THE SALINITY ORIGIN OF THE SURFACE WATER IN THE WATERSHED DAM ZARDEZAS, EASTERN ALGERIA

Sami KEMOUKH
Batna 2 Mostfa Ben Boulaïd University, Faculty of Technology,
Department of Hydraulics, N 3 RN3, Algeria; e-mail: s.kemoukh@centre-univ-mila.dz

Ali ATHAMENA*
Batna 2 Mostefa Ben Boulaïd University, Institute of Earth and Universe Sciences,
Department of Geology, N 3 RN3, Algeria; e-mail: a.athamena@univ-batna2.dz

Fouad DJAIZ
Batna 2 Mostefa Ben Boulaïd University, Institute of Earth and Universe Sciences,
Department of Geology, N 3 RN3, Algeria; e-mail: f.djaiz@univ-batna2.dz

Halima BELALITE
Mila University Centre, Institute of Natural and Life Sciences,
Departments of Earth and Universe Sciences BP 26 RP, Mila 43000, Algeria;
e-mail: halima.belalite@centre-univ-mila.dz

Malika ATHAMENA
Batna 2 Mostfa Ben Boulaïd University, Faculty of Technology, Department of Hydraulics,
N 3 RN3, Algeria; e-mail: athamena_malika@yahoo.fr

Abstract: The deterioration of the physico-chemical quality of surface waters in the Algerian Northeast is caused by several factors. Our study aims to fill the knowledge gap on the control of hydro-chemical evolution of surface waters in wetlands. The main focus is on major elements in surface waters of the Skikda region in northeastern Algeria. To address this issue, we received 45 samples during the 09 campaigns conducted during the period of low and high water of the year 2015-2016, distributed over five points, namely the tributary Oued Khemakhem, Oued Bouadjeb, Oued Safsaf, reservoir of the Zerdazas dam and the downstream of the Zerdazas dam. First, we studied the variation of physical elements such as pH and EC. Then, using PCA and FA, we characterized the physicochemical properties of the water to demonstrate the relationship between

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* Corresponding Author

the elements and the factors controlling the distribution of the major elements and the heavy metals Pb^{2+}, Fe^{2+} and Sr^{2+}. The specific formula of the dominance of the different concentrations in the surface waters of the study area followed the sequence: Ca-Mg-Na-K and Cl-SO_4-HCO_3 from which a predominant specific facies emerges on 67% of the samples, is of the chloride and sulfate-calco-Magnesian facies.

Key words: Algeria, Chemical, Surface Waters, Principal component, Zerdezas Dam, Skikda

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INTRODUCTION

The acquisition of surface water chemistry is a complex phenomenon because of the different possible sources of the mechanism, the triggers of the phenomenon and its consequences on water quality. Water, whether surface or groundwater, has a natural chemical facies that varies according to the lithology of the formations, whether they are traversed by runoff or infiltration and the residence time of the water in contact with them. Anthropogenic action leading to a change in the morphometric parameters of a watershed induces a gradual process leading to a change in the chemical composition of the overlying water.

The construction of dams is one of the solutions adopted by decision makers, when reducing the deficit in water is their primary strategy, regarding crucial water needs during drought events (Ali, Redha, Fouad, & Halima, 2019; Gaagai et al., 2022). In addition, the generalization of irrigation is being spread over large agricultural perimeters, where the productive potential of the soil is closely linked to the availability of water during the summer period (stretching) (Belalite, Menani, & Athamena, 2022). In the Constantinois coastal watershed, located in northeast of the country, Algeria has had to build many dams; among these works, the Zerdazas dam (Figure 1).

The overall mineralization of surface waters is often linked to the nature of geological formations, heavy precipitation and the dilution effect. Several studies have been carried out on this subject around the world (Durozoy Guy, 1952; Mehta & Parchure, 2000; Kemoukh, 2008; Khelfaoui & Zouini, 2010; Zaoui, Benslama, Hursthouse, & Kahit, 2016; Liang et al., 2017; Athamena & Menani, 2018; Chen et al., 2019; Gaagai et al., 2023), where they showed the role of these latter factors in increasing water mineralization. Consequently, the elements, which are in the solution, are informative on the nature of the lithology (Belalite, 2021; Athamena et al., 2023).

Among the in organic contaminants of the river water, heavy metals are getting importance for their non-degradable nature and often accumulate through tropic level causing a deleterious biological effect (Jain, 1978). Anthropogenic activities like mining, ultimate disposal of treated an d untreated waste effluents contain in toxic metals as well as metal chelates (Ammann, 2002) from different industries, e.g. tannery, steel plants, battery industries, thermal power plants etc. and also the indiscriminate use of heavy metal containing fertilizers and pesticides in agriculture resulted in deterioration of water quality rendering serious environmental problems posing threat on human beings (Lantzy & Mackenzie, 1979; Nriagu, 1979; Bradshaw & Ross, 1995) and sustaining aquatic biodiversity (Ghosh & Vass, 1997; Das, Samantaray, & Rout, 1997). Though some of the metals like Pb, Fe, and Sr are essential as micronutrients for life processes in plants and microorganisms, but they are proved detrimental beyond a certain limit (Marschner, 2012; Bruins, Kapil, & Oehme, 2000; Talbi & Kachi, 2019) which is very much narrow for some elements like Fe (0.30 mg/L), Pb (0.10 mg/L) (Indian Standards, 1982). The deadlier diseases like edema of eyelids, tumor, congestion of nasal mucous membranes and pharynx, stuffiness of the head and gastrointestinal, muscular, reproductive, neurological and genetic malfunctions caused by some of these heavy

metals have been documented (Johnson, 1998; Tsuji & Karagatzides, 2001; Kumar & Khan, 2020). Therefore, monitoring these metals is important for safety assessment of the environment and human health in particular.
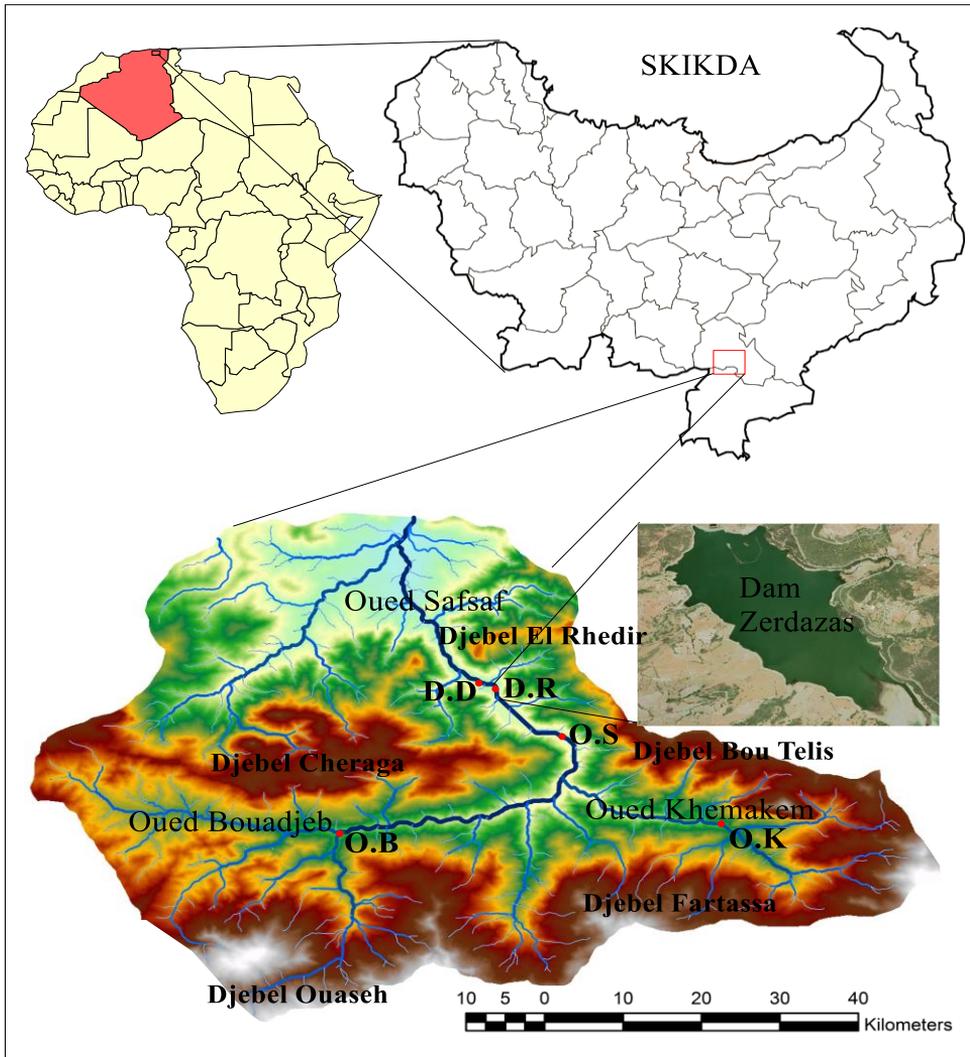
Figure 1. Study area location and hydrographic map and sampling points

GENERAL SETTING

The Zerdazas watershed is located south of the province of Skikda, northeastern Algeria, about 345 km east of Algiers (Figure 1). It is part of the coastal watersheds of the Constantinois and is among the wettest regions of Algeria. Morphologically, the watershed is located in the wet folded mountains of the littoral and characterized by a rugged relief, (figure 3-5). In fact, the mountainous massifs cover more than 50% of the watershed, especially in the southern part.

The watershed, upstream of the Zerdazas dam and elongated in shape and spread over an area of 340 km² and with a perimeter of approximately 94 km. The main Thalweg Oued Safsaf is about 33.22 km long with a high hydrographic density (3.2 Km/Km²) and temporary flows. The morphometric parameters of the watershed are listed in the table above (Table 1).

Table 1. Morphometric parameters of the watershed
(Data source: Kemoukh, 2008)

Parameter	values	Unity
Planned Area	339.86	Km^2
Stylized Perimeter	93.97	Km
Compactness Index	1.42	/
Mean Altitude	608.63	m
Median Altitude	590	m
Maximum Altitude	1166	m
Minimal Altitude	189	m
Single Slope	650	m
Overall Slope Index	15.90	m/Km
Roche Slope Index	1.27	m/Km
Specific Height Difference	293.12	m
Length of the Main Thalweg	33.5	Km
Concentration Time	7.56	Heur
Drain Density	3.22	Km/Km^2
Permanent Drainage Density	0.32	Km/Km^2
Temporary Drainage Density	2.91	Km/Km^2

The region is one of the wettest regions of Algeria and has a sub-humid climate, with an average annual precipitation of 667 mm, and an average annual temperature of 18°C. The analysis of hydrological variables allows the evaluation of water resources and their variability, with an average annual flow of around 1.35 m3/s, i.e. a contribution of 39.34 hm^3/year. The watershed has modest water potential with an infiltration of about 79 mm or 12% of annual precipitation and runoff is 124 mm which represents 19% of annual precipitation (Remenieras, 1961; Roche, 1963; Dubreuil, 1974; Kemoukh, 2008; ANRH, 2024).

The region is characterized by a very heterogeneous lithology due to its position in the Tellian Atlas to the eastern Tell (Kabylie of Collo). This zone is characterized by a litho-structural complexity, of which the oldest formations are from the Permo-Triassic and the most recent are from the Quaternary (Figure 2). The dominant lithology is represented by limestone, marl, sandstone and clay (David, 1956; Bouillin, 1977). The structure is a gravity dam commissioned in 1945 and raised in 1974. The structure is located in a difficult geological context. The foundation of the dam is made up of limestone, pudding stone and sandstone of fairly poor quality.

The dam ensures the irrigation of 1000 hectares of the perimeter of the SafSaf plain and the supply of drinking water to the city of Skikda and the urban centers of Zerdaza, El-harrouch, Aïn Bouziane and Mzedj Edchich as well as the industrial zone (oil refinery) from Skikda. In addition to the water supply, the Zerdazas dam regulates the flow of Oued Safsaf at times of destructive floods. The presence of carbonate formations rich in heavy metals on the surface has strongly influenced the quality of surface water stored in the dam and intended for consumption or irrigation. Determining the origin of these elements and their connection with geology is of great importance.

MATERIALS AND METHODS

To achieve the desired results, 51 water sampling were collected (wet and dry season) through 5 stations: Oued Khemakhem (O. K), Oued Bouadjeb (O. B), Oued Safsaf (O. S), reservoir of the Zerdazas dam (D.R) and the downstream of the Zerdazas dam (D. D). The samples were collected in glass bottles of 1 liter capacity. The water samples for each collection were kept in two

bottles. The first is acidified to a pH < 2 using pure nitric acid, intended for the analysis of cations. The second bottle did not undergo any treatment and was intended for anion analysis. All water samples were filtered at 45 μm using sterile syringe filters (SFCA). Monitoring was done for 45 samples (from June 2015 to February 2016). Only high pure chemicals and double distilled water were used for preparing solutions for analysis. Physical parameters like pH, TDS and EC were determined at the site with the help of digital portable water analyzer kit (CENTURY-CK-710), and measured in situ. Determination of major cations and anions were realized in the laboratory using the analytical methods shown in (Table 2) (Clesceri, Greenberg, & Trussell, 1990; Rodier & Legube, 2016). For analysis of three heavy metals Sr, Fe and Pb, using atomic absorption spectrophotometer (GBC -902, Australia). The data obtained were subject to statistical analysis to test the analysis of variance (Free Statistica) and correlation among all the parameters using SPSS statistical package. All the results are compared with standard limits recommended by WHO (World Health Organisation, 2017).
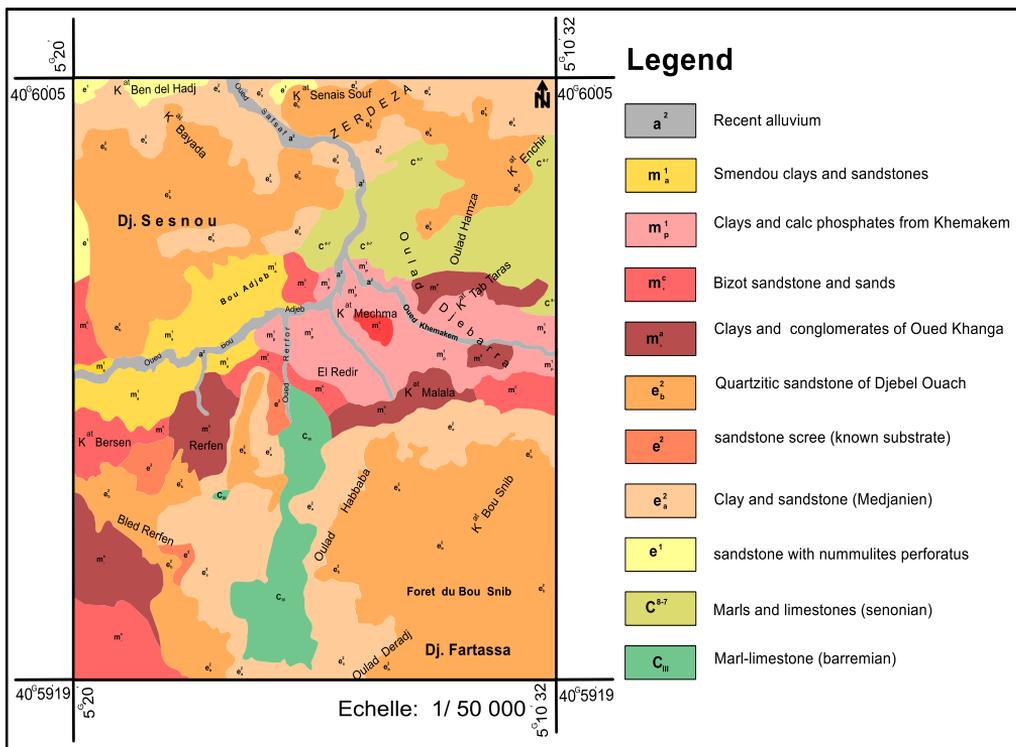
Figure 2. Extract of the geological map of Smendou, scale 1/50000
(Source: detailed geological map Algeria, sheet no. 52, redrawn by the authors)

RESULTS AND DISCUSSION
Chemical Characteristics

We have presented and interpreted the physic-chemical properties trends to make the results easier to use. Therefore, we provide interpretation results to determine the origin of the elements found descriptive statistic of physical-chemical analyzes of the Zerdazas watershed surface water (Tabel 3) is intended to summarize the observations on the state of its quality. It has been revealed that for the average values, there is a predominance of the HCO_3^-, Cl^-, SO_4^{2-}, Ca^{2+} and Mg^{2+} elements over the other parameters.

Figure 3. Photo of Dam of Zerdazas
(Source: https://ebourse.dz/wp-content/uploads/2020/10/zerdazas.jpg)

Figure 4. Photo of Dam of Zerdazas
(Source: https://encrypted-tbn0.gstatic.com/images?q=tbn:ANd9GcTL1c_zyTP6VhRV3gv5am5jF9JRdnDCLCuIiA&s)

In this case, the water temperature varies between 5.5 and 25 °C throughout the study area. This variation is a direct function of the ambient air temperature depending on the season, summer temperatures vary between 19 and 25 °C while in winter they drop to 5.5 °C. The maximum values are observed at the dam reservoir and downstream of the dam due to the static state of the water due to the lack of water dynamism (no flow). The WHO (2017) has not recommended limit values, but a higher temperature of 15°C facilitates the development of microorganisms and at the same time intensifies sensory parameters such as smell and taste.

Figure 5. Photo of Dam of Zerdazas
(Source: https://fr.geneawiki.com/images/d/d2/Barrage_de_Zardezas.jpg)

Tabel 2. Analys method used for each parameters
(Data source: Clesceri et al., 1990; Rodier & Legube, 2016)

Parameters	Method Used
Chloride (as Cl in mg/l)	Argentometric titration
Carbonate (as CO3 in mg/l)	Titrimetry
Bicarbonate (as HCO3 in mg/l)	Titrimetry
Magnesium (as Mg in mg/l) EDTA	Titration
Calcium (as Ca in mg/l) EDTA	Titration
Sodium (as Na in mg/l)	Flame photometric method
Potassium (as K in mg/l)	Flame photometric method
Sulfate (as SO4 in mg/l)	Spectrophotometric method
Nitrate (as NO3 in g/l)	Spectrophotometric method
Strontium(as Sr in mg/l)	Spectrometry of Mass
Lead (as Pb in mg/l)	Atomic absorption spectrophotometer
Iron (as Fe in mg/l)	Atomic absorption spectrophotometer

Note : All values are in mg/l except pH, T (°C), and EC (µS/cm).

EC shows slightly variable values ranging from 455 µS/cm measured at Oued Safsaf point in the North to 1215 µs/cm measured at Oued Bouadjeb in the West, with a maximum average value of 1005.49 µS/cm and a standard deviation (SD) of 188.55 (Tabel 3). However, all sample values were found above the guideline value for human consumption limited to 1500 µS/cm according to WHO (2017). The temporal distribution of the EC shows that the low values were recorded during the period of high water flows following rains which dilute the concentrations. Spatially, the high conductivities are measured at the level of Oued Bouadjeb following the leaching of saline lands (Triassic).

The TDS coincides with the spatio-temporal distribution of the conductivity. This configuration suggests that the period of heavy rainfall and high flow dilutes the concentration of water in dissolved salts. In contrast to the Period of low flows, the waters are more enriched in dissolved salts, especially at the level of Oued Bouadjeb where the leaching of saline soils (Triassic) and the lack of dilution promotes the enrichment of dissolved salts.

The Calcium ion concentration in the surface water samples varied from 58.3 to 147.7 mg/L, with a max average concentration of 143.04 mg/L (Tabel 3). The calcium values at all samples have been above the guide value of 150 mg/L for drinking water, which prescribed in WHO (2017). For the spatial variation of Ca^{2+}, the highest contents were located in the amount of the dam Zerdazas. These concentrations indicate that these waters are influenced by the dissolution of gypsum formations along the two tributaries Oued Bouadjeb and Oued Khemakem.

In the case of the magnesium, the Mg^{2+} ions in water samples ranged from 42.3.8 to 137.3 mg/L, with a max average value of 110.91 mg/L in all surface water samples of the study area (Tabel 3). The highest concentration was found in the Oued Bouadjeb. The guide value of magnesium concentration for human consumption is 70 mg/L WHO (2017). The majority of samples show concentrations below the 2017 WHO standard, except at the Oued Bouadjeb point where the evolution over time shows a high concentration during low water periods followed by a dilution phenomenon during high water periods. These Magnesium contents lead us to think of an enrichment following the dissolution of evaporites and salt formations such as clays rich in Mg^{2+} following the leaching of soils rich in magnesium minerals.

The weathering of rock-forming minerals and agricultural activities may be the main sources of Na in groundwater (Athamena & Menani, 2018). Na^+ concentration is in the range of 1.99 to 59.9 mg/L, with a max average of 52.29 mg/L. All the samples has Na concentration less than the value guide of drinking water quality of 200 mg/L, (Tabel 3). As the spatial distribution of sodium, the highest Na^+ concentration was located in the upstream of the Dam. These concentrations testify to a salt supply from the evaporites formations rich in halite.

In general, potassium rarely exceeds 10 or 15 mg/l in natural waters. The highest contents of potassium are probably induced by weathering of potash feldspars minerals (Mokadem, Dennis, & Dennis, 2021). The minimum and maximum concentrations of potassium in the surface waters samples of the study area varied from 4.03 to 11.98 mg/L with a max average of 10.38 mg/L (Tabel 3). Accordingly, WHO (2017) suggests the value guide of K^+ in the drinking water as 12 mg/L. As the spatial distribution the highest K concentration was located in the upstream of the Dam These potassium levels come from the alteration of potassic clays and the dissolution of chemical fertilizers (NPK), which are used massively by farmers in the region.

The HCO_3^- concentration are in the range of 195.2 to 494.1 mg/L, with a max average of 388.38 mg/L (tabel 3). The highest bicarbonate concentration (494.1 mg/L) was recorded at Oued Bouadjeb in the West parts of the study area and the lowest is 195.2 mg/L at RD, in the upstream parts of the study area. The Major source of HCO_3^- ion in the water is silicate weathering and dissolution of carbonate rocks such as calcite [CaCO3] and dolomite [CaMg(CO$_3$)$_2$].

Sulfate values in water samples ranged from 141 to 239 mg/L with a maximum average of 221.91 mg/L (Table 3). The highest concentrations of SO_4^{2-} were observed in the southern parts of the study area. In addition, all groundwater samples have a SO_4^{2-} concentration below the guideline value of the WHO (2017) drinking water quality guidelines (250 mg/L). Thus, the spatial distribution of sulphate ions suggests to us the dissolution of gypsum formations, the degradation of organic matter in the soil, as well as agricultural inputs (anthropic origin)

Chloride concentrations ranged from 16.39 mg/L to 88.75 mg/L, with a max average value of 65.44 mg/L (Table 3). The highest contents (1462.6 mg/L) were registered in Oued Bouadjeb in the West part of the study area. All the surface water samples have Cl^- concentration lower than the value guide of WHO (2017. The chloride concentrations in the surface water samples in particular of the Oued Bouadjeb, may be due to salt inputs from evaporitic formations and wastewater discharges can be the cause of this element (Athamena & Menani, 2018; Athamena et al., 2023).

In the analyzed surface water, the nitrate content was revealed in the range from 0.2 mg/L to 0.8 mg/L. This content may reflect a lower No_3^- concentration. We believe that the mechanisms of nitritation (the basis of the biological phenomena that lead to the formation of nitrates from ammonia (nitrification)) may be incomplete and may be stopped at different stages, due to the change in the state of the land (fallow, fallowing etc).

Trace amounts Strontium was found in all analyzed water samples with content from 0.075 to 0.435 mg/l. These values remain below 7 mg/l (proposed by the Federal-Provincial-Territorial Committee on Drinking Water (CEP) of Canada). Chemically, strontium is similar to calcium, which it replaces in carbonate rocks. Sedimentary environment seems to be the most favorable contexts for the occurrence of strontium in water, in particular, evaporite levels rich in strontianite $SrCO_3$ and celestine ($SrSO_4$) a mineral often associated with Triassic gypsum ($CaSO_4$ $2H_2O$).

In surface waters, iron is generally present in the ferric state (Fe^{3+}), in well-aerated waters, the concentration is rarely high, but when the conditions necessary for a reduction are met, as is the case in the waters of lakes and dam, and in the absence of sulphides and carbonates, the concentration of soluble ferrous metal can be high. In our case, the average iron concentrations in the waters of the Zerdazas watershed show levels close to the allowable levels. The highest concentrations were observed at Oued Bouadjeb (0.36 mg/L) and Oued Safsaf (0.38 mg/L). Excluding the value superior to 0.30 mg/L of iron (Fe^{+3}), which exceeds the content set by OMS 2017, observed concentrations are generally between 0.101 and 0.295 mg/L and remain below the standard 0.3 mg/L.

Lead is found in many minerals, the most important of which is galena (lead sulfide) and in the environment it exists mainly in mineral form, but small amounts of organic lead additionally come from gasoline additives. The natural lead content of lakes and rivers is estimated at between 1 and 50 µg/l. the WHO requires a limit of 0.1 mg/l for aquatic life and 5 to 50 µg/l for drinking water. Trace amounts lead was found in all analyzed water samples with content from 0.076 to 0.896 mg/l. These values remain higher 0.1 mg/l recommended. These concentrations are surely due to an accumulation by concentration along its course in the watershed. The highest levels are observed on the downstream side of the Zerdazas dam with a maximum value equal to 0.896 mg/l.

For all the elements analyzed, the highest values are observed during the low water period, on the other hand, during the high water period, a dilution is recorded which causes the contents to drop, following dilution phenomena.

Tabel 3. Summary statistics of the analytical data of surface water of Zerdazas watershed

	T				Ca				Cl			
	Min	Max	Mean	SD	Min	Max	Mean	SD	Min	Max	Mean	SD
O. K	6.5	23	13.42	6.41	68.13	96.19	80.7	8.64	28.4	56.8	41.92	9.56
O. B	5.5	23	15.04	7.66	96.19	147.7	143.04	25.96	53.25	88.75	65.44	11.18
O. S	7	25	17.92	6.49	60.12	72.14	65.61	4.1	17.75	49.7	30.87	9.83
D. R	7	25	18.03	6.41	58.3	70.54	64.64	4.11	17.75	64.5	34.19	13.7
D. D	10	25	17.84	4.79	58.76	72.14	65.68	16.50	16.39	39.05	29.83	8.44
	pH				Mg				SO$_4$			
O.K	7.1	7.6	7.37	0.21	51.33	77.31	63.98	8.12	162	175	167.1	4.72
O.B	6.8	7.7	7.41	0.21	64.99	137.3	110.91	24.5	187	239	221.91	15.53
O.S	7.3	7.9	7.65	0.21	43	59.28	48.98	4.57	142	182	166.23	11.35
R.D	7.2	7.9	7.64	0.21	42.68	55.64	47.84	4.5	147	193	170.61	15.98
D. D	7.3	7.8	7.55	0.21	42.3	54.34	49.54	4.16	141	184	159.01	14.02
	EC				Na				HCO$_3$			
O.K	475.28	685.41	589.91	76.35	36.4	45.7	39.76	2.91	231.84	376.6	313.81	60.21
O.B	654.72	1215	1005.49	188.55	40.8	59.9	52.29	7.16	283.04	494.1	388.38	58.76
O.S	455	622.37	546.32	57.99	28.4	36.2	30.6	2.08	197.64	257.9	235.98	19.72

R.D	460	621.32	551.29	59.84	28.6	49.2	42.38	8.19	195.2	257.4	236.46	18.33
D. D	459.75	617.85	550.48	61.73	1.99	18.8	20.82	18.68	199.1	298.9	240.24	26.09

	TDS				K				NO$_3$		
O.K	450	890	573.42	232.26	8.54	11.6	10.24	1.02	0.3	0.8	0.51	0.18
O.B	510	1040	920.83	144.12	9.32	11.98	10.38	0.69	0.2	0.7	0.41	0.21
O.S	270	730	514.61	139.5	8.33	10.73	9.47	0.62	0.2	0.8	0.55	0.2
R.D	270	480	390	58.45	5.98	11.6	8.98	1.82	0.2	0.8	0.43	0.18
D. D	270	460	361.53	60.94	4.03	10.44	5.95	1.97	0.2	0.6	0.37	0.15

	Pb				Fe				Sr		
O.K	0.081	0.524	0.222	0.207	0.139	0.243	0.196	0.035	0.132	0.3345	0.217	0.063
O.B	0.096	0.742	0.352	0.23	0.185	0.36	0.226	0.054	0.146	0.435	0.258	0.087
O.S	0.093	0.659	0.328	0.237	0.175	0.38	0.252	0.068	0.075	0.39	0.203	0.099
R.D	0.076	0.652	0.298	0.24	0.146	0.289	0.228	0.056	0.111	0.27	0.175	0.056
D. D	0.082	0.896	0.358	0.297	0.101	0.295	0.221	0.068	0.091	0.216	0.164	0.067

Note : O.K: Oued Khemakem, O.B: Oued Bouadjeb, O.S: Oued Safsaf, D.R: reservoir of the Zerdazas dam and the D.D: downstream of the Zerdazas dam.

Water-chemical facies

The presentation of the chemical analysis results on the Piper diagram (Piper, 1944) made it possible to reveal that the dominant chemical facies of the waters are the chloride and sulfate-calco-Magnesian facies, and bicarbonate-Calco-Magnesian (Figure 6). The two facies indicate that natural mineralization is probably the result of the influence of lithology (such as saliferous earth, clays, gypsum,...) to acquire ionic mineralization in surface waters. These waters are more mineralized in chlorides and sulfates in contact with the terrigenous saliferous formations because of the dissolution of the mineral salts, the basic exchange with the clays and the concentration of the water in chemical elements according to the direction of the runoff.

However, the anthropogenic origin of chlorides, sulfates and potassium is not excluded. High concentrations in the analyzed water are caused by domestic water discharges, fertilizer use and irrigation water discharges. The first facies was observed in Oued Bouadjeb and the upstream part of the watershed. This is due to the proximity of the Triassic formations and the influence of the Triassic saliferous land rich in halite. The further downstream the watershed, along the Saf-Saf river, the influence of the Triassic slows down and the facies becomes rather bicarbonate calco-magnesian, reflecting the carbonate matrix of the eastern and southeastern edge, which constitutes a limit to the incoming flow (natural filling by meteoric waters).

Multivariate statistical analysis

The acquisition of salinity mechanism has been studied mainly using the correlations of different chemical elements with EC. Correlation coefficient is a measure commonly used to establish the relationship between independent and dependent variables (Nair, Bohjuari, Al-Mariami, Attia, & El-Toumi, 2006). Applying the Pearson's correlation matrix for the physicochemical data of the 45 samples, using Free STATISTICA software, revealed moderate the high correlation value (0.58–0.97) between EC, and Ca^{2+}, Mg^{2+}, Cl^-, Na^+, HCO_3^- and SO_4 (Tabel 4). This indicates that these elements are the main components of salinity.
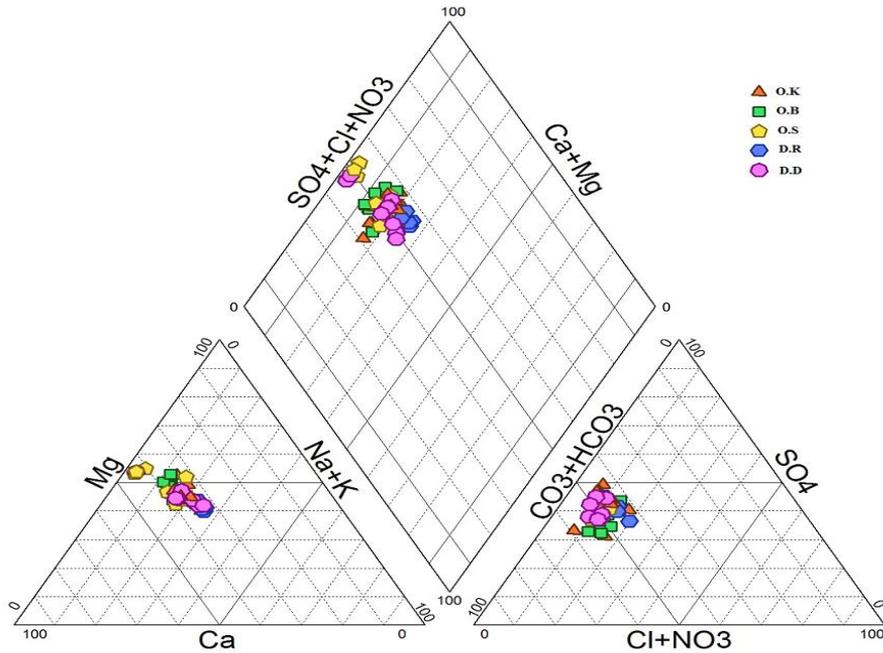
Figure 6. Piper diagram of the analyzed samples

The strong bond between electrical conductivity and calcium, magnesium, chlorides, bicarbonates, and to a lesser degree with sulfates and sodium, which gives water of the chlorinated and sulfate calcium-magnesium type.

In general, electrical conductivity is related to evaporates (Na^+, Cl^-, SO_4^{2-}) and carbonate formations (Ca^{2+}, Mg^{2+}, HCO_3^-). The presence of these elements is due to the dissolution of evaporates such as NaCl, KCl, [$CaSO_4$, $2H_2O$], and carbonates such as $CaCO_3$, Ca, Mg (CO_3). Calcium has a double bond, the first with carbonate elements and the second with saline elements.

This association suggests a double origin, which we can discuss further. Like magnesium, it also appears on two bonds, one carbonate and the other salt, which could also suggest a double origin, as for calcium. The salt elements (Na, Cl, SO_4) seem to correlate with the bicarbonate (Ca, Mg, HCO_3). The presence of evaporates is confirmed by the correlation between sodium and chloride ions (r = 0.57), (Table 4).

A strong correlation between Ca^{2+} and Mg^{2+} (r=0.99= is conditioned by the dolomitization phenomenon. The correlation between Ca^{2+} and Na^+ (r = 0.58), Mg^{2+} and Na^+ (r = 0.57), can be explained by the dissolution of silicates, which is a probable source of Na+ in the waters as well as the base exchange between Ca^{2+} or Mg^{2+} and Na^+. The good connection between Ca^{2+}, Mg^{2+}, Na^+, Cl^-, SO_4^{2-} and HCO_3^- suggests that these elements may have a common origin.

The anthropogenic origin (engrais, sanitation), is visible Afterwards, good similarities appeared between K^+, SO_4^{2-}, Na+ and Cl^-. The trace metals (lead and iron) evolve in a polar manner with the temperature (Table 4), which seems normal since the dissolution of these elements increases with temperature. These elements are also well correlated suggesting that they may also have the same origin.

Principal components analysis (PCA), as a multivariate data analytic technique, reduces a large number of variables (measured physical parameters, major anions and cations in water samples) to a small number of variables which are the principal components (PCs). More concisely, PCA combines two or more correlated variables into one variable.

Tabel 4. Surface water correlation matrix in the Zerdazas Watershed

Variable	Ca	Mg	Na	K	Cl	SO$_4$	HCO$_3$	NO$_3$	Pb	Fe	Sr	T	pH	Ec
Ca	1.00													
Mg	**0.99**	1.00												
Na	**0.58**	**0.57**	1.00											
K	0.41	0.40	**0.68**	1.00										
Cl	**0.84**	**0.84**	**0.57**	0.39	1.00									
SO$_4$	**0.72**	**0.71**	**0.62**	**0.62**	**0.71**	1.00								
HCO$_3$	**0.94**	**0.94**	**0.52**	0.36	**0.88**	**0.71**	1.00							
NO$_3$	-0.14	-0.15	-0.18	0.26	-0.12	-0.02	-0.10	1.00						
Pb	0.06	0.06	-0.23	-0.07	0.29	-0.04	0.16	0.20	1.00					
Fe	-0.01	0.00	-0.26	0.09	0.19	-0.07	0.12	0.43	**0.60**	1.00				
Sr	0.41	0.43	0.23	0.43	0.41	0.31	0.34	0.23	0.38	0.25	1.00			
T	0.00	0.03	-0.02	0.07	0.25	-0.03	0.09	0.12	**0.73**	**0.48**	0.22	1.00		
pH	-0.46	-0.47	-0.06	0.01	-0.05	-0.21	-0.29	0.25	0.30	0.32	-0.09	0.31	1.00	
EC	**0.96**	**0.97**	**0.58**	0.41	**0.89**	**0.72**	**0.96**	-0.10	0.10	0.03	0.45	0.09	-0.33	1.00

Note : EC: electrical conductivity, T: temperature, pH : a number that shows how strongly acid or alkaline a substance

This approach has been used to extract related variables and infer the processes that control water chemistry. Varimax rotation is applied to the PCs in order to determine factors that can be more easily explained in terms of hydrochemical or anthropogenic processes (Helena et al., 2000). This rotation is called Varimax because the goal is to maximize the variance (variability) of the ''new'' variable, while minimizing the variance around the new variable. The number of PCs extracted (to explain the underlying data structure) is defined by using the ''Kaiser Criterion'' (Kaiser, 1958) where only the PCs with eigen values greater than unity are retained. In other words, unless a PC extracts at least as much information's as the equivalent of one original variable, it is dropped. The reader is referred to the work of Davis (1966) for an in-depth account of the theory. The analytical results of PCA were performed for the 45 samples and 14 variables. The analysis was carried out on three factors and more than 75.7 % of the total variance having been expressed, the parameter weights for the three components from the PCA of the dataset are given in (Tabel 5).

The factorial analysis revealed that factor 1 explains the greatest amount of the variance (45.19%) and is characterized by highly positive loadings in EC, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, Na^+ and, to a lesser extent by potassium, (Table 5, Figure 7). The EC association with these elements is due to the different hydrochemical processes that increase the water salinity, so this is the factor of the mineralization. Factor 2 explains 20.15 % of the total variance of the dataset and shows significant highly positive loadings in lead, iron and the temperature. This factor shows that the element does not influence the total mineralization of the water and predicts the contamination by trace elements accentuated by temperature (Table 5; Figure 7).

The Factor 3 explains 9.89% of the total variance of the dataset and shows significant positively loading in potassium and nitrates, which predicts the association of this factor with chemical fertilizers. Factor analysis revealed that factor 1 explains most of the variance (45.19%) and is characterized by very positive charges in EC, Ca^{2+}, Mg^{2+}, HCO_3^-, Cl^-, SO_4^{2-}, Na^+ and, to a lesser extent, potassium, (Table 5; Figure 6). The association EC with these elements is due to the different hydrochemical processes that increase the salinity of the water, so it is the factor of mineralization.

The Factor 2 explains 20.15% of the total variance of the dataset and shows significant very positive loadings in lead, iron and temperature. This factor shows that the element does not influence the total mineralization of the water and predicts contamination by trace elements accentuated by temperature (Table 5; Figure 7).

The Factor 3 explains 10.36% of the total variance of the dataset and shows a significant positive charge in potassium and nitrates, which predicts the association of this factor with chemical fertilizers. Commonly used mineral fertilizer inputs in the region are NPK.

Tabel 5. Principal component weights

Variable	F1	F2	F3
Ca	**0.961**	-0.102	-0.172
Mg	**0.961**	-0.089	-0.189
Na	**0.691**	-0.243	0.425
K	**0.568**	0.087	**0.727**
Cl	**0.900**	0.203	-0.121
SO$_4$	**0.820**	-0.103	0.247
HCO$_3$	**0.936**	0.035	-0.203
NO$_3$	-0.092	**0.502**	**0.507**
Pb	0.106	**0.859**	-0.320
Fe	0.039	**0.817**	-0.036
Sr	0.499	0.401	0.167
T	0.100	**0.765**	-0.180
pH	-0.326	**0.528**	0.344
EC	**0.967**	-0.009	-0.141

Note : F1, F2, F3 : factorial analysis
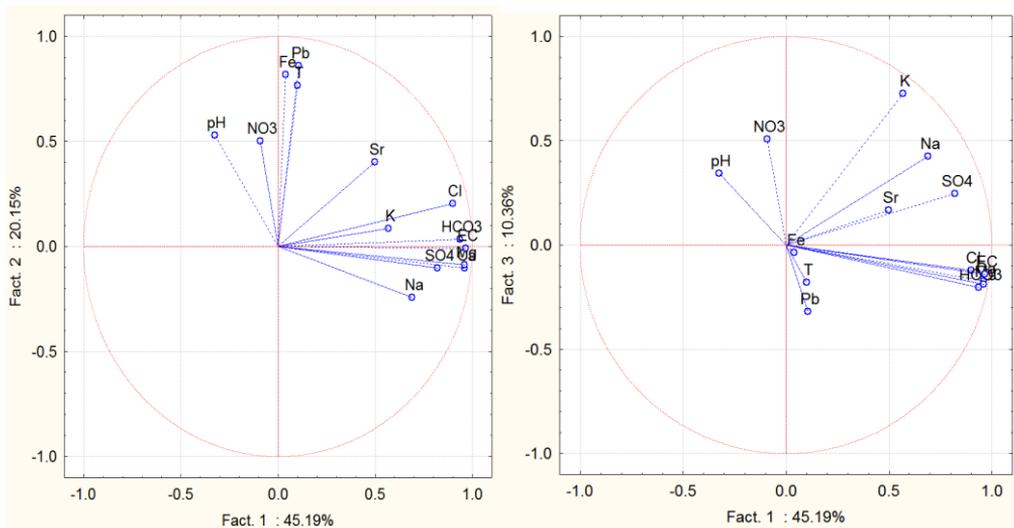
Figure 7.   Circular correlation graphs of variables

Water-rock interaction

Water-rock interactions and water circulation are recognized as the main agents of mobilization and transport of elements. Thus, the chemical composition of the water reflects the

mineralogical composition of the host rocks. Water chemistry can also provide information on water-rock interaction processes (Bensoltane, Zeghadnia, & Hadji, 2021). The origin of the predominant elements in the majority of the sampled points is sought with binary relations between elements.

The molar ratio Na^+/Cl^- reveals the origin of these elements from the dissolution of halite (NaCl). The (Figure 8) shows that all samples are above the line of slope 1.

This latter reflects the presence of a second origin.
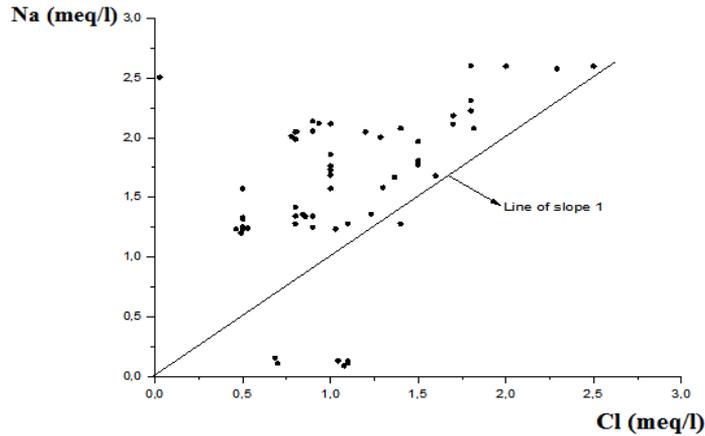
Figure 8. Diagram Na^+ Vs Cl^-

Sodium ions, which have increased the concentration of sodium compared to chloride, this additional contribution could come from weathering of sodium silicates. To demonstrate this phenomenon, it has intervened a diagram Na/Cl - Ca/(HCO₃ + SO₄). Examination of this diagram Na/Cl - Ca/(HCO₃ + SO₄), (Figure 9) shows that over 90% of the samples undergo an exchange basis which could justify the excess sodium by this phenomenon (Mermoud, 2002).
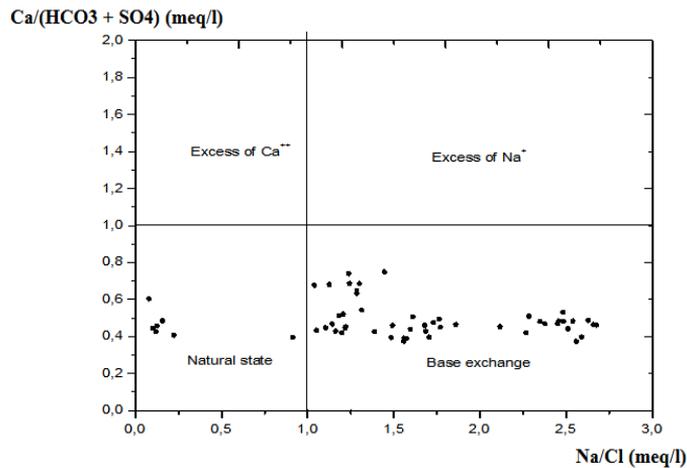
Figure 9. Basis exchange

Figure 10 show that all the sampled points are located at the top of the line of slope 1, which demonstrates an excess of sulphate compared to sodium. This is explained by a higher dissolution of gypsum than that of halite.

The projection of points on the diagram (Mg^{2+} / Ca^{2+}) and SO_4^{2-}, (Figure 11) shows that 45 samples have a ratio of Mg^{+2} / Ca^{+2} greater than one, it allows us to say that magnesium the outweighs its calcium and cannot be due to the dissolution of evaporate ($MgSO_4$). The stabilization of this report despite the higher concentration of sulfate can explain only by precipitation of the element Mg^{++}.
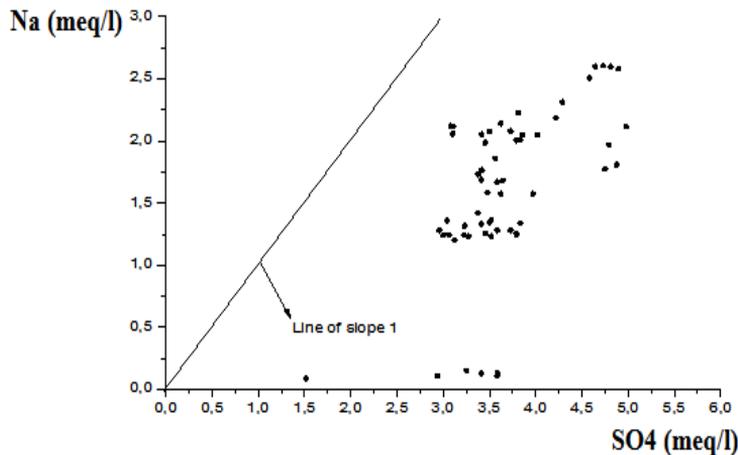
Figure 10. Diagram Na^+ Vs SO_4^{2-}
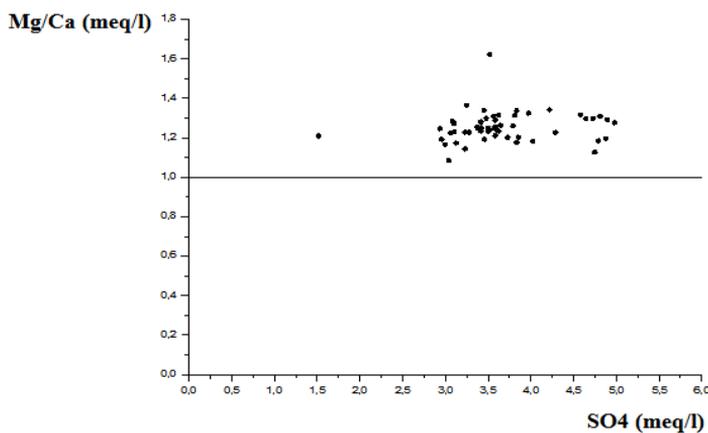
Figure 11. Diagram Mg^{2+}/Ca^{2+} Vs SO_4^{2-}

The first representation, (Figure 12.a) shows that calcium has two possible origins for the content of HCO_3^-<6meq/L, the origin of calcium was carbonate, and the content of HCO_3^->6 meq/L HCO_3^- there was an excess of calcium that can be evaporate. Examination of (Figure 12.b) on the evolution of limestone according to sulfates shows 65% of the samples had an excess of sulfates, which confirms the original evaporate.

Origin of salinity

The salinity acquisition mechanism has been studied mainly using the ratio of HCO_3^-/(Cl^-+ SO_4^{2-}) Vs conductivity. This report reveals two poles, (Figure 13). The carbonate pole characterized

by a dominance of carbonate ions HCO_3^-, it covers only 24% of sampled water and the other represents the evaporation pole and asserts a dominance of Cl^- and SO_4^{2-} and includes 76% points. Thus, the conductivity is largely due to the evaporated elements.
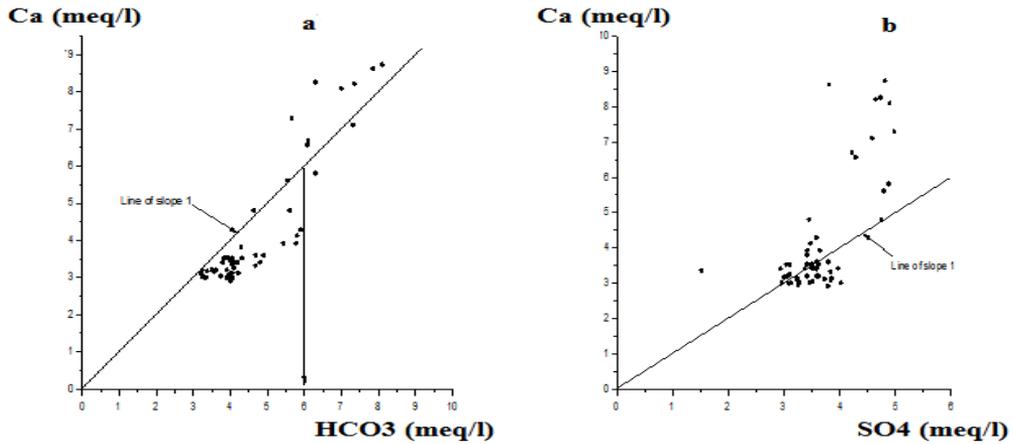
Figure 12. Origin of the Calcium Ca^{2+} (a - left & b - right)
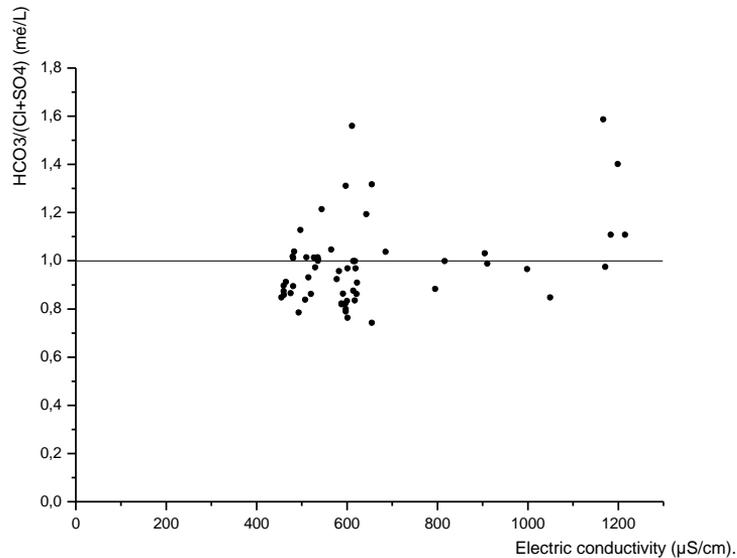
Figure 13. Origin of salinity

Furthermore, the acquisition of the salinity mechanism has been studied mainly using Strontium which is a tracer related to evaporation. A high Sr^{2+} content in the waters can only be explained by the dissolution of Celestite ($SrSO_4$), a mineral that is associated with gypsum; Sr is therefore a good tracer of the existence of evaporites. The Sr^{2+}/Ca^{2+} ratio is characteristic of an evaporitic origin if it is equal to or greater than 1‰ (Bakalowicz, 1988; (Meybeck & Fabre, 1986).

Strontium analyses in the waters show that most points have low Sr^{2+} contents (0.075-0.435 mg/L) (Tabel 3). Water from Wadi Bouadjeb has a much higher content (0.146 - 0.435 mg/L). According to the Sr^{2+}/Ca^{2+} ratio (‰), two groups can be distinguished: the carbonate-related points without relation to the salt formations, have a low Sr^{2+}/Ca^{2+} ratio (< 1‰, Tabel 6), the second group determined by the waters that have crossed the salt formations, have a Sr^{+2}/Ca^{+2} ratio between 1 and 2. 9 ‰; points in the dam reservoir (RD) and downstream of the dam (DD) are located downstream of the watershed have Sr^{2+}/Ca^{2+} ratios varinat from 0. 78 to 2.11 ‰). These values, are characteristic of water that has flowed through the sandstone and dolomitic layers of the limestone that is observed at the eastern outcrop of the Oued Safsaf River that drains the central part of the limestone range (Figure 8-10). And influenced by meteoric water that falls on the water body of the reservoir. From the above, we can conclude that the origin of salinity in our case is related to the evaporites.

Tabel 6. Ratio Sr/Ca

Ratio (Sr/Ca) (‰)	Ratio (Sr/Ca) (‰)	Ratio (Sr/Ca) (‰)	Ratio (Sr/Ca) (‰)
OK	**OB**	**OS**	**RD and DD**
1.1146	**1.3204**	**1.4206**	**1.3318**
1.9077	**1.0800**	**1.3516**	**1.6781**
0.7672	**1.1146**	**2.9245**	**2.1142**
0.9587	**1.1059**	**2.7126**	**1.9204**
1.2769	**1.2386**	0.9346	**1.3290**
1.5278	**1.0460**	**1.3803**	**1.2232**
1.1507	**1.0893**	**1.1789**	0.9902
1.1626	**1.0795**	0.6292	0.7831
1.5094	**1.3612**	0.8290	0.7885

CONCLUSIONS

The hydro-geochemical behavior of surface waters of the Zerdazas watershed was studied using hydrochemical and statistical tools. Although the waters of the watershed are less loaded with a low total mineralization below 1200 mg/L.

The use of the statistical tool allows to highlight significant relationships between the electrical conductivity and the different chemical elements Ca, Mg, Na, Cl, SO_4, and HCO3, showing the strong participation of sulfates, chlorides and sodium in the acquisition of salinity. The trilinear plot shows that most of the surface water samples fall in the range of Cl-SO_4-Ca-Mg and HCO_3-Ca-Mg water types. EC shows a good positive correlation, which indicates the participation of these elements in the mineralization of the waters.

The application of the principal component analysis, as well as the binary relation elucidated the origin of these facies, which is strongly related to the lithology of the watershed and showed the existence of two origins of the chemical elements diluted in the watershed. A natural origin, conditioned by the dissolution of carbonate and evaporite formations, and an antropic origin, conditioned by the sanitation and the agricultural use of fertilizers. Also the existing basic exchange is highlighted.

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