



Hydrochemical characteristics and water quality evaluation of the Srou River and its tributaries (Middle Atlas, Morocco) for drinking and agricultural purposes

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ABSTRACT

The present study was conducted to evaluate the surface water quality of the Srou River and its tributaries for drinking and agricultural purposes. For this, 18 parameters including temperature, pH, electrical conductivity (EC), turbidity, total hardness (TH), dissolved oxygen (DO), chlorides (Cl), sulfate (SO_4^{2-}), calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), carbonates (HCO_3^-), nitrate (NO_3^-), nitrite (NO_2^-), ammonia (NH_4^+), and trace elements were monitored on 12 sampling points. The results showed that EC, TH, Cl, SO_4^{2-} , Ca^{2+} , Mg^{2+} , Na^+ , and some heavy metals such as Al, Cd, Fe, and Pb exceed widely the Moroccan and WHO standards for drinking water. The pH, DO, K^+ , NO_3^- , NO_2^- , and NH_4^+ contents are within the Moroccan and WHO guidelines for drinking water. Therefore, we concluded that the Srou River was potentially unsafe for drinking and domestic use. The abundance of cations and anions were in the order of $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{CO}_3^{2-}$ that leads to Cl⁻, SO_4^{2-} , Ca^{2+} , Mg^{2+} hydrochemical facies type. The multivariate statistical methods including Pearson's correlation, principal component analysis, and cluster analysis show that the variations in water compounds' concentration are mainly related to the effects of the lithology of the basin (weathering of soil, rock, and leaching of minerals). The SAR, salinity, KI, and MH were also used to assess the river water quality for agricultural purpose. The sodium absorption ratio, KI, and MH values suggested that the Srou River water had an acceptable quality for irrigation. However, high salinity values indicate that these waters could pose hazards in irrigated soils and should not be used for irrigation without special management plan.

Keywords: Srou River; Surface water; Physicochemical parameters; Multivariate statistical techniques; Sodium absorption ratio (SAR); Salinity; Kelley index (KI); Magnesium hazard (MH)

1. Introduction

Water is an important natural resource of the Earth and has been essential for the existence of all living things. Human society and water have always had an intimate relationship with the fact that the world's major civilizations developed along rivers. However, with the rapid growth of the world population and industry, the quality and quantity

of available water resources have become a major global concern [1]. Therefore, serious issues relating to pollution of water has attracted particular interest, because of its direct adverse impact on landscapes and ecosystems and human health. Those problems bring more attention nowadays by the implement of rigorous water policy and establish a new decision maker to slow down the progression of the contamination of water resources, even sometimes to make it regress.

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The hydrochemical composition of surface water is dependent on natural factors such as lithology of the basin and especially the availability of easily soluble minerals such as calcite (Ca–HCO₃ dominant), halite (Na–Cl dominant), and gypsum (Ca–SO₄ dominant) [2], atmospheric inputs, climatic conditions [3]. Anthropogenic intervention has also significant effects on surface water quality [4–6]. Some polluting behaviors, such as the discharge of domestic, industrial, urban and other wastewater into the watercourse without any previous treatment makes its quality to deteriorate [7,8]. Therefore, controlling and reducing inputs of hazardous substances, nutrients, and other water pollutants is becoming a necessity in order to record any alteration in its quality and to avoid any problems of health that could rise. Naturally, water quality refers to some physicochemical and hydrochemical characteristics, usually present at the optimum level for suitable growth of plants and animals and human uses.

In Morocco, which is a semi-arid country, the surface water occupies a prominent place in the development of various economic sectors and forms an important source of water supply for drinking, agricultural, and industrial purposes. As important surface water resources, some rivers need to be carefully managed to satisfy the growing demand. Oum Er Rbia watershed, drained by Oum Er Rbia River, is one of the Moroccan watersheds blessed by an abundant water resource that is used in various purposes such as the crop irrigation, hydroelectric power production, industrial and drinking water, and aggregate resources [9]. Oum Er Rbia River belonging to this basin catches its origin in the middle atlas near to the Khenifra City. It extends for about 550 km long. Several rivers, associated with this watershed, Srou, El Abid, Lakhder, ensure almost the totality of the recharge. The Oum Er Rbia River and their tributaries drain some rural, urban, agricultural, and industrial regions that constitute the main source of pollutant loads including domestic wastewater, agricultural runoff, animal husbandry, and industrial effluents, discharged into Oum Er Rbia River [10,11].

In this study, the Srou River was focused, a tributary of the Oum Er Rbia River, whose water has been used for a wide range of purposes such as domestic use, irrigation, and livestock. However, the quality of water from the Srou River is certainly threatened every day by the human population situated in a mid-mountain environment which suffers from a general lack of equipment [12]. Except for a few studies that have been conducted on Oum Er Rbia River's water, no detailed study has been carried out on the assessment of water quality of the Srou River yet.

The aim of the study is to investigate the surface water quality in the region since surface water resources are widely used for drinking and agricultural purposes. Therefore, the main objectives of this work are: (i) to assess the hydrochemical characteristics of the Srou water and its tributaries, (ii) to explain and identify the contamination affecting water quality and their potential sources using multivariate statistical methods, (iii) to determine the suitability for drinking and irrigation purposes.

2. Material and methods

2.1. Sampling and analysis

Water samples were collected from 12 sampling stations distributed at key point alongside the Srou River and its tributaries

(Fig. 1). Sampling was done on wet season. All samples were transported in bottles pre-rinsed with effluent water; bottles were conserved at 4°C. Different parameters such as temperature (T), pH, electrical conductivity (EC), and total hardness (TH) were recorded in the field using a portable multiparameter meter (Thermo Scientific Orion 4-Star Plus). Turbidity (NTU) was determined by turbidimeter; chloride (Cl⁻), dissolved oxygen (DO), calcium (Ca²⁺), and magnesium (Mg²⁺), were determined by volumetric titrimetry, and sulfates (SO₄²⁻) were analyzed by spectrophotometry using the turbidimetric method. Sodium (Na⁺) and potassium (K⁺) are measured using BWB flame photometer after calibrating the instrument with known standards. Nitrite (NO₂), nitrates (NO₃), and ammonium (NH₄) were estimated by a spectrophotometric technique. In order to analyze the metal content, water samples were digested with 1 mL of nitric acid (HNO₃) and 0.5 mL of hydrochloric acid (HCl), analyses were performed using ICP-AES technique.

All samples were analyzed in the Georesources and Environment Laboratory of the Faculty of Science and Techniques, Beni Mellal, and the Laboratory of National Office of Electricity and Water (ONEE), Morocco. The physico-chemical analysis was performed following the standard methods [13].

2.2. Statistical methods

All statistical computations in this study were implemented using Microsoft Excel 2010 and IBM SPSS 21 to prepare the correlation matrix of the surface water parameters. The data obtained were subjected to multivariate analyses techniques in order to facilitate consistent evaluation of the multiple variables, through Pearson's correlation, principal component analysis (PCA), cluster analysis (CA). Pearson's correlation coefficient (r) gives an idea about the possible relationships between variables. A correlation coefficient (r) of +1 indicates that two variables are perfectly related in a positive linear sense, but $r = -1$ indicates a negative linear correlation. However, no relationship between two variables exists if $r = 0$. Thus, two variables having a positive correlation coefficient infer that they have a common source, while negative correlation coefficient indicates different source [14,15]. It provides information on the most significant parameters used to describe the entire data set, data reduction, and to summarize the statistical correlation among constituents in the water with a minimum loss of original information [16–18]. PCA has been used on a correlation matrix of rearranged data to explain the structure of the underlying dataset and to identify the unobservable, latent pollution sources [19]. Cluster analysis is a group of multivariate techniques whose primary purpose is to assemble objects based on the characteristics they possess [20,21]. It provides intuitive similarity relationships between any one sample and the entire data set, and is typically illustrated by a dendrogram [6,13,31]. The resulting clusters of objects should then exhibit high internal (within-cluster) homogeneity and high external (between cluster) heterogeneity [21–23].

2.3. Geological setting

The Srou River is the main water body crossing the Middle Atlas in the high Oum Er-Rbia watershed. The Srou basin covers an area of about 1,443 km² between 32°35' to

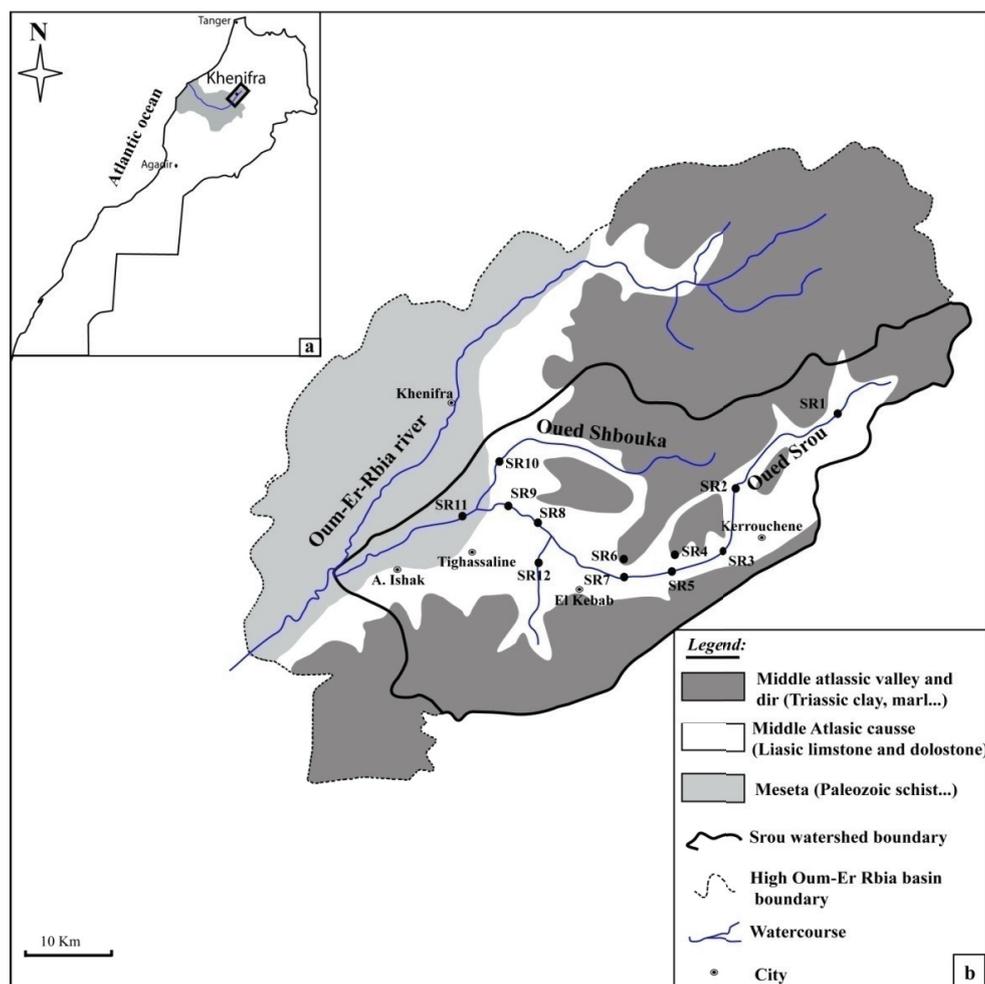


Fig. 1. (a) Geographical situation of the Oum-Er-Rbia basin (Morocco map). (b) Geological sketch and main hydrographic network of the Srou basin in high Oum-Er-Rbia basin. Source: Modified from El Jihad [27].

33° latitude north and 5°05' to 5°50' longitude west and lies in the west by the Hercynian massif, Causse of Ajdir at the north, and the high Moulouya plain at the south-east [24]. The Srou River originates near Senoual at 2,200 m altitude and flows North-East to South-West direction. Chbouka river is the main tributary of the Srou River which is located on its right bank [25] (Fig. 1). The geology of the study area exhibits diverse lithological features and ages based mainly on cretaceous sub-tabular limestone, liassic dolostone limestone and triassic red clay with saliferous and evaporite formations, doleritic basalt and Paleozoic schist, gray, and quartzite [24]. The hypsometric data reflect its mountainous character with a very strong and uneven relief. Its altitude varies from 700 m at the SW and 2,350 m at the NE.

2.4. Climate

The region is characterized by a semi-arid to sub-humid climate which is distinguished by irregular distribution, spread irregularly from October–November to April–May with predominance in December and January, and is almost non-existent in July and August except for occasional

summer rainfall. Consequently, we distinguish two seasons: a dry season and wet season. The study of rainfall through 12 rainfall stations located in high Oum Er-Rbia basin (including the Srou basin) and neighboring areas shows irregular rainfall in time and space with 480 mm at the SW and 805 mm at the NE of the basin [26]. The temperature varies from the low value near to 0°C in winter and high value in summer.

3. Results and discussion

3.1. Water quality evaluation

The hydrochemical results of water from all studied samples are summarized in Table 1 and Fig. 2. To determine the drinking quality of surface water samples, the data collected were compared with Moroccan Standards [28] and World Health Organization [29] standards to determine the suitability of this water for drinking and irrigation purposes. All the water quality parameters are expressed in mg/L, except pH, electrical conductivity (EC) ($\mu\text{S}/\text{cm}$), and temperature ($^{\circ}\text{C}$).

The temperature of the water shows a considerable variation among the water body due to the fact that ambient temperature differed as water progressed and between morning

Table 1
Hydrochemical analysis of water samples of the Srou and environs compared with Moroccan [28] and WHO [29] standards

| Samples | T °C | pH | EC μS/cm | Turbidity (NTU) | TH (mg/L) | DO (mg/L) | Cl ⁻ (mg/L) | SO ₄ ²⁻ (mg/L) | NO ₂ ⁻ | NO ₃ ⁻ | NH ₄ ⁺ | Na ⁺ (mg/L) | K ⁺ (mg/L) | Ca ²⁺ (mg/L) | Mg ²⁺ (mg/L) | HCO ₃ ⁻ (mg/L) | CO ₃ ²⁻ (mg/L) |
|--------------------|-------|---------|-------------|--------------------|--------------|--------------|---------------------------|-----------------------------------------|------------------------------|------------------------------|------------------------------|---------------------------|--------------------------|----------------------------|----------------------------|-----------------------------------------|-----------------------------------------|
| SR1 | 11.8 | 8.4 | 1,910 | 38.7 | 1,430 | 8.48 | 447.3 | 305.5 | 0.0233 | 0.1506 | 0.055 | 336.6 | 3.41 | 307.1 | 273.09 | 311.1 | 30 |
| SR2 | 14.8 | 8.6 | 1,800 | 90 | 1,380 | 8.48 | 497 | 440 | 0.0231 | 0.1731 | 0.042 | 338.3 | 3.8 | 306 | 261.20 | 293.75 | 42 |
| SR3 | 13 | 8.4 | 1,520 | 110 | 1,070 | 8.64 | 390.5 | 417.3 | 0.026 | 0.0809 | 0.03 | 275.9 | 3.4 | 264.6 | 195.87 | 311.1 | 48 |
| SR4 | 17.2 | 8.3 | 1,070 | 4.24 | 785 | 8 | 156.2 | 769.6 | 0.0122 | 0.0896 | 0.026 | 260.6 | 3.2 | 260.3 | 127.61 | 317.2 | 0 |
| SR5 | 13.5 | 8.5 | 1,450 | 74 | 1,100 | 8.48 | 383.4 | 457.6 | 0.0181 | 0.0714 | 0.03 | 250.4 | 3.3 | 245.2 | 207.89 | 311.1 | 18 |
| SR6 | 14.2 | 8.1 | 720 | 69.4 | 530 | 8.64 | 113.6 | 280.8 | 0.0138 | 0.1184 | 0.01 | 266.3 | 4.7 | 258.6 | 66.00 | 317.2 | 0 |
| SR7 | 12 | 8.3 | 1,600 | 89.5 | 1,220 | 8.96 | 383.4 | 464.1 | 0.0224 | 0.0658 | 0.027 | 279.3 | 5 | 260.4 | 233.37 | 305 | 36 |
| SR8 | 12.3 | 8.2 | 1,960 | 117 | 1,460 | 8.8 | 475.7 | 663.9 | 0.0194 | 0.2319 | 0.02 | 324.6 | 4.1 | 289.6 | 284.64 | 317.2 | 24 |
| SR9 | 13.2 | 8.4 | 2,000 | 170 | 1,488 | 8.96 | 497 | 536.9 | 0.0937 | 0.1482 | 0.06 | 394.7 | 3.8 | 333 | 280.90 | 305 | 24 |
| SR10 | 18.6 | 8.6 | 1,250 | 3.87 | 920 | 8.64 | 440.2 | 369.2 | 0.0135 | 0.0759 | 0.026 | 212.3 | 1.42 | 216.8 | 171.02 | 305 | 18 |
| SR11 | 16.7 | 8.1 | 1,830 | 71.7 | 1,350 | 8.8 | 433.1 | 409.2 | 0.241 | 0.134 | 0.62 | 291.7 | 3.09 | 266.8 | 263.43 | 293.75 | 0 |
| SR12 | 15 | 8.3 | 2,890 | 14.3 | 2,000 | 8.24 | 816.5 | 885.3 | 0.0259 | 0.1612 | 0.037 | 483.3 | 4.18 | 381.2 | 393.69 | 329.4 | 18 |
| Mean | 14.36 | 8.35 | 1,666.67 | 71.06 | 1,227.75 | 8.59 | 419.49 | 499.95 | 0.04 | 0.13 | 0.08 | 309.5 | 3.62 | 282.47 | 229.89 | 309.73 | 21.5 |
| Moroccan standards | 20 | 6.5–8.5 | 2,700 | 5 | 300 | 5–8 | – | – | 0.5 | 50 | 0.5 | – | – | 100 | – | – | – |
| WHO standards 2011 | – | 6.5–8.5 | – | 5 | 500 | – | 200 | 250 | 0.9 | 11 | 0.2 | – | – | 75 | 50 | – | – |

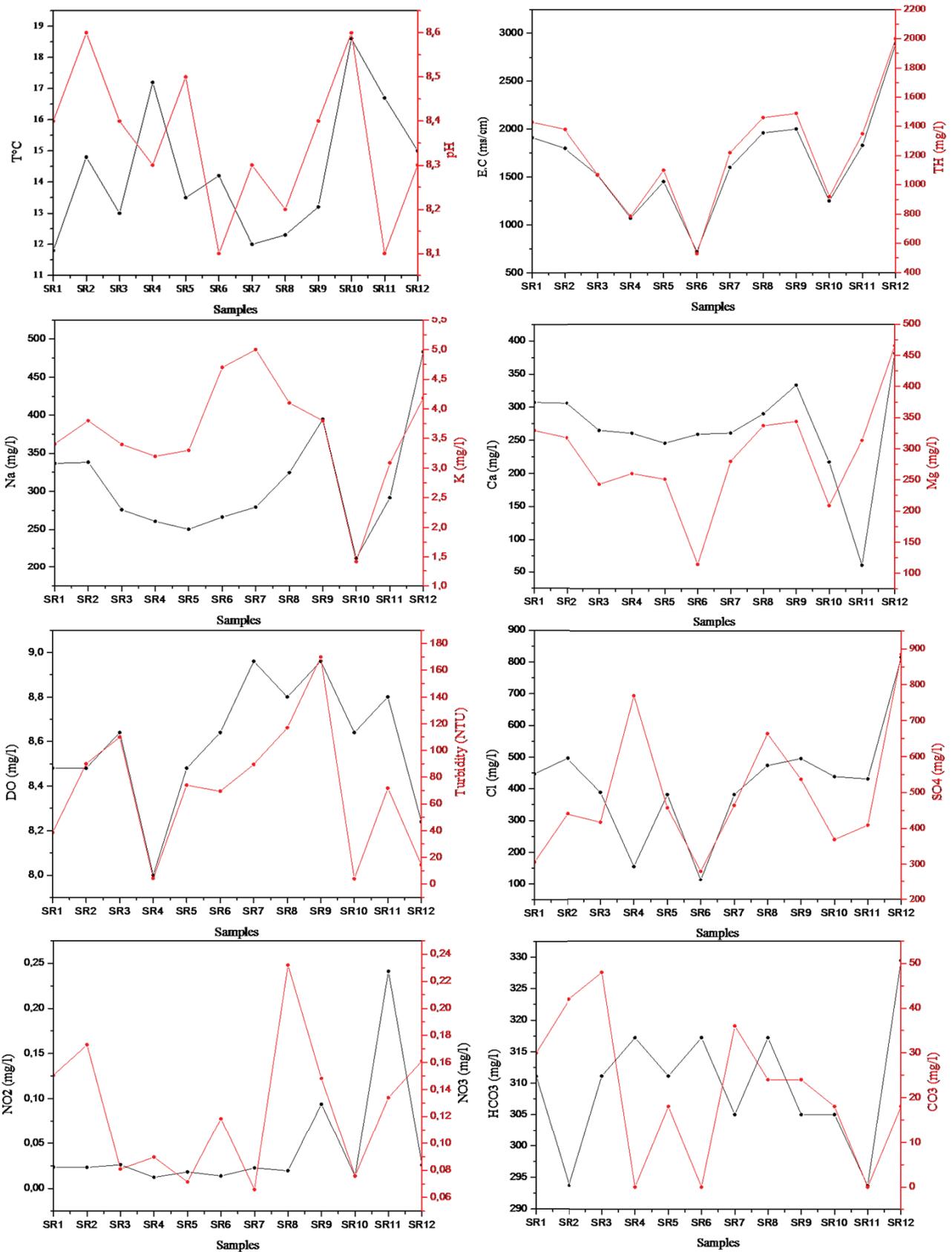


Fig. 2. Representation of physicochemical parameters at sampling sites.

and afternoon. However, the observed temperature did not exceed 18.6°C and was well within the safe limit for drinking (Moroccan standards).

The pH values ranged from 8.1 to 8.6 which were within the recommended range for drinking water referring to Moroccan and to the WHO limits. The pH values are alkaline in nature. Slight difference in the observed pH was noted between each sample. This could be explained, probably, by the carbonate nature of the geological outcrops traversed by the waters of the Srou River and its tributaries.

The EC is an index that represents the concentration of soluble salts in water [30]. The increase in water salinity and EC has been attributed principally to chloride, sodium, calcium, magnesium, and sulfate in groundwater [31]. In the study area, EC varies from 720 to 2,890 $\mu\text{S}/\text{cm}$ with an average of 1,660.6 $\mu\text{S}/\text{cm}$ and remarkable variations between each site. The minimum value of EC recorded at site SR6, can be explained by the origin of the stream, while the maximum value registered at site SR12 (2,890 $\mu\text{S}/\text{cm}$) and cross Moroccan and WHO limits. The latter is characterized by a sharply salty taste and it is assigned to the leaching of minerals from outcrops crossed by the stream. This increase in salinity has been attributed principally to chloride, sodium, calcium, magnesium, and sulfate.

Turbidity is a measure of the relative clarity or cloudiness of water [32,33]. Turbidity may result from mobilization of particulate matter such as sediments, mineral precipitates, biomass and its occurrence may be permanent or seasonal [34]. The observed values of turbidity are between 3.87 and 170 NTU. According to the Moroccan and WHO standards, all samples have turbidity values greater than the maximum permissible limits for drinking water by 5 NTU except for SR10. In our study, the turbidity comes from the source, adjacent outcrops and is probably a consequence of clay, marl, and chalk particles or of insoluble precipitations moved during rainfall and storms, human activity such as several stone careers that are very common in this region especially in downstream.

Dissolved oxygen in water, used by microorganisms in the biological oxidation of organic matter, is one of the most sensitive parameters indicating organic pollution. Its value provides information on the degree of pollution and therefore the degree of self-purification of streams. In our study, the DO concentrations fluctuated, in the normal range, between a minimum of 8 mg/L in SR4, and a maximum of 8.96 mg/L in SR7 and SR9.

The total hardness is caused by the presence of too many minerals primarily soluble salts of calcium and magnesium. It was found to be in the range of 530 mg/L to up than 2,000 mg/L and exceeds the Moroccan and WHO limit fixed at 300 and 500 mg/L, respectively. The Srou River samples have relatively high TH value. The minimum value registered at the Srou tributaries in SR4, SR6, and SR10 sampling sites with the exception of the SR12 site where the TH reached a maximum value higher than 2,000 mg/L. The content of Ca and Mg in all water samples ranges between 216.8–381.2 and 66–393.6 mg/L with an average of 282.46 and 229.89 mg/L, respectively. All samples present Ca and Mg higher than the standard limit admissible fixed at 75 mg/L for Ca and 50 mg/L for Mg according to WHO and Moroccan standard. The availability of magnesium and calcium ions registered in water of the Srou River could be explained by the composition of the

underlying bedrocks (dolomite and limestone) crossed water bodies (the Srou River and its tributaries).

Carbonate and bicarbonate concentration are varying from 0 to 48 mg/L and 293.75 mg/L to 329.4 mg/L, respectively. No standard limits have been provided by the Moroccan and WHO limits of carbonate and bicarbonate in drinking water.

Sodium shows a high value that ranges between 212.3 and 483.3 mg/L. The maximum value recorded at SR12 in accordance with EC and TH, while the potassium indicates very low values. Sodium must have entered the water system through natural sources including weathering of feldspar (albite), leaching of clay minerals [35,36], and rainwater [37].

The measured values for the chlorides concentrations in this study are very high in all sampling sites except SR4 and SR6 where the values are below the critical value recommended by WHO (200 mg/L). The maximum value recorded is 816.5 mg/L at SR12 site. Chlorides occur in all natural waters with different concentrations [34] and under two most common formulas in nature NaCl and KCl minerals. It is due to the dissolution of the Triassic saliferous formations. High concentration of chloride leads to bad taste in water and responsible for the saline taste if it is combined with the sodium [38].

Sulfate is widely distributed in nature and may be present in natural waters at concentrations ranging from a few to several hundred milligrams per liter. Its contents exceed widely, in all water samples, the standards (250 mg/L) recommended by WHO [29], which can be due to the dissolution of the gypsum formations ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and to the discharge effluent for the riverine population, animal excrement, and livestock waste.

The high levels of nitrates and nitrite in drinking water may cause harmful health effects such as cancer risks [14,39,40], increased starchy deposits, and hemorrhage of the spleen [41]. Nitrate and nitrite in the water samples are found to be in a range of 0.066 to 0.232 mg/L and 0.0122 to 0.241 mg/L, respectively. In SR12, the registered value is slightly high compared with other samples, but it is still minimal. This watercourse received domestic wastewater effluents via their tributaries from El Kebab city. According to the Moroccan and WHO standards, all the data satisfy the recommended values for drinking water.

Ammonia is an indicator of elevated pollution from organic substances [42]. A limit of 0.2 mg/L has been prescribed by the WHO for drinking water supplies. All samples are within the desirable limit for drinking water supplies except SR11 where the value reaches 0.62 mg/L at the confluence between the Srou River and Chbouka river. This value was attributed to local wastewater input and livestock waste.

3.2. Heavy metal

Studies of heavy metals in water (rivers, lakes, wells, and sediments) have been a major environmental focus, especially in the last decades. Heavy metals are regarded as a serious pollution of the aquatic ecosystem because of their environmental persistence and toxicity effects on living organisms, also it can be detrimental to human health when their concentrations exceed the permissible limits. Water pollution by trace metal can be a result of a natural process and human behaviors. The former can contribute through debris, geological formation [43], Snow and rainwater which contain

particulate minerals and some gaseous pollutants from the atmosphere, while the latter resulting from effluents discharged from industries and urban sewage and drinking water distribution materials [43].

The concentrations of heavy metals (Table 2) were in the ranges of 22–3,280; 6–18; 6–104; 3–2,114; 1–31; 3–23; 9–24; and 2–29 µg/L for Al, Cd, Cu, Fe, Mn, Ni, Pb, and Zn, respectively. Cu, Mn, Ni, and Zn fall within the WHO desirable limits, while Al, Cd, Fe, and Pb reveal higher concentration values and exceed widely the suitable value recommended by WHO for drinking water. All heavy metal measurements show a little variability in concentration except for Al and Fe which recorded the greatest values, especially in SR7 and SR8 in compared with the other sampling site. The supposed origin of heavy metal in sampling water might be dependent on the bedrock via which the water flows from anthropogenic activities, agricultural drainage water, sewage effluents, and industrial wastes remained poorly developed.

3.3. Hydrochemical facies

A piper trilinear diagram [44] is a graphical representation classifying water. It consists of two lower triangles that show the percentage distribution of the major base cations (K^+ , Na^+ , Ca^{2+} , Mg^{2+}) and the major anions (Cl^- , SO_4^{2-} , CO_3^{2-} , HCO_3^-) and a diamond-shaped part above that summarizes the dominant cations and anions to indicate the final water type. In Fig. 3 it can be seen in the water samples fall under a Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} hydrochemical facies. In our study, the geological formations particularly rock types, water–rock interaction and relative mobility of ions are prime factors influencing the geochemistry of surface water.

3.4. Correlation analysis

Pearson's correlation used to assess the relationship between two variables. Table 3 presents the values of Pearson's correlation coefficient ($p < 0.01$) for pairs of variables at all

sampling stations. The obtained results indicate that temperature was negatively correlated with turbidity ($r = -0.606$), K ($r = -0.677$) and CO_3^{2-} ($r = -0.552$); pH showed a negative correlation with K ($r = -0.505$) and positive correlation with CO_3^{2-} ($r = 0.556$). Turbidity showed a positive correlation with DO ($r = 0.724$) and DO presented a positive correlation with turbidity but no apparent strong correlation between DO and other parameters. A significant positive correlation was found between EC and TH ($r = 0.994$), Cl ($r = 0.944$), Ca ($r = 0.836$), Na ($r = 0.871$), Mg ($r = 0.988$), SO_4^{2-} ($r = 0.528$), and NO_3^- ($r = 0.547$) suggest that these elements are the principal source of salinity. The similar significant positive correlation is shown between TH and EC, Cl ($r = 0.933$), Ca ($r = 0.819$), Mg ($r = 0.997$), and Na ($r = 0.851$). HCO_3^- showed a positive correlation with SO_4^{2-} ($r = -0.570$) and a negative correlation with NH_4^+ ($r = -0.516$), and CO_3^{2-} presented a negative correlation

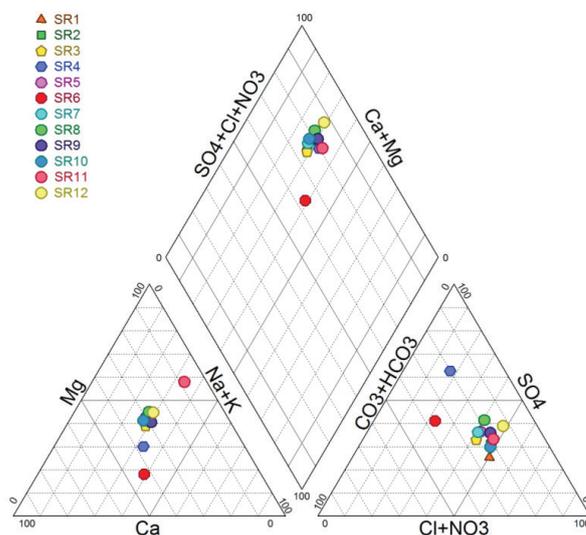


Fig. 3. Piper diagram of surface water samples.

Table 2
Metal concentrations in water of studied sites

| Sample | Ag | Al | Ba | Cd | Cr | Cu | Fe | Mn | Ni | Pb | Zn |
|-----------------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| | mg/L | | | | | | | | | | |
| SR1 | – | 0.229 | 0.045 | 0.017 | 0.014 | 0.05 | 0.732 | 0.003 | 0.011 | 0.01 | 0.011 |
| SR2 | 0.022 | 0.422 | 0.055 | 0.017 | 0.015 | 0.032 | 0.598 | 0.002 | 0.003 | 0.012 | 0.011 |
| SR3 | 0.022 | 0.321 | 0.051 | 0.017 | 0.012 | 0.037 | 0.457 | 0.004 | 0.018 | 0.024 | 0.013 |
| SR4 | – | – | – | – | – | – | – | – | – | – | – |
| SR5 | 0.021 | 0.361 | 0.051 | 0.017 | 0.013 | 0.014 | 0.313 | 0.001 | 0.019 | 0.009 | 0.004 |
| SR6 | – | – | – | – | – | – | – | – | – | – | – |
| SR7 | 0.023 | 3.28 | 0.054 | 0.017 | 0.012 | 0.006 | 2.114 | 0.031 | 0.018 | 0.015 | 0.002 |
| SR8 | 0.021 | 1.899 | 0.053 | 0.015 | 0.014 | 0.038 | 1.153 | 0.023 | 0.02 | 0.014 | 0.006 |
| SR9 | 0.018 | 0.328 | 0.053 | 0.006 | 0.014 | 0.104 | 0.375 | 0.004 | 0.019 | 0.011 | 0.029 |
| SR10 | 0.022 | 0.022 | 0.016 | 0.018 | 0.017 | 0.058 | 0.006 | 0.01 | 0.022 | 0.015 | 0.005 |
| SR11 | 0.021 | 0.028 | 0.041 | 0.018 | 0.018 | 0.059 | 0.003 | 0.01 | 0.022 | 0.016 | 0.002 |
| SR12 | 0.021 | 0.238 | 0.044 | 0.018 | 0.015 | 0.049 | 0.408 | 0.006 | 0.023 | 0.014 | 0.028 |
| WHO standards 2011 | – | 0.2 | – | 0.003 | – | 2 | 0.3 | 0.1 | 0.07 | 0.01 | 0.5 |

Table 3
Correlation matrix of water quality parameters (Pearson correlation coefficients [*r*])

| | T | pH | EC | Turbidity | TH | DO | Cl ⁻ | SO ₄ ²⁻ | NO ₂ ⁻ | NO ₃ ⁻ | NH ₄ ⁺ | Na ⁺ | K ⁺ | Ca ²⁺ | Mg ²⁺ | HCO ₃ ⁻ | CO ₃ ²⁻ | |
|-------------------------------|---------------|---------------|--------------|--------------|--------------|--------|-----------------|-------------------------------|------------------------------|------------------------------|------------------------------|-----------------|----------------|------------------|------------------|-------------------------------|-------------------------------|--|
| T | 1.000 | | | | | | | | | | | | | | | | | |
| pH | 0.123 | 1.000 | | | | | | | | | | | | | | | | |
| EC | -0.240 | 0.042 | 1.000 | | | | | | | | | | | | | | | |
| Turbidity | -0.606 | -0.084 | 0.112 | 1.000 | | | | | | | | | | | | | | |
| TH | -0.278 | 0.071 | 0.994 | 0.161 | 1.000 | | | | | | | | | | | | | |
| DO | -0.395 | -0.161 | 0.015 | 0.724 | 0.064 | 1.000 | | | | | | | | | | | | |
| Cl ⁻ | -0.098 | 0.255 | 0.944 | 0.032 | 0.933 | 0.042 | 1.000 | | | | | | | | | | | |
| SO ₄ ²⁻ | 0.137 | -0.130 | 0.528 | -0.182 | 0.486 | -0.467 | 0.427 | 1.000 | | | | | | | | | | |
| NO ₂ ⁻ | 0.234 | -0.418 | 0.206 | 0.229 | 0.220 | 0.369 | 0.118 | -0.123 | 1.000 | | | | | | | | | |
| NO ₃ ⁻ | -0.253 | -0.232 | 0.547 | 0.285 | 0.570 | 0.076 | 0.432 | 0.291 | 0.120 | 1.000 | | | | | | | | |
| NH ₄ ⁺ | 0.317 | -0.434 | 0.140 | 0.026 | 0.149 | 0.236 | 0.065 | -0.154 | 0.959 | 0.074 | 1.000 | | | | | | | |
| Na ⁺ | -0.281 | -0.102 | 0.871 | 0.168 | 0.851 | -0.090 | 0.759 | 0.557 | 0.088 | 0.613 | -0.032 | 1.000 | | | | | | |
| K ⁺ | -0.677 | -0.505 | 0.169 | 0.415 | 0.178 | 0.208 | -0.019 | 0.162 | -0.131 | 0.265 | -0.190 | 0.410 | 1.000 | | | | | |
| Ca ²⁺ | -0.311 | -0.088 | 0.836 | 0.169 | 0.819 | -0.141 | 0.707 | 0.537 | 0.052 | 0.626 | -0.065 | 0.993 | 0.426 | 1.000 | | | | |
| Mg ²⁺ | -0.267 | 0.089 | 0.988 | 0.155 | 0.997 | 0.088 | 0.938 | 0.468 | 0.235 | 0.549 | 0.172 | 0.811 | 0.142 | 0.776 | 1.000 | | | |
| HCO ₃ ⁻ | -0.152 | -0.276 | 0.172 | -0.326 | 0.097 | -0.472 | 0.111 | 0.570 | -0.530 | 0.104 | -0.516 | 0.340 | 0.266 | 0.337 | 0.064 | 1.000 | | |
| CO ₃ ²⁻ | -0.552 | 0.556 | 0.301 | 0.415 | 0.332 | 0.270 | 0.369 | -0.152 | -0.342 | 0.049 | -0.390 | 0.158 | 0.135 | 0.178 | 0.343 | -0.209 | 1.000 | |

Bold values represent significant correlation.

with temperature ($r = -0.552$) and a positive correlation with pH ($r = 0.556$). The measured Ca concentration showed significant positive correlation with EC, TH, Na ($r = 0.993$), Mg ($r = 0.776$), Cl ($r = 0.707$), NO_3^- ($r = 0.626$), and SO_4^{2-} ($r = 0.537$) while Mg showed a good positive correlation with EC, TH, Na ($r = 0.811$), Ca ($r = 0.776$), and Cl ($r = 0.938$). This indicates that Ca and Mg are likely due to the leaching of minerals from the basin rock. Na showed significant positive correlation with EC, TH, Ca ($r = 0.993$), Mg ($r = 0.811$), and Cl ($r = 0.759$) while potassium presents negative correlation with temperature and pH. Cl correlated reasonably well with EC, TH, Na, Ca ($r = 0.707$) and Mg ($r = 0.938$). As also shown in Table 3 there was a positive correlation between SO_4^{2-} and Ca ($r = 0.537$), HCO_3^- ($r = 0.570$) and EC ($r = 0.528$). NO_3^- showed positive correlation with EC, and Ca and NO_2^- correlated positively well with NH_4^+ ($r = 0.959$), whereas NH_4^+ was positively correlated with NO_2^- and negatively correlated with HCO_3^- ($r = -0.516$).

3.5. Spatial similarity and site grouping

Cluster analysis was used to detect the similarity groups between the sampling sites. It yielded a dendrogram, grouping all 12 sampling sites of the basin into three clusters (Fig. 4). The stations in each group have similar water contamination types, greatness [11] and natural background of the water quality characteristics [45].

The Cluster 1 included stations SR1, SR2, SR3, SR5, SR7, SR8, SR9, and SR11 that located in the Srou River and SR10 located in the Chbouka River. This cluster shows the similar quality characteristics and corresponds to moderate water quality. The Cluster 2 consisted of stations SR4 and SR6 that sampled in tributaries situated in the right bank of the Srou River. This cluster recorded low values in all monitoring parameters and correspond to good water quality. The Cluster 3 included only one station SR12. It shows the highest values in all monitoring parameters and corresponds to highly polluted cluster. In our case study, the parameters responsible for water quality variations are mainly related to natural process such as soluble salts (especially Triassic saliferous, and evaporite formations, leaching of minerals from outcrops crossed by

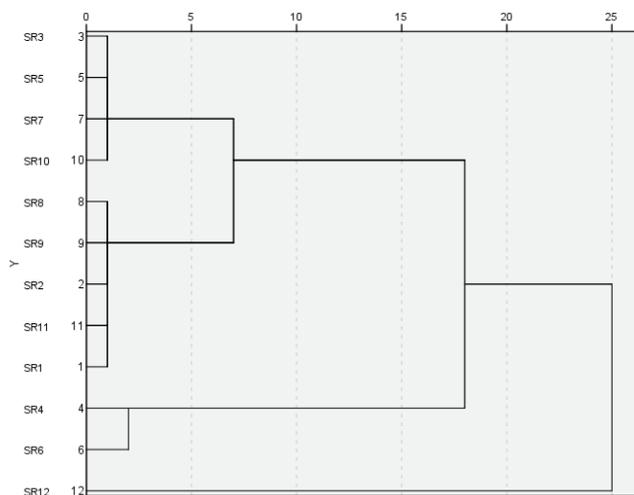


Fig. 4. Dendrogram based on hierarchical clustering (wards method) for complete stations.

the stream and the erosion from upland areas during rainfall events. Therefore, the CA technique is useful in offering reliable classification of surface waters and it will provide more insights on the design of sampling and monitoring network for effective management of reservoir water quality [46].

3.6. Source identification of monitored variables

PCA was performed on the normalized data set to compare the compositional pattern between the water samples and to identify the factors influencing each one [46]. Thus the scree plot was used to identify the number of PCs to be retained. An eigenvalue 1 or greater are considered significant [21] while variables with eigenvalues lower than 1, were removed due to their low significance [47]. In the present study, the scree plot (Fig. 5) showed a pronounced change of slope after the fourth eigenvalue; four components were retained with 86% of the total variance in the water dataset. Liu et al. [48] classified the factor loadings as 'strong', 'moderate', and 'weak' where the absolute loading values are greater than 0.75, between 0.75 and 0.50, and between 0.50 and 0.30, respectively. Loading of four retained PCs are expressed in Table 4.

The first factor (PC1), accounting 38.17% of the total variance, showed a high positive loading of EC, TH, Na, Ca, Mg, and Cl, moderate positive loading of SO_4^{2-} and NO_3^- , weak negative loading of T and pH and weak positive loading of DO, K, and CO_3^{2-} . This factor can be interpreted as a mineral component of the river water and points to a common origin for these minerals, likely from dissolution of limestone and gypsum soils [49]. Similar observation was found by Han et al. [50] in Xiangxi river basin, China.

The second factor (PC2) explained 18.38% of the total variance and had a strong positive loading on DO and NO_2^- and strong negative loading on HCO_3^- moderate positive loading of turbidity and NH_4^+ and moderate negative loading on SO_4^{2-} . This factor including organic and nutrient variables may be associated to influences from domestic sources and/or livestock operations and manure [51].

The third factor (PC3), which described 16.58% of the total variance, had strong positive loading on T and strong

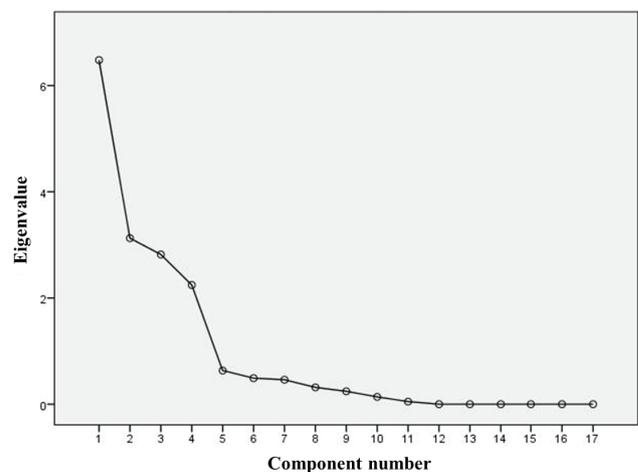


Fig. 5. Scree plot of the eigenvalues.

negative loading on CO_3^{2-} , moderate positive loading of NO_2^- and NH_4^+ , and moderate negative loading of turbidity and HCO_3^- and weak negative of DO and K and weak positive of NO_3^- . PC3 is an indicator of mixed source of contamination comprising natural processes as well as anthropogenic inputs [11].

The fourth factor (PC4) explaining 13.20% of the total variance and had strong positive loading on pH, moderate negative loading on K and moderate positive loading on CO_3^{2-} , and weak negative loading on HCO_3^- and weak positive loading on Cl. This factor points to common sources of natural processes of dissolution of soil constituents mainly carbonates [22].

4. Irrigation quality of water from the study area

To evaluate the suitability of water for irrigation, the most important water quality parameters for irrigation should take into consideration: Sodium adsorption ratio (SAR), salinity hazard, Kelley index (KI) [52], and magnesium hazard (MH) (Table 5).

4.1. Sodium hazard

Some natural constituents determine the suitability of water for irrigation. Example of such constituents is the sodium which with a large concentration can lead to damage of the soil by causing dispersion and swelling. As Purushothaman et al. [53] confirmed that high sodium concentration in shallow and deep groundwater in Bist-Doab region (Punjab, India) affects crop yield and permeability of

Table 4
Loading of experimental variables (16) on principal components for the whole datasets

| | PC1 | PC2 | PC3 | PC4 |
|----------------|--------------|---------------|---------------|---------------|
| T | -0.378 | -0.202 | 0.772 | 0.274 |
| pH | -0.033 | -0.248 | -0.269 | 0.894 |
| EC | 0.965 | 0.026 | 0.152 | 0.162 |
| Turbidity | 0.241 | 0.642 | -0.544 | -0.142 |
| TH | 0.962 | 0.083 | 0.116 | 0.187 |
| DO | 0.034 | 0.809 | -0.358 | -0.021 |
| Cl | 0.870 | -0.018 | 0.140 | 0.391 |
| SO_4 | 0.552 | -0.523 | 0.296 | -0.197 |
| NO_2 | 0.108 | 0.762 | 0.607 | -0.080 |
| NO_3 | 0.658 | 0.123 | 0.033 | -0.225 |
| NH_4 | 0.011 | 0.682 | 0.691 | -0.062 |
| Na | 0.939 | -0.103 | 0.060 | -0.133 |
| K | 0.359 | 0.079 | -0.469 | -0.686 |
| Ca | 0.920 | -0.128 | 0.024 | -0.146 |
| Mg | 0.943 | 0.108 | 0.124 | 0.224 |
| HCO_3 | 0.249 | -0.750 | -0.050 | -0.461 |
| CO_3 | 0.323 | 0.100 | -0.703 | 0.514 |
| Eigenvalues | 6.480 | 3.126 | 2.819 | 2.244 |
| % of variance | 38.117 | 18.386 | 16.583 | 13.202 |
| % cumulative | 38.117 | 56.502 | 73.085 | 86.287 |

Bold values represent significant correlation.

the soil. Soil dispersion can harden the soil and decrease infiltration rates at the surface and reduce the hydraulic conductivity of the soil [54,55]. The ratio of sodium ions to calcium and magnesium ions is called the SAR. The main role of SAR is to evaluate the sodium hazard for irrigation water supply [56]. Indeed if SAR increases, the sodium hazard increases; therefore, the suitability of water for irrigation purposes decreases. The SAR was calculated using the following equation given by Richards [57]:

$$\text{SAR} = (\text{Na}^+) / \sqrt{1/2(\text{Ca}^{2+} + \text{Mg}^{2+})} \quad (1)$$

where Na^+ , Ca^{2+} , and Mg^{2+} represent concentrations expressed in milli-equivalents per liter for each constituent.

For the study area, the SAR values (Table 5) are generally low. It lies between 2.15 and 3.47 with an average of 2.72 and falls in S1 class which revealed a low sodium hazard (Table 6). The Srou River water is, therefore, suitable for irrigation purposes. Yidana et al. [58] suggested that the low values of the SAR in the Southwestern and Coastal River Systems in Ghana are attributed to the relatively higher concentrations of alkaline earth metals than the alkali metals.

4.2. Salinity hazard

Electrical conductivity measurements give a strong indication of overall salinity. Extremely high salinities in irrigation waters have several adverse effects on both the

Table 5
SAR, KI, and MH values of the studied samples

| Samples | Na (meq/L) | Ca (meq/L) | Mg (meq/L) | SAR | KI | MH |
|---------|---------------|---------------|---------------|------|------|-------|
| SR1 | 6.73 | 6.14 | 5.46 | 2.79 | 0.58 | 47.06 |
| SR2 | 6.77 | 6.12 | 5.22 | 2.84 | 0.60 | 46.03 |
| SR3 | 5.52 | 5.29 | 3.92 | 2.57 | 0.60 | 42.55 |
| SR4 | 5.21 | 5.21 | 2.55 | 2.65 | 0.67 | 32.88 |
| SR5 | 5.01 | 4.90 | 4.16 | 2.35 | 0.55 | 45.90 |
| SR6 | 5.33 | 5.17 | 1.32 | 2.96 | 0.82 | 20.33 |
| SR7 | 5.59 | 5.21 | 4.67 | 2.51 | 0.57 | 47.28 |
| SR8 | 6.49 | 5.79 | 5.69 | 2.71 | 0.57 | 49.56 |
| SR9 | 7.89 | 6.66 | 5.62 | 3.19 | 0.64 | 45.77 |
| SR10 | 4.25 | 4.34 | 3.42 | 2.16 | 0.55 | 44.09 |
| SR11 | 5.83 | 5.34 | 5.27 | 2.53 | 0.55 | 49.69 |
| SR12 | 9.67 | 7.62 | 7.87 | 3.47 | 0.62 | 50.79 |
| Mean | 6.19 | 5.64 | 4.60 | 2.73 | 0.60 | 44.92 |

Table 6
Classification of irrigation water based on SAR values

| SAR class | Range of values | Sodium hazard |
|-----------|-----------------|---------------|
| S1 | <10 | Low |
| S2 | 10–18 | Medium |
| S3 | 18–26 | High |
| S4 | >26 | Very high |

irrigation soil and the crops being irrigated. High salinities affect plants both physically and chemically, reduce the osmotic ability of plants and thus interfere with the capacity of plants to absorb water from the soils and transport it to the branches and leaves [59]. In the study area, EC is ranging from 720 to 2,890 $\mu\text{S}/\text{cm}$. This value means a high salinity which is unsuitable for irrigation to soils of restricted drainage (Table 7).

In addition, the classification of USSL [57] is based on the salinity of studied water represented by EC and SAR to comprehensively classify irrigation waters. As is described earlier, SAR is low in the study area whereas the electrical conductivity shows a high value. Following USSL [57] diagram one sample (SR6) plot within C2-S1 (low sodium-medium salinity) zone denoting good quality of water for irrigation. Ten samples (SR1, SR2, SR3, SR4, SR5, SR7, SR8, SR9, SR10, and SR11) plot within the C3-S1 (low sodium-high salinity) zone which qualified as good to moderate quality of water for irrigation. The remaining sample SR12 plots within the C4-S2 (medium sodium-very high salinity) zone (Fig. 6) indicating high salinity and low sodium water which can be inappropriate to use for irrigation in almost all types of soil. According to

Tiwari and Singh [60], the good water (C2S1) can be used for irrigation with little danger of harmful levels of exchangeable sodium and salinity. The moderate water (C3S1) may be used to irrigate salt tolerant and semi-tolerant crops under favorable drainage conditions. The bad water with high salinity and medium to high alkalinity (C4-S2, C4S3, and C4S4) are generally undesirable for irrigation and such water should not be used on clayey soils of low permeability.

4.3. Kelley index

Kelley's index is the ratio of $\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})$ which is also used for the classification of water for irrigation. Water with >1.0 Kelley's ratio indicate an excess level of sodium and unsuitable for irrigation water with Kelley's ratio of <1.0 are only considered suitable for irrigation [59,61]. Kelly index was calculated by using the following Equation. $\text{KI} = [\text{Na}^+ / (\text{Ca}^{2+} + \text{Mg}^{2+})]$. In the present study area, KI values varied from 0.55 to 0.82 with a mean value of 0.61 suggest that surface water of the area is suitable for irrigation (Table 5).

4.4. Magnesium hazard

Magnesium ratio (MR) is another parameter used to assess the suitability of waters for irrigation. Increasing values reduce the suitability of waters for irrigation. MR values should be below 50% to be considered for irrigation [62]. MR is calculated by the following formula: $\text{MR} = [\text{Mg}^{2+} / (\text{Ca}^{2+} + \text{Mg}^{2+})]$. All the Srou water samples had MR values from 20.33% to 50.79 % (average 44.92%; Table 5). Hence the water is very suitable for irrigation purposes.

5. Conclusion

This study assessed the hydrochemical characteristics of the Srou water and its tributaries for drinking and agricultural purposes from 12 different locations. The results presented here demonstrate that temperature, pH, DO, potassium, nitrates, nitrites, and ammonia fell below within the permissible values according to Moroccan and WHO standards while the electrical conductivity, TH, chlorides, sulfate, calcium, magnesium, sodium, and some heavy metals (Al, Cd, Fe, and Pb) values exceed largely the maximum concentration allowed for surface waters by the WHO and the Moroccan standards. Based on the mean values of the chemical parameters, the cations were in the order of abundance as $\text{Na}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{K}^+$ while the anions reveal the order of abundance as $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^- > \text{CO}_3^{2-}$. This order leads to Cl^- , SO_4^{2-} , Ca^{2+} , Mg^{2+} hydrochemical facies type.

Multivariate statistics including Pearson's correlation, PCA and CA were employed to evaluate spatial variations of surface river water quality data and to identify the sources of pollution on the water quality in the Srou River and its tributaries. Cluster analysis CA grouped 12 different sampling sites into three clusters of similar water quality characteristics. This suggests that it is possible to design a future, optimal sampling strategy, which could reduce the number of sampling stations and cost of sampling. PCA helped in identifying the factors, sources responsible for water quality variations, and reduces the original data matrix into four components that explains 86% of the total variance. Therefore, the

Table 7
Classification of irrigation water based on EC values

| Class | EC $\mu\text{S}/\text{cm}$ | Salinity hazard | Suitability criteria |
|-------|----------------------------|-----------------|---------------------------------------------|
| C1 | <250 | Low | Suitable for most crops and soils |
| C2 | 250–750 | Medium | Suitable for the soil of moderate drainage |
| C3 | 750–2,250 | High | Unsuitable for soils of restricted drainage |
| C4 | >2,250 | Very high | Unsuitable for average condition |

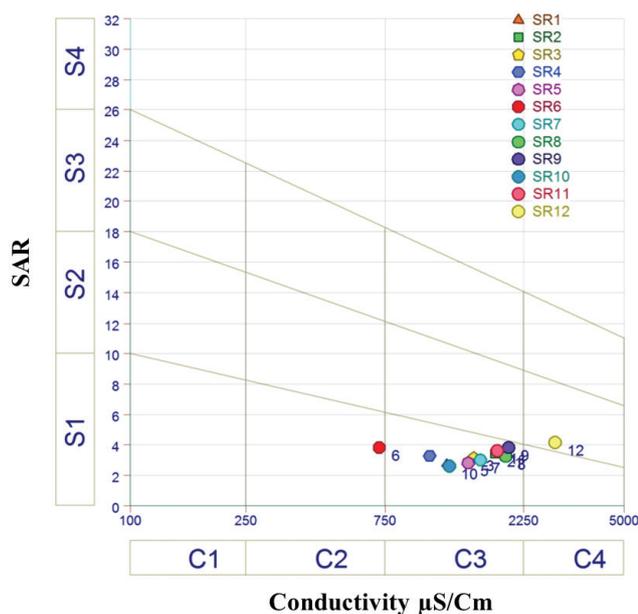


Fig. 6. Classification of irrigation water based on EC value.

observed pollution can be attributed, on one hand to diverse effects of geological formations (saliferous and evaporate beds), precipitation, weathering, and water–rock interaction and on the other hand, to the domestic waste and livestock waste and manure but it remains minimal. Thus, the surface water of the Srou River should be treated with caution.

Suitability of irrigation has been envisaged by studying SAR, salinity, KI, and MH. Due to the low SAR, KI, and MH values, the water from the Srou River is suitable for irrigation but jointly to the high salinity this water can pose negative effects and further irreversible damage in irrigated soils.

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