of a given aquifer, and therefore can give stakeholders and the mineral water industry management important indications to prevent pollution and/or overexploitation of the water resource. However, they require detailed information (e.g. boundary conditions, hydraulic conductivity, porosity, etc...) which are usually not available. As an alternative, the analysis of atmospheric transient tracer concentrations in groundwaters can provide important basic information on their residence time and mixing.

As a development arising from tritium, which can be used as a transient tracer as a result of ^3H injection into the atmosphere from the atmospheric testing of nuclear devices in the 50's and early 60's, the ^3H - ^3He dating method offers a direct measure for the time since groundwater had its last gas exchange with the atmosphere. The ^3H - ^3He pair is of particular interest because tritium and its daughter helium-3 are assumed to be fully conservative tracers, and also because the ^3H - ^3He radioactive clock only relies on the in-situ $^3\text{H}/^3\text{He}$ ratio. Hence, it is independent of the history of tritium input to the aquifer (Schlosser et al., 1988, 1989; Poreda et al., 1988; Solomon et al., 1991, 1993; Stute et al., 1997).

Like tritium, ^{14}C was also a by-product of atmospheric nuclear tests. Hence, the resultant transient spike in atmospheric $^{14}\text{CO}_2$ can also be used as a transient tracer (Stewart, 2012; Baudron et al., 2013).

The CFCs and SF_6 methods are based on the direct comparison of the groundwater tracer concentration with the concentration of these tracers in the atmosphere, and hence in groundwater recharge. Because their atmospheric concentration has changed through time, this provides the basis for travel time determination (Thompson and Hayes, 1979; Cook and Solomon, 1995; Busenberg and Plummer, 1992, 2000; Goody et al., 2006; Darling et al., 2012).

Each tracer has its own atmospheric input function and each tracer method relies on its own specific set of assumptions and caveats. There are significant differences in the reliability of the derived tracer ages. Some caveats are the result of hydrogeology. For CFCs and ^{14}C additional uncertainties of the infiltration conditions influence the resulting ages. Therefore the combination of several tracer methods in parallel is highly preferable to the use of a single method (Szabo et al., 1996; Beyerle et al., 1999; Plummer et al., 2001; Corcho Alvarado et al., 2005, 2007; Massmann et al., 2008; Solomon et al., 2010; Mayer et al., 2014; Kralik et al., 2014; Delbart et al., 2014; Battle-Aguilar et al., 2017). Ideally measured tracer concentrations in a groundwater can be matched simply to a particular year of recharge. However, this requires that the groundwater moves as a result of simple piston flow, that is along parallel flowlines from recharge to discharge. In reality, groundwaters are often a mixture of water of different ages due to the complexity of the hydrogeological network and/or the internal structure of the aquifer. One basic way of resolving flow processes is to plot one tracer versus another (see for instance Figure 3 in Darling et al., 2012). On these plots, simple piston flow and binary mixing between young

recharge waters and old tracer-free waters are opposite extremes of groundwater behaviour. In most cases however, groundwater flow may be more complicated and one must test a variety of modeled reservoirs connected to each other serially or in parallel with or without dead volumes, cross flow in between or bypass flow (see Ozyurt and Bayari, 2003 and references therein).

Here we report the application of such a multi-tracer approach to a suite of mineral waters of Northern and Central Tunisia among the main commercial brands. The region is characterized by a semi-arid climate with mild wet winters and hot dry summers (monthly average temperatures vary from $10\pm 1^{\circ}\text{C}$ in January to $28\pm 2^{\circ}\text{C}$ in August), and relatively low annual rainfall in the range 300 mm – 600 mm. For this study, we selected eleven bottled water production sites (Table 1), exploiting local aquifers nested in karstified limestone and/or sandstone formations (see Appendix A). Very little is known by the operators concerning the actual extent of their mineral groundwater resources and the sustainability of their business. Comparison of mineral water withdrawal rates and recharge rates estimated from precipitation figures and catchments' surface area shows that the rate of water withdrawal exceeds the present-day recharge rate. This overexploitation of the local mineral groundwater reservoirs may have serious implications in term of water quality and economic consequences for the mineral water industry. Note that the issue of groundwater overexploitation in Tunisia is not restricted to mineral waters: Tunisia, being a semi-arid to arid country, is facing water shortage of increasing severity as a result of population growth, rising living standards and increasing water consumption by the agricultural sector (Frija et al., 2014)

The present work aims at exploring the potential of the selected suite of transient tracers (tritium/helium-3, SF₆, CFCs and radiocarbon) to gain insight into the hydrogeological characterization of these different water reservoirs.

1. Sample collection and analytical methods

The sampled sites are shown in Fig. 1, and their main characteristics (climatic conditions, elevation, ...) are summarized in Table 1. Groundwaters were analyzed for ¹⁸O/¹⁶O, D/H, ³H, ³He, ⁴He, ²⁰Ne, CFCs (F-11, F-12, F-113), SF₆ and ¹⁴C. Apart from Marwa-2009 which shows a high neon supersaturation (see below), the samples were taken at the water extraction point (at the well-head for pumped waters and at the capture point for natural springs) so that contact of the water with the atmosphere can be excluded. With the exception of a few tritium/helium and ¹⁴C samples taken in October 2009, all the water samples were collected in September/October 2010.

CFCs and SF₆ samples were collected in air tight stainless steel cells of 30 and 500 ml respectively and were analyzed at the University of Rennes (Labasque et al., 2006; Ayraud et al., 2008). The CFC and SF₆ concentrations were determined by Purge and Trap (PT) extraction and analysed with a gas chromatograph equipped with an electron capture detector (GC/ECD). The uncertainty is 3% for water equilibrated with the present-day atmosphere for CFC and 5% for SF₆ (see Table 2).

Noble gas samples (He, Ne) were collected using standard refrigeration grade 3/8" copper tubes equipped with metal clamps at both ends. ³H samples were collected in 500 ml pyrex bottle, baked at 75°C and pre-filled with argon. The tritium and noble gas isotopic analyses (³He, ⁴He, ²⁰Ne) were carried out at LSCE (CEA-

Saclay) with a MAP-215 mass spectrometer using standard procedures. Helium and neon dissolved in the water samples were first extracted under vacuum into sealed glass tubes. The accuracy is $\pm 0.8\%$ for helium and neon concentrations, and $\pm 0.4\%$ for the $^3\text{He}/^4\text{He}$ ratio. Water for tritium determination was degassed and stored during 9 to 12 months to allow for ^3He ingrowth. Uncertainty on tritium determination is given in Table 2. Technical details concerning laboratory treatments and analytical methods are available in Jean-Baptiste et al., 1992, 2010.

Carbon-14 samples were taken in 500 ml stainless steel cells and analyzed by accelerator mass spectrometry at the French Radiocarbon National facility (CEA-Saclay), with an accuracy between ± 0.1 pmC and ± 0.2 pmC (see Table 2). Delta ^{13}C was measured by IRMS at Paris-Sud University, with an accuracy of ± 0.1 ‰.

Water for stable isotope analysis was collected in 15 ml glass bottles. Deuterium and oxygen-18 were analysed at LSCE (CEA-Saclay) by laser spectrometry. Uncertainties are ± 0.15 ‰ and ± 0.7 ‰ for oxygen-18 and deuterium respectively.

3. Results

Analytical results are shown in Table 2. Stable isotopes are between -50.5‰ and -31.6‰ for D/H and between -7.66 and -5.10 for $^{18}\text{O}/^{16}\text{O}$, respectively. The lowest values correspond to the El Kef region and reflect the altitude effect of this more elevated area (altitude > 850 m – see Table 1) on the water isotopes composition of rainwaters (Ambach et al., 1968; Siegenthaler and Oeschger, 1980). The results are consistent with precipitation isotopic data for northern and central Tunisia represented by the Tunis and Sfax Local Meteoric Water Lines (Fig. 2),

indicating that the rainfall contributing to the recharge did not undergo any significant evaporation before infiltration.

All waters are tagged to various degree with environmental tracers of the post-1950 era (Table 1). In spite of this, all carbon-14 values (range : 2.2 to 68.7 pmC) are well below the natural modern pre-nuclear value of 100 pmC. The lowest value corresponds to the carbo-gaseous waters of Ain Garci ($[\text{HCO}_3] = 19.8 \text{ mmol/l}$), clearly showing the influence of the ^{14}C dilution by dead carbon on the ^{14}C result. $\delta^{13}\text{C}_{\text{TDIC}}$ data were used to correct measured ^{14}C activities for dead carbon dilution due to bicarbonate formation during the reaction between carbonic acid originating from soil CO_2 and carbonate minerals (Clark and Fritz, 1997; Han and Plummer, 2016). For this correction, the initial $\delta^{13}\text{C}$ value in groundwater recharge prior to leaving the water-soil gas interaction zone is set to -12 ‰ (Clark and Fritz, 1997; Fourré et al., 2011) and the $\delta^{13}\text{C}$ of the marine carbonate limestone formations (see Appendix A) is assumed to be 0 ‰ (Clark and Fritz, 1997).

Neon excess relative to solubility equilibrium at the recharge temperature and elevation ranges from -0.4% to 50.1% (mean value of 21.4%), with the exception of Marwa which show a very large excess in 2009 (230%). This large anomaly, which is confirmed by the analysis of a backup sample, is not seen in 2010 (26.6%). The most probable explanation for the difference between 2009 and 2010 is the sampling location : inside the bottling building in 2009 and at the well head in 2010. The neon data are used to correct all tracer gas concentrations (^3He , ^4He , CFCs and SF_6) for excess air (Aeschbach-Hertig et al., 1999) prior to age calculations and tracer comparisons. In addition, all tracer concentrations are normalized to sea-level pressure and a common temperature of 15°C to allow the comparison of all sites.

CFCs and SF₆ ages were determined from the direct comparison of the groundwater tracer concentration with the time-dependent concentration of the tracer in the groundwater recharge.

The ³H/³He age τ is defined as $\tau = \lambda^{-1} \ln(1 + {}^3\text{He}_{\text{tri}}/{}^3\text{H})$, where λ is the decay constant of tritium and ³H the measured tritium concentration. It is usually expressed in tritium units (TU) : 1 TU corresponds to a ³H/H ratio of 10⁻¹⁸. ³He_{tri} is the fraction of the total ³He that is produced by ³H decay, i.e. the difference between the measured concentration ³He_{meas} and the concentrations of other ³He components : ³He_{atm} of atmospheric origin, and ³He_{ter}, the terrigenic component : ${}^3\text{He}_{\text{tri}} = ({}^3\text{He}_{\text{meas}} - {}^3\text{He}_{\text{atm}} - {}^3\text{He}_{\text{ter}})$. ³He_{atm} and ³He_{ter} are deduced from the measured concentrations of helium and neon. A terrigenic ratio ³He_{ter}/⁴He_{ter} of 2×10⁻⁸ typical isotope ratio for radiogenic helium production in rocks was used, according to the work of Fourré et al. 2011 which shows the absence of mantle helium in the studied area (except for Ain Garci – see below). Note that ³He_{ter} is very small, therefore ³He_{tri} is relatively insensitive to the value of this terrigenic ³He/⁴He ratio.

Tracer ages are reported in Table 2 and Figure 3. (Fig. 3). SF₆ ages are younger and F-11 ages older than ³H/³He, F-12 and F-113 ages, possibly due to in-situ terrigenic SF₆ production and F-11 breakdown (see section 4 below). For Ain Garci, ³H-³He dating was problematic due to the presence of mantle ³He (³He/⁴He = 2.4 × Ra – see Fourré et al., 2011). ³H/³He, F-12 and F-113 ages range from 10 to 58 years but tracer ages show substantial discrepancies. Age calculations assume that groundwater moves along independent flowlines analogous to pipes (piston flow). However, tracer-tracer plots (see section 4 below) indicate that the groundwaters are a mixture of modern waters with older (tracer-free) waters. Therefore, the piston flow conditions are not valid here and under these conditions it

is not possible to assign ages to tracer concentrations. Therefore tracer ages reported here are not true ages but “apparent” ages (Suckow, 2014). Actual tracer concentrations are modified by this mixing which, in turn, variously affects tracer ages, thus explaining the substantial discrepancies among tracers.

4. Discussion

Figure 4a displays the mean annual atmospheric concentrations of CFCs, SF₆ and ¹⁴C as a function of time for the northern hemisphere. For tritium, the past history of its concentration in precipitation in Tunisia was constructed using all historical measurements from Central Mediterranean stations in the IAEA Global Network of Isotopes in Precipitation database (at <https://nucleus.iaea.org/wiser/gnip.php>), including the times-series of tritium in rainwater for Tunis and Sfax (Fig. 4b). Tunis data agree with Central Mediterranean IAEA stations between 1970-1980 and then seems to be overestimated, possibly due to data quality problems (some contamination or analytical problems may be suspected). Sfax is on the lower side of the IAEA central Mediterranean dataset, which is consistent with its southern location. C-14 and tritium data are averaged using a polynomial function. The curves in Figure 4a and 4b provide the basis for model calculations of the theoretical relationships between the concentrations of the different transient tracers in groundwater under various mixing assumptions.

Figure 5 compares the groundwater concentrations of F-11, F-12, F-113 and SF₆ for all groundwaters with the piston flow (PF) model, i.e. along tubular flow lines from recharge to discharge with no mixing of the flow lines. Each curve (in black) represents the relationship between a given tracer pair for recharge dates going back

in time from the sampling date (2010) to the pre-1950s years corresponding to waters beyond the time-scale of the transient tracers. As a variante to this simple piston flow model, we have also calculated the tracer-tracer relationships (blue curves) for the PF model with a typical dispersion coefficient of 10^{-4} cm²/sec along the direction of the flow (PF+DIS). Figure 5 shows that at all sites the groundwater concentrations disagree with both models and are better explained (dotted line) by a simple binary mixing (BM) between “modern” waters (upper right corner) and “old” tracer free waters (lower left corner). The PF and BM curves define the region that should contain all tracer data if no additional process other than mixing affects the tracer concentration (permitted region). In Figure 5b and 5c, most SF₆ and F-11 concentrations are somewhat outside the permitted region. As already noted above when comparing the tracer ages (section 3), this indicates a small but significant additional SF₆ component likely due to in-situ production (Harnisch and Eisenhauer, 1998; Busenberg and Plummer, 2000; Deeds et al., 2008; Lapworth et al., 2015) as well as some F-11 in-situ degradation (Oster et al., 1996; Shapiro et al., 1997; Höhener et al., 2003).

This mixing trend defined by CFC tracer plots is also apparent on the tritium-F12 and tritium-radiocarbon diagrams (Fig. 6a and 6b). This latter diagram also suggests that, for the various studied sites, the old water ¹⁴C endmember is in the range 5 – 50 pmC, corresponding to radiocarbon ages between one and four radiocarbon half-lives (approximately 5000 to 20000 years). Radiogenic ⁴He was plotted against these radiocarbon ages (not shown) since one would expect radiogenic ⁴He coming with the old water. However, as already noticed in the above Results section, for all the sites ³He_{ter} and ⁴He_{ter} are very small and do not provide any clear evidence of a

correlation with ^{14}C ages. This is probably because the old waters are too shallow to pick-up significant crustal helium.

The fraction of old water present at each site, estimated from the F113 - F12 or tritium - F12 diagrams, is shown in Fig. 7.

Qualitatively, one may say that this factor of dilution by the old waters is an indication of size of the reservoir, and therefore of the sustainability of groundwater resource. More quantitatively, the evolution of the tracer concentration C_n at year n (for a well-mixed deep reservoir) can be deduced from the tracer concentration C_{n-1} at year $n-1$ by writing the following tracer balance equation:

$$AH_n C_n = AH_{n-1} C_{n-1} + [A r (C_{\text{surf}})_n - A w C_{n-1}] \Delta t \quad (1)$$

where Δt equals 1 year, r (in m/year) is the water recharge rate and w (in m/year) is the withdrawal rate (both natural and anthropic). A (in m^2) is the surface area of the recharge zone, (AH_n) and (AH_{n-1}) are the volume of groundwater at year n and $n-1$ (in m^3) and $(C_{\text{surf}})_n$ is the tracer concentration in the recharge water of the year n .

In a similar way, the time-evolution of the volume of groundwater obeys the following equation:

$$AH_n = AH_{n-1} + (A r - A w) \Delta t \quad (2)$$

If one introduces the renewal time τ_n of the groundwater defined by $\tau_n = H_n/r$, equations (1) and (2) can be rewritten as follows :

$$C_n \tau_n = C_{n-1} \tau_{n-1} + \Delta t [(C_{\text{surf}})_n - C_{n-1} w/r] \quad (1')$$

$$\tau_n = \tau_{n-1} + \Delta t (1 - w/r) \quad (2')$$

Note that for tritium, a radioactive decay is applied to the concentrations every year (not shown in the above equations).

The concentration C_{2010} of each tracer at the year of sampling (2010) is determined by solving equations (1') and (2') as a function of the initial renewal time τ_{init} of the undisturbed reservoir (before the commissioning of the bottling plant) for various w/r . The value of w/r , which is not known precisely, is assumed equal to 1 in natural conditions. For all the sites where groundwater is pumped from a well, different values of w/r between 1 and 10 are tested. Since C_{2010} must be equal to the measured concentration, a value of τ_{init} can be determined for each tracer. Calculations start in 1950 for CFC's with an initial concentration set to zero. For tritium, an additional spin-up phase going from 1900 to 1950 is necessary to allow for the establishment of the natural concentration in the groundwater reservoir. Table 3 displays the value of the renewal time at each site calculated for each tracer for $w/r=1$ and $w/r=10$. One can see that the impact of the value chosen for w/r remains limited. This unexpected result is due to the fact that tracer infiltration started in the 1950's, that is well before the commissioning of most of the sites (see Table 1); as a consequence, because of the small withdrawal time compared to the tracer infiltration history, the influence of the withdrawal rate has not enough time to really make a strong difference. Tritium-based renewal times are systematically higher than those of F-12 and F-113. For the majority of the studied sites, renewal times are in the range 50-150 years and, as expected, increase to several centuries (and even millenia) for the sites that show the highest dilution by old waters (Jannet, Hayet, Sabrine, Marwa).

The discrepancy between tritium-based and F-12 / F-133-based renewal times indicates that the well-mixed reservoir hypothesis is clearly oversimplified, thus explaining why the renewal time is affected by the temporal shape of the tracer input function. In actuality, the deep reservoirs are most likely characterized by vertical

gradients in tracer concentration. Therefore, analysing tracer concentrations at various depth as well as monitoring tracer concentrations in the mineral waters as a function of time would be very helpful to get a better view of the actual characteristics of groundwater reservoir at each site.

5. Conclusion

We have analysed anthropogenic tracers (tritium/helium-3, SF_6 , CFCs and radiocarbon) in eleven mineral waters of northern and central Tunisia.

The analysis of the tracer results show that SF_6 and F-11 are not entirely reliable due to an additional SF_6 component likely originating from in-situ production and a slight but significant F-11 loss attributed to in-situ degradation. All carbon-14 values are well below the natural modern value clearly showing the influence of the ^{14}C dilution by dead Dissolved Inorganic Carbon. Therefore, the tracer analysis focussed mainly on tritium, F-12 and F-113.

Tracer-tracer plots indicate that the analysed groundwaters are a mixture of “modern” rainwater with older waters of pre-1950s ages, which constitute the main groundwater reservoir. ^{14}C data suggest that the age of these old waters is of the order of radiocarbon half-life or more.

The degree of dilution by these old waters is a qualitative indication of size of the reservoir, and therefore of the sustainability of groundwater resource. More quantitatively, the renewal time of each mineral groundwater was estimated using a well-mixed reservoir hypothesis. Most of the studied sites have groundwater renewal times in range from 50-150 years. For the sites where tracer concentrations are the most diluted by old waters, this value increase to several centuries. However one

observes some serious discrepancies between tritium based and F-12 / F-133 based results, clearly showing that the well-mixed reservoir hypothesis is oversimplified and calling for additional tracer data and a better resolution of well screens to define the vertical gradients in tracer concentration in the various reservoirs.

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Appendix A. Geological setting

The Tunisian mineral waters are found in various geological domains, trapped in the Jurassic, Upper Cretaceous and Eocene limestone reservoirs as well as the Mio-Pliocene detrital reservoirs.

The Marwa mineral waters are captured by an inclined borehole, upstream of Ain el Hammam natural spring. The latter was captured by the Romans via galleries. The Upper Cretaceous fractured and karstified carbonate aquifer forms a large NE-SW synclinal structure affected by faults in the same direction. The centre of the structure is occupied by Paleocene marls providing partial protection of the aquifer against pollution. The aquifer is supplied by infiltration of precipitation waters through widespread carbonates outcropping and forming the Anntra and El Hara massifs.

Crystalline and Aqualine mineral waters are captured in the Jurassic limestones by two deep drillings of 187 and 96 m respectively, both located to the NW side of the Zaghouan massif. The waters are supplied by infiltration of precipitation in the

Zaghouan massif affected by numerous faults: the Zaghouan fault on the SE side and by smaller faults on the NW side (Turki, 1985). The underground flows of Jurassic aquifers waters are oriented towards the NW (mineral water catchment area) and the SE of the Zaghouan massif (Zeriba thermal springs).

The Ain Garci mineral waters are captured by a gallery dug in the Eocene limestones. They are probably mixed with the ascending waters of the upper Cretaceous aquifers (Campanian and Cenomanian-Turonian limestones). The physical-chemical characteristics of the mineral waters suggest a deep supply in relation to volcanic rocks (basalt alkaline) associated with the Cenomanian-Turonian carbonates recorded in Jebel Fadhloun and jebel Abid (Raaf and Althuis, 1952; Laaridhi-Ouazaa, 1994). Ain Garci mineral waters show the highest radioactivity, confirming the influence of volcanic rocks (Ben Belgacem, 2011).

The mineral water Safia (Ain Mizeb) is captured by a recent gallery in continuity with a Roman gallery and also by drillings (Ain Ksiba). Ain Mizeb is located about 50 km south of El Kef and 800 m above sea level. The aquifer is housed in the Eocene limestones of Sra Ouertène (Jellouli). It is a vast limestone plateau resting on the phosphatic layers and covered in places by marls and lumachelles. This plateau is affected by numerous faults and the source (Ain Mizeb) is associated with a fault bringing the Eocene limestone sediments into contact with the marls. The drilling (SO12) capturing Ain Ksiba is located on the edge of the collapsed part of the massif of Sra Ouertene.

The mineral water Dima is recovered by a drilling upstream of the Ain M'rada at the level of the wadi Lassoued syncline. This structure is formed by the Eocene limestones and the central part is occupied by the Upper Eocene-Oligocene sediments. It is affected by a series of oblique faults, the most important of which is

that of Ain Sassi. This structure constitutes an important hydraulic unit from which emerges several sources: Ain Sassi, Ain Badi and Ain M'rada along the faults. The Eocene limestones constitute the Dima mineral water aquifer. The direction flow of groundwater is SW-NE, so water capture is located in the upstream part of the aquifer.

Mineral waters of Fourat, Janet, Sabrine and Hayet are captured by drillings in the Miocene detrital Formation: the water table of Janet aquifer is tapped by a 360 m deep drilling intersecting the Mio-Pliocene detrital Formation near Haffouz (Kairouan) which is in direct contact with Eocene limestone formations.

The Fourat mineral water comes from a source located at Ksar Lemsa in the delegation of Oueslatia. The mineral water of Fourat is captured by a deep drilling crossing the Mio-Pliocene formations which are in direct contact with the Eocene limestone.

Sabrine waters are captured by a 154 m deep drilling in the southern part of the Chougafia aquifer. It is trapped in a synclinal basin, the core of which is formed by the Mio-Pliocene siliceous sands and is fed by the reliefs surrounding the structure. The water flow of this aquifer is directed SW-NE (Farid et al., 2015) and the drilling, collecting the mineral water is located in the upstream part of the aquifer.

Hayet mineral waters are captured by a 226 m deep drilling located at Baten El Ghazel in the delegation of Jelma, 45 km away from Sidi Bouzid. The aquifer is housed in the Miocene sandstone and sealed by marls. Water supply through infiltration occurs throughout sandstones outcropping on the flanks of jebels Labeidh and M'Rihla.

7. References :

399

400 Aeschbach-Hertig, W., Peeters, F., Beyerle, U., Kipfer, R., 1999. Interpretation of
401 dissolved atmospheric noble gases in natural waters. *Water Resour. Res.*, 35,
402 2779-2792.

403 Ambach W, Dansgaard W, Eisner H, Mollner J., 1968. The altitude effect on the
404 isotopic composition of precipitation and glacier ice in the Alps: *Tellus* 20, 595-
405 600.

406 Ayraud, V., Aquilina, L., Labasque, T., Pauwels, H., Molenat, J., Pierson-Wickmann,
407 A.C., Durand, V., Bour, O., Tarits, C., Le Corre, P., Fourre, E., Mérot, P., Davy,
408 P., 2008. Compartmentalization of physical and chemical properties in hard rock
409 aquifers deduced from chemical and groundwater age analyses. *Appl. Geochem.*
410 23, 2686–2707.

411 Battle-Aguilar, J., Banks, E.W., Batelaan, O., Kipfer, R., Brennwald, M.S., Cook,
412 P.G., 2017. Groundwater residence time and aquifer recharge in multilayered
413 semi-confined and faulted aquifer systems using environmental tracers. *J. Hydrol.*
414 546, 150-165.

415 Baudron, P., Barbecot, F., Gillon, M., Arostegui, J.L.G., Travi, Y., Leduc, C., Gomariz
416 Castillo, F., Martinnez-Vicente, D., 2013. Assessing groundwater residence time
417 in a highly anthropized unconfined aquifer using bomb peak ^{14}C and
418 reconstructed irrigation ^3H . *Radiocarbon* 55, 993-1006.

419 Ben Belgacem, S., 2011. Les activités alpha et bêta globales dans l'eau minérale
420 tunisienne. PFE Chimie Industrielle INSA Tunis, 61 pp.

- Beyerle, U., Aeschbach-Hertig, W., Hofer, M., Imboden, D.M., Baur, H., Kipfer, R.,
1999. Infiltration of river water to a shallow aquifer investigated with $^3\text{H}/^3\text{He}$, noble
gases and CFCs. *J. Hydrol.* 220, 169–185.
- Bullister, J.L., 2011. Atmospheric CFC-11, CFC-12, CFC-113, CCl_4 and SF_6
Histories. http://cdiac.ornl.gov/ftp/oceans/CFC_ATM_Hist/. Carbon Dioxide
Information Analysis Center, Oak Ridge National Laboratory, US Department of
Energy, Oak Ridge, Tennessee.doi: 10.3334/CDIAC/otg.CFC_Hist.
- Busenberg, E. and Plummer, N.L., 2000. Dating Young Groundwater with Sulfur
Hexafluoride: Natural and Anthropogenic Sources of Sulfur Hexafluoride, *Water
Resour. Res.* 36 (10), 3011-3030.
- Busenberg, E., Plummer, L.N., 1992. Use of chlorofluorocarbons (CCl_3F and CCl_2F_2)
as hydrologic tracers and age dating tools: the alluvium and terrace system of
central Oklahoma. *Water Resour. Res.* 28, 2257–2283.
- Busenberg, E., Plummer, L.N., 2000. Dating young groundwater with sulfur
hexafluoride: natural and anthropogenic sources of sulfur hexafluoride. *Water
Resour. Res.* 36, 3011–3030.
- Celle-Jeanton, H., Zouari, K., Travi, Y., Daoud, A., 2001. Isotopic characterisation of
the precipitation in Tunisia. Variations of the stable isotope compositions of rainfall
events related to the origin of air masses. *Compte-rendus de l'Académie des
Sciences, série IIa*, 333, 625-631.
- Clark, I. and Fritz, P., 1997. Environmental isotopes in hydrogeology. Lewis
Publishers, CRC Press, New York, 331pp.

- Cook, P.G., Solomon, D.K., 1995. Transport of trace gases to the water table: Implications for groundwater dating with chlorofluorocarbons and krypton-85. *Water Resour. Res.* 31, 263–270.
- Corcho Alvarado, J.A., Purtschert, R., Hinsby, K., Trolborg, L., Hofer, M., Kipfer, R., Aeschbach-Hertig, W., Arno-Synal H., 2005. ^{36}Cl in modern groundwater dated by a multi-tracer approach ($^3\text{H}/^3\text{He}$, SF_6 , CFC-12 and ^{85}Kr): a case study in quaternary sand aquifers in the Odense Pilot River Basin, Denmark. *Appl. Geochem.* 20, 599-609.
- Corcho Alvarado, J.A., Purtschert, R., Barbecot, F., Chabault, C., Rueedi, J., Schneider, V., Aeschbach-Hertig, W., Kipfer, R. and Loosli, H. H., 2007. Constraining the age distribution of highly mixed groundwater using ^{39}Ar : A multiple environmental tracer ($^3\text{H}/^3\text{He}$, ^{85}Kr , ^{39}Ar and ^{14}C) study in the semiconfined Fontainebleau Sands Aquifer (France). *Water Resour. Res.* 43, W03427, doi:10.1029/2006WR005096.
- Craig, H., 1961. Isotopic variation in meteoric water. *Science* 133, 1702-1703.
- Darling, W.G., Goody D.C., MacDonald A.M., Morris B.L., 2012. The practicalities of using CFCs and SF_6 for groundwater dating and tracing. *Appl. Geochem.* 27, 1688-1697.
- Deeds, D.A., Vollmer, M.K., Kulongoski, J.T., Miller, B.R., Mühle, J., Harth, C.M., Izbicki, J.A., Hilton, D.R. and Weiss, R.F., 2008. Evidence for Crustal Degassing of CF_4 and SF_6 in Mojave Desert Groundwaters, *Geochim. Cosmochim. Acta* 72, 999-1013.
- Delbart, C., Barbecot, F., Valdes, D., Tognelli, A., Fourré, E., Purtschert, R., Couchoux, L., Jean-Baptiste, P., 2014. Investigation of young water inflow in karst

aquifers using SF_6 –CFC– $^3\text{H}/\text{He}$ – ^{85}Kr – ^{39}Ar and stable isotope components. Appl. Geochem. 50, 164-176.

Farid, I., Zouari, K., Rigane, A., Beji, R., 2015. Origin of the groundwater salinity and geochemical processes in detrital and carbonate aquifers: Case of Chougafiya basin (Central Tunisia). J. Hydrol. 530, 508-532.

Fourré E., Di Napoli, R., Aiuppa, A., Parello, F., Gaubi, E., Jean-Baptiste, P., Allard, P., Calabrese, S., Ben Mammou, A., 2011. Regional variations in the chemical and helium-carbon isotope composition of geothermal waters across Tunisia. Chemical Geology 288, 67-85.

Frija, A., Chebil, A., Speelman, S., Faysse, N., 2014. A critical assessment of groundwater governance in Tunisia. Water Policy 16, 358-373.

Gat, J.R. and Carmi, I., 1970. Evolution of the isotopic composition of atmospheric waters in Mediterranean Sea area, J. Geophys. Res. 75, 3039-3048.

Gooddy, D.C., Darling, W.G., Abesser, C., Lapworth, D.J., 2006. Using chlorofluorocarbons (CFCs) and sulphur hexafluoride (SF_6) to characterise groundwater movement and residence time in a lowland Chalk catchment. J. Hydrol. 330, 44-52.

Harnisch, J. and Eisenhauer, A., 1998. Natural CF_4 and SF_6 on Earth. Geophys. Res. Lett. 25 (13), 2401-2404.

Han, L.F., Plummer, L.N., 2016. A review of single-sample-based models and other approaches for radiocarbon dating of dissolved inorganic carbon in groundwater. Earth Science Reviews 152, 119-142.

Höhener, P., Werner, D., Balsiger, C., Pasteris, G., 2003. Worldwide occurrence and fate of chlorofluorocarbons in groundwater. Water Resour. Res. 33, 1-33.

- Jean-Baptiste, P., Mantisi, F., Dapoigny, A., Stievenard, M., 1992. Design and performance of a mass spectrometric facility for measuring helium isotopes in natural waters and for low-level tritium determination by the ^3He ingrowth method. *Int. J. Radiat. Appl. Instrum.* 43, 881-891.
- Jean-Baptiste, P., Fourré, E., Dapoigny, A., Baumier, D., Baglan, N., Alanic, G., 2010. ^3He mass spectrometry for very low-level measurement of organic tritium in environmental samples. *J. Environ. Rad.*, 101, 185-190.
- Kralik, M., Humer, F., Fank, J., Harum, T., Klammler, G., Goddy, D., Sültenfuß, J., Gerber, C., Purtschert, R. 2014. Using $^{18}\text{O}/^2\text{H}$, $^3\text{H}/^3\text{He}$, ^{85}Kr and CFCs to determine mean residence times and water origin in the Grazer and Leibnitzer Feld groundwater bodies (Austria). *Appl. Geochem.* 50, 150-163.
- Laaridhi-Ouazaa, N., 1994. Etude minéralogique et géochimique des épisodes magmatiques mésozoïques et miocènes de la Tunisie. PhD Thesis, Univ. Tunis II, 457 pp.
- Labasque, T., Ayraud, V., Aquilina, L., Le Corre, P., 2006. Dosage des composés chlorofluorocarbonés et du tétrachlorure de carbone dans les eaux souterraines. Application à la datation des eaux. Editions Géosciences Coll Cahiers Techniques. ISBN:2-914375-38-7.
- Lapworth, D.J., MacDonald, A.M., Krishan, G., Rao, M.S., Goddy, D.C. and Darling, W.G., 2015. Groundwater recharge and age-depth profiles of intensively exploited groundwater resources in northwest India, *Geophys. Res. Lett.*, 42, 7554–7562, doi:10.1002/2015GL065798.
- Lucas, L.L., Unterwieser, M.P., 2000. Comprehensive review and critical evaluation of the half-life of tritium. *J. Res. Natl. Inst. Stand. Technol.* 105, 541-549.

- 515 Massmann, G., Sültenfuß, J., Dünnebier, U., Knappe, A., Taute, T., Pekdeger, A.,
516 2008. Investigation of groundwater residence times during bank filtration in Berlin:
517 a multi-tracer approach. *Hydrol. Process.* 22, 788–801.
- 518 Mayer, A., Sültenfuß, J., Travi, Y., Rebeix, R., Purtschert, R., Claude, C., Le Gal La
519 Salle, C., Miche, H., Conchetto, E., 2014. A multi-tracer study of groundwater
520 origin and transit-time in the aquifers of the Venice region (Italy). *Appl. Geochem.*
521 50, 177-198.
- 522 Nydal, R., and K. Lövseth. 1996. Carbon-14 Measurements in Atmospheric CO₂ from
523 Northern and Southern Hemisphere Sites, 1962-1993. ORNL/CDIAC-93, NDP-
524 057. Carbon Dioxide Information Analysis Center, Oak Ridge National Laboratory,
525 Oak Ridge, Tennessee. 67 pp. doi: 10.3334/CDIAC/atg.ndp057
- 526 Oster, H., Sonntag, C., Munnich, K.O., 1996. Groundwater age dating with
527 chlorofluoro-carbons. *Water Resour. Res.* 32 (10), 2989-3001.
- 528 Plummer, L.N., Busenberg, E., Böhlke, J.K., Nelms, D.L., Michel, R.L., Schlosser, P.,
529 2001. Groundwater residence times in Shenandoah National Park, Blue Ridge
530 Mountains, Virginia, USA: a multi-tracer approach. *Chemical Geology* 179, 93-
531 111.
- 532 Plummer, L.N. and Glynn, P.D., 2013. Radiocarbon dating in groundwater systems.
533 In: *Isotope methods for dating old groundwater*, International Atomic Energy
534 Agency, Vienna, STI/PUB/1587, Chapter 4, 33-89.
- 535 Poreda, R.J., Cerling, T.E. and Solomon, D.K., 1988. Tritium and helium isotopes as
536 hydrologic tracers in a shallow unconfined aquifer. *J. Hydrol.*, 103, 1-9.

- 537 Raaf, J.F.M. and Althuis, S.P., 1952. Présence d'ophites spilitiques dans le Crétacé
538 des environs d'Enfidaville. 19th International Geological Congress, Algiers, 2^d Ser.
539 Tunisia 6, 127-137.
- 540 Schlosser, P., Stute, M., Dörr, H., Sonntag, C. and Münnich, K.O., 1988. Tritium/³He
541 dating of shallow groundwater. *Earth Planet. Sci. Lett.*, 89, 353-362.
- 542 Shapiro, S.D., Schlosser, P., Smethie, W.M., Stute, M., 1997. The use of H-3 and
543 tritogenic He-3 to determine CFC degradation and vertical mixing rates in
544 Framvaren Fjord, Norway. *Marine Chemistry* 59 (1–2), 141-157.
- 545 Siegenthaler, U. and Oeschger, H., 1980. Correlation of ¹⁸O in precipitation with
546 temperature and altitude, *Nature* 285, 314–317.
- 547 Solomon, D.K. and Sudicky, E.A., 1991. Tritium and helium-3 isotope ratios for direct
548 estimation of spatial variations in groundwater recharge. *Water Resour. Res.*,
549 27(9), 2309-2319.
- 550 Solomon, D.K., Schiff, S.L., Poreda, R.J. and Clarke, W.B., 1993. A validation of the
551 ³H/³He method for determining groundwater recharge. *Water Resour. Res.*, 29(9),
552 2951-2962.
- 553 Solomon D.K., Genereux D.P., Plummer L.N., Busenberg E., 2010. Testing mixing
554 models of old and young groundwater in a tropical lowland rain forest with
555 environmental tracers. *Water Resour. Res.* 46, W04518,
556 doi:10.1029/2009WR008341.
- 557 Stewart, M.K., 2012. A 40-year record of carbon-14 and tritium in the Christchurch
558 groundwater system, New Zealand: dating of young samples with carbon-14. *J.*
559 *Hydrol.* 430, 50-68.

- Stute, M., Deák, J., Révész, K., Böhlke, J.K., Deseö, E., Weppernig, R., Schlosser, P., 1997. Tritium/³He dating of river infiltration: an example from the Danube in the Szigetköz Area, Hungary. *Groundwater* 35 (5), 905–911.
- Suckow, A., 2014. The age of groundwater – Definitions, models and why we do not need this term. *Appl. Geochem.* 50, 222-230.
- Szabo, Z., Rice, D.E., Plummer, L.N., Busenberg, E., Drenkard, S., Schlosser, P., 1996. Age dating of shallow groundwater with chlorofluorocarbons, tritium/helium-3, and flow path analysis, southern New Jersey coastal plain. *Water Resour. Res.* 32 (4), 1023–1038.
- Thompson, G.M. and Hayes J.M., 1979. Trichloromethane in groundwater: A possible tracer and indicator of groundwater age. *Water Resour. Res.*, 15, 546-554.
- Turki M.M., 1985. Polycinématique et contrôle sédimentaire associé sur la cicatrice Zaghuan- Nebhana. PhD Thesis, Univ. Tunis. C. ST-INRST Ed., 7, 252 pp.

Figure captions

Fig.1 : Map of Northern and Central Tunisia showing the location of the groundwater sampling sites.

Fig.2 : Comparison of the stable isotopic composition of precipitation with the isotopic composition of the groundwaters. Tunis and Sfax Local Meteoric Water Lines (dotted lines) are from Celle-Jeanton et al. (2001). The Global Meteoric Water Line (GMWL) and Mediterranean Meteoric Water Line (MMWL) are from Craig (1961) and Gat & Carmi (1970), respectively.

Fig.3 : Tracer ages comparison : ^3H - ^3He (light blue), F-11 (red), F-12 (yellow), F-113 (green), SF_6 (dark blue)

Fig.4 : Atmospheric concentration of the transient tracers for the northern hemisphere as a function of time. CFC and SF_6 curves (a) are from Bullister (2011) and ^{14}C data are from Nydal & Lövseth (1996). Tritium content of rainwater in Tunisia (b) was constructed using all historical measurements from Central Mediterranean stations in the IAEA Global Network of Isotopes in Precipitation database (at <https://nucleus.iaea.org/wiser/gnip.php>), including the times-series of tritium in rainwater for Tunis and Sfax.

Fig.5 : CFC and SF_6 tracer plots showing F-113 versus F-12 (a), SF_6 versus F-12 (b) and F-11 versus F-12 (c). The black and blue curves correspond to the PF model and the PF model + dispersion respectively (see text). Numbers are travel times (in

year) in the PF model. The dotted line represents the mixing between a recharge water of the year 2010 (upper right corner) and an old water endmember with zero tracer concentration (lower left corner).

Fig.6 : (a) ^3H versus F-12. The black and blue curves correspond to the PF model and the PF model + dispersion respectively (see text). Tritium values prior to 2010 are decay-corrected using a tritium half-life of 4500 d (Lucas and Unterweger, 2000). Dotted curve represent mixing between old waters and a recharge water of the year 2010 . (b) ^3H versus ^{14}C (corrected for carbonate dissolution). NB: the initial ^{14}C value of recharge waters, as given by the ^{14}C input function (Fig. 4a), can be modified by interaction of infiltrating water with soil CO_2 from plant root respiration and microbial degradation of soil organic matter. In semi-arid to arid environments however, those biological interactions are minimal (Plummer and Glynn, 2013) so this effect is neglected here.

Fig.7 : Comparison of the fraction of old water present at each site, estimated from the F113 - F12 and tritium - F12 diagrams.

Table captions

Table 1 : Summary of the main relevant parameters for the sampled sites

Table 2 : Tracer results. CFCs and SF₆ tracer concentrations have been corrected from excess air as defined by neon data and normalized to sea-level pressure and a common temperature of 15°C to allow the comparison of all sites (note that the uncertainty on CFC and SF₆ ages do not take into account the uncertainty on the air excess correction, mostly because of the lack of knowledge of the exact recharge altitude).

Table 3 : Estimated groundwater renewal time for the various sites based on tritium, F-12 and F-113 data, assuming a well-mixed reservoir (see text).

Site	Geographic zone	Catchment type	Well depth (m)	Year of commissioning	Altitude of the site (m)	Average temperature (°C)		Average precipitation (mm)			Recharge temperature (°C) (precipitation weighed)	pH	HCO ₃ (mmol/l)
						January	July	January	July	Annual			
Marwa	Bizerte	well	72	1993	300	11,3	25,2	77	3	558	13,1	7,2	4,17
Safia (Ain Mizab)	El Kef	surface	0	1968	880	7,1	26,5	65	9	509	12,9	7,3	3,87
Safia (Ain Ksiba)	El Kef	well	62	1992	900	7,1	26,5	65	9	509	12,7	7,0	3,71
Dima	El Kef	well	~50	2009	750	7,1	26,5	65	9	509	13,7	7,5	4,04
Cristaline	Zaghouan	well	187	2003	200	9,6	27,0	68	5	496	15,2	7,4	3,79
Aqualine	Zaghouan	well	96	2006	200	9,6	27,0	68	5	496	15,2	7,6	4,40
Ain Garci	Zaghouan	surface	0	1900	110	9,6	27,0	68	5	496	15,2	6,6	19,84
Sabrine	Kairouan	well	154	1991	106	11,7	29,1	23	5	306	17,6	7,5	3,80
Fourat	Kairouan	well	~150	2003	400	11,7	29,1	23	5	306	16,1	7,2	4,80
Hayet	Kairouan	well	226	1996	420	11,7	29,1	23	5	306	16,0	7,5	2,15
Jannet	Kairouan	well	360	2002	400	11,7	29,1	23	5	306	16,1	7,6	3,75

Table 1

Site	Tritium	Neon excess	3H-3He age	F-11		F-12		F-113		SF6		F-11 age		F-12 age		F-113 age		SF6 age		2-H	18-O	14-C		delta 13-C	14-C corrected
	(TU)	(%)	(year)	(pmol/L)		(pmol/L)		(pmol/L)		(pmol/L)		(year)		(year)		(year)		(year)				(pmC)		(permil)	(pmC)
Marwa (2009)	1,44 ± 0,13	230,1	34,6 ± 1,4																			52,27 ± 0,21	-11,14	56,30	
Marwa	1,35 ± 0,05	26,6	23,9 ± 0,6	0,69 ± 0,12		0,549 ± 0,07		0,081 ± 0,01		7,99E-04 ± 1,2E-04		42 ± 2		40 ± 3		32 ± 2		20 ± 2		-35,7	-6,45				
Safia-Ain Mizeb (2009)	3,29 ± 0,15	11,0	10,4 ± 2,4																	-49,1	-7,84	55,07 ± 0,19	-11,82	55,90	
Safia-Ain Ksiba	3,34 ± 0,06	7,3	9,98 ± 1,1	2,08 ± 0,12		1,320 ± 0,07		0,208 ± 0,01		1,27E-03 ± 1,2E-04		34 ± 2		31 ± 2		25 ± 2		13 ± 2		-49,9	-7,66	58,01 ± 0,22	-12,36	58,01	
Dima	3,03 ± 0,08	50,1	12,9 ± 1,0	1,43 ± 0,12		1,067 ± 0,07		0,176 ± 0,01		1,33E-03 ± 1,2E-04		37 ± 2		34 ± 2		26 ± 2		12 ± 2		-50,5	-7,62	68,72 ± 0,24	-12,22	68,72	
Cristaline	3,10 ± 0,08	34,5	19,8 ± 0,7	1,64 ± 0,12		1,134 ± 0,07		0,165 ± 0,01		1,66E-03 ± 1,2E-04		36 ± 2		33 ± 2		24 ± 2		8 ± 1		-36,3	-6,51	67,93 ± 0,24	-10,47	77,86	
Aqualine	3,16 ± 0,12	31,1	19,5 ± 0,6	1,64 ± 0,12		1,069 ± 0,07		0,166 ± 0,01		1,73E-03 ± 1,2E-04		36 ± 2		34 ± 2		26 ± 2		7 ± 1		-36,0	-6,52	66,43 ± 0,21	-10,57	75,42	
Ain Garci (2009)	0,49 ± 0,04	-0,4																		-31,7	-5,65	2,25 ± 0,09	-0,75	36,00	
Sabrine	0,23 ± 0,05	10,9	37,1 ± 1,7	0,14 ± 0,12		0,061 ± 0,07		0,034 ± 0,01		1,84E-04 ± 1,2E-04		51 ± 2		56 ± 3		37 ± 2		33 ± 2		-31,6	-5,26	31,30 ± 0,14	-8,50	44,19	
Fourat	2,53 ± 0,05	8,2	26,8 ± 1,0	1,30 ± 0,12		0,894 ± 0,07		0,136 ± 0,01		1,20E-03 ± 1,2E-04		38 ± 2		36 ± 2		28 ± 2		14 ± 2		-38,8	-6,59	60,66 ± 0,20	-11,35	64,13	
Hayet	0,10 ± 0,06	38,8	55,7 ± 17,7	0,25 ± 0,12		0,185 ± 0,07		0,031 ± 0,01		2,33E-04 ± 1,2E-04		48 ± 2		51 ± 3		43 ± 2		31 ± 2		-32,2	-5,10	34,54 ± 0,16	-10,94	37,89	
Jannet	0,12 ± 0,07	16,3	48,1 ± 16,3	0,12 ± 0,12		0,045 ± 0,07		0,025 ± 0,01		3,02E-04 ± 1,2E-04		52 ± 2		58 ± 3		39 ± 2		29 ± 2		-37,2	-6,32	3,62 ± 0,10	-7,49	5,80	

Table 2

Site	Tritium-based renewal time (yr)		F12-based renewal time (yr)		F113-based renewal time (yr)	
	w/r = 1	w/r = 10	w/r = 1	w/r = 10	w/r = 1	w/r = 10
Marwa	329	360	131	215	125	215
Safia-Ain Mizeb	108	n.a	-	-	-	-
Safia-Ain Ksiba	106	186	41	183	38	183
Dima	122	135	57	69	49	61
Cristaline	118	134	52	89	53	90
Aqualine	114	129	57	75	53	72
Ain Garci	950	n.a	-	-	-	-
Sabrine	2100	2100	1320	1390	320	400
Fourat	155	171	72	102	68	100
Hayet	4500	4500	430	470	350	400
Jannet	4100	4100	1800	1800	440	470

Table 3

Figure 1

Figure 2

Figure 3

Figure 4

Figure 5a

Figure 5b

Figure 5c

Figure 6a

Figure 6b

Figure 7

^3H - ^3He , CFCs, SF_6 and ^{14}C were analyzed in commercial mineral groundwaters of Tunisia

All studied groundwaters are a mixture of modern rainwater with old groundwaters

Radiocarbon ages of these old groundwaters are in the range 5000-20000 years

Most groundwaters have renewal times between 50 years and several centuries