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Groundwater geochemistry of a small reservoir catchment in Central Tunisia

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Abstract

Due to the scarcity of water resources in semiarid sedimentary basins, hill reservoirs are often constructed to recharge groundwater and limit runoff induced water loss. The impact of such reservoirs on groundwater chemistry is investigated in the aquifers of the El Gouazine watershed, Central Tunisia. Three groundwater types are recognised, Ca–HCO₃, Na–Cl and Ca–SO₄. The strong similarity between host rock and groundwater chemistries indicates significant rock–water interaction. A flowpath, along which the chemical composition of the groundwater evolves, can be identified using the contrast in stable isotope signature between upstream and downstream groundwater. Shallow upstream groundwater is recharged by the infiltration of rainwater with the rate of recharge strongly linked to the permeability of the host lithology. Calcium and HCO₃ are supplied to an alluvial aquifer from a more rapidly recharged limestone aquifer with the concentration of Ca and HCO₃ ions decreasing by dilution. The alluvial aquifer is also enriched in Ca and SO₄ during the downstream flow of groundwater through gypsiferous materials. There is evidence of mixing between meteoric groundwater and evaporated reservoir water. Below the reservoir and partly responsible for reservoir leakage is a sandy aquifer, formed by weathering and erosion of a sandstone host which also supplies water to the alluvial aquifer. © 2002 Elsevier Science Ltd. All rights reserved.

1. Introduction

A perennial problem for farmers and herdsman in semiarid areas without permanent rivers is the scarcity of water owing to the low and erratic rainfall. In the last century, global population expansion has tremendously increased the pressure on water resources. To secure water supply and intensify agricultural production, water harvesting is traditionally used to combat the problems of varying rainfall rates and population densities.

One technique of water harvesting, floodwater harvesting (FWH), also called large catchment water harvesting or spate irrigation, is widely developed. When floodwater is harvested in the stream bed, the water flow is dammed and stored in temporary or permanent surface reservoirs. Water is forced to infiltrate and, as a result, to recharge the aquifer, with recharge concentrated

mainly in the valley downstream from the reservoir (Prinz, 1999). FWH is a relatively inexpensive technique providing water for the development of agriculture and agroforestry, and reducing the use of other valuable water resources such as groundwater. Water supply is not always even and secure during the year depending on the climatic variability. Large evaporation losses and loss of storage by siltation and pollution are the main limitations of FWH. Social problems like conflict between water users are a further drawback to this style of water harvesting.

In the Mediterranean basin, water harvesting played an important role in ancient civilisations such as the Roman and Egyptian empires (Prinz, 1999). During the 20th century, modern techniques (groundwater drilling, large reservoir construction etc.), which are favoured by government policy, slowly replaced traditional harvesting techniques. High demands for water during the agricultural growing season, which coincides with the dry period of the Mediterranean climate, has resulted in the depletion of the groundwater table in some areas. The low renewal rate of groundwater resources and the

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poor water quality of permanent rivers in the Mediterranean basin make it necessary to find other water supplies and to revive traditional systems of water harvesting.

Since the early 1990s, the Tunisian Government has undertaken the implementation of the “National Strategy of Surface Runoff Mobilization” which aims at building numerous large dams, small earth dams, and other works for irrigation and water table recharge. More than 500 small earthworked reservoirs, called *hill reservoirs* in North Africa, have already been constructed and the construction policy is still in progress. They are mainly localized in the central part of the country, along the Atlas mountain range within the semiarid zone that receives from 250–500 mm of rainfall annually. Hill reservoirs show a high diversity in capacity, ranging from a few ten thousand m³ to several hundred thousand m³, and watershed areas vary from a few hectares to several dozen km². Land use in the watershed consists of a varied proportion of forestry and agriculture (Albergel et al., 1999). According to the Food and Agriculture Organization (FAO, 1997), the area of irrigated land under FWH in Tunisia amounts to 30,000 hectares. About 20 Mm³ of water are annually harvested covering 4250 ha (Prinz, 1999).

The functions assigned to these reservoirs are: to decrease soil loss caused by runoff, to reduce reservoir sedimentation and to replenish the groundwater tables (Talineau et al., 1994; Selmi, 1996; Albergel and Rejeb, 1997). At present, 30 reservoirs are monitored using a hydrological network within one catchment allowing the calculation of water budgets and modelling of catchment water flows.

Although hydrochemical investigation sometimes combined with hydrogeological inventory is well established throughout the Mediterranean basin (Adar et al., 1992; Armengol et al., 1994; Marc et al., 1996; Ben Othman et al., 1997; Petelet et al., 1997; Stigter et al., 1998), little is known in Tunisia about the influence of hill reservoir construction on groundwater flow and chemistry. A chemical and regional classification of hill reservoir water, recently performed by Rahaingomanana (1999), gives a general framework for more detailed studies such as the present one which is included in the European Union sponsored project Hydro-med.

The El Gouazine reservoir was chosen for the present study because the annual water balance is strongly negative, ranging from –47,522 m³ in 1997–1998 (Tunisian hydrological year, conventionally starting in September and ending in August) to –273,435 m³ in 1995–1996 (CES/ORSTOM, 1996, 1997a, 1997b, 1999), suggesting that water loss by infiltration is an important process. Leakage of the reservoir and concomitant recharge of the alluvial aquifer is attested by the appearance of marshy fields downstream of the reser-

voir. No saline spots, which could have been attributed to intensive evaporation from the saturated soils, were observed in the vicinity of the reservoir.

The goals of the present paper are threefold: (i) to spatially characterize water chemistry at a given time; (ii) to explain how the different geological and pedological parts of the watershed contribute to the chemistry of the reservoir water; (iii) to define how the construction of reservoirs can lead to alluvial aquifer recharge.

2. Study description

The El Gouazine watershed is about 50 km NW of the city of Kairouan (35°55'N–9°45'E) (Fig. 1). The watershed area is about 18.1 km² and is covered by steppe vegetation. The Mediterranean climate is marked by distinct summer (warm and dry) and winter (cool and humid) seasons. The mean annual rainfall in the watershed is 339 mm (estimated from 1994–1998, after Montoroi et al., 2000), more than 70% of this falling during the autumn and winter period (September–February). The mean annual air temperature is 19.1 °C with a 10.4 °C minimum in January and a 28.6 °C maximum in August. In the El Gouazine region, potential evapotranspiration on a yearly basis far exceeds the annual rainfall with a mean annual amount of approximately 1460 mm estimated from 1993 to 1995 (Riou, 1980). Class-A pan evaporation in the watershed was on the order of 1775 mm a⁻¹ during the 1996–1998 period, the monthly mean value ranging from 55.4 mm in January to 314 mm in July. The El Gouazine river watershed belongs to the Nebhana river network whose outlet occurs in the Kelbia endoreic depression (known as *sebkha* in Tunisia).

The El Gouazine watershed is located at the east boundary of the SW–NE orientated Ousseltia syncline. Pedological formations have developed on Tertiary sedimentary units (marly calcareous and gritty deposits), which were intensely folded by Atlasian tectonic movements resulting in rock layers dipping steeply SE to nearly vertical in the eastern part of the watershed (Castany, 1951; Jauzein, 1967; Fournet, 1969). The southeastern part of the basin is formed by Eocene marine sediments that include a mostly carbonaceous deposit composed of marl and nummulitic limestone of Ypresian or lower Lutetian age, and a mostly clayey deposit composed of marl and shelly limestone of upper Lutetian age. The northwestern part of the basin is formed from Oligocene sediments whose detrital facies is mostly gritty and known as the *Fortuna formation*. Layers of shelly limestone (containing oyster and/or gastropod fossils), limey sandstone and marl outcrop in some areas of the catchment. During the Quaternary, the sediments that comprise the syncline were eroded by the rivers (locally known as oued or wadi). Gravelly and

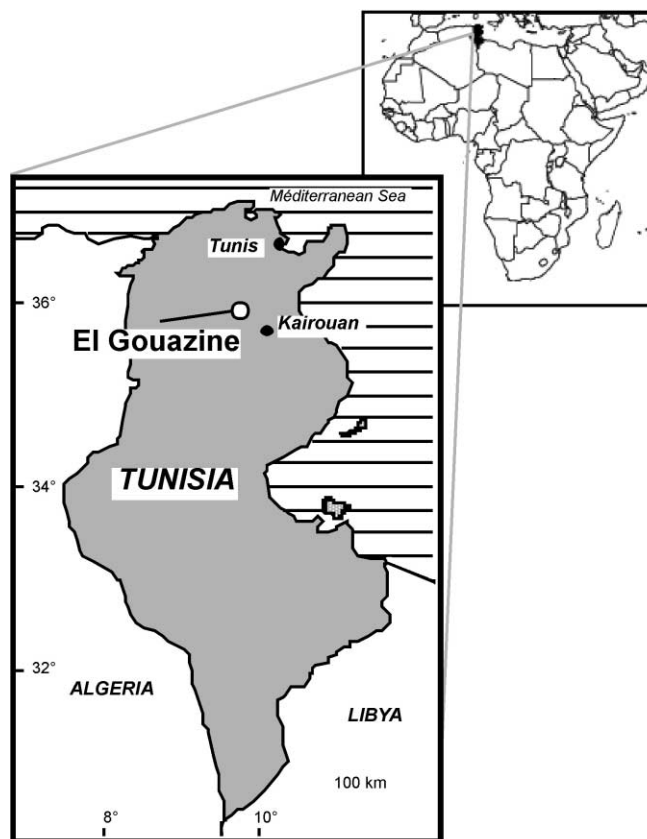


Fig. 1. Location of the El Gouazine watershed in Tunisia (North Africa).

pebbly colluviums were extensively deposited and subsequently cemented as calcretes. The geomorphology of the catchment is characterized by 575 m high hills along the eastern boundary of the watershed. The elevation regularly decreases to 375 m in the vicinity of the reservoir and the mean slope of the El Gouazine river is 18 m km^{-1} . Most soils are highly calcareous and clayey and locally calcified. On the hillslopes, colluvium is found with a high stone content. According to the World Reference Base for Soil Resources (ISSS Working group RB, 1998), the main soils in the catchment include calcrete calcisols and calcaric cambisols. Cambisols are mainly formed from marl deposits and locally from limey sandstone deposits.

Over the years, a large part of the native vegetation, consisting primarily of Alep pines and Carob trees, has been progressively replaced by rain fed cereals and by irrigated agricultural crops. Alep trees occupy only the poor calcareous soils at the top of the hills. This change in land use has likely affected the hydrological equilibrium, and hence the flows of water. Water conservation techniques such as the construction of benches, called *tabia* in Tunisia, are used in the watershed to limit

soil erosion. The high density of benches combined with the highly variable rainfall has contributed to a lack of runoff water available to replenish the reservoir (Nasri, 1999).

In 1990, the El Gouazine hill reservoir was formed by constructing a 232 m long earth dyke rising 10.6 m in the valley axis. The spillway overflows at a 8.28 m maximum water level and the reservoir surface in overflow situation is $9.597 \cdot 10^{-2} \text{ km}^2$ defining a 233,370 m^3 maximum capacity and a 0.53% watershed surface rate. Annual sedimentation is on the order of 2290 m^3 and actually corresponds to a maximum of 3 m as shown by a thick sediment deposit near the dyke. Owing to the low sedimentation, the reservoir is predicted to remain sustainable for more than 100 a (CES/ORSTOM, 1996, 1997a, 1997b, 1999).

3. Methodology

Surface waters were collected from 3 places: close to the dam for the open water surface of the reservoir (s1/1 and s1/2), in a small upstream pond dammed by the

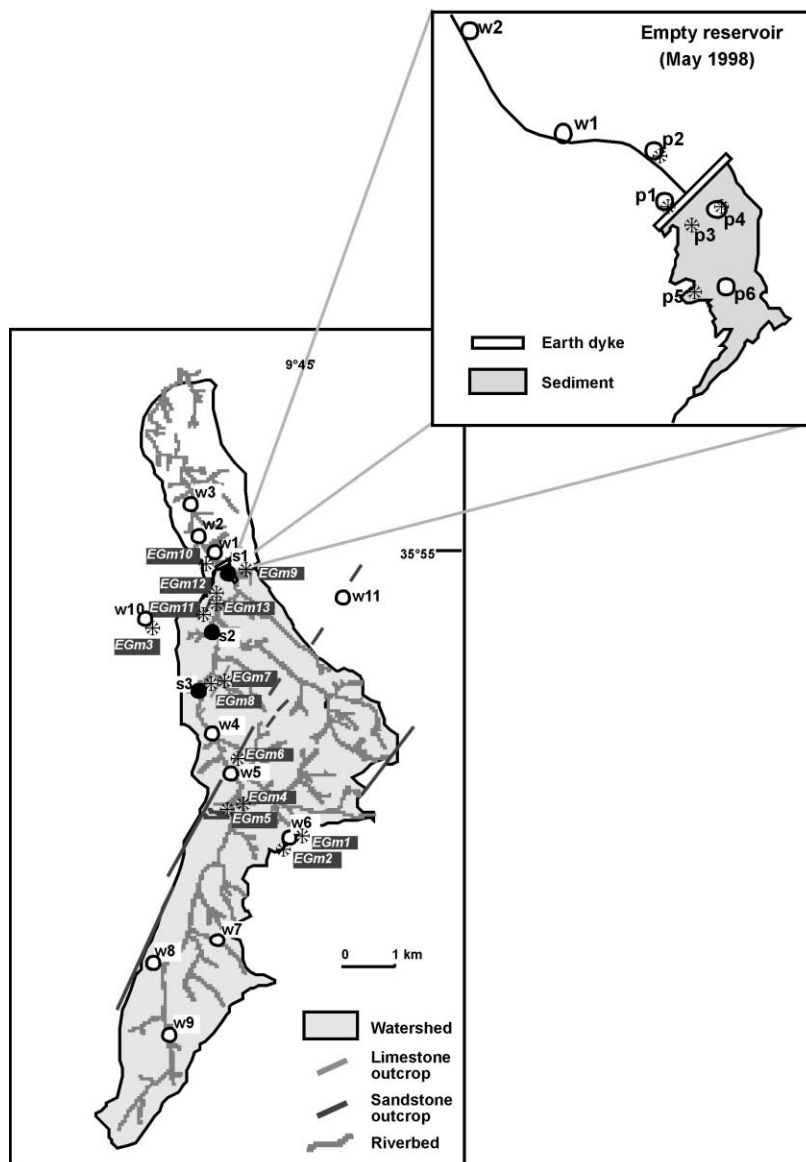


Fig. 2. Map of the El Gouazine watershed showing the main geological features and the sampling location points for sediments, soils, rocks (*) and waters (● surface waters, ○ ground waters).

road (s2), and in an affluent river that is potentially supplied by temporary, local groundwater seepage (s3) (Fig. 2). Underground waters were collected using a 1 l glass bottle which was slowly plunged and promptly opened in water. Sampling was performed within and beyond the catchment from 11 well locations, the water table depth ranging from 1.5 (w5) to 8.4 m (w6) under the ground surface. Groundwater was sampled without previous water discharge from 1 m below the water table surface and, for some wells, at the base of the well whose depth ranges from 2.3 (w3) to 15 m (w1). Sam-

pling was carried out in May 1998 during the dry period when the hill reservoir was almost empty. Up to 20 samples were collected and immediately filtered on site using a Nalgene filtration unit with a Millipore membrane (47 mm diameter cellulose nitrate filter stored in polyethylene boxes) of 0.2 μm pore size. Dissolved O_2 content, pH and electrical conductivity at 25 °C (EC) were measured in the field before and after filtration using WTWTM devices. All procedures (sampling, filtration, storage) were conducted in a manner designed to minimize potential sample contamination.

The major cation (Ca, Mg, Na and K) and anion (Cl, SO₄) concentrations were determined by liquid-ion chromatography (HPLC) on a Dionex chromatograph DX 120 located at the IRD centre of Bondy (France). The chromatograph was equipped with columns CS 12A and CG 12A for cations, using H₂SO₄ as eluant, and columns AS 14 and AG 14 for anions, using Na₂CO₃ and NaHCO₃ as eluant. The overall detection limit for ions was 0.05 mg l⁻¹. Aqueous silica (Si(OH)₄)^o concentration was measured by ICP-AES with a detection limit of 5 µg l⁻¹. The alkalinity was measured by titration with 0.1N HCl (in field) and 0.02N H₂SO₄ (in laboratory). The total analytical precision varied within 10%.

The analysis of stable isotopes in the water samples was conducted at the Paris XI-Orsay University using the Epstein-Mayeda technique (Epstein and Mayeda, 1953) as described by Taylor (1973) for ¹⁸O and the Zn reduction procedure for ²H (Coleman et al., 1982). Isotope ratios were measured using a mass spectrometer and expressed as δ-values, the deviations in parts per mil (‰) from the International Standard V-SMOW. The analytical precision is better than 0.2‰ for ¹⁸O and 2‰ for ²H.

As the dam was almost empty, 4 pits (p3, p4, p5 and p6) were dug in the dried reservoir sediments and sediment samples were collected in p3, p4 and p5 pits (EGp3, EGp4 and EGp5). Two others pits (p1 and p2) were dug on the downstream side of the dam for sampling (EGp1 and EGp2). Groundwater samples were collected in 4 pits (p1, p2, p4 and p6) and the above chemical analyses were conducted. The different lithologies cropping out in the catchment were collected in the vicinity of the wells where the groundwater was sampled (EGm1, ..., EGm13). The chemical and mineralogical analyses of the sediment, soil and rock samples were carried out at the IRD laboratory of Bondy, France. Major element composition was determined by ICP-AES after a fusion treatment with lithium borate. Analytical uncertainties are less than 10% for most elements. X-ray diffractometry (XRD) was performed for mineral characterization and identification of clay minerals using a D500 Siemens diffractometer.

4. Results

4.1. Geochemical and mineralogical features of solid phases

An existing geological map of the area at 1:200,000 scale (Maktar sheet) and a visual inspection of the catchment led to identify 4 main lithologies for sampling: limestone, marl, gypsiferous marl and sandstone. The XRD analysis confirms the field determination and

precise mineral content (Table 1). The presence of gypsum and the lack of calcite in two supposed marl samples (EGm8 and EGm12) allow the inference of the presence of a fifth parental rock, this was called gypsiferous mudstone. In addition to calcite, limestone samples contain a small amount of quartz, and traces of smectite and kaolinite. Quartz is abundant in all the other sampled catchment materials and, as expected, clay minerals and calcite characterize marl samples. Traces of illite are detected in the sandstone sample and feldspar is abundant. Reservoir sediments and riverbed soils are quartz-rich and contain varied abundances of calcite, smectite and kaolinite. Gypsum likely dissolved and removed by water flows is absent, and traces or low abundances of feldspar are most likely derived from erosion of sandstone, as evidenced by the mineralogical data. The EGp3r, EGp4r and EGp2r samples, corresponding to the gravel and pebble fractions, are limestone in origin.

Chemical composition in the parental rock, soil and sediment samples is displayed in Table 2. Limestone samples show that the lithology is Ca-rich (over 50%), and contains very low amounts of Mg and a variable amount of SiO₂ ranging from 2.8 to 10.3 g 100 g⁻¹. Sandstone is dominated by SiO₂ with nearly 90% while small amounts of Al₂O₃ and K₂O are also found, corresponding to the mineral illite, which has been identified in the sandstone by X-ray diffraction (Table 1). Marl and mudstone rock-types are clay-rich with a high amount of SiO₂ (37–55%), Al₂O₃ (13–16%) and Fe₂O₃ (5–7%), and variable amounts of cations. TiO₂ content is higher in the marl and mudstone than in the limestone. The 60–75 cm depth EGp3 and EGp5 samples have amounts of SiO₂ and CaO very similar to the sandstone rock-type suggesting a parental link in soil and sediment formation. In turn, the 125–150 cm depth EGp3, EGp4, EGp1 and EGp2 samples have a lower amount of SiO₂ and a higher amount of CaO, and are generally linked to marl samples.

4.2. Geochemical features of catchment waters: the influence of lithology

The results of chemical analysis of water samples are presented in Tables 3 and 4. The overall chemical characteristics of water measured in the field show a high contrast between reservoir water and watershed groundwater. The total dissolved solids (TDS) and the electrical conductivity (EC) of surface water (samples s1-s3) range from 0.6 (s1) to 6.0 (s3) g l⁻¹ and from 0.9 (s1) to 7.7 (s3) mS cm⁻¹. Reservoir water (s1/1 and s1/2) is highly oxygenated (dissolved O₂ content ranging from 9 to 12 mg l⁻¹) and weakly carbonated (alkalinity ≈ 2 mmolc l⁻¹). The pH of all the surface water samples is nearly neutral and can be higher (pH ≈ 10) in reservoir water. The TDS and EC of the groundwater, located

Table 1

Chemical composition (major elements) in the parental rock, soil and sediment samples. Values are in %

Sample	Quartz	Calcite	Gypsum	Feldspar	Smectite	Kaolinite	Illite
<i>Limestone</i>							
EGm1	XX	XXX	–	–	–	–	–
EGm2	XX	XXX	–	–	X	X	–
EGm7	XX	XXX	–	–	X	X	–
EGm3	X	XXX	–	–	–	–	–
EGm6	X	XXX	–	–	–	–	–
EGm11	X	XXX	–	–	X	X	–
<i>Marl</i>							
EGm4	XXX	XXX	–	–	XXX	XX	–
EGm5	XXX	XXX	X	–	XXX	XX	–
<i>Gypsiferous marl</i>							
EGm9	XXX	XXX	XXX	–	XX	XXX	–
EGm10	XXX	XXX	XXX	–	XX	XXX	–
<i>Gypsiferous mudstone</i>							
EGm8	XXX	–	XX	X	XXX	XX	–
EGm12	XXX	–	XXX	–	XX	XXX	–
<i>Sandstone</i>							
EGm13	XXX	–	–	XXX	–	–	X
<i>Reservoir sediment</i>							
EGp3 60–75	XXX	X	–	X	–	X	–
EGp3 125–150	XXX	XXX	–	X	XX	XX	–
EGp3r	XXX	XXX	–	X	–	–	–
EGp4 110–120	XXX	XXX	–	XX	XX	XX	–
EGp4r	XXX	XXX	–	X	X	X	–
EGp5 20–30	XXX	XX	–	XX	X	X	–
EGp5 50–70	XXX	X	–	X	X	X	–
<i>Riverbed soil</i>							
EGp1 2.50	XXX	XXX	–	XX	XX	XX	–
EGp2 2.00	XXX	XXX	–	X	XX	XX	–
EGp2r	XXX	XXX	–	X	X	X	–

within the watershed, varies from 0.6 (w8) to 6.2 (w4) g l⁻¹ and from 0.8 (w8) to 8.3 (w4) mS cm⁻¹. The pH values range between 6.9 (p6) and 7.7 (p4). Dissolved O₂ content, ranging from 1.3 (p6) to 7.5 mg l⁻¹ (w7/5 and w9/2), is higher in the ground waters than in the surface waters. Alkalinity in all groundwater samples is highly variable ranging from 3.7 (w8) to 10.7 (w4) mmol_c l⁻¹. Silica concentrations in the water samples, expressed as Si(OH)₄^o, show relatively small variations ranging from 22.3 (w6) to 27.0 (w4) mg l⁻¹ except for one pit (p4) in the reservoir sediments where Si concentration is very low (6.6 mg l⁻¹). Beyond the watershed and downstream of the reservoir, chemical data vary in the same range. These data are in agreement with the values given by Rahaingomanana (1999) for watersheds in the same geological environment. The chemistry of s3 surface water and w4 groundwater are very similar suggesting that the surface water is probably influenced by groundwater seepage (Tables 3 and 4).

Three groups of groundwater can be distinguished on the basis of major ion concentrations (Fig. 3). The first type (Ca–HCO₃), weakly mineralized, is represented by 3 wells located on a limestone outcrop (w6, w8 and w11). Bicarbonate and Ca, which range respectively from 50–65% mmol_c l⁻¹ and from 45 to 70% mmol_c l⁻¹, are the major ions and result from chemical weathering and erosion of the limestone. The second type of groundwater (Na–Cl) includes 5 wells (w4, w5, w7, w9 and w10), located in the marly lowlands between limestone outcrops, and is characterized by a lower concentration of Ca and HCO₃ coupling with a higher concentration of Mg. Sodium is the major cation in w9 and w10 wells whereas Cl dominates in w4, w5, w7 and w9 wells. In the lower part of the watershed, the third type of groundwater (Ca–SO₄) is draining a gypsiferous deposit and is dominated by Ca and SO₄ ions. These ions are less concentrated in the downstream part of the dam suggesting that upstream groundwater flow is diluted by reservoir water (Fig. 3).

Table 2

Relative importance of major minerals in the parental rock, soil and sediment determined by XRD analysis. XXX : highly abundant; XX : less abundant; X : trace; - : absent

Sample	SiO ₂	Al ₂ O ₃	TiO ₂	Fe ₂ O ₃	K ₂ O	Na ₂ O	MgO	CaO	MnO	P ₂ O ₅	H ₂ O ⁺	H ₂ O ⁻	Σ
<i>Limestone</i>													
EGm1	6.76	1.86	0.10	1.38	<0.01	<0.01	0.44	50.08	0.07	<0.03	0.52	39.22	100.4
EGm2	8.62	3.32	0.15	0.98	<0.01	<0.01	0.58	45.55	0.01	<0.03	1.40	38.29	98.9
EGm7	10.28	1.55	0.10	1.21	0.05	<0.01	0.27	49.12	0.11	<0.03	0.51	38.50	101.7
EGm3	2.83	0.59	0.05	0.87	<0.01	<0.01	0.34	53.62	0.10	<0.03	0.20	42.12	100.7
EGm6	2.99	0.65	0.05	0.25	<0.01	<0.01	0.62	54.46	<0.03	<0.03	0.25	42.44	101.7
EGm11	5.06	1.56	0.07	1.69	0.09	0.04	0.56	51.27	0.05	<0.03	0.32	41.15	101.9
<i>Marl</i>													
EGm4	41.99	13.51	0.56	5.23	0.78	<0.01	3.43	9.98	0.04	<0.03	5.50	17.09	98.1
EGm5	40.80	14.06	0.52	5.69	0.62	0.12	3.26	10.91	0.02	<0.03	6.45	15.75	98.2
<i>Gypsiferous marl</i>													
EGm9	42.46	15.25	0.63	6.76	0.74	<0.01	1.40	10.02	0.04	0.13	6.08	14.66	98.2
EGm10	37.10	13.27	0.61	5.72	0.71	<0.01	1.05	12.62	0.10	<0.03	5.89	16.79	93.9
<i>Gypsiferous mudstone</i>													
EGm8	54.66	16.19	0.85	7.07	0.92	0.25	2.10	1.76	0.06	<0.03	5.92	9.39	99.2
EGm12	42.36	15.93	0.76	5.37	1.42	0.04	1.42	6.23	0.01	<0.03	5.46	13.92	92.9
<i>Sandstone</i>													
EGm13	89.53	3.78	0.22	1.93	1.10	0.35	0.10	0.41	0.05	<0.03	0.37	1.44	99.3
<i>Reservoir sediment</i>													
EGp3 60–75	85.43	3.64	0.24	1.79	<0.01	<0.01	0.34	2.26	0.02	<0.03	1.24	4.47	99.4
EGp3 125–150	58.94	7.65	0.39	3.50	0.77	<0.01	1.05	9.25	0.03	<0.03	3.01	13.49	98.1
EGp4 110–120	62.95	6.48	0.35	3.06	0.51	<0.01	0.82	10.26	0.03	<0.03	2.29	12.67	99.4
EGp5 20–30	81.73	3.45	0.22	1.63	0.12	<0.01	0.35	2.58	0.01	<0.03	6.01	4.80	100.9
EGp5 50–70	87.81	3.07	0.20	1.61	<0.01	<0.01	0.28	1.09	0.01	<0.03	1.07	3.20	98.3
<i>Riverbed soil</i>													
EGp1 2.50	69.00	4.51	0.27	2.61	<0.01	<0.01	0.53	10.37	0.03	<0.03	1.32	10.40	99.0
EGp2 2.00	58.21	8.02	0.41	3.66	0.41	<0.01	0.88	10.07	0.03	<0.03	2.83	13.67	98.2

4.3. Weathering reactions

The abundance of carbonate rock in the basin, and the lithology's rapid weathering and erosion rate suggests that dissolution of carbonate minerals will add significant amounts of Ca and Mg to the reservoir. The most common weathering reaction for calcite is simple dissolution (Drever, 1988) giving a 1/2Ca:HCO₃ equivalence ratio of 1:1. Fig. 4A shows that only w6, w8 and w11, located on limestone, fall, either on, or just above the 1:1 line. All the other groundwater and surface water samples are above the line indicating another source of Ca must be present possibly from weathering and erosion of gypsum and/or clay.

In mudstone and marl, the dissolution of gypsum is the source of SO₄ and additional Ca in waters. A plot of Ca and SO₄ (Fig. 4B) shows that most of the ground water samples fall above the 1:1 line, indicating another source of Ca as previously shown. Downstream wells and well sample w10 fall below the 1:1 Ca:SO₄ line suggesting Ca may have been incorporated and removed from the system during clay formation. Only reservoir

water (s1), s2 surface water and w4 well water appear to be affected by weathering and erosion of gypsum.

If Na was only derived from dissolution of evaporite minerals, then Na should balance Cl. A plot of Na and Cl (Fig. 4C) illustrates that Na is in excess for all the downstream well samples and the nearby w10 well. One potential source of excess Na is weathering of feldspars such as those found in samples of sandstone. Sodium balances Cl for w5, w6, w8 and w11 ground water samples and reservoir water sample (s1). Sodium is depleted versus Cl in w4, w7 and w9 wells, a potential sink for Na ions being clay formation. Hence the chemistry of the surface and ground water samples appears to be dominantly controlled by the dissolution and reprecipitation of minerals in the catchment's host lithologies.

4.4. Watershed hydrochemical functioning

Different types of groundwater in the watershed (Ca-HCO₃, Na-Cl and Ca-SO₄), as identified by their differing chemistries are represented in Fig. 5 showing a cross-section of the riverbed. The alluvial aquifer is

Table 3
Selected chemical species in samples of surface water

Sample	pH	EC ^a	O ₂ ^a	T ^a	Alk ^a	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	F ⁻	Br ⁻	NO ₃ ⁻	Si(OH) ₄	TDS	δ ¹⁸ O‰	δ ² H‰
		mS cm ⁻¹	mg l ⁻¹	°C	mmol l ⁻¹	mg l ⁻¹										mg l ⁻¹	g l ⁻¹	vs SMOW	
s1/1	10.13	0.859	12.3	28.7	2.0	109.1	11.0	66.2	11.7	78.3	64.1	292.8	1.26	0.05	0.05	6.86	0.64	+10.9	+~45.4
s1/2	9.93	0.878	9.1	29.2	1.9	107.6	9.3	60.3	8.50	114.3	54.6	278.9	27	0.05	0.05	5.45	0.64	–	–
s2	6.88	2.845	3.9	20.2	1.7	722.8	30.2	80.1	12.0	120.7	0.61	1298.3	0.85	0.05	0.64	17.0	2.68	+1.9	+5.3
s3	7.03	7.665	7.6	22.45	10.2	672.4	351.6	731.0	3.47	520.3	1445.7	2167.1	1.54	6.56	0.85	18.6	6.02	-4.5	-24.3

^a Field measurement.

Table 4
Selected chemical species in samples of groundwater

Sample	Depth ^a	Depth ^b	pH ^c	EC ^c	O ₂ ^c	T ^c	Alk ^c	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	F ⁻	Br ⁻	NO ₃ ⁻	Si(OH) ₄ ^c	TDS	δ ¹⁸ O‰	δ ² H‰
	m			mS cm ⁻¹	mg l ⁻¹	°C	mmol l ⁻¹	mg l ⁻¹										mg l ⁻¹	g l ⁻¹	vs SMOW	
<i>Downstream the reservoir</i>																					
w1/1	3.3	1.0	7.00	2.240	3.0	18.7	6.2	211.4	69.9	191.5	2.37	381.0	217.0	637.7	1.10	1.30	0.90	22.4	1.74	-2.1	-13.2
w1/2	3.3	15.0	7.15	2.450	7.2	17.8	6.2	203.4	82.2	220.9	2.27	317.3	2721.7	776.6	1.29	1.49	0.99	20.7	1.90	–	–
w2/1	2.7	1.0	7.04	2.130	2.9	17.8	6.3	209.6	72.9	180.5	2.01	441.0	167.3	636.5	1.09	0.72	<0.05	22.7	1.73	-2	-13
w2/2	2.7	2.5	7.08	2.130	2.5	17.3	6.6	253.4	72.6	185.8	2.00	440.0	162.6	644.4	0.95	0.60	0.55	22.9	1.79	-1.6	-13.3
w3/1	1.7	1.0	7.10	2.990	4.6	17.7	6.8	203.2	97.0	374.8	1.68	437.2	308.3	827.0	1.36	1.35	<0.05	24.0	2.28	-2.6	-15.1
w3/2	1.7	2.3	7.11	2.990	4.2	17.7	7.1	311.9	102.9	383.5	2.00	448.5	427.8	870.8	1.42	1.77	0.74	24.0	2.58	-1.9	-10.7
p1	2.5	0.1	7.38	1.888	3.9	18.7	4.0	177.2	46.4	175.8	3.72	360.1	232.4	351.5	1.43	1.81	5.61	28.2	1.38	-1.3	-9.1
p2	1.9	0.1	7.05	2.720	3.7	17.2	6.2	334.0	83.3	201.2	1.87	264.2	395.0	581.7	2.17	2.18	4.07	22.6	1.89	-2.2	-15.5
<i>Within the watershed</i>																					
w4	2.7	1.0	7.02	8.300	6.5	17.0	10.7	769.6	375.8	856.9	8.37	529.4	1826.9	1811.5	1.00	8.95	3.38	27.0	6.22	-4.1	-25.5
w5	1.5	1.0	6.98	2.240	3.8	20.0	6.2	235.0	66.87	279.1	–	396.7	377.2	299.5	0.64	2.15	27.10	25.5	1.71	-5.3	-31.1
w6	8.4	1.0	7.34	1.212	2.6	16.1	4.5	118.8	21.8	94.5	1.99	301.5	144.2	92.2	1.67	<0.5	<0.5	22.3	0.80	-5.44	-28.9
w7/1	nd	1.0	7.13	3.240	7.5	19.3	5.3	214.1	85.8	250.8	1.30	323.4	779.6	262.4	0.68	4.67	58.85	29.0	2.01	–	–
w7/2	nd	5.5	7.10	3.250	6.9	18.1	5.0	214.3	87.2	252.9	1.23	305.1	776.2	261.9	0.68	4.89	59.34	25.6	1.99	-4.7	-32.0
w8	nd	–	7.61	0.753	8.8	21.7	3.7	83.9	16.8	61.3	2.33	253.6	77.9	81.3	0.58	0.49	10.0	23.0	0.61	-5.2	-33.9
w9/1	3.2	1.0	7.26	3.230	5.6	17.1	6.9	254.9	106.3	439.9	1.64	475.6	815.4	427.9	1.22	4.17	61.2	22.8	2.61	–	–
w9/2	3.2	8.3	7.30	3.230	7.5	17.2	6.0	184.3	96.7	302.3	1.51	366.1	629.5	428.8	1.24	4.44	95.1	22.7	2.13	-4.4	-23.5
p4	2.0	0.1	7.72	2.020	5.3	25.6	5.2	196.0	46.8	191.2	7.04	300.1	175.5	575.6	0.64	2.75	24.2	6.62	1.52	-1.1	-7.7
p6	2.3	0.1	6.85	4.910	1.3	16.8	8.4	568.7	145.8	442.9	5.50	448.8	829.6	1239.5	1.97	3.29	7.70	21.4	3.72	-3.6	-22.1
<i>Beyond the watershed</i>																					
w10	3.4	1.0	7.23	4.180	5.5	18.4	5.6	297.2	131.2	511.1	6.03	406.3	408.3	1389.2	0.96	2.12	1.67	20.8	3.17	-4.2	-28.0
w11/1	4.0	1.0	7.26	0.833	3.3	17.0	6.5	120.1	15.8	45.8	1.16	396.6	57.2	47.4	<0.05	<0.05	5.21	19.9	0.71	–	–
w11/2	4.0	4.0	7.25	0.835	3.7	16.8	5.7	115.7	16.0	46.0	1.18	347.8	57.4	47.5	<0.05	<0.05	3.98	19.5	0.66	-5.3	-31.7

^a Depth of groundwater level below ground surface.

^b Sampling depth below groundwater level.

^c Field measurement. In bold characters, alkalinity data measured in field. nd: not determined.

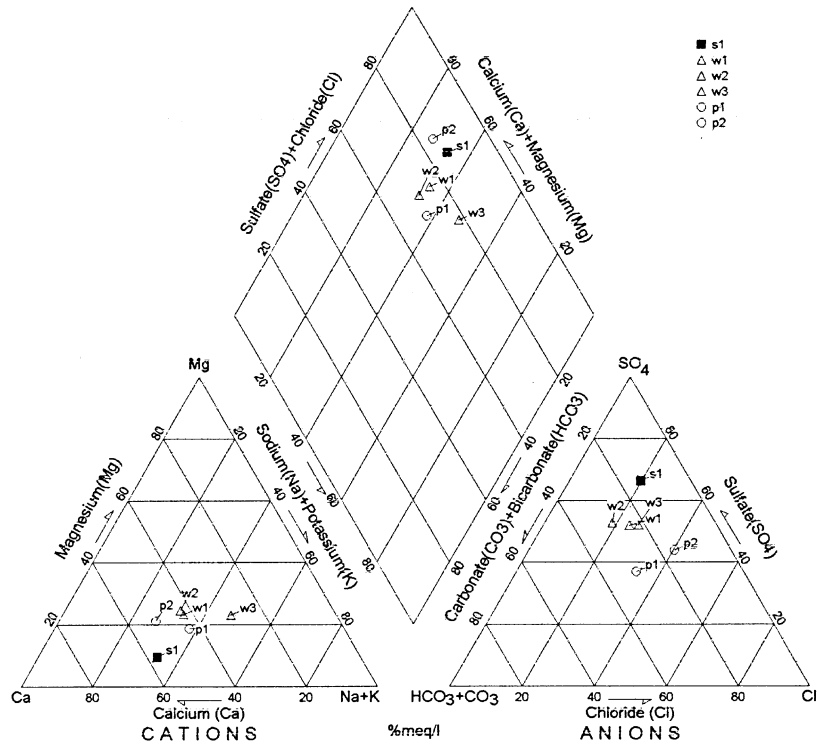
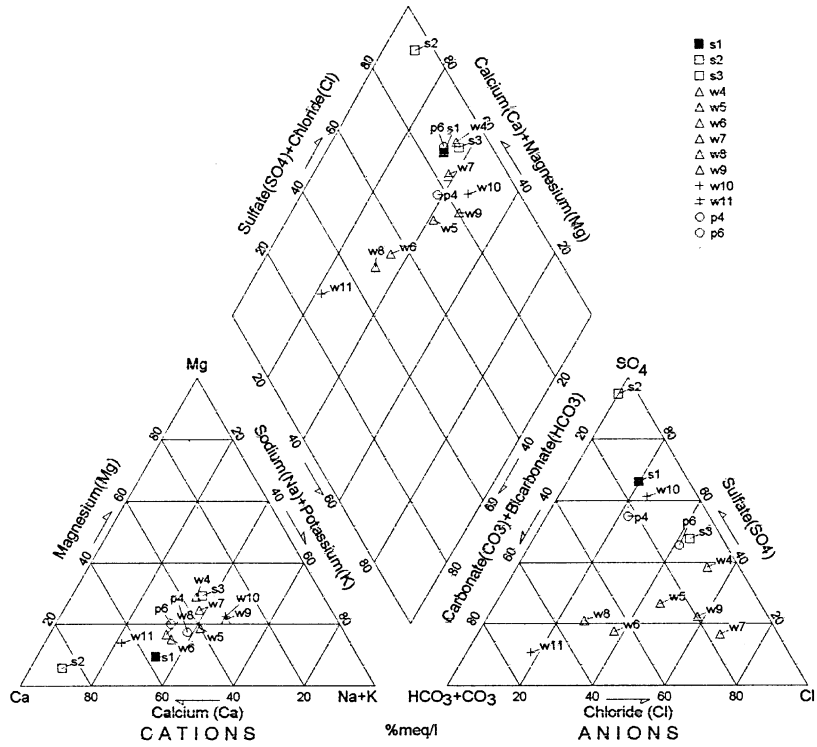


Fig. 3. Piper diagram showing the major ion composition of the surface water and groundwater samples collected in the El Gouazine watershed (Piper, 1944). Values for ions are given as % mmol_e l⁻¹. Top: reservoir water and upstream groundwater; bottom: reservoir water and downstream groundwater; w10 and w11 samples collected beyond the watershed were added as external reference.

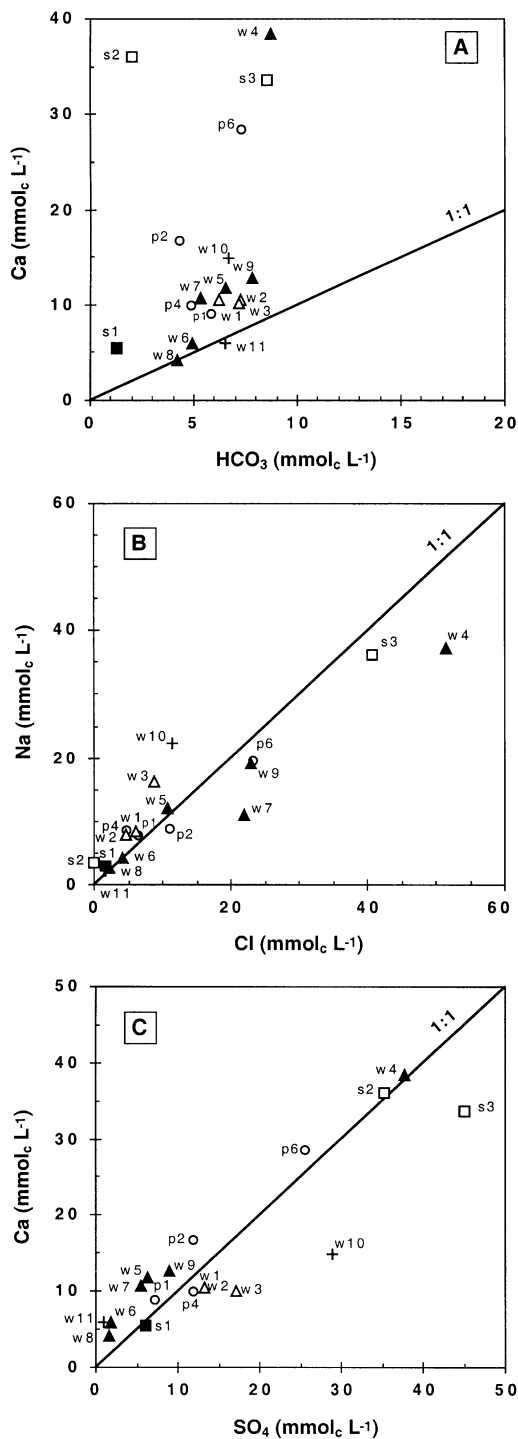


Fig. 4. Chemical relationships for samples of the surface water and groundwater (A): Ca vs. HCO_3 ; (B): Ca vs. SO_4 ; (C): Na vs. Cl. ■ = reservoir water; □ = surface waters; ▲ = ground waters from upstream wells; △ = ground waters from downstream wells; ○ = ground waters from pits; + = ground waters from wells beyond the watershed. Ion concentrations are in mmolc L^{-1} .

supplied by shallow groundwater stored in limestone aquifers leading to a strong decrease in electrical conductivity. Due to the high porosity of the limestone, these aquifers can accumulate high water contents and rapidly recharge or discharge. The hill reservoir seems to have the same effect as the limestone aquifer on the concentration of proximal groundwater. It means that both systems containing a high volume of water can dilute the alluvial groundwater. In turn, the alluvial groundwater, which flows through the less permeable but soluble mineral-rich argillaceous materials, such as gypsum, contains a strong concentration of elements and ions. The lack of additional groundwater data in the catchment does not allow validation of this result. By extension, the spatial relationships between aquifers, including relative rates of recharge and supply of water from one to the other, cannot be clearly established.

4.5. Alluvial aquifer recharge

Values of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ for samples of surface water and ground water are plotted in Fig. 6A. Most of the groundwater samples fall on or near the global meteoric water line ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ as reported by Craig, 1961) and the West Mediterranean meteoric water line ($\delta^2\text{H} = 7.2 \delta^{18}\text{O} + 6.1$ as reported by Celle, 2000), indicating that they originated from infiltrating precipitation that was not subject to surface or subsurface alteration of its isotopic composition. Groundwater sampled from limestone outcrops (w5, w6, w8 and w11) is less enriched in stable isotopes and values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ are nearly -31.4‰ and -5.3‰ , respectively. Surface water samples (s1 and s2) show ^2H and ^{18}O enrichment (positive values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$), which is typical for water that has been subject to open surface evaporation. The slope of the evaporation line is nearly 4.6. Downstream groundwater (w1, w2, w3, p1 and p2) and sediment groundwater (p4) are weakly enriched in H and O isotopic composition, values of $\delta^2\text{H}$ and $\delta^{18}\text{O}$ values respectively ranging from -7.7‰ to -15.5‰ and from -1.1‰ to -2.6‰ . The plot displacement on the evaporation line suggests mixing of meteoric groundwater with the evaporated water of the reservoir. Values of $\delta^{18}\text{O}$ versus chlorine are given in Fig. 6B. Reservoir water (s1) has a relatively low concentration of Cl (64 mg L^{-1}) and is enriched in ^{18}O ($\delta^{18}\text{O} = 10.9\text{‰}$) suggesting a water mixing and/or a reservoir leakage. In turn, upstream ground waters show a depletion in isotopic values ($\delta^{18}\text{O} \approx -4.9\text{‰}$) and a varied Cl content ranging from 78 (w8) to 1827 mg l^{-1} (w4), depending on the lithology. Downstream groundwater is more Cl-rich than reservoir water as groundwater is far away from the reservoir.

Physical and pedological clues suggest that the reservoir is leaking (Fig. 7). A sandy layer nearly 1.5 m thick (over 70% of sand), situated on the western embank-

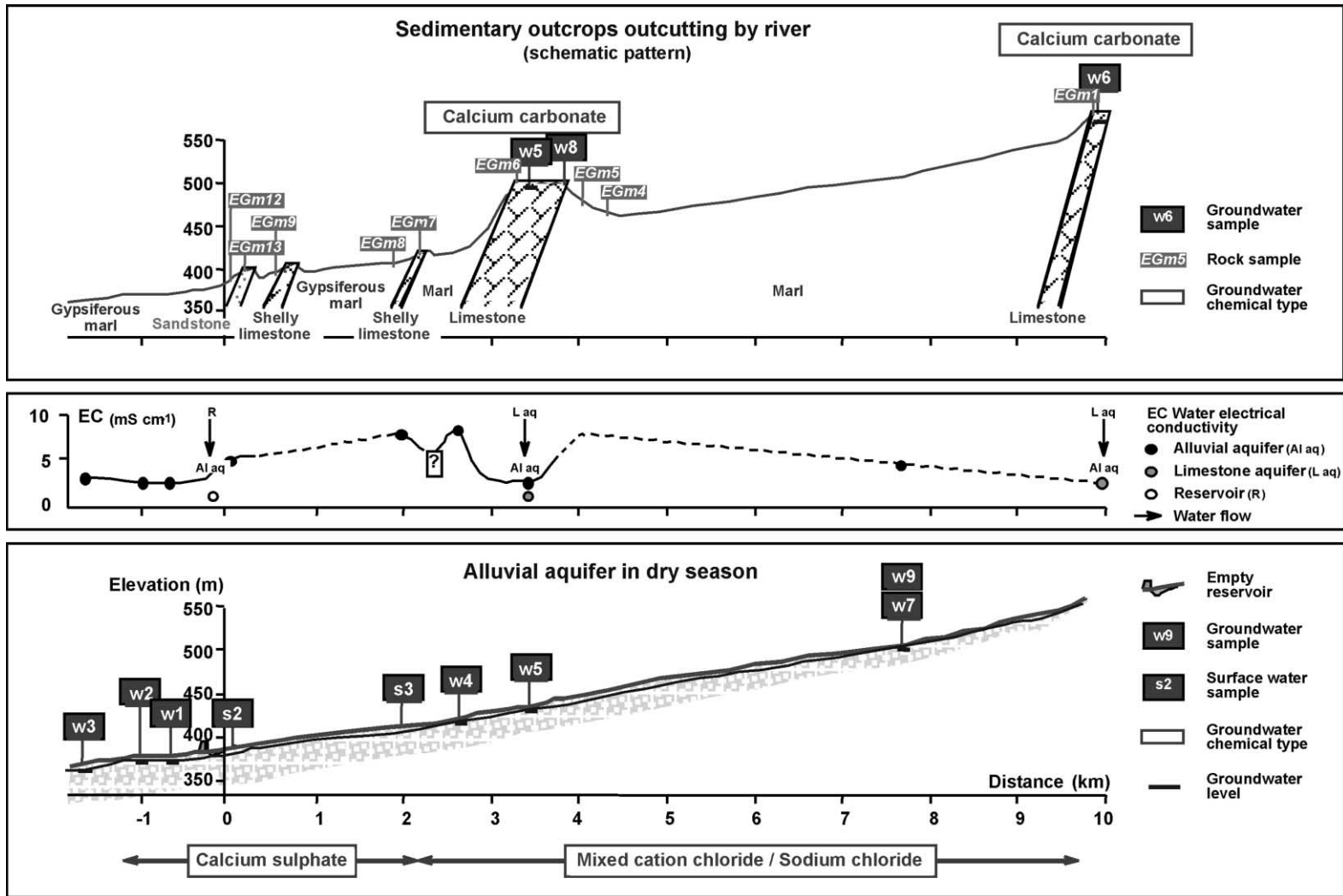


Fig. 5. General hydrogeological features of the El Gouazine basin showing the electrical conductivity variations in relation to watershed geology.

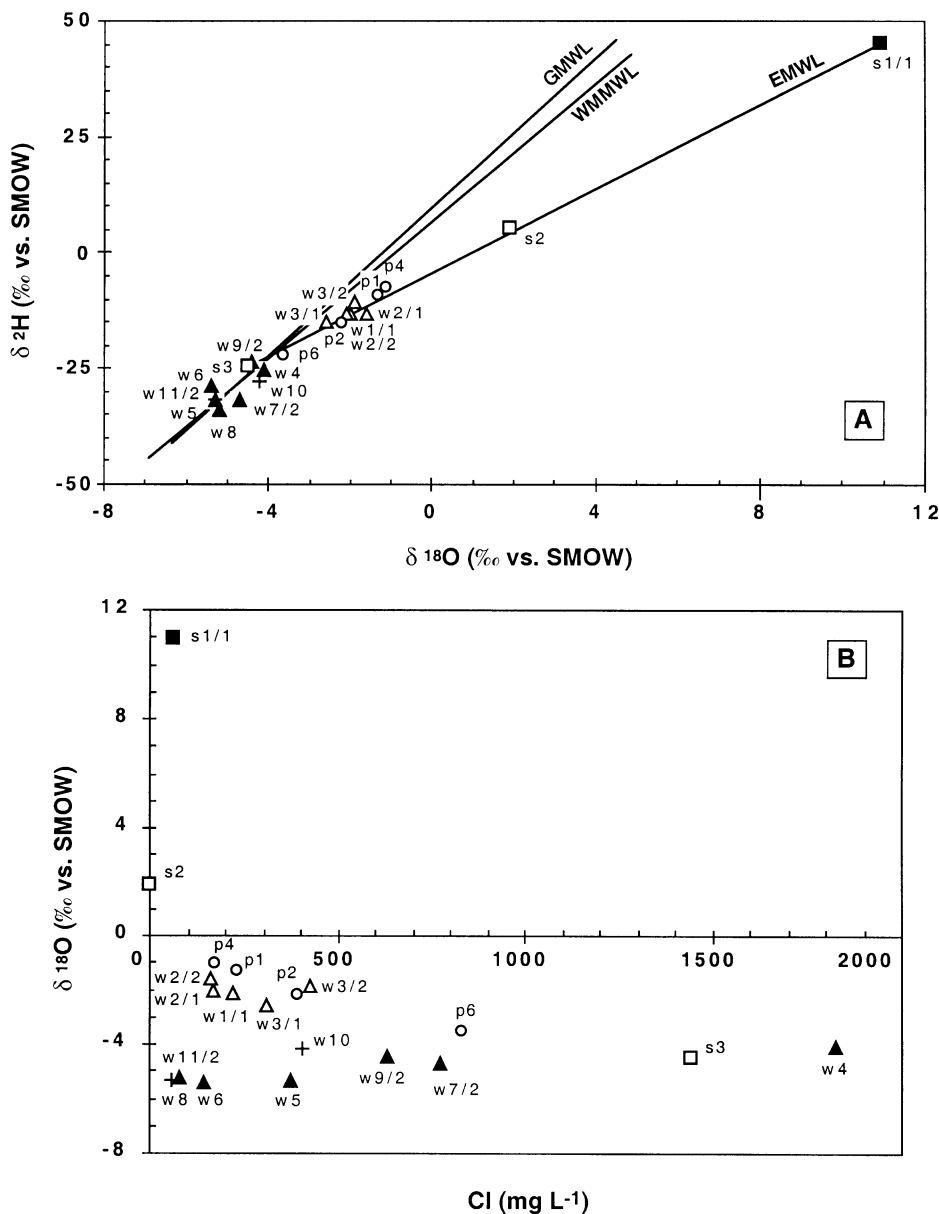


Fig. 6. Isotopic relationships for samples of the surface water and groundwater (A): ^2H versus ^{18}O ; (B): ^{18}O versus Cl. Symbols as in Fig. 4. GMWL: Global Meteoric Water Line ($\delta^2\text{H} = 8 \delta^{18}\text{O} + 10$ after Craig, 1961); WMMWL: West Mediterranean Meteoric Water Line ($\delta^2\text{H} = 7.2 \delta^{18}\text{O} + 6.1$ after Celle, 2000); EML Evaporation and Mixing Line ($\delta^2\text{H} = 4.6 \delta^{18}\text{O} - 3.9$).

ment and in the sediment of the reservoir, forms an aquifer. The formation of the aquifer may result from weathering and erosion of the sandstone host rock that is connected with the downstream alluvial aquifer. The high permeability of the sandy layer, being at a 5 m elevation above the reservoir bottom, partly explains the high water loss from the reservoir, especially when the reservoir water level exceeds 4.5 m, which also corre-

sponds to a deep change in daily groundwater balance (Montoroi et al., 1999). The piezometric levels of pits and wells, located in the reservoir sediments and in the riverbed, show the water supply of the downstream alluvial aquifer from the reservoir (Fig. 7). The corresponding chemical data, previously discussed, give a summarized overview of the groundwater chemistry change due to the reservoir.

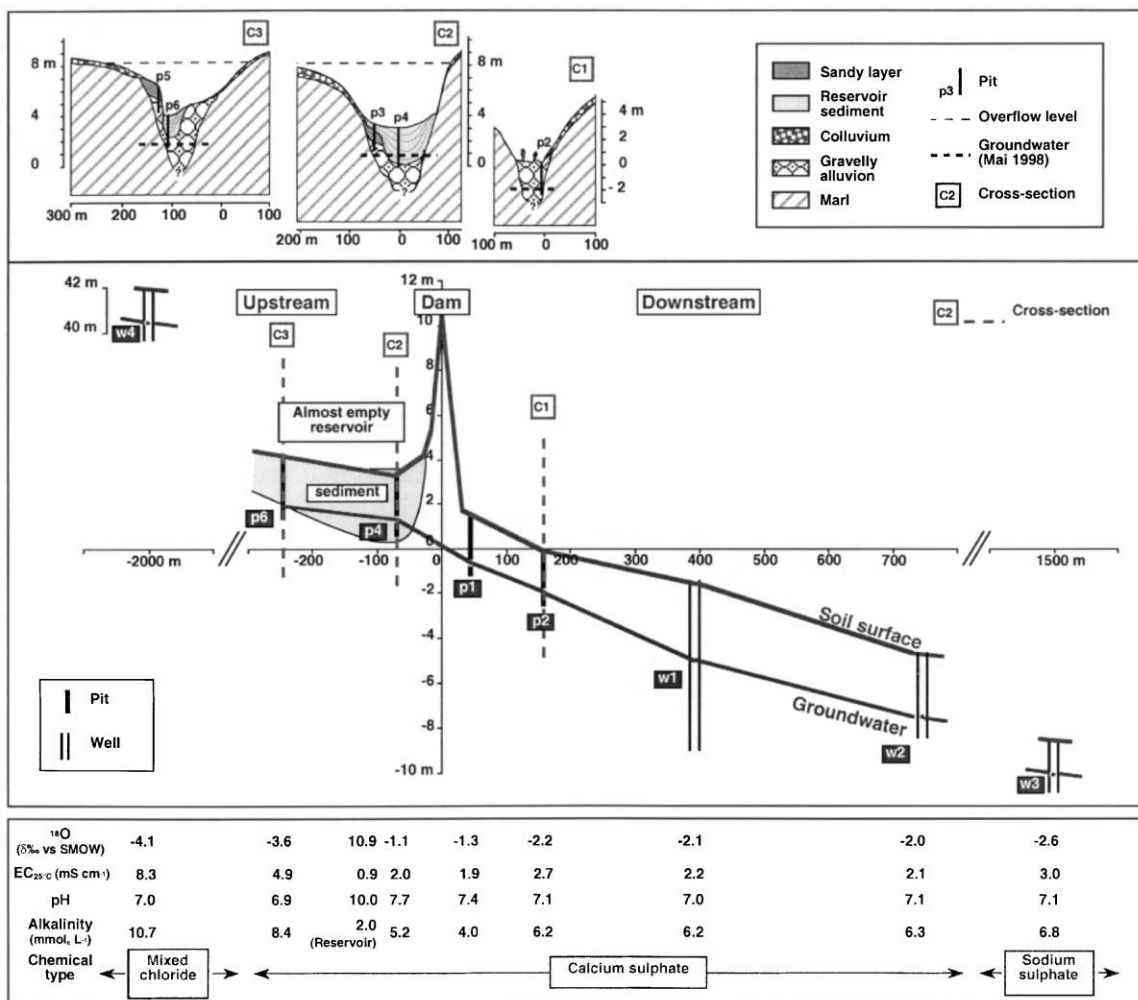


Fig. 7. Groundwater chemical characteristics, piezometric profile and general pedological features in the vicinity of the reservoir.

5. Conclusion

For hydrological balance calculations, it is assumed that the reservoir is filled by direct precipitation and runoff from the riverbed, with the permanent negative water budget suggesting water loss by infiltration. The chemical characterization (major elements and stable isotopes) of the catchment waters during the dry period show that in the semiarid sedimentary El Gouazine watershed: (i) 3 shallow groundwater bodies (Ca-HCO₃, Na-Cl, Ca-SO₄) can be identified and are meteoric in origin, the groundwater infiltrates soil and rock and groundwater chemistry is strongly linked to the lithology by mineral weathering and erosion and/or formation of new minerals; (ii) the meteoric groundwater and the evaporated reservoir water are mixing; (iii) the alluvial aquifer recharge below the reservoir is due to a shallow sandy drain formed by weathering and

erosion of the host sandstone, which partly leads to the mixture of reservoir water and alluvial groundwater.

Further chemical and isotopic analyses from water samples collected during the catchment's flow period will allow a better understanding of the geochemical functioning of the watershed and will allow modelling of water-soil-rock interactions. The results of such a study could be extended to explain the catchment chemistry and dynamics of similar infiltrating reservoirs.

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