

# Using Major Ion and Stables Isotopes to Characterize Groundwater Recharge and Hydrochemical Processes in a Mountain-Plain Area: A Case Study in High-Atlas of Marrakech, Morocco

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## Abstract

Piedmont landscape is especially important as groundwater recharge zones. Determination groundwater recharge origin and qualitatively, evaluate their contribution on groundwater in piedmont area of Haouz plain was based on the use of geochemical and isotopic analysis of groundwater, surface water and springs of the contact zone between the High-Atlas Chain and the Haouz plain. The correspondence in the space evolution of the various chemical elements of evaporitic origin ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$ ,  $\text{Sr}^{2+}$ ) in groundwater, piedmont springs, and surface water reveals the existence of recharge water from the adjacent High-Atlas Chain. The various recharge modes of the different aquifers (High Atlas and Haouz plain) determined by isotopic analysis, shows that the source of groundwater both for the alluvial aquifer of Haouz and piedmont seems to be composite between a direct infiltration on the High-Atlas tributaries and a remote recharge from the bordering High Atlas aquifers. Remarkable mountain bloc recharge was observed in the piedmont area near the axis of syncline structures, which have layers of Mesozoic and Cenozoic deposits and control groundwater mineralization both in piedmont and plain.

**Keywords:** Groundwater recharge, Interaction groundwater-river, Mountain block recharge, Isotopic signature, Hydrochemical process

## 1. Introduction

In semiarid area, groundwater is the primary resource for drinking, irrigation and industry. However, climate changes and population growth are showing the great pressure on water resources in recent years. To satisfying human and ecosystem needs, sustainable management of aquifers will require accurate estimates of groundwater recharge (Yuan & al., 2011; Liu and Yamanaka, 2012). A significant component of recharge to basin aquifers occurs along the mountain front. Even under semiarid climates, groundwater in plains aquifers is recharges along stream channels and the mountain front (Boukhari & al., 2014). A thorough understanding of recharge is usually a prerequisite for effective groundwater management. Identifying recharge source, hydrochemical process and their corresponding contributions are critical hydrological parameters to water resource management. In piedmont area, direct infiltration of local precipitation and mountain-front constitute generally the main tool of groundwater recharge in piedmont landscape (Liu & Yamanaka, 2012). Mountain-front recharge can be also distinguish by (i) surface and subsurface components, with the stream channels represent river seepage from water surface to shallow groundwater and (ii) mountain block recharge, which is the water flow diffuse movement of groundwater along mountain to adjacent basin, through the underlying mountain block. In one hand, previous study has demonstrated that river water seepage is an important recharge mechanism along river reaches (Shahul Hameed & al., 2015). However, water level towards the stream, has been depleted during dry periods, as a result of groundwater abstraction, thus, can decline groundwater and deterioration of their quality from highly part of river into the downstream area. In the other hand, mountain block recharge can be described by their geological structure, (fault and/or syncline). According to the faults, a significant role can be played in the flow behavior by its characteristics as a conduit for the transfer of precipitation and/or deep aquifer in mountain area to plain. In the other hand, a syncline structure play an important role (i) in transmitting block recharge, and mountain block recharge which suppressed river channel seepage into the mountain, and (ii) to controlling groundwater chemical in the plain adjacent.

Geochemical and isotopic analysis have been largely used and have been of great significance to investigate geochemical evolution of groundwater at basin scales due to its great helps in better understanding spatial and temporal distribution of groundwater chemistry and in efficiently managing groundwater resources for domestic, industrial and agricultural water supplies in arid and semiarid regions.

Although the large alluvial plain of Haouz in central Morocco is a water scare region, it is still one of the largest agricultural production area in Morocco and one of the most developed of tourism (Marrakech city receive more than 2.5 million tourists/year). Focusing of this heavily depends on development of groundwater, source and altitude of recharge and origin of salinity in the plain has been analysed (Boukhari & al., 2014). However, no agreement has been reached in piedmont area. For a better understanding of recharge regime and hydrochemical evolution of the aquifer, which is usually a prerequisite for an accurate estimate of recharge,

should be determined firstly.

In this paper we present a case study of groundwater recharge origin, groundwater-river interaction and hydrochemical process in a mountain-plain transitional area with syncline geological setting. The essential aims of the present study are to identify recharge origin of groundwater and qualitatively evaluate their contribution on groundwater in plain.

## 2. Géological and hydrogeological setting

The High-Atlas is an intracontinental belt in the south of Haouz plain (Fig. 1), with peak over than 4000 m. It is formed by a Precambrian and Paleozoic basement and a Mesozoic-Cenozoic succession.

Eocene and Cretaceous terrains (Senonian, Cenomanian and Turonian) are located in low mountain areas and also form a vast carbonate plateau beyond the western limit of the plain. The Eocene is composed of limestone and marls. The Cretaceous layers consist of gypsiferous marls of the Senonian intercalating between the Eocene and the limestone and dolomite of the Turonian–Cenomanian. The Eocene and the Turonian–Cenomanian constitute deeper aquifers and are tapped by deep wells or boreholes in the western Haouz plain whenever the overlying alluvial aquifer productivity is insufficient. Little knowledge is available on the hydrogeological characteristics of these aquifers. The Jurassic and Permo-Triassic terrains are largely present in the Eastern part of the study area. The Jurassic is composed mainly of limestones. The Permo-Triassic is composed of clay alternating with sandstone beds and salt deposits which could constitute a source of water salinization. The Jurassic limestones form an aquifer drained by several springs in the High-Atlas valleys. Groundwater of these formations can also flow into the alluvial aquifer in the South-East of the plain. The Permo-Triassic underlies the Jurassic but towards the north it lies beneath the Miocene or the Plio-Quaternary alluvial deposits due to the absence of the Eocene and Cretaceous formation.

## 3. Methodology

The present study relies on geochemical and isotopic data. Field measurements (temperature, electrical conductivity (EC), pH) and geochemical sampling were carried out during the wet period of January February 2011.

17 water samples were taken analyzed for stable isotopes, geochemical analyses and 7 were analyzed for tritium (Fig. 2 and Tab. 1). The geochemical sampling points were distributed according to their geographical distribution and aquifer type in the piedmont area. Within the distribution of samples, three zones are distinguished (Fig. 2): Eastern part (MoE), Middle part (MoM) and Western part of piedmont (MoW).

Total alkalinity was determined by titration. Major ions and trace elements (Br, Sr) were measured in the Center of Analyses and Characterisation (CAC) of Cadi Ayyad University by high-performance liquid chromatography (HPLC). The stable isotopes ( $^{18}\text{O}$  and  $^2\text{H}$ ) were analyzed in the Ecolab laboratory (<http://shiva.univ-tlse3.fr>). Samples of water were collected in 10-mL tight-capped glass vials for  $\text{d}^{18}\text{O}$  and  $\text{d}^2\text{H}$  measurements and were kept at a stable temperature of  $20\text{ }^{\circ}\text{C}$  until analysis. In the laboratory, 0.2 mL aliquots of the water were taken in capped 3.7-mL Exetainer vials (Labco Ltd, High Wycombe, UK). To measure the  $\text{d}^{18}\text{O}$  values of the water samples, the samples and the internal standards were flushed offline with a gas mixture of 5 %  $\text{CO}_2$  in He. The Exetainer vials were then left to equilibrate at  $40\text{ }^{\circ}\text{C}$  for about 8 h. The analytical precision of the measurements by this system, Multiflow, was 0.25 per mil. To measure the  $\text{d}^2\text{H}$  values of the samples, Hokko beads were added to the Exetainer vials containing the water samples and the internal standards before the vials were flushed offline with a gas mixture of 5 %  $\text{H}_2$  in He. The Exetainer vials were left to equilibrate at  $40\text{ }^{\circ}\text{C}$  for about 8 h. The analytical precision of the measurements was 2.5 per mil. The spectrometer Elementar Isoprime-100 was calibrated using four working standards that are traceable to the primary reference standards V-SMOW2 (Vienna-Standard Mean Ocean Water) and V-SLAP2 (Vienna-Standard Light Antarctic Precipitation). Tritium analyses were performed in the laboratory of Hydrogeology of Avignon using a liquid scintillation counter after electrolytic enrichment.

## 4. Results and Discussion

### 4.1 Mechanism of recharge

Due to the over-pumping of groundwater, water table declines greatly in the alluvial plain area, which may change the recharge conditions of the alluvial aquifer. The growth of water demands and the succession of droughts during the last decades have led to increasing groundwater abstractions. A modeling study operating was carried out for the water resources in the plain (Le Page & al. 2012). During the simulation period (1971–2008) the gross agricultural demand was estimated by remote sensing to 650–700  $10^6\text{ m}^3\text{ year}^{-1}$  accounting for about 90 % of the total water demand. The net groundwater abstraction was assessed around  $400 \times 10^6\text{ m}^3\text{ year}^{-1}$ . The cumulative budget deficit for this period was assessed to about 1.1 billion  $\text{m}^3$ , highlighting the importance of groundwater depletion in the area. The water potential decreased from about 10 m to more than 20 m between 1998 to 2011, in the central part of plain (Fig. 3). Piedmont area is identified as the recharge zone receiving a

various recharge's mechanism. Their potential resource shows an increasing from 10 to 20 m between 1998 and 2011 (Fig. 3). However, it may be hard to receive direct recharge in the alluvial plain area under the impact of intensive human activities and the climate semi-arid.

The situation can be clarified by isotopic signature. Previous observations both in the mountain and plain (Boukhari., 2014; Boudelaire N'da et al., 2016) have shown heterogeneous values (24.4% to 110.7% for  $d^2H$  and -5.5% to -15.6% for  $d^{18}O$ ) representing isotopic variation of rainfall and snowmelt from the plain to the High-Atlas mountain. Our data of groundwater isotopic content (Tab. 1) of piedmont area (samples and springs) varies within -5,08 % to -7,99 % for  $^{18}O$  and -27,82 % to -54,84 % for  $^2H$ .

A local meteoric water line (LMWL) with a deuterium excess of 13.5% was drawn using these values. Due to the scarcity of rain isotopic measurements used for the LMWL, the  $d^{18}O$  and  $d^2H$  values from the water samples of the present study are plotted and compared both to the LMWL and the global meteoric water line GMWL with a deuterium excess of 10% (Fig. 4). Groundwater samples from the different parts of piedmont are scattered around the MWLs, indicating generally meteoric origin of groundwater. The direct infiltration of precipitation could form the dominant and rapid recharge in the hilly area in mountain, owing to the large depth to the water table. However, it is supposed that the local precipitation is not alone process of recharge, and most of infiltration is discharged by evapotranspiration before it reaches the water tables in the piedmont and plain. In figure 4, some samples in the plain, including wells and springs in the East part of piedmont (MoE1 and MoE3), one sample in the Middle part of piedmont (MoM1) and one sample of western part of piedmont (MoW14), enriched in isotopes and located below the meteoric water lines, which could reflect an evaporation effect. It should be noted that other samples, of Middle part of piedmont plot slightly to the left of the MWLs. This could be linked to isotope content variation in the rainfall recharging the aquifers (as the meteoric water line is a linear relationship of average values). In arid regions the humidity related kinetic isotope effect could result in meteoric waters being enriched in deuterium and thus plotting to the left of the GMWL (Maliva & Missimer, 2012).

#### 4.2 Groundwater residence time

Tritium ( $^3H$ ) is a commonly used tracer in hydrology for determining relative ages of recent groundwater. In general, groundwater with  $^3H$  content higher than 2TU represents waters that were recharged during the last 40 years (Clark and Fritz., 1997). The tritium concentration measured on wells and springs at different parts of piedmont varies between 1.30 and 3 UT (Tab.1). These values indicate recent groundwater recharge and they correspond to the contents expected in high altitude areas indicating that have short residence time.

Silicate content in groundwater may also display some informations about groundwater residence time. It comes from: i) interaction with igneous rocks and/or ii) mixture process between surface water and deep aquifer. Their hydrolysis process is slow and the resulting changes in water chemistry are gradual (but less developed in carbonate aquifers) (Santoni et al., 2016).  $SiO_2$  and  $Ca/HCO_3$  may hence constitute good indicators to demonstrate the intensity of water-rocks interactions, and are supposed to increase along the flow lines with the residence time. The  $SiO_2$  versus  $Ca/Mg$  (Fig. 5) displays two groups. The first one, including almost of samples of different part of piedmont and wadis Lakhdar and Tassaoute show an increasing in  $Ca/Mg$  with weak values of Silicate. However, the second group, including three samples of Middle part, two samples of Western part of piedmont and rest of wadis present a positive correlation, and has higher values of  $SiO_2$ . Enrichment of Silicate in wadis can be explained by contribution of recharge by deep aquifer. Indeed, chaponière, 2005 demonstrated that deep aquifer comes from high altitude enriched largely the water river in the spring and summer. The positive correlation with samples in Middle and Western part of piedmont and wadis indicate a hydraulic connection between them and most of these wadis through igneous rocks in the hilly area. In the contrast, the first group suggests that carbonate dissolution is a main process which dominated in groundwater mineralization, and it could be linked by domination of carbonate rocks in the Eastern part of piedmont. Thus suggest that groundwater residence time in Western and Middle part of piedmont is longer than Eastern part. Weighted groundwater residence time in different section of study area (mountain, piedmont and plain) need more tritium and  $^{14}C$  analysis, practice other methods such us CFC and CF (Santoni et al., 2016) and applied different models of this parameter for a sustainable management.

#### 4.3 Interaction of groundwater and river water

Generally, river water seeps through the streambed and recharges the shallow groundwater. The hydrological regime of the main rivers from the High Atlas is influenced by both rain and snowmelt, the annual floods can be due to rapid snowmelt and/or heavy rainfall (Jarlan & al., 2015). In one hand, the snow cover area of the Atlas mountains was monitored from 2000 to 2014 using remote sensing (Marchane & al., 2015). The annual snow cover area shows strong intra-seasonal and inter-annual variability, both in terms of maximum snow surface and total amount, and in terms of distribution of events and duration of the season. Their accumulation cover between 1500 and 4000 m asl, usually from November to May. The monthly average snow cover varied between

5 km<sup>2</sup> (for May 2005) and 14,894 km<sup>2</sup> (for January 2006) (Boudelaire N'da et al., 2016). Rainfall varies between 600 to 700 mm from 1973 to 2011 in the mountain area (Fninguire & al., 2014; 2016). therefore, floods are frequent in mountainous semi-arid environment. The flash floods was estimated. Peaks of 103 m<sup>3</sup>/s for example occur every 2 years, and floods of around 485 m<sup>3</sup>/s have a return period of 10 years. The abruptness and violence of the extreme flows are the main hazards which always threaten the valleys.

The general ground flow of Haouz plain (Boukhari & al., 2014) reveals interactions between groundwater and other wadis as well. The wadis N'Fis, Assif el Mal and Chichaoua seem to drain groundwater in some places, whereas upstream of the Middle Haouz, groundwater mounds are linked to the wadis of Rheraya and Ourika, most likely indicating recharge from wadis during floods and generally through river bed infiltration. The south-eastern sector located between Lakhdar and Tassaouate wadis and the south-western sector located between Chichaoua and Assif el Mal wadis also seem to be recharge areas. Therefore, the recharge of the alluvial aquifer and piedmont area seems to be mainly insured by the wadi floods or dam releases coming from the High-Atlas mountains which receive important precipitation either as rainfall and snowfall.

The major factors controlling the contribution ratio of the river water at groundwater are the distance from the river, slope and hydrogeological conditions such as syncline structure. High Atlas of Marrakech is a geographic area composed by the following several watersheds (N'Fis, Gheraya, Ourika, Zat and Ghdat). They are exposed to the atlantic humid air masses which condenses easily on the upper watersheds. In the upper, central and southern border Haouz piedmont of different rivers drainage basin were respectively characterized by highly erosional debris flow deposits, fluvial terraces and alluvial fans. They characterized also steep slopes and an anastomosed river system, which result high matrix porosity and permeability. consequently river-aquifer interaction changes along the piedmont with some areas behaving as gaining streams (mainly in the upper parts of the basin) and other areas as losing streams.

The chemical compositions of the river Rdat, Zat, Ourika, Rheraya, N'Fis, Assif el Mal and Chichaoua and the groundwaters samples near of these wadis are very similar (Fig. 6). It demonstrates the close hydraulic connection between the river water and the groundwater in the piedmont. In addition, the isotopic compositions in groundwater enriched in heavier isotopes (Tab. 1) were similar to that of rivers water, which indicates the same source of the waters. Thus, it is inferred that river water seeps through the river bed and dries up eventually in the piedmont, and then overflowed in the plain. Although the d-excess, high concentration of silica and tritium of rivers water and groundwater (Tab. 1) showed a weak variation, which indicate recent recharge and their contribution by deep aquifer. These features suggest that the mean residence times of river water and groundwater in mountain and piedmont may considerably long (at least > 1 year).

#### 4.4 Hydrochemical characteristic

The EC reflects the total dissolved ion concentrations in water, and to a certain extent, the length of flow paths and residence times underground. The EC values of groundwater ranged from 200 to 3792  $\mu\text{S}/\text{cm}$ , while those of river water are respectively 1025, 1414, 6720, 362, 363, 717, 303, 100 and 475  $\mu\text{S}/\text{cm}$  for wadis Lakhdar, Tassaoute, Rdat, Zat, Ourika, Rheraya, N'Fis, Assif el Mal and Chichaoua. The average EC is 1534  $\mu\text{S}/\text{cm}$  for Eastern part of piedmont, 1616  $\mu\text{S}/\text{cm}$  for Middle part of piedmont and 636  $\mu\text{S}/\text{cm}$  for Western part of piedmont. These values reveals the regional flow and the mixture behavior in shallow groundwater and different rivers. Generally, the EC value of groundwater increased when elevation decreased (Xing & al., 2013). In the study area the trend is also observed only in the eastern part. However, the Middle and Western part both in plain and piedmont showed that the fresh groundwater were largely exposed (Boukhari & al., 2014). It could be linked by hydraulic connection between rivers and shallow groundwater through the stream and/or snowmelt. The snowmelt plays an important role in recharging aquifers, lakes, and rivers on the southern and northern sides of the Atlas mountains, which allows the dilution of salinity in adjacent aquifers (Boudelaire N'da & al., 2016).

Piper digram (Fig. 7) suggest that SO<sub>4</sub>-Ca is the dominant hydrochemical facies in the study area. In the scatter plot of Ca vs SO<sub>4</sub> (Fig. 8) show a linear correlation, which indicate the same source of these elements. Piedmont area along the East to West part expose the Cenozoic and Mesozoic terrains, which largely enriched by evaporate and carbonate rocks.

#### 4.5 Hydrochemical processes

The determination of possible mineral phases is very important to understand hydrochemical processes, which is based on mineral compositions of aquifer sediments, groundwater chemical components and the occurrence condition of aquifers. The minerals contained in aquifer sediments are the first priority of the possible mineral phases. In the study area, sediments are mainly composed of calcite, dolomite, Aragonite, halite and gypsum. In addition, the cation ex-changes between Ca<sup>2+</sup> and Na<sup>+</sup>, Mg<sup>2+</sup> and Na<sup>+</sup> may very important during groundwater chemical evolution processes. Clay minerals were considered as adsorbents for cation ex-changes. Possible mineral phases and their dissolution reactions are shown in Table 2.

The results of inverse modeling in groundwater of different parts of piedmont are shown in Table 3.

Simulation results showed that the hydrogeochemical processes were variables in different zonations. In Eastern part of piedmont, groundwater system experienced dissolution of dolomite, calcite, aragonite and gypsum, cation-exchange (between  $K^+$  and  $Na^+$  in sediments and  $Ca^{2+}$  in water), dissolutions of halite and evaporation process are stronger in this part, such as in the Rdat wadi and groundwaters in piedmont and plain. In Middle and Western part of piedmont, it experienced precipitations of calcite, dolomite and aragonite and dissolutions of halite and gypsum. It also experienced cation exchange, and low evaporation. The simulation results showed that cation-exchange, evaporation, halite and gypsum dissolution were generally occurred in all zones of groundwater systems. Based on inverse modeling. Calcite and dolomite precipitations were expected to take place in Eastern and Middle part of piedmont.

#### 4.5.1 Evaporation process and halit dissolution

Ratio Br/Cl via Cl is an important invaluable tracers for geochemical process. It can distinguish between evaporation from halit dissolution. Inland basins, especially in arid or semi-arid areas, may have higher Br/Cl ratios due to the tendency for  $Cl^-$  to be removed by deposition of marine aerosols in coastal areas. In the other hand, Br/Cl ratios of halite are commonly in the order of 1–0.1 %, because halite could prevent more bromine from entering its mineral lattice. In this case, halite dissolution will produce a rapid decrease in Br/Cl ratios with increasing Cl concentrations.

Average concentration of bromide in different part of piedmont is very low. It was found respectively 0.0052 mmol/l, 0.0016 mmol/l and 0.0018 mmol/l in Eastern, Middle and Western part of piedmont respectively. The range of Br/Cl ratios in groundwaters was between 0 and 0.0030. Relatively lower ratios were observed in Middle part of piedmont (<0.0010), in comparison with those in Western and Eastern part of piedmont (Fig. 9b). Since all samples were unsaturated with respect to halite, with SIHalite between -4 and -0.5, except two samples of Eastern and Middle part of piedmont (Fig.9c). In addition, Br- concentration has positively correlation with Cl- in the most samples of different parts of mountain (Fig. 9a). Thus, evaporation process is may generally occurred in the groundwater system in the piedmont.

In Fig. 9b, it was observed that clearly separate three groups of samples. The first one has higher values of Br/Cl ratio, similar to rainfall values. This group corresponds to groundwater sampled in the Eastern, Middle and Western part of piedmont. The second group is depleted in bromide inducing lower values of Br/Cl ratio. This group corresponds to groundwater from the Middle part of piedmont. The third group, including one sample of Eastern part of piedmont and two samples of Middle part, have higher values of Cl, with lower values of Br/Cl ratio with even close to 0 %. Thus, suggest that halit dissolution may generally occurred in theses parts of piedmont. The distinction between evaporation and salt dissolution can be also showed, using the plot of 18O vs Cl (Fig. 9d). Salt dissolution will cause horizontal lines in the plot showing only increase in Cl and not in 18O. However, evaporation will display almost vertical lines, affecting 18O much more significantly than Cl, as can be proven by applying the rayleigh equation for oxygen isotope fractionation. The result demonstrate that several samples of different parts of piedmont affected by evaporation, one sample in the Middle part of piedmont affected by salt dissolution and one in the Eastern part of piedmont seem to be affected by both processes. It was suggested that groundwaters in different parts of piedmont are relatively affected by evaporation and weakly affected by salt dissolution.

#### 4.5.2 gypsum dissuloution process

The release of sulfate occurs rapidly by dissolving gypsum sediment. It results (i) an increase in its saturation index and (ii) a positive correlation between Ca, Mg and  $SO_4$  by the progressive release of  $SO_4$  and then Ca and finally Mg.

A good correlation observed in figure 8, which shows this process. It indicates that these elements have the same origin. Groundwater had relatively high  $SO_4$  contents than rivers water. The  $SO_4$  and Ca likley originated from sediments deposited in the differents suncline structure in the piedmont

Similarly, the saturation index with respect to gypsum (Fig. 10) shows an alignment between  $SO_4$  and Ca and a tendency of sub-saturation, confirming the similar origin of these elements.

In addition, strontium (Sr) is used as it is often associated to gypsum as celstite ( $SrSO_4$ ). Figure 11 sohow good correlation between Sr and  $SO_4$  in all parts of piedmont. It is suggest that gypsum dissolution is the main process of sulfate contamination. Gypsum is present in the gypsiferous marls of the Senonian wich forms the basement of the Eocene aquifer and the top of Turonian layers in differents synclines structures in piedmont. Consequently, groundwater in these aquifers could be affected by sulfate contamination.

#### 4.5.3 Ion exchange process

Ion exchange between  $Ca^{2+}$ ,  $Mg^{2+}$  and  $Na^+$  in groundwater systems is very important for groundwater hydrochemical evolution. The soluble ions in natural waters mainly come from the rocks and soils weathering, anthropogenic input, and partly from the atmosphere input. Groundwaters of piedmont and plain,  $Na^+$  concentration and  $[Na]/[Ca]$ ,  $[Na]/[Mg]$  molar ratios gradually increased from mountain, through piedmont, to plain (Tab.4). Average molar ratios of  $[Na]/[Ca]$  and  $[Na]/[Mg]$  increased from 2.9 and 2.2 in Eastern part of piedmont, 1.49 and 2.86 in Middle part of piedmont and from 0.79 in Western part of piedmont to 2.47 and 2.39

in plain, respectively (Tab.4). These increases were expected to result from ion exchange between adsorbed  $\text{Na}^+$  and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from solution.

Gibbs diagram could be used to analyze the genesis mechanisms of water chemistry (Xing & al., 2013). According to Gibbs (1970), rivers may have an assemblage of dissolved loads that reflect dominant effects of precipitation, rock weathering, or evaporation in dry regions.

Ratios of  $\text{Na}^+(\text{Na}^+ + \text{Ca}^{2+})$  were mostly less than 0.5 in groundwaters coming from Western part of piedmont, some samples of Middle part of piedmont and one sample of Eastern part of piedmont, with low TDS values (Fig. 12). This suggested that rock weathering (RWD) was the dominant mechanism. Three samples including one sample of Middle part of piedmont, one of Eastern part of piedmont and wadis Rdat have increasing of  $\text{Na}^+(\text{Na}^+ + \text{Ca}^{2+})$ , with the values more than 0.8 and with high TDS (80 and 180 mmol/l) which suggested that the groundwater chemistry was not only controlled by rock weathering and/or atmospheric precipitation, but also by mixing of saline water or evaporation (ECD).

The molar ratio of  $\text{Na}^+$  to  $\text{Cl}^-$  can be used to reflect the ion exchange degree (Li, 2010). Most of groundwater of piedmont samples have  $\text{Na}^+/\text{Cl}^-$  ratios greater than 1 (Fig. 13a). In addition,  $\text{Na}^+/\text{Cl}^-$  ratio showed a decrease trend with an increase in  $\text{Cl}^-$  concentration. The reason for the weak ion exchange in high  $\text{Cl}^-$  groundwater was that  $\text{Na}^+$  concentration increased due to evaporation and became high enough to balance the adsorbed  $\text{Na}^+$  for ion exchanged cations, although the increase in TDS would be driving force for cation exchange. It indicated that evaporation would gradually suppress ion exchange between aqueous  $\text{Ca}^{2+}$  and adsorbed  $\text{Na}^+$ . Besides,  $\text{Mg}^{2+}$  in groundwaters could be involved into the ion exchange, which was supported by meq ratio of  $\text{Na}^+$  to  $(\text{Na}^+ + \text{Ca}^{2+} + \text{Mg}^{2+})$ . The ratio increased in all zones of piedmont, and exhibited higher in Middle and Eastern part of piedmont (Fig. 13b).

#### 4.6 Relation between piedmont and plain

The hydrochemical facies both in plain (Boukhari & al., 2014) and piedmont (showed in present study) show three types of waters:  $\text{HCO}_3^- \text{Ca}$ ,  $\text{SO}_4 \text{Ca}$  and  $\text{NaCl}$ . The geologic map (Fig. 1) show a lateral variance of Mesozoic and Cenozoic layers, and relative absence of these formations in plain. The heterogeneity of hydrochemical facies is may linked by Mesozoic and Cenozoic formation of High-Atlas enriched by evaporitic rocks. However, hydrochemical evolution and mechanism of recharge which linked by of (High-Atlas and Plain) will still interpreted.

Sulfate and calcium variation on different parts of study area, show a decrease of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$  from mountain through the piedmont to plain. It's indicate a variety's mechanism of recharge, with mixture between these types of waters. Moreover, Western part show an increase on average of these elements. Thus refer that Cretaceous formation is continued under Mio-Plio-Quaternary deposits in plain of Mejjate.

The presence of  $\text{NaCl}$  anomaly both in piedmont and plain indicate the contribution of other parameter of recharge with regard to unique recharge through high-atlasic aquifers. Boukhari & al., 2014 and the present study shows a composite origin in  $\text{Na}^+$  and  $\text{Cl}^-$  concentration between halite dissolution, evaporation process and Ion exchange. In contrast, the decrease of  $\text{NaCl}$  in profil S-N in central part of study area can be explained by water dilution coming from wadis. The wadis Ghmat, Baaja and Nfis usually carry water of lower salinity from the mountains.

The dynamic of underground flows and the chemistry of the above-mentioned waters, shows that feeding the caters of the plain from the High-Atlas to plain seems to have a composite origin between waters abutment underground of piedmont and direct infiltration of stream flow which slashes the southern slope of High-Atlas through plain.

However, the spatial analysis of the chemical parameters ( $\text{SO}_4^{2-}$ ,  $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Cl}^-$  and  $\text{SiO}_2$ ) of the water of the sheet shows a decrease in the concentrations following the substantially oriented profiles SN at the level of the drainage axis of the central part of the study area. This result confirms the hypothesis of feeding from the High Atlas and also demonstrates a continuous dilution effect that occurs from fresh water. A third feeding area for the plain from the extrem Eastern and Western part of the plain may be envisaged. In addition, Sr/Ca ratio can be used to demonstrate the origin of evaporitic rocks of each formation. Indeed, Bakalowicz, 1988, show that when Sr/Ca is high or equal than 1‰, the ratio comes from evaporitic formations. However, when it higher or equal than 5‰, it may attribute of alpin triassic evaporite. It is found also in the formations of High-Atlas and plain adjacent of Souss that groundwater has four types of waters: the first group have the value of Sr/Ca less than 2‰ which linked by Paleozoic formation, the second group have Sr/Ca between 2,3 et 3,65‰, which the waters linked by Cretaceous and Eocen formations, the third group have Sr/Ca between 3,70 et 4,7‰ which linked by Triassic terrain and the last group have the values higher than 5,3‰ which influenced by evaporitic terrains riches on gypsiferous mineral of Liassic terrain. In this area, figure 14 display that all samples both of piedmont and plain have values of Sr/Ca plot between 0,1‰ and 2‰, which suggests the influence of Paleozoic terrains.

Therefore, based on the behavior of the chemical parameters ( $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{Sr}^{2+}$ ,  $\text{Na}^+$  and  $\text{Ca}^{2+}$ ) mainly related

to the dissolution of gypsum ( $\text{CaSO}_4$ ), halite ( $\text{NaCl}$ ) and Celestine ( $\text{SrSO}_4$ ) In the lithological formations of the High Atlas and relatively absent in the plain (exception plain of Mejjate in the west), it has been shown that the supply of water that feeds the mountain to the plain can have several origins: i) a contribution by underground abutment between the boundary layers of the two estates, ii) intakes from high-atlasic tributaries, during high-water periods, by direct infiltration into the piedmont, And iii) a supply from the limestone discharge waters at the Marmouta anticline in the extrem West and East of the plain. It seems that groundwater in plain is the results of mixture between the variance type of waters comes from different origins.

## 5. Conclusion

The aquifer of the piedmont in High Atlas gain direct and indirect recharge. Isotopes signature reflect that it receives significantly direct recharge in the hilly area (more than 2000 m of altitude). Rivers water seeps through the river bed and dries in the piedmont and plain. Within the piedmont, tritium analysis show a presence of recent groundwater recharge. Stable isotopes data indicates that recharge may be dominated by high-altitude meteoric originating from the High-Atlas mountain. High silicate content in groundwater indicate also that recharge may realise by a deep aquifer. The recharge water transferred from the mountains to the piedmont by the wadis that cross the mountain from south.

Evaporation, ion ex-change and gypsum dissolution are the main process controlling groundwater hydrochemical characteristics. Thus, groundwater mineralization resulting from groundwater flow in carbonate formation of Paleozoic, Mesozoic and Cenozoic deposits both mountain, piedmont and sandstone and conglomerate of dejection cone in plain. These results indicate an influence of water coming from High-Atlas on groundwater chemical in plain. Correlation between Br and Cl, and  $^{18}\text{O}$  and Cl shows that evaporation process is may generally occurred in the groundwater system in piedmont, one sample present halite dissolution is minor process and probably local especially in the Middle part of piedmont and both process are marked in one sample in Eastern part of piedmont.

Dissolution of gypsum mineral is responsible of enrichment of  $\text{SO}_4^{2-}$  and  $\text{Ca}^{2+}$ . It can be linked by syncline structure influences, which widely expose gypsum mineral in Eocene and Cretaceous formations.

Groundwaters of piedmont and plain,  $\text{Na}^+$  concentration and  $[\text{Na}]/[\text{Ca}]$ ,  $[\text{Na}]/[\text{Mg}]$  molar ratios gradually increased from mountain, through piedmont, to plain. These increases were expected to result from ion exchange between adsorbed  $\text{Na}^+$  and  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from solution.

Analysis in one hand of geologic and piezometric maps between high-atlas and plain (Boukhari & al., 2014) and spatial evolution of hydrochemical elements of evaporitic origin ( $\text{SO}_4^{2-}$ ,  $\text{Cl}^-$  and  $\text{Sr}^{2+}$ ) in the other hand indicate the presence of : i) composite of recharge of shallow groundwater both in piedmont and plain between direct infiltration in river channel seepage through by High-Atlas, ii) recharge through Mesozoic and Cenozoic aquifer presented in different structure syncline (mountain block recharge) and iii) a mixture process of different origins and dilution of salt groundwater presented in plain adjacent High-Atlas mountain

The present study highlights the spatial structure of the groundwater-rivers interactions and the influence of syncline structure setting on mountain block recharge. Evaluate qualitatively and quantitatively of End-Member Analysis (EMMA) and their contribution of recharge, with temporal hydrochemical analysis, combined by other approaches such as numerical simulation is necessary to further the sustainable management groundwater of Haouz plain.

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Table 1. Chemical and isotopic analysis

Number	GW Unit	Type	Z	pH	T° C	EC (µS/Cm)	Na (mmol/l)	K (mmol/l)	Ca (mmol/l)	Mg (mmol/l)	Cl (mmol/l)	SO4 (mmol/l)	HCO3 (mmol/l)	Br (mmol/l)	Sr (mmol/l)	SiO2 (mg/l)	deltal8 O	Delta D	3H(UT)
1	MoE	Well	1043	7.1	16.0	1788	40.39	0.36	8.29	7.78	53.40	4.52	6.83	0.00	0.03	0.00	-5.08	-40.72	
2	MoE	Spring	1170	6.7	22.3	1251	6.29	0.13	5.81	5.83	7.28	8.73	4.85	0.01	0.10	2.87	-6.51	-52.81	
3	MoE	Spring	1151	7.1	13.2	1564	1.28	0.05	3.99	3.14	1.56	3.86	4.08	0.00	0.10	3.98	-5.19	-32.82	2.70
4	MoM	Spring	1209	7.2	17.3	1061	1.20	0.07	2.24	0.87	0.67	0.38	6.17	0.00	0.01	2.13	-6.50	-44.16	2.10
5	MoM	Spring	1373	7.7	17.7	2080	2.94	0.78	2.52	2.53	4.26	1.05	7.09	0.00	0.03	1.48	-6.19	-36.97	1.30
6	MoM	Well	1195	7.6	15.2	3792	35.29	0.26	4.66	2.39	39.94	1.49	5.33	0.01	0.01	3.04	-6.90	-37.30	2.20
7	MoM	Spring	1174	7.6	13.5	738	0.59	0.07	1.74	0.48	0.36	0.33	4.84	0.00	0.01	7.19	-6.11	-39.59	
8	MoM	Well	1205	7.1	13.5	1203	8.97	0.10	2.41	1.55	9.31	0.64	4.69	0.00	0.00	0.83	-7.99	-48.36	
9	MoM	Well	1221	7.5	13.2	2060	1.47	0.13	9.13	4.97	1.42	12.48	5.01	0.00	0.03	2.99	-5.29	-33.86	
10	MoM	Spring	1279	7.4	19.4	1307	0.47	0.05	4.68	2.79	0.34	5.46	4.07	0.00	0.05	11.77	-5.93	-34.27	
11	MoM	Spring	1282	7.2	20.0	312	0.67	0.12	3.88	2.77	0.56	4.48	4.62	0.00	0.04	1.55	-5.61	-43.19	2.20
12	MoM	Well	1208	7.2	15.0	2541	1.38	0.03	1.51	0.43	0.45	0.11	5.21	0.00	0.00	1.97	-5.69	-27.82	
13	MoM	Spring	1188	8	16	1061	1.20	0.06	4.77	2.40	0.95	4.98	5.29	0.00	0.09	9.38	-7.2	-49.58	
14	MoW	Spring	1021	7.5	17.0	200	0.81	0.08	2.14	1.30	0.41	1.22	5.96	0.00	0.02	7.76	-6.29	-51.38	5.20
15	MoW	Spring	1292	7.5	19.5	1036	1.19	0.05	4.47	2.30	0.85	4.78	5.20	0.00	0.08	10.87	-6.81	-44.27	3.00
16	MoW	Well	1298	7.8	14.3	834	2.21	0.16	4.29	3.24	2.20	3.91	4.73	0.00	0.02	0.57	-5.82	-34.82	
17	MoW	Spring		8	17	475	1.22	0.07	2.25	0.89	0.68	0.39	6.13	0.00	0.02	2.33	-6.3	-49.4	
18	MoE	WLakhdar	932	7.1	17.0	1025	0.55	0.07	1.67	1.34	0.42	1.22	2.77	0.00	0.03	3.47	-8.29	-52.35	
19	MoE	WTassaout	1021	7.8	16.7	1414	4.28	0.07	1.38	1.03	4.21	0.79	3.44	0.00	0.01	4.36	-7.78	-52.68	
20	MoE	WRdat	1017	7.5	17.1	6720	36.16	0.42	4.37	1.52	37.69	2.85	3.77	0.00	0.05	5.94	-5.15	-39.80	
21	MoM	W.Zat	1001	7.6	10.6	362	0.62	0.06	0.77	0.23	0.41	0.13	2.44	0.00	0.00	9.15	-6.94	-44.50	
22	MoM	WOurika	1038	7.8	11.5	363	0.39	0.03	0.76	0.22	0.23	0.13	2.15	0.00	0.00	6.15	-8.75	-56.63	5.20
23	MoM	WRheraya	1014	6.6	16.2	717	5.84	0.06	1.76	1.01	5.96	0.44	3.42	0.00	0.01	7.14	-8.23	-50.55	
24	MoM	WNFis	1096	7.2	17.9	303	0.57	0.06	0.94	0.42	0.37	0.16	2.99	0.00	0.00	6.68	-8.17	-51.01	
25	MoW	Mal	1064	7.9	16.0	100	0.65	0.10	2.81	1.18	6.89	0.38	2.13	0.00	0.01	13.44	-7.80	-52.42	
26	MoW	W.Chichaoua	1072	7.8	11.8	475	0.75	0.05	1.40	0.93	0.64	0.80	3.66	0.00	0.02	9.32	-6.57	-46.60	

Table 2. Possible mineral phases and their dissolution reactions

Mineral phases	Dissolution reactions
Calcite	$CaCO_3 = Ca(2+) + CO_3(2-)$
Dolomite	$CaMg(CO_3)_2 = Ca(2+) + Mg(2+) + 2CO_3(2-)$
Halite	$NaCl = Na(+) + Cl(-)$
Gypsum	$CaSO_4 \cdot 2H_2O = Ca(2+) + SO_4(2-) + 2H_2O$
Cation exchange	$Ca^{2+} + 2Na^+ \rightleftharpoons Ca^{2+} + 2Na^+$

Table 3. Results of inverse modelings of groundwaters (in mmol/l)

Mole transfers	Eastearn part of piedmont	Middle part of piedmont	Western part of piedmont
Dolomite	-0,0845	0,3305	0,6475
Calcite	-0,0331	0,3039	0,4417
Aragonite	-0,1827	0,1538	0,2920
Halite	-1,0204	-2,3072	-2,7149
Gypsum	-0,7881	-1,4105	-1,2941
ion exchange	0,1669	-0,5147	-0,5761

Table4. Average molar ratios of [Na]/[Ca] and [Na]/[Mg] in groundwaters from different zones

	[Na/Ca]	[Na/Mg]
Eastern part of piedmont	2,09242278	2,227059
Middle part of piedmont	1,49304295	2,868867
Western part of piedmont	0,79936781	0,799368
Plain	2,47539047	2,39154
Wadis	1,96966121	4,596656

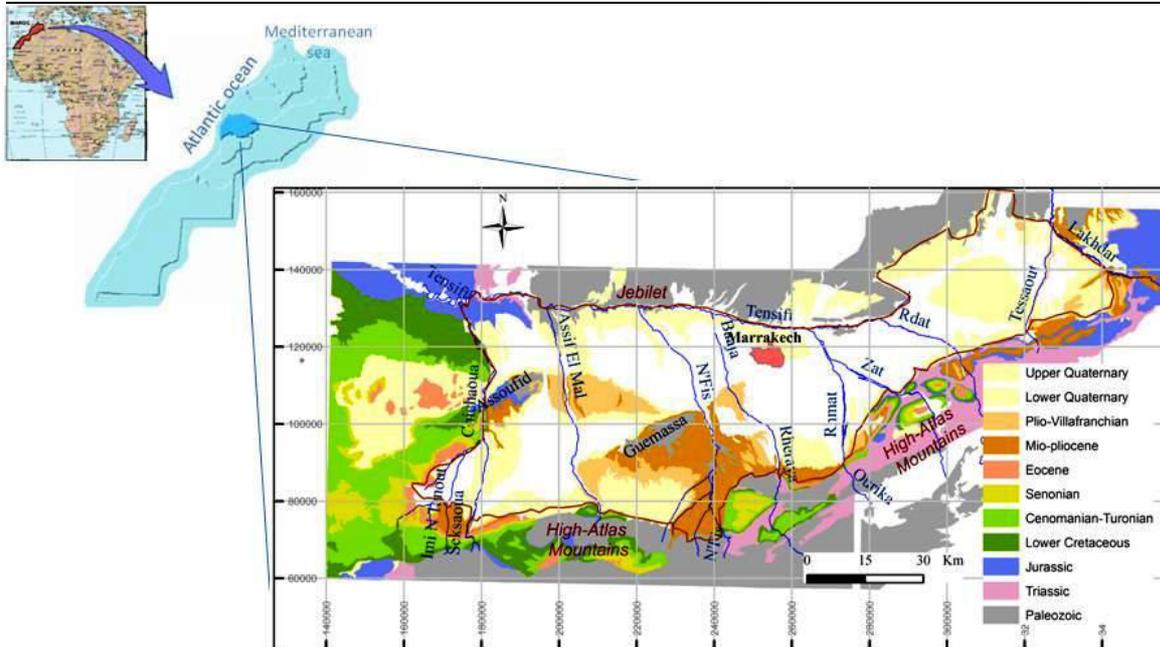


Figure .1 Location map of the Haouz plain, piedmont and High-Atlas mountain in Morocco. The figure shows also the geology within and around the plain as well as the network of wadis which come from the High-Atlas Mountains and cross the plain from south to north

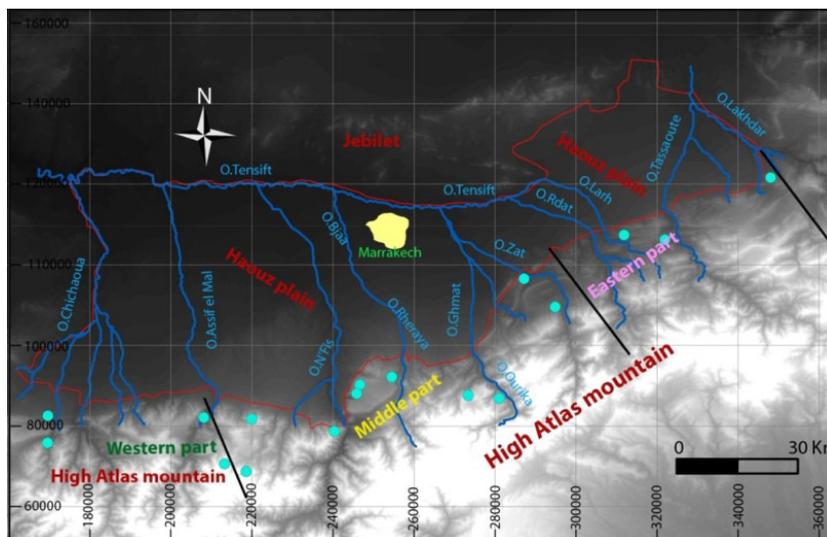


Figure .2 Sampling points of springs and of groundwater sorted by their geographical distribution. Three zones are distinguished in the piedmont area: West (MoW), Middle (MoM) and East (MoE)

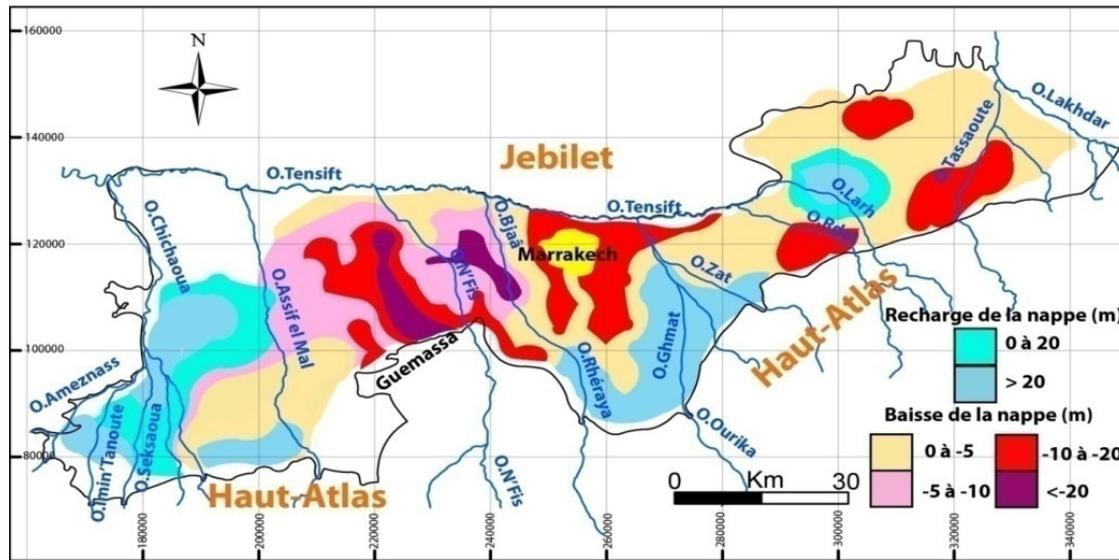


Figure .3 Groundwater decrease between 1998 to 2011

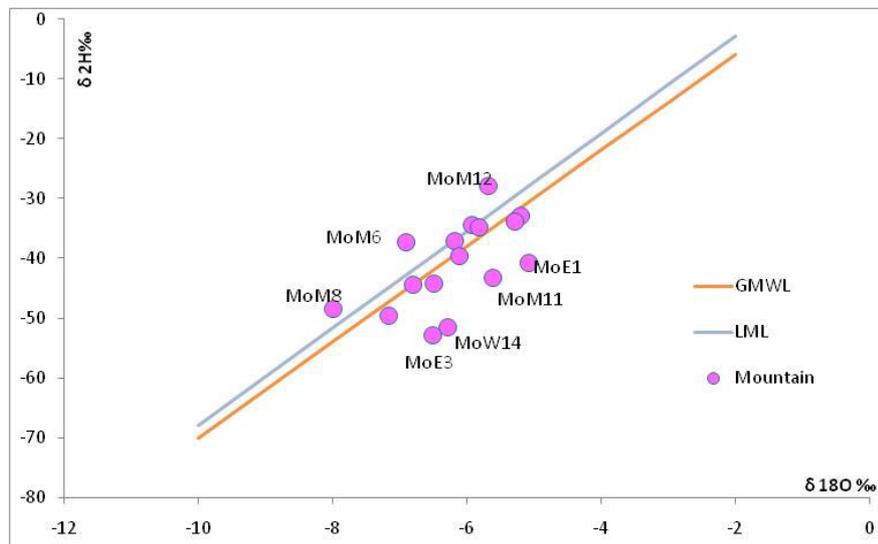


Figure .4  $\delta^2\text{H}$  vs  $\delta^{18}\text{O}$  values of sampled, springs and surface waters of mountainous as compared to the global and local meteoric water lines

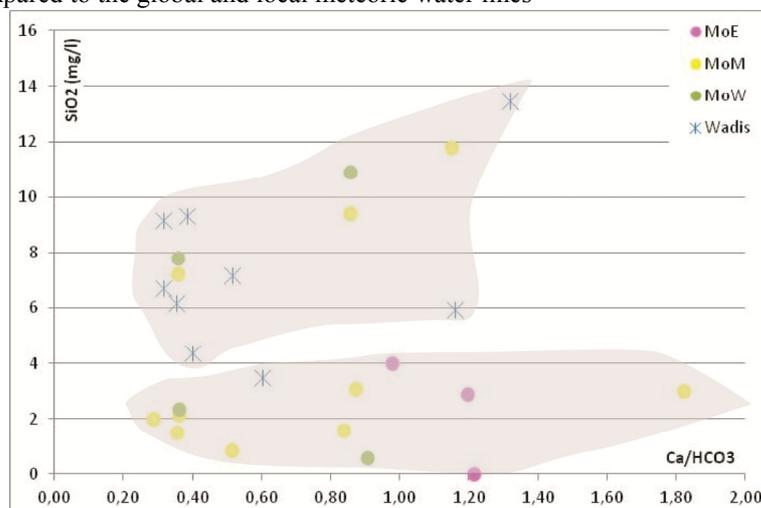


Figure .5 Scatter plot of  $\text{Ca}/\text{HCO}_3$  vs  $\text{SiO}_2$

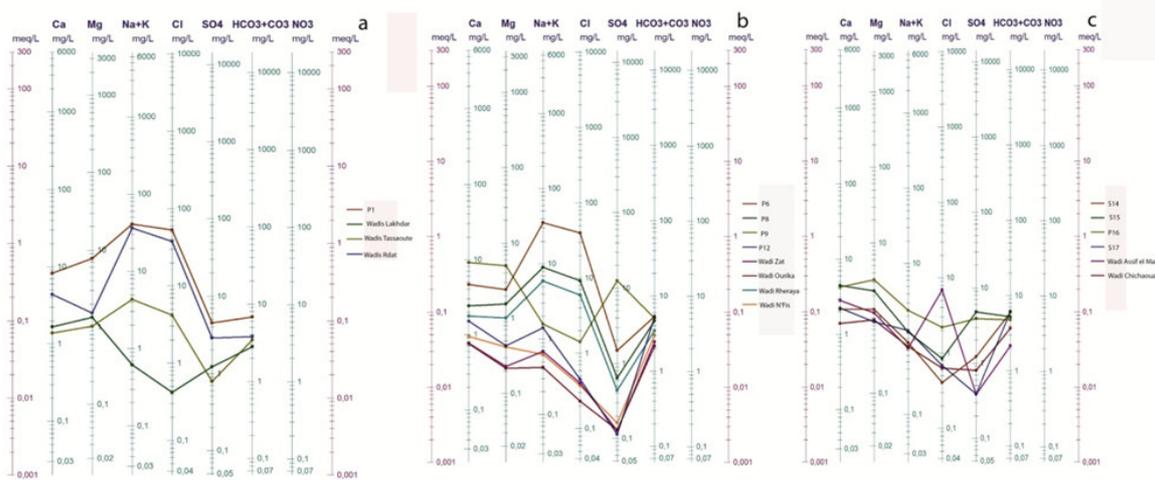


Figure .6 Fingerprint plot of chemical compositions of water samples. The chemical composition of river water very close to those of groundwater

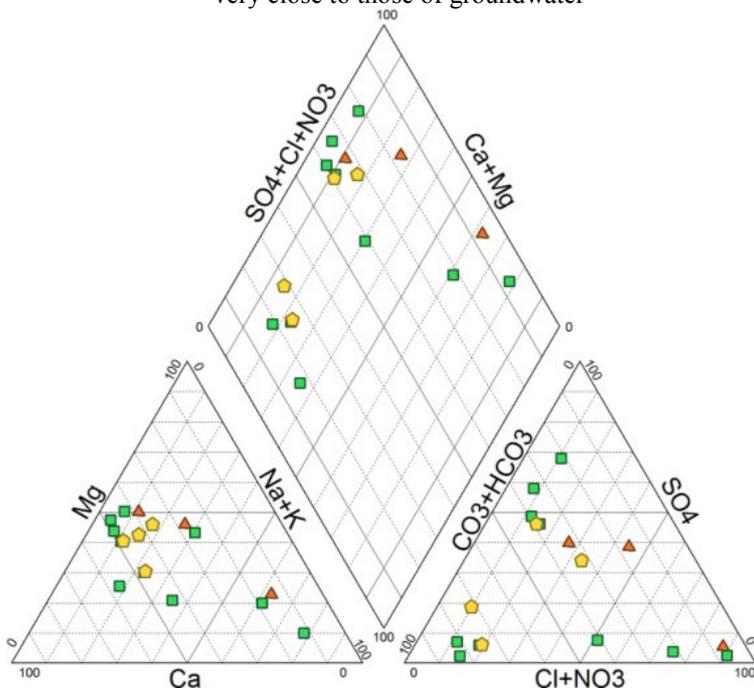


Figure .7 Piper diagram of the chemical composition of sampled groundwater

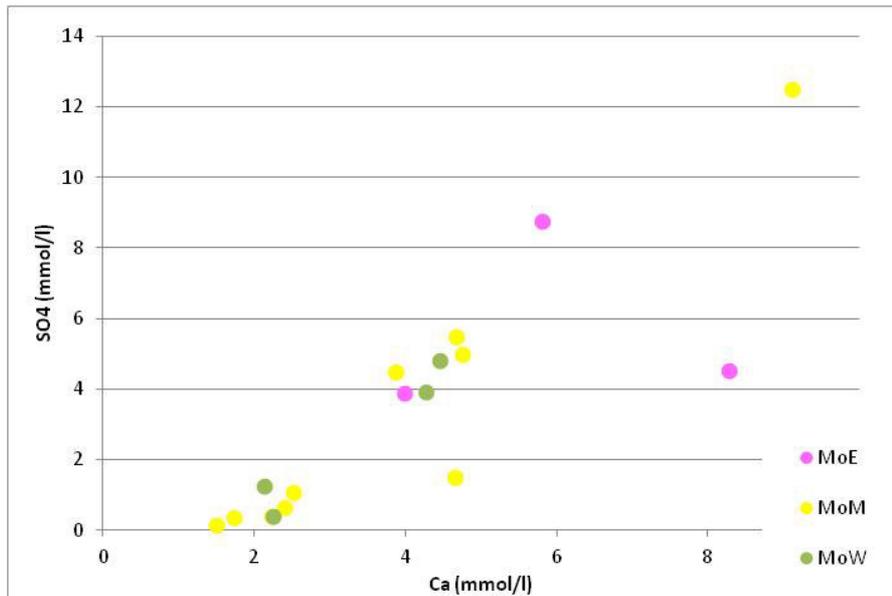


Figure .8 Scatter plot of Ca vs SO4

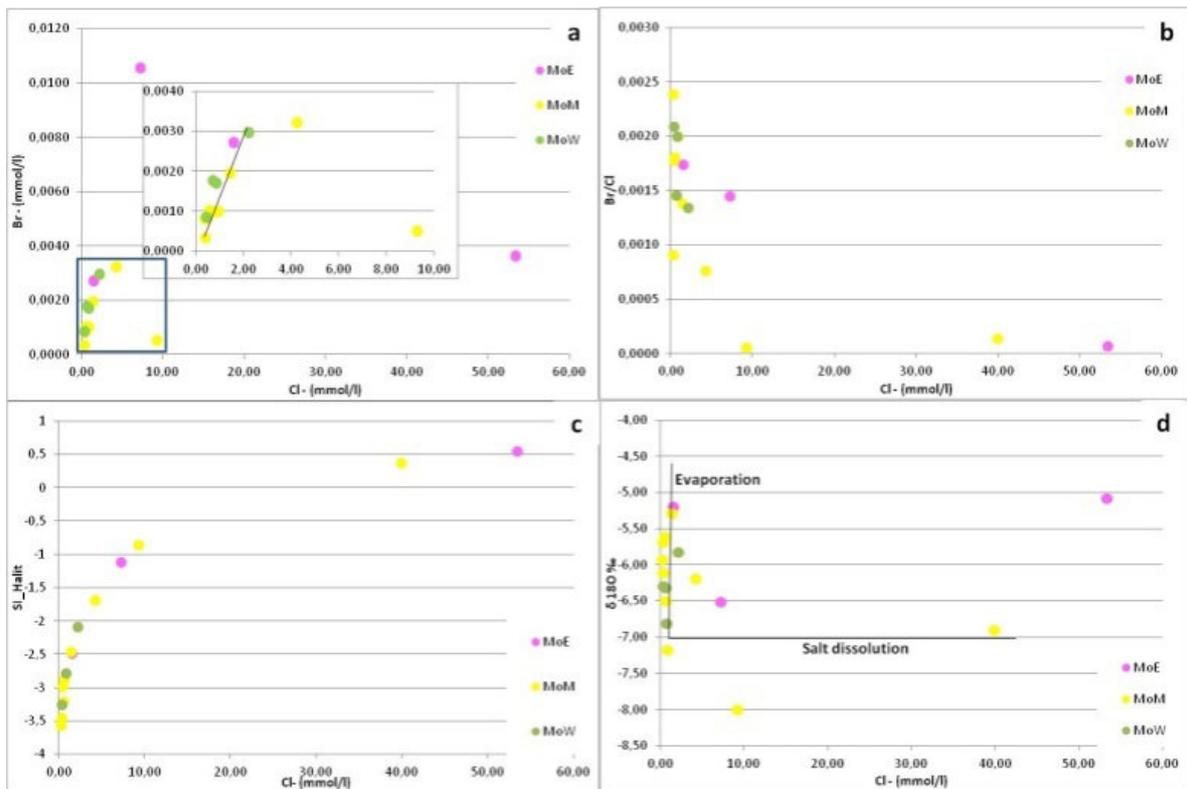


Figure .9 a) Scatter plot of Br vs Cl; b) Scatter plot Br/Cl vs Cl; c) Scatter plot of saturation index vs Cl and d) Scatter plot of 18O vs Cl concentrations in the study area

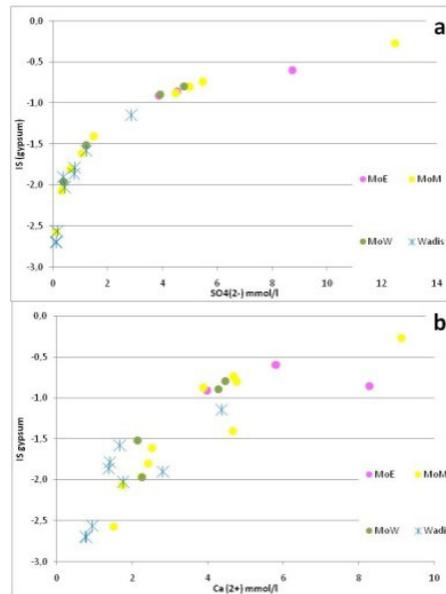


Figure .10 Scatter plot of saturation index of gypsum vs SO<sub>4</sub> (a) and Ca (b)

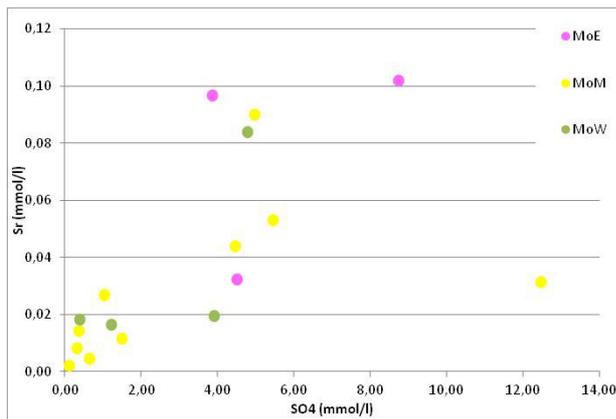


Figure .11 Scatter plot of Sr vs SO<sub>4</sub>

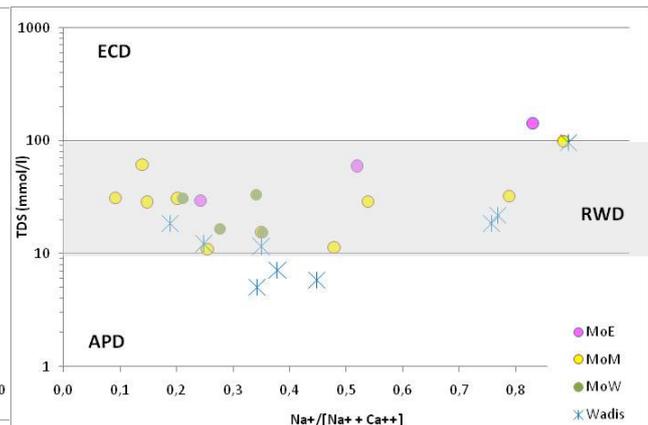


Figure .12 Gibbs diagram of groundwater samples in the piedmont area of High-Atlas

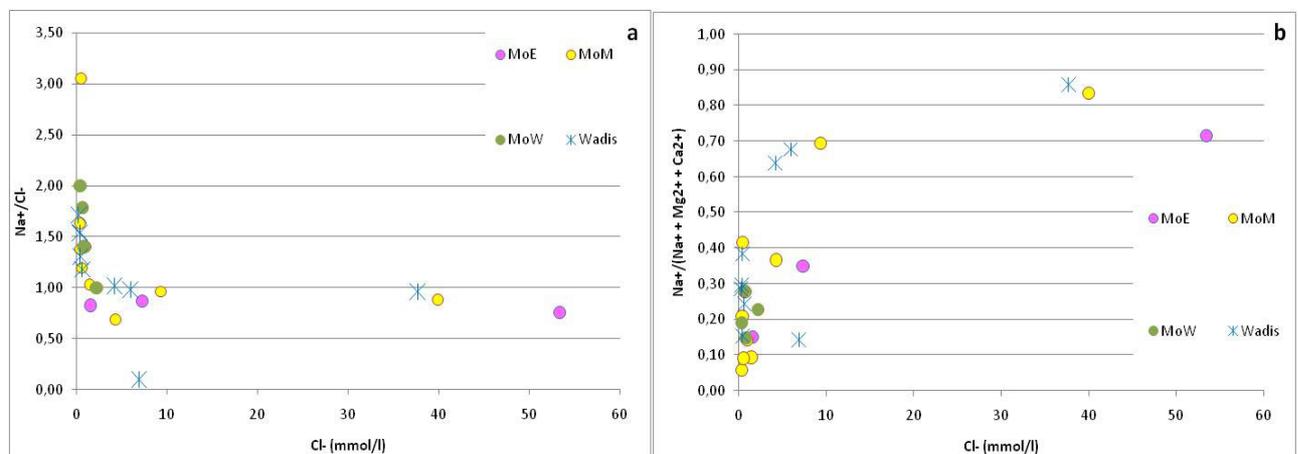


Figure .13 Variation of Cl concentration with Na/Cl ratio (a) and Na/(Na + Ca +Mg) ratio (b) in groundwaters of the piedmont area of High-Atlas mountain

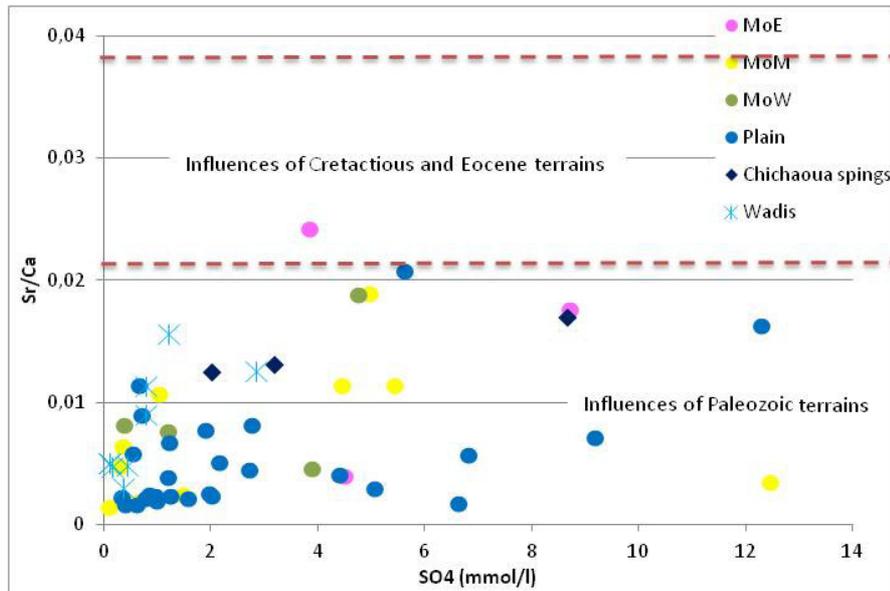


Figure .14 Variation of SO<sub>4</sub> concentration with Sr/Ca

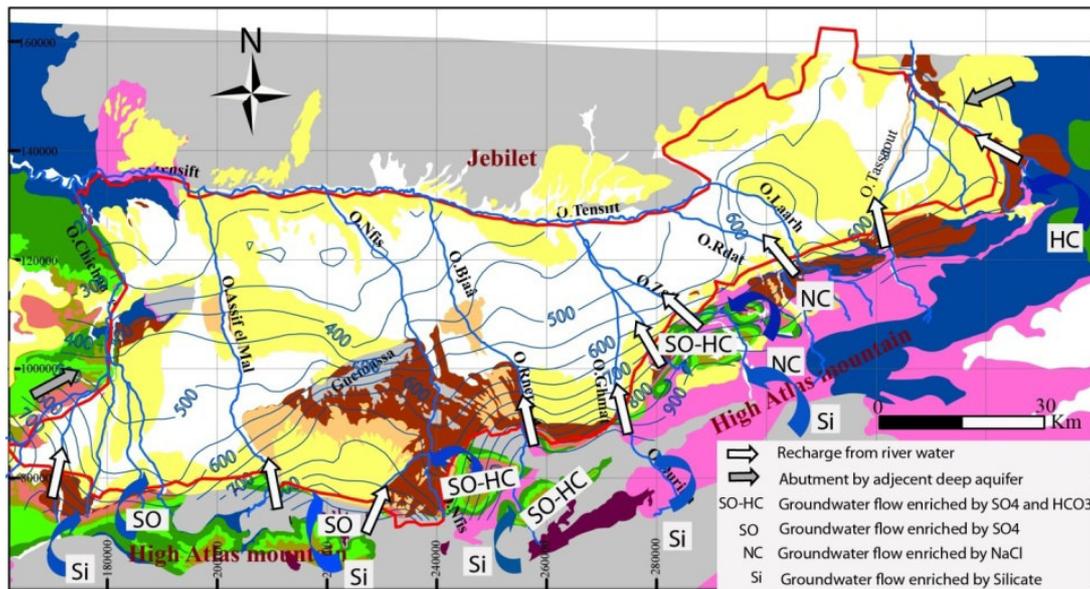


Figure .15 Mode of recharge and mineralization of groundwater in piedmont area of High-Atlas mountain and their adjacent Haouz plain.