

Full Length Research Paper

Characterization of groundwater in the Souss upstream basin: Hydrochemical and environmental isotopes approaches

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The hydrochemistry of major ions and environmental isotope compositions (^{18}O , ^2H) of water samples have been used to identify the chemical characteristics and the origin of groundwater in the Souss upstream basin. The total dissolved solids (TDS) did not exceed 1000 mg.L^{-1} with an average of 635 mg.L^{-1} . Two chemical water types were observed: A calcium and magnesium bicarbonate type ($\text{Ca}^{2+}\text{-Mg}^{2+}\text{-HCO}_3^-$), forming the dominant water type generally observed in the plain along the Souss river and towards the piedmont of the Anti-Atlas Mountains; and a calcium sulphate type ($\text{Ca}^{2+}\text{-SO}_4^{2-}$), from the northwest of the study area, linked to the presence of phosphatic gypseous marls and limestone marls (Upper Cretaceous). The calculations of saturation indexes versus the main mineral phases have been carried out, using the PHREEQC program. The groundwater is saturated and slightly oversaturated with respect to carbonate minerals and under saturated with respect to evaporite minerals; surface waters show an oversaturation with respect to carbonate mineral phases, mainly dolomite. The groundwater composition is largely controlled by the dissolution of carbonate rocks known in this part of the basin. Stable isotope contents of groundwaters ranged from -7.96 to -6.26‰ for $\delta^{18}\text{O}$ and from -49.47 to -39.28‰ for δD . The hydrogen (δD) and oxygen ($\delta^{18}\text{O}$) isotope signatures indicate a low evaporation of precipitations during infiltration and that the aquifer is highly influenced by the contribution of recharge water recharge from the High Atlas Mountains.

Key words: Groundwater, hydrochemistry, stable isotopes, arid climate, Souss, Morocco.

INTRODUCTION

The Souss basin is one of the most important basins in Southern High Atlas Mountains in Morocco and includes a plain which covers a surface extent of about 4150 Km^2 .

The climate is semi-arid to arid; it varies from humid to cold in winter on the summits of the Western High Atlas Mountain to the pre-Saharan to fresh in winter in the plain. The rainfall presents a large spatial and temporal variability: From 300 to 600 mm/year in the High Atlas to

approximately 200 mm/year in the plain. The water balance of the Souss aquifer is irregular, because of the high climatic variability, but in last decades, this balance became in continuous deficit (D.R.P.E, 2004), due to the combined effect of drought and aquifer overexploitation. Continuous decrease of water level in almost all of the aquifer poses the problem of the quality and the renewal of the water resources in this semi-arid area.

Physico-chemical data reported in the plain of the Wadi Souss show a wide variation in space. Several sources of salinity have been identified in the Souss Basin: Sea water intrusion along the coastal areas, recycling of agricultural return flows in the lower and middle plain of the

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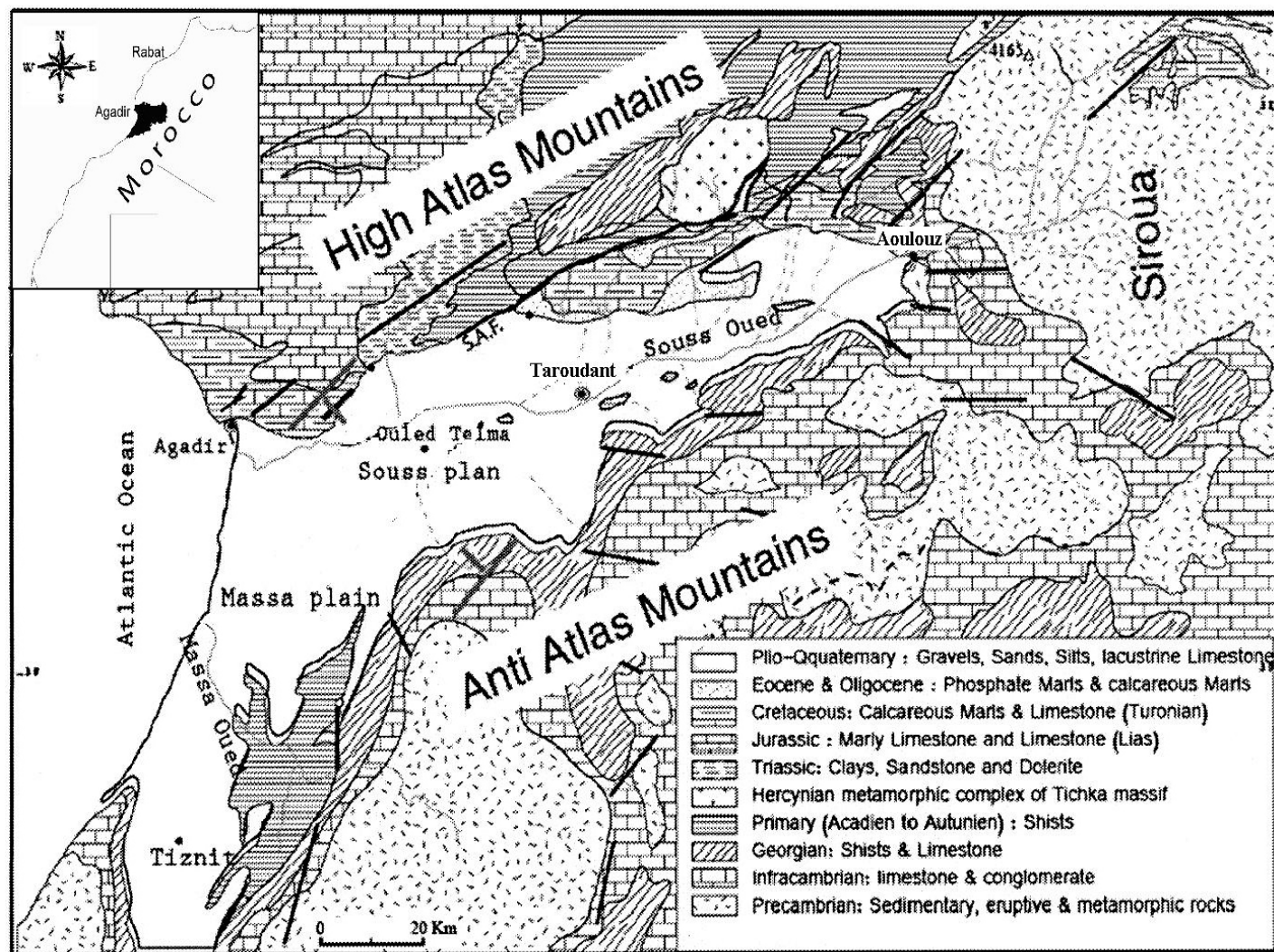


Figure 1. Location and geological map of the study area.

aquifer, and dissolution of evaporites along the outcrops of the high Atals Mountains (Bouchaou et al., 2008).

Previous studies (Boutaleb et al., 2000; Hsissou et al., 2002; Dindane et al., 2003; Krimissa et al., 2004; Bouchaou et al., 2003, 2005) showed a degradation of water quality in downstream and medium part of the plain and in western High Atlas Mountains, have suggested that groundwater quality is controlled mainly by: water-rock interactions and anthropogenic pollution, and have also shown that most of the natural recharge in the Souss comes from the High Atlas which receives a significant rainfall especially in its upstream part.

The present study deals with the general problems of water in the arid areas and comes in addition to the aforementioned studies. The main objective is to better delineate the chemical characteristics and origin of groundwater in the Souss upstream basin which constitutes a zone of recharge, and to study the mode of acquisition of mineralisation and its distribution.

MATERIALS AND METHODS

General characteristics of the study area

The study area (Figure 1) is located between longitudes 30 and 31 ° and latitudes 8 and 9°. The Souss upstream basin is bounded to the north by the High Atlas Mountains, to the south by the Anti-Atlas Mountains, the Siroua crystalline massive to the east and the transition to the medium part of the plain near Taroudant city to the west.

The climate is semi-arid to arid; it varies from humid to cold in winter on the summits of the Western High Atlas Mountain to the pre-saharian to fresh in winter in the plain. The Souss basin contains a shallow unconfined aquifer which constitutes the major groundwater resource in the region. The Souss plain is an alluvial depression between the High Atlas Mountains with Palaeozoic, Mesozoic and Cenozoic rocks in the north and the Anti-Atlas Mountains with Precambrian and Palaeozoic rocks in the south. Both Atlasic domains are interconnected in a complex way beneath the Souss valley, and are covered with thick detrital formations and calcareous marls of Plio-quaternary deposits. These overlie a Cretaceous-Eocene syncline.

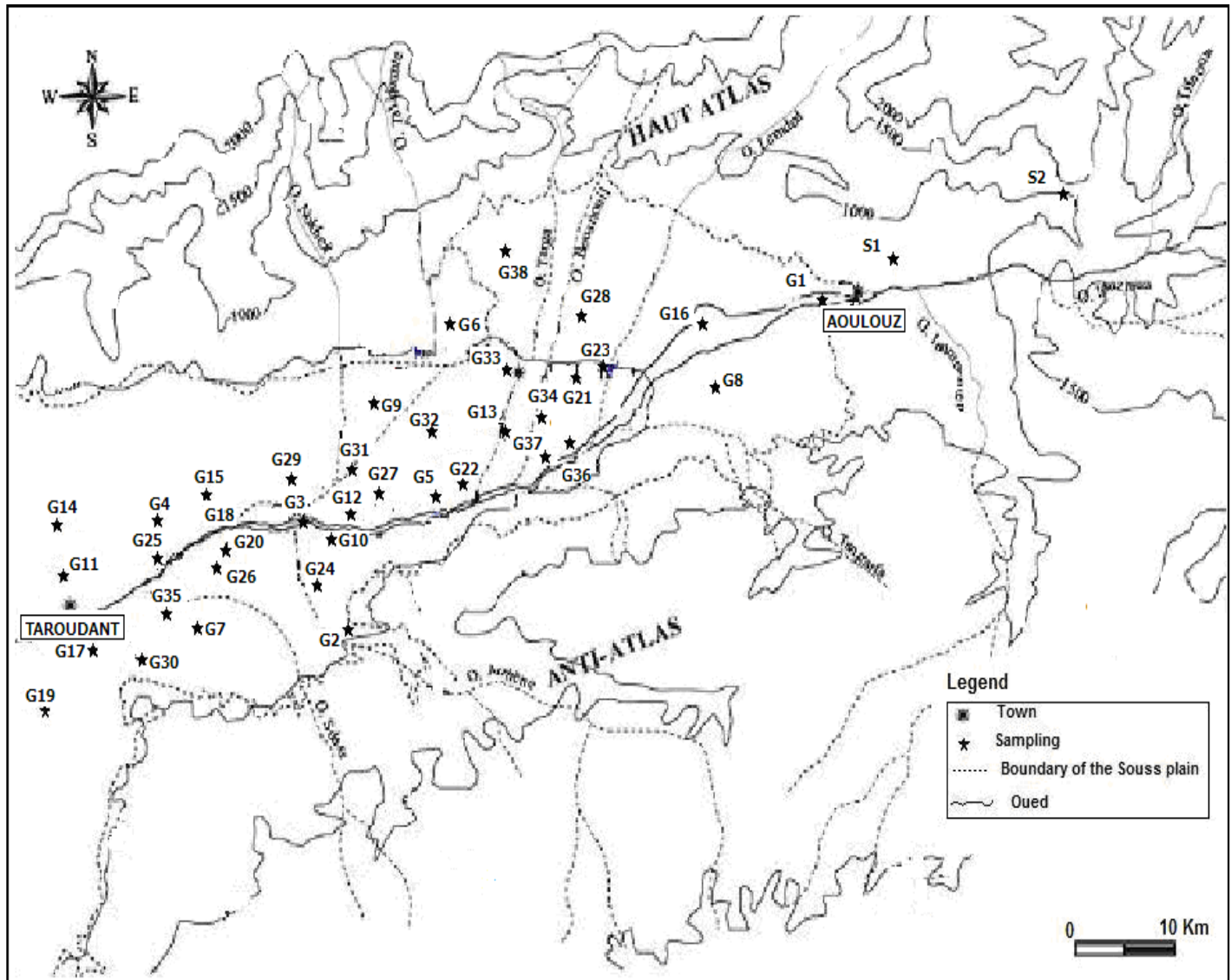


Figure 2. Location of sampling water points collected in the Souss upstream basin in 2005.

The syncline axis is oriented on east west direction, its northern flank outcrops vertically in the high Atlas and marks a vertical fault. Its southern short flank outcrops slightly in the centre of the basin. The high Atlas shows an alternation of permeable and impermeable Mesozoic formations. Some layers contain evaporates minerals (gypsum in Jurassic and Cretaceous, and halite in Triassic formations).

The quaternary sequence consists of two lithological types, continental and fluvio-lacustrine facies (conglomerate, limestone, marls, sandstone), called "Souss formation". The basement of the valley consists of Palaeozoic, Mesozoic and Eocene rocks (Ambroggi, 1963).

The Anti-Atlas Mountains are characterized by carbonate and crystalline formations. The presence of evaporite layers in the Mesozoic formations of the southern side of the High Atlas is likely to influence the water quality of the rivers (called locally oueds) that drain this side of the aquifers and those of the piedmonts. Groundwater occurs under unconfined conditions in the Pliocene and Quaternary formations of the plain, often overlying one or several confined sub-aquifers, like the Turonian aquifer (Dijon,

1969; Combe and El Hebil, 1977).

Sampling and analysis

During May and July, 2005, two sampling campaigns were done to collect 57 water samples from surface water (Aoulouz and Mokhtar Soussi dams), wells, boreholes and springs in the Souss basin within its upstream part between Aoulouz and Taoudant city.

All samples (Figure 2) have been subjected to physical and chemical analyses. Physico-chemical parameters (temperature, pH, electrical conductivity, EC) were measured in the field, alkalinity in the laboratory shortly after sampling, and other ions (Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , NO_3^-) analyzed in the Applied Geology and Geo-Environment laboratory at the University of Agadir (Morocco). Analytical error as inferred from the balance between cations and anions did not exceed 5%.

33 samples were chosen for an isotopic investigation of oxygen-18 (^{18}O) and deuterium (^2H) (Aoulouz (S1) and Mokhtar Soussi dam (S2) representing actual recharge, Tiout spring (G2) representing a

Table 1. Elementary statistics of chemical data (mg.L⁻¹) of waters in the Souss upstream basin.

Statistical calculations	T (°C)	pH	CE (µs.cm ⁻¹)	mg.L ⁻¹								
				TDS	Na ⁺	K ⁺	Ca ²⁺	Mg ²⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Groundwater (n = 55)												
Minimum	20.2	6.93	467	358.0	7.0	1.00	51.2	6.3	195.2	12.4	14.2	0.4
Maximum	28.1	7.73	1341	994.0	54.0	3.7	192.0	65.6	549.0	78.1	306.8	29.4
Mean	23.9	7.25	811.84	635.5	29.2	2.0	97.1	32.3	343.3	37.5	79.5	14.4
Standard deviation	1.9	0.18	207.54	154.3	9.9	0.7	29.9	11.8	78.4	13.0	69.9	6.1
Surface water (n = 2)												
Minimum	13.2	7.9	366.0	275.0	23.0	1.9	26.0	16.5	158.6	21.3	17.7	0.4
Maximum	26.1	8.7	390.0	294.0	26.0	2.7	32.0	19.1	170.8	24.9	24.1	3.8
Mean	13.2	8.3	378.0	284.5	24.5	2.3	29.0	17.8	164.7	23.1	20.9	1.6
Standard deviation	9.1	0.6	17.0	13.4	2.1	0.6	4.2	1.9	8.6	2.5	4.5	1.9

Table 2. Chemical elements and physical parameters correlation matrix.

	CE	TDS	T°C	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
CE	1											
TDS	0.98	1										
T°C	0.41	0.44	1									
pH	-0.72	-0.76	-0.20	1								
Ca ²⁺	0.90	0.87	0.27	-0.68	1							
Mg ²⁺	0.68	0.70	0.40	-0.50	0.33	1						
Na ⁺	0.77	0.76	0.29	-0.46	0.62	0.48	1					
K ⁺	0.17	0.24	0.44	0.02	0.01	0.29	0.29	1				
HCO ₃ ⁻	0.66	0.77	0.41	-0.72	0.47	0.66	0.54	0.43	1			
Cl ⁻	0.70	0.68	0.32	-0.50	0.54	0.54	0.74	0.17	0.50	1		
SO ₄ ²⁻	0.76	0.68	0.22	-0.34	0.80	0.35	0.49	-0.10	0.08	0.36	1	
NO ₃ ⁻	0.24	0.32	0.32	-0.47	0.11	0.37	0.15	0.07	0.49	0.29	-0.13	1

recharge from Anti-Atlas and boreholes from upstream toward downstream part of the plain and near of the Souss river). Isotopic analyses (¹⁸O and ²H) were performed in both laboratories of the IAEA in Vienna (Austria) and IDES in Orsay (France). The hydrogen and oxygen isotopic ratios are expressed as relative differences (δ values) from standard mean ocean water (SMOW) in parts per mil (‰) (Fontes, 1976). The δ¹⁸O and δD were measured by a mass spectrometer referenced to the V-SMOW. The analytical precision is better than 0.2% for δ¹⁸O and 2% for δD.

RESULTS AND DISCUSSION

Chemistry of groundwater

Groundwater mineralization is determined by the total dissolved solids (TDS). For all water samples, TDS does not exceed 1000 mg.L⁻¹.

Elementary statistics (minimum, maximum, mean and standard deviation) of physico-chemical data of all samples are reported in the Table 1.

The correlation matrix (Table 2) shows the significant values (non diagonal) in the threshold alpha = 0.05 for a total of individuals n = 57.

The relationship between EC and TDS is highly significant (r = 0.98, n = 57). Mineralization variations are mainly controlled by calcium (r = 0.87), sodium (r = 0.76), bicarbonates (r = 0.77) and magnesium (r = 0.70) concentrations. Sulphate and chloride also present a relatively important contribution in the total mineralization of the analysed waters.

We also notice that sulphate correlate with calcium (r = 0.80), chloride with sodium (r = 0.74) and bicarbonates with magnesium (r = 0.66).

Piper diagram (Figure 3) allows a global visualisation of the chemical water types while identifying potential chemical evolutions.

Among the major cations, groundwater samples are almost totally located close to the (Ca²⁺ + Mg²⁺) end. Among the major anions, waters are mainly located in the bicarbonate end, with a migration toward the sulphate

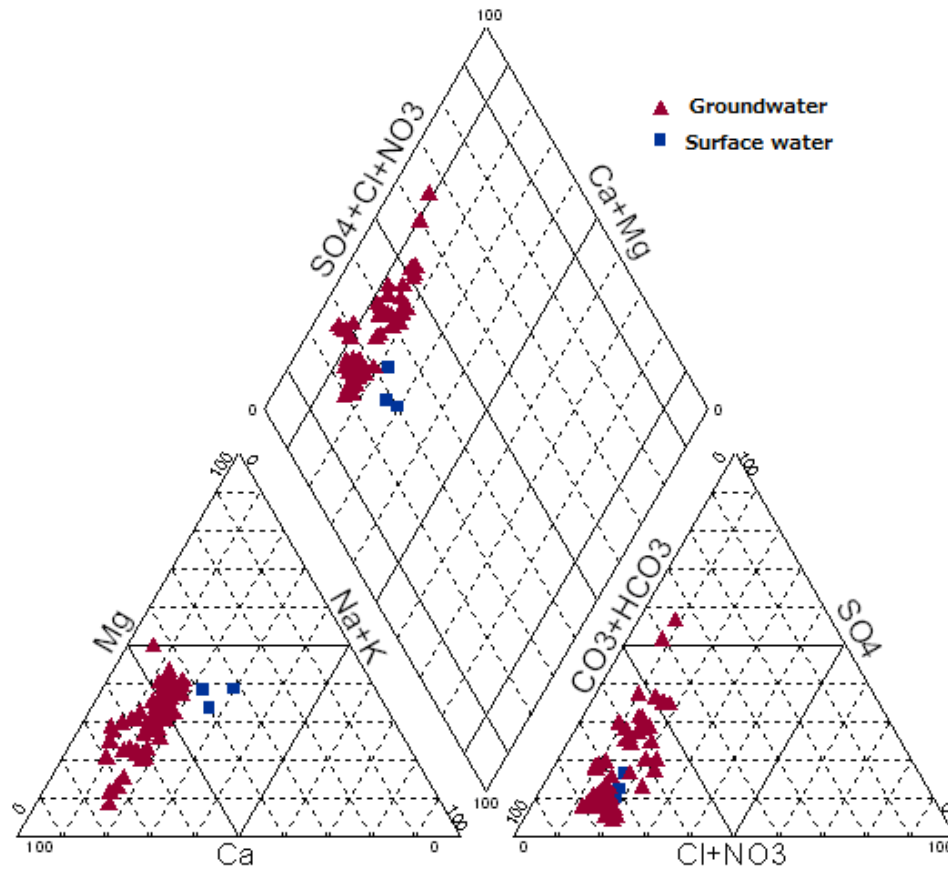


Figure 3. Piper diagram of the chemical composition of samples collected during 2005.

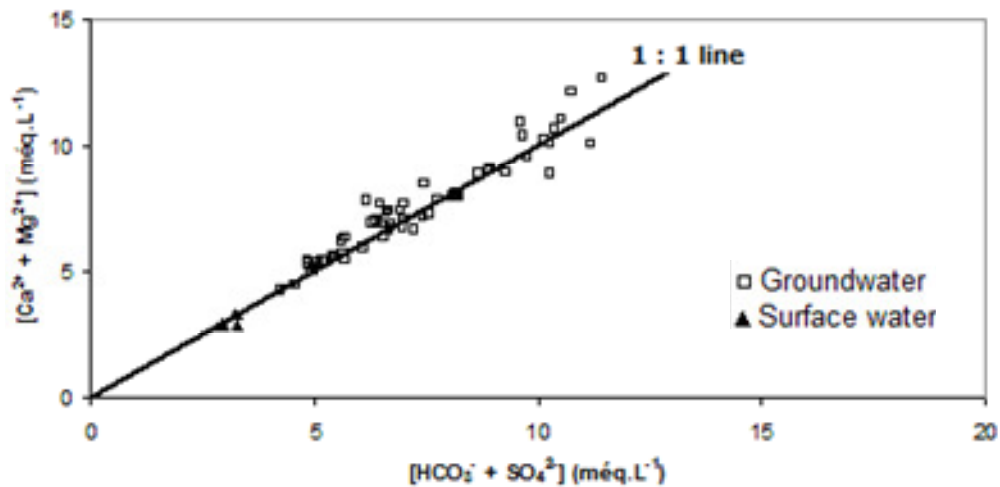


Figure 4. (Ca+Mg) vs. (HCO₃+SO₄) contents (in meq.L⁻¹) in the investigated samples.

end. HCO₃⁻ is dominant with 72% of the sum of anions; the SO₄²⁻ and Cl⁻ are secondary and represent respectively, 17 and 8%.

Two groundwater types were determined: Ca²⁺-Mg²⁺-HCO₃⁻ type water in most of samples, generally observed

in the plain along the Souss River and towards the piedmont of the Anti-Atlas Mountains; and Ca²⁺-SO₄²⁻ type in the northern part of the study area.

The sum of Ca and Mg was therefore plotted versus (HCO₃+SO₄) (Figure 4), points are well scattered around

the 1:1 line. The good correlation suggests the dissolution of carbonate and gypsum rocks. This corresponds to the lithology in the basin drained by water from the Atlas Mountain and mixed with water hosted in the aquifer.

The PHREEQC geochemical code (Parkhurst and Appelo, 1999) was used to compute the saturation index (SI).

$$SI = \log (IAP.K_{sp}^{-1})$$

where IAP is ion activity product of the species that compose the mineralization and K_{sp} is solubility product of the associated mineral.

A SI of zero indicates equilibrium; a positive value indicates oversaturation and a negative value under saturation, with respect to the solid phases.

Groundwater samples vary from saturated to oversaturated with respect to dolomite, calcite and aragonite (Table 3). Surface water samples are oversaturated with respect to carbonate mineral phases, mainly dolomite ($+0.07 < SI < +2.06$). All the samples (Table 3) are under-saturated with respect to evaporitic mineral phases suggesting that evaporite mineral phases are minor in the host rocks. Only carbonate minerals tend to allow precipitation of dolomite. This suggests that the mineralization of groundwaters is controlled by the dissolution of carbonate rocks and by the long residence time in the aquifer. The water composition is controlled by the composition of sedimentary rocks in the basin and hydrologic characteristics such as the flow path and residence time.

Stable isotope composition

In the study area, the stable isotopic contents of groundwaters ranged from -7.96 (G29) to -6.26‰ (G2 Tiout) for $\delta^{18}O$, from -49.47 (G29) to -39.28‰ (G30) for δD .

In surface water (samples from Aoulouz and M.Soussi dams), the stable isotope contents ranged from -6.9 to -5.35‰ for $\delta^{18}O$ and from -45.27 to -38.23‰ for δD .

The $\delta^{18}O$ versus δD ratios have been plotted in Figure 5. In absence of the Regional Isotopic Gradient Line (RIGL), we have drawn the global meteoric water line (GMWL) with a slope 8 and a relation ^{18}O versus 2H with a deuterium excess of nearly 10 (Craig, 1961). It characterizes rainfalls of an oceanic origin.

On this figure, waters are generally located on or slightly above the GMWL with a deuterium excess equals or slightly above 10. This shows that waters are just a little, or not at all, evaporated. They have a meteoric origin from the Atlantic Ocean, and their saline charge is then free from evaporitic component.

The evaporated water is not shown, except for samples S1 (Aoulouz dam) and G36 (shallow well from the

southern margin of the Souss upstream basin). Evaporation is then only detectable for the samples that have undergone a superficial retention stage. The data suggest that the aquifer records a high altitude isotopic signal.

The quasi-absence of evaporation during infiltration implies a significantly rapid infiltration before evaporation and that isotopic effect due to evaporation was unimportant compared to that induced by the altitude variations.

In order to assess the contribution of irrigation water to the water balance within the study area, a relationship between nitrate contents in $mg.L^{-1}$ and ^{18}O had been established (Figure 6).

This figure shows clearly that there is no correlation between nitrate and $\delta^{18}O$ values. This finding suggests that there is no significant contribution of agricultural return flows in the study area.

Conclusion

The jointly use of hydrochemistry and environmental isotope methods to investigate the origin and the characteristics of surface water and groundwater in the upstream part of Souss basin, has so far permitted to extract the following major conclusions:

Two main water types are identified: (1) Calcium-magnesium and bicarbonate type which primarily reflects the predominance of dissolution of limestone and dolomite rocks and which corresponds to the majority of wells, and also to surface water but with some enrichment in sodium, and (2) Calcium-sulphate type, along the outcrops of the High Atlas Mountains, originating from an evaporate source (cretaceous evaporites of the High-Atlas mountains).

The chemical components of the aquifer water vary according to the lithology of adjacent Atlasic formations.

The water quality is generally fresh ($TDS < 1000 mg.L^{-1}$); less saline in the upstream and progressively becomes more saline going downstream.

Mineral saturation indexes suggest that the dissolution of carbonates is significant in the groundwater indicating a long residence time.

The study of stable isotopes of water has shown the presence of an Atlantic origin of precipitations. Hydrogen and oxygen isotopes signatures reveal that none of these waters is marked by significant evaporation; this suggests a rapid infiltration before evaporation of meteoric waters. The depletion in groundwater stable isotopes shows a recharge under different conditions, during wet periods than the current one and/or that the precipitation altitude was higher.

Surface waters are more enriched in ^{18}O and 2H , which indicates a re-start of rainfall evaporation before infiltration. Evaporation is then detectable for the samples that have undergone a superficial retention stage.

Table 3. Saturation indexes of samples collected from the Souss upstream basin during 2005.

Code	Saturation index						Code	Saturation index					
	Calcite	Aragonite	Dolomite	Gypse	ANHYDRITE	Halite		Calcite	Aragonite	Dolomite	Gypse	Anhydrite	Halite
S1	0.91	0.77	2.06	-2.60	-2.81	-7.76	G22	0.39	0.24	0.59	-1.88	-2.10	-7.58
S2	0.09	-0.06	0.07	-2.59	-2.84	-7.84	G23	0.37	0.22	0.48	-1.64	-1.87	-8.02
G1	0.36	0.21	0.67	-2.22	-2.46	-7.72	2G23	0.32	0.18	0.37	-1.63	-1.86	-8.02
G2	0.23	0.09	0.53	-2.50	-2.72	-7.64	G24	0.17	0.03	0.18	-1.44	-1.66	-7.27
2G2	0.21	0.07	0.55	-2.42	-2.64	-7.66	G25	0.16	0.02	0.35	-1.52	-1.75	-7.34
G3	0.47	0.32	0.59	-2.11	-2.34	-7.73	2G25	0.19	0.04	0.14	-1.45	-1.67	-7.32
G4	0.34	0.19	0.59	-1.14	-1.36	-6.99	G26	0.28	0.14	0.56	-1.81	-2.04	-7.46
G5	0.30	0.16	0.40	-1.77	-1.99	-7.47	2G26	0.32	0.17	0.72	-2.12	-2.34	-7.49
2G5	0.40	0.25	0.68	-1.93	-2.15	-7.50	G27	0.38	0.24	0.69	-1.99	-2.21	-7.58
G6	0.35	0.20	0.34	-1.56	-1.78	-7.40	2G27	0.41	0.27	0.85	-2.10	-2.32	-7.57
G7	0.14	0.00	0.23	-2.17	-2.40	-7.77	G28	0.50	0.35	0.86	-1.08	-1.29	-7.84
G8	0.47	0.33	0.90	-1.79	-2.00	-7.37	G29	0.20	0.06	0.04	-1.65	-1.88	-7.71
G9	0.27	0.13	0.21	-1.93	-2.16	-8.46	2G29	0.20	0.06	0.04	-1.65	-1.88	-7.71
G10	0.28	0.13	0.39	-2.23	-2.46	-7.83	G30	0.20	0.05	0.49	-2.37	-2.58	-7.52
G11	0.36	0.22	0.64	-1.29	-1.49	-7.48	2G30	0.38	0.23	0.81	-2.32	-2.54	-7.52
2G11	0.43	0.29	0.77	-1.31	-1.53	-7.22	G31	0.44	0.29	0.00	-1.86	-2.09	-7.53
G12	0.44	0.29	0.16	-1.04	-1.27	-7.40	2G31	0.18	0.03	-0.30	-1.80	-2.03	-7.57
G13	0.24	0.10	0.39	-1.69	-1.92	-7.42	G32	0.38	0.23	0.42	-1.15	-1.37	-7.13
2G13	0.51	0.37	0.84	-1.69	-1.91	-7.43	2G32	0.22	0.08	-0.10	-1.11	-1.34	-7.23
G14	0.28	0.13	0.20	-1.62	-1.84	-7.90	G33	0.17	0.02	-0.10	-1.98	-2.21	-8.47
2G14	0.19	0.04	0.02	-1.65	-1.88	-7.84	G34	0.33	0.18	0.68	-2.27	-2.50	-7.91
G15	0.29	0.14	0.52	-1.81	-2.03	-7.51	2G34	0.50	0.36	0.90	-2.35	-2.58	-7.83
G16	0.11	-0.04	0.27	-2.39	-2.62	-7.80	G35	0.43	0.29	0.85	-2.21	-2.43	-7.50
G17	0.27	0.13	0.60	-2.15	-2.37	-7.49	2G35	0.38	0.24	0.69	-2.10	-2.32	-7.54
G18	0.21	0.06	0.40	-1.21	-1.44	-7.13	G36	0.18	0.04	0.38	-1.92	-2.13	-7.46
G19	0.22	0.08	0.50	-2.27	-2.49	-7.49	2G36	0.23	0.08	0.35	-1.82	-2.03	-7.45
G20	0.36	0.21	0.34	-2.19	-2.42	-7.80	G37	0.30	0.15	0.70	-1.83	-2.05	-7.45
2G20	0.33	0.19	0.34	-2.07	-2.30	-7.61	G38	0.18	0.04	0.49	-2.07	-2.31	-8.47
G21	0.35	0.21	0.51	-1.33	-1.56	-7.65							

G: Groundwater; 2G: Groundwater collected in the second sampling campaign; S: Surface water.

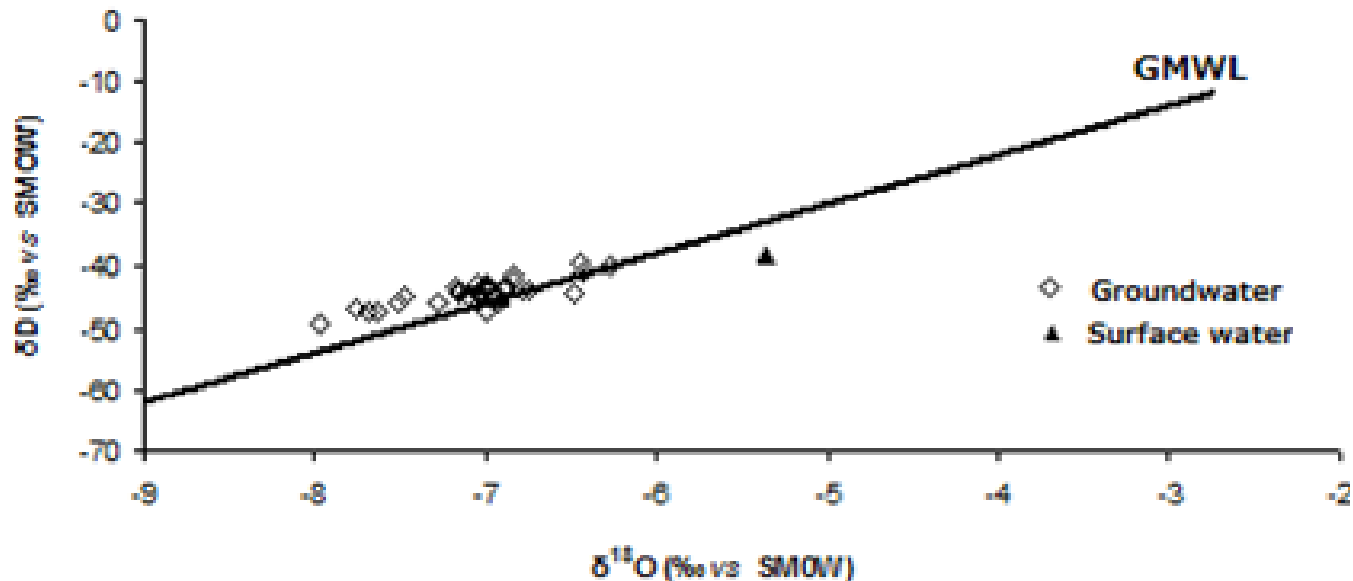


Figure 5. $\delta^{18}\text{O}$ versus δD values of samples investigated in this study as compared to the Global Meteoric Water Line (GMWL).

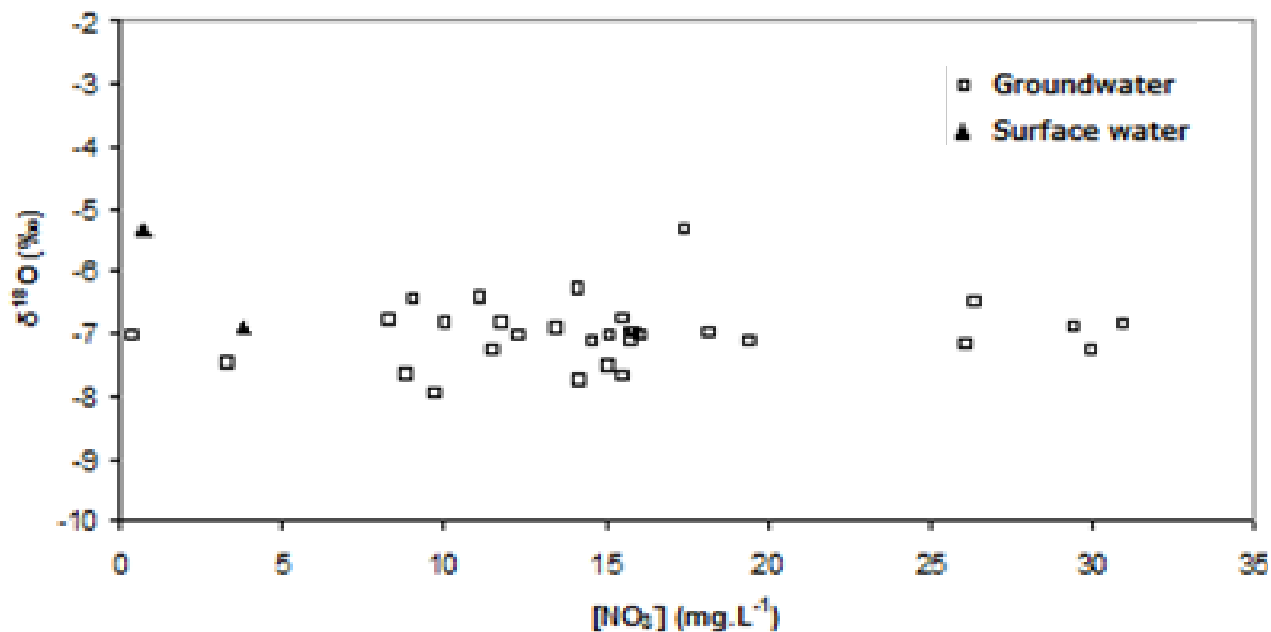


Figure 6. Variations of $\delta^{18}\text{O}$ values vs. nitrate concentrations of groundwater and surface water investigated in this study.

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