Journal of Fundamental and Applied Sciences

ISSN 1112-9867

Available online at http://www.jfas.info

Research Article

APPLICATION OF STATISTICAL METHODS TO THE STUDY OF THE SPATIO-TEMPORAL EVOLUTION OF THE PHYSICO-CHEMICAL PARAMETERS OF THE SURFACE WATERS OF THE CHERF WADI BASIN. ALGERIA

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Received: 21 May 2020/ Accepted: 27 April 2021 / Published online: 01 May 2021

ABSTRACT

The physico-chemical parameters of the surface waters of the Cherf wadi watershed experience considerable variations over space and time under the influence of natural or anthropogenic phenomena. The application of the Kruskal-Wallis test for the comparison of the physico-chemical parameters showed that there were very significant intersite differences for pH, electrical conductivity, bicarbonate, chloride and sodium; as well as significant differences between the dates for all the studied variables. The typology highlighted by principal component analysis and Hierarchical Classification Analysis is linked to the availability of mineral elements by the anthropic activities of variable intensity depending on the sites, is added a natural process of mineralization related to the contact water- rock and throughfall phenomena. Statistical processing also revealed two types of water. The first type represents waters with very strong mineralization with very high sodium and chloride values characterizing the waters of site 5. The second type is marked by strong mineralization with high contents of Calcium. It characterizes the sites receiving discharges coming respectively from certain agglomerations not connected to the wastewater system and from the treatment plant.

Key words: Discharge, Watershed, Mineralization, Spatio-temporal variablity.

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doi: http://dx.doi.org/10.43 14/jfas.v13i2.27

1. INTRODUCTION

The chemical composition of a watershed waters is often used as an indicator of the flow of water from the rain downstream to the river. It allows to determine the origin of each chemical element and its evolution along the river.

This study aims to highlight the spatio-temporal evolution of the water quality of Oued Cherf and its influents, as well as the natural and anthropogenic origin of these chemical species.

Several research projects around the world [1.2. 3] and in Algeria [4.5.6] have shown the effect of these anthropogenic activities on the degradation of the physico-chemical quality of the waters of the watershed.

Additionally, a number of geological works were carried out in the region [7.8.9] have shown the complexity of the geological composition.

In this context, the use of the Principal Component Analysis, the Hierarchical Classification and the Kruskal - Wallis test for the interpretation of the data seems an interesting solution for a better understanding of the spatio-temporal evolution of the chemical elements. These techniques have as well the advantage of identifying and linking the different factors influencing the water quality of the watershed.

2. MATERIAL AND METHODS

2.1. Field of study

The watershed of Oued Cherf is drained by several rivers. On the east, Oued Tiffech follows the axis of the synclinal plain of the same name. The syncline; which forms the plain of Khemissa; is crossed by Oued Crab grown by Oued Behezz, Oued Ain Sfa and Oued Es Souk towards which flows the waters coming from the southern slope of the Atlas chain. Oued Crab which flows into Oued Tiffech becomes Oued Hamimine downstream. The latter and Oued Crab meet in the South-West of Sedrata and yield Oued Cherf which passes at the foot of the Jebel Zouabi , then comes Oued Ain Snob which has its source in the chott El Magéne and the Jebel Teraguelet at the farthest points of the great basin of the Seybouse. Oyued Settara composed of Oued Ain Babouche and Oued El Mebdoua; these influents are fed by the small streams descending from Jebel Sidi Reghiss north of Oum El Bouaghi and the eastern flank of the Chebkat Sellaoua range [10] (fig.1).

The geology of the region is characterized by sedimentary formations, whose oldest age is the Triassic to the Quaternary. It is generally composed of limestones, clays, marls, sandstones, gravel and alluvium [11].

It is among the regions that suffer the most from drought and water stress. It is subject to a semi-arid climate characterized by irregular rainfall with periods of intense and persistent drought. The annual rainfall is of the order of 166 to 535 mm and the high temperatures are more and more felt in recent years.

The watershed is subject to pollution generated by domestic wastewater discharges from the two cities of Sedrata and M'Daourouch. It receives daily more than 5313 m^3/day of waste water, of which 5000 m^3 are treated by the STEP in Sedrata and more than 313 m^3 are discharged directly without any prior treatment.

2.2. Sampling and analysis

To study the influence of the lithology of Oued Cherf watershed and the anthropogenic discharges on the water mineralization, Eighteen sampling campaigns with an average time step of five days were carried out during a period that extends from February 2016 to the month of April 2017 for six sample sites including (fig. 1):

Crab wadi (S1 et S2);

Hamimine wadi (S3) ;

Trouch wadi(S5),

Cherf wadi upstream (S4) and downstream (S6).

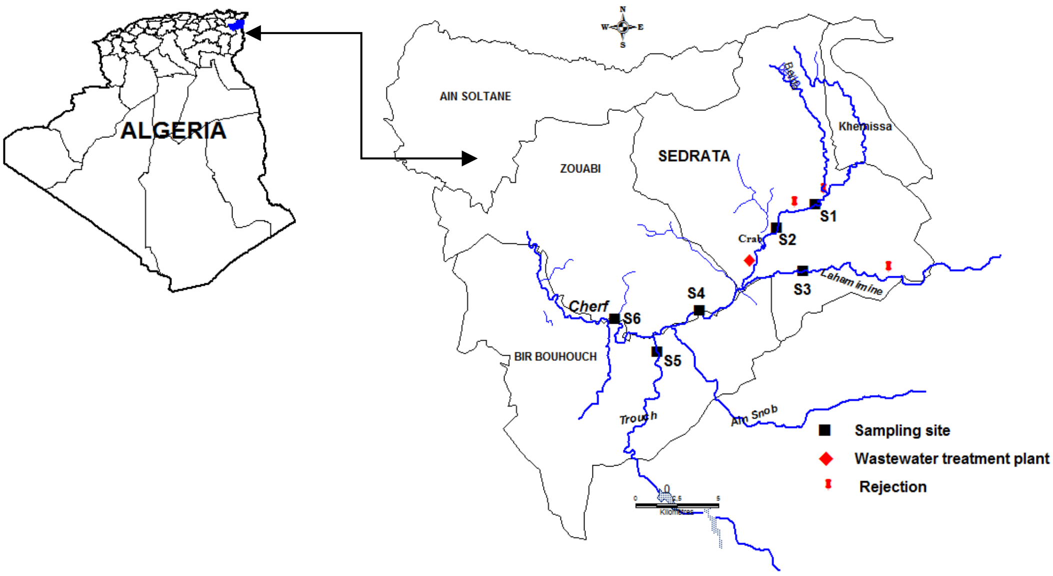

Fig.1. Map of location of sites and study area

During sampling campaigns for water samples, we have respected the standards of sampling "filtration (0.45 µm filter), acidification (5 mL of HCl or HNO_3) and preservation (4◦C)" (AFNOR / T91E).

The physico-chemical parameters (pH, temperature, conductivity) are measured in situ using a multi-parameter WTW device (multi 340i / SET). The chemical elements were analyzed by volumetric (Cl^-), atomic absorption with flame and colorimetry.

2.3. Statistical analysis

The principal component analysis (PCA) is widely used to interpret the hydro-chemical data of the surface waters as well as the Hierarchical Ascending Classification (AHC) are carried out using the software R.

The Kruskal-Wallis non-parametric test is also applied using the same software to test the significance of differences in physico-chemical parameters, between sites on one hand and months on the other hand.

3. RESULTS AND DISCUSSION

The water chemistry of the study area is naturally influenced by the composition of the matrix, but also by the different discharges. The results of chemical analyses of these waters are given in table 1.

Table1. Mean and extended values of the measured physico-chemical parameters

Site		pH	T	Cond	HCO_3^-	SO_4^{2-}	Ca^{2+}	Mg^{2+}	Cl^-	K^+	Na^+
			+C	Us/cm	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
	Min	7,18	6,8	630	237,9	4,89	19,24	0,72	88,62	0,1	9,4
	Max	8,16	22,9	2610	483,12	85,71	145,9	135,4	603,55	15,6	184
S1	Moy	7,8444	15,111	1310,83	312,591	50,87	79,16	44,1	214,13	7,6	81,33
	Min	7,09	8,3	790	140,3	6,88	20,84	0,729	106,35	0,2	23
	Max	8,23	23,3	2300	397,72	132,4	238,9	121,3	957,05	18,2	287,5
S2	Moy	7,7844	16,544	1470,56	291,309	57,86	101	41,92	339,26	9,81	130,7
	Min	6,75	9,3	630	214,964	4,31	8,818	1,216	141,8	0,1	34,5
	Max	8,28	22,4	4960	918,66	104,5	200,8	130,5	856,19	39	345
S3	Moy	7,5867	16,361	1625	401,665	50,74	102,8	41,74	362,9	12,4	170,4
	Min	6,84	7,4	800	262,3	7,34	51,3	1,945	177,25	3,9	46
	Max	8,43	22,3	3050	613,66	150	226,9	97,73	1061,3	15,6	253
S4	Moy	7,5561	15,367	2051,39	376,031	58,29	129	49,59	388,84	9,76	158,2
	Min	7,09	8	2970	193,98	8,4	30,46	1,216	354,5	7,8	49,8
	Max	8,14	25,4	8570	808,86	189,8	325	157	1501,3	23,4	750
S5	Moy	7,73	16,472	5466,94	412,224	47,92	159,1	75,05	965,72	14,7	449,5
	Min	7,44	7,5	1270	140,3	8,28	35,27	3,16	124,08	0,7	23
	Max	8,83	27,6	3570	501,42	138,3	161,9	159,2	531,75	21,5	253
S6	Moy	8,0611	16,756	2522,5	255,658	56,56	103,4	78,98	365,33	9,92	104,3

Discharges of purified and wastewater are characterized by high levels of Cl^-, HCO_3^- and Na^+. In the Piper cation diagram, all the points have a remarkable tendency towards the sodium pole; while in the anion diagram, the points form a cloud relatively close to the chloride pole (fig. 2).

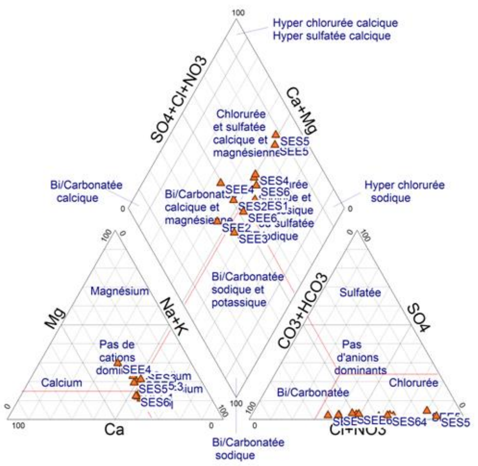

Fig.2. Piper diagram of purified water

Figure 3 shows the different facies depending on the hydrological regime and the groups of stations. Two chemical facies characterize most of the sodium chloride (45 %) and calcium chloride (39 %) points; some calcium bicarbonate points (12 %) and four sodium bicarbonate points.

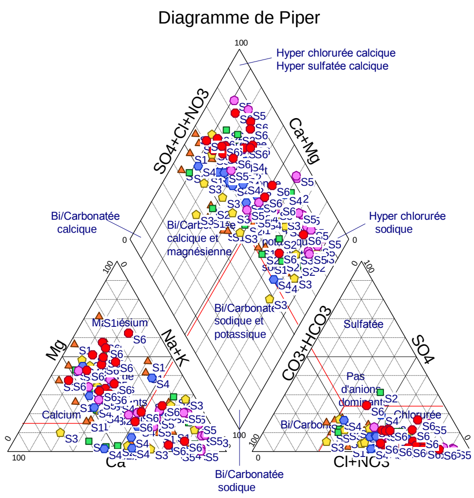

Fig.3. Piper diagram show hydrochemical facies according to hydrology

The spatial distribution of facies shows a certain peculiarity between two groups of stations. In fact, the waters of station 5 have a dominant sodium chloride facies; this is due to the influence of the geology of the region on the water quality of Trouch wadi. While for the other stations it is clear, in addition to geology, the influence of the discharges on the quality of the water, from which we have two almost similar chemical facies, sodium chloride and calcium chloride.

The data processing by PCA, using as variables T °, pH, Conductivity, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-} , SO_4^{2-} and HCO_3^{-}; and as readings, the 108 samples taken from the 6 stations surveyed on the watershed system of the Cherf wadi watershed reveal several axes. The first two express the maximum of the variance (56.43 %). The information given by axis 1, corresponds to 31,6 % of the variance and the axis 2 represents 24,83 %.

The distribution of physico-chemical variables according to the F1-F2 plan (fig. 4) presented on the positive side of the F1 axis reveals a positive correlation with the conductivity, chloride and sodium. This axis reflects a combination of native ions and elements reflecting the mineralization of waters associated with human activities. According to F2, the distribution presents on the positive side a correlation with parameters Ca^{2+}, Mg^{2+} and SO_4^{2-} and on the negative side a correlation with the temperature. This F2 axis reflects the dissolution of carbonate and gypsum rocks, characterized by a high concentration of indigenous ions which indicates a natural pollution.

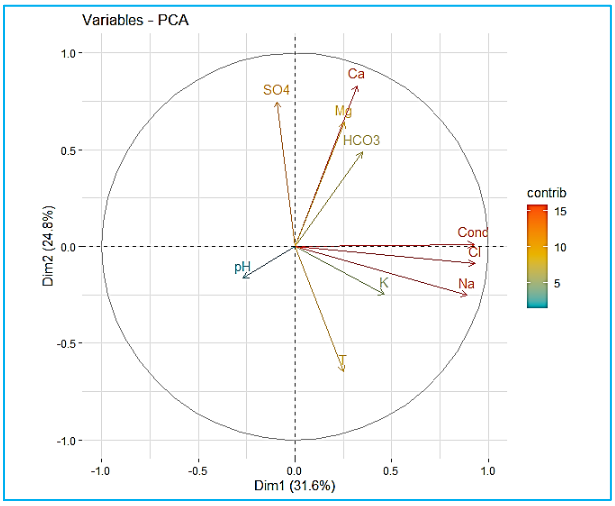

Fig.4. Correlation circle of physico-chemical variables

The final reconstitution of the distribution of the stations, allowed us to define the factorial axes responsible for this distribution, and consequently, to bring out the affinity between the different stations and to deduce the parameters that characterize them at best. Thus, the projection of the stations on the F1 and F2 plan makes it possible to carry out a significant regrouping in relation to the mesological parameters (fig. 5).

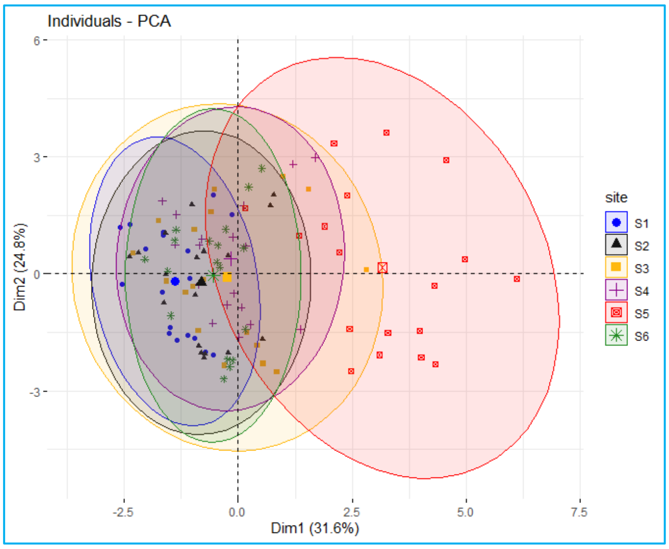

Fig.5. Individual correlation circle

The first axis F1 makes it possible to distribute on the positive side, the stations according to their very strong concentrations in Cl^- and Na^+ which reflect in some ways the rate of very high mineralization relative to the S5 station prospected on the Trouch wadi. Thus, stations with high salinity are placed on the negative side of the F1 axis. They are mainly represented by Cherf , Crab and Hamimine wadis.

An ascending hierarchical classification made from individuals of a collection cycle allowed to complete the information of the PCA and to classify the sites into two groups. In figure 6, we identify two main groups:

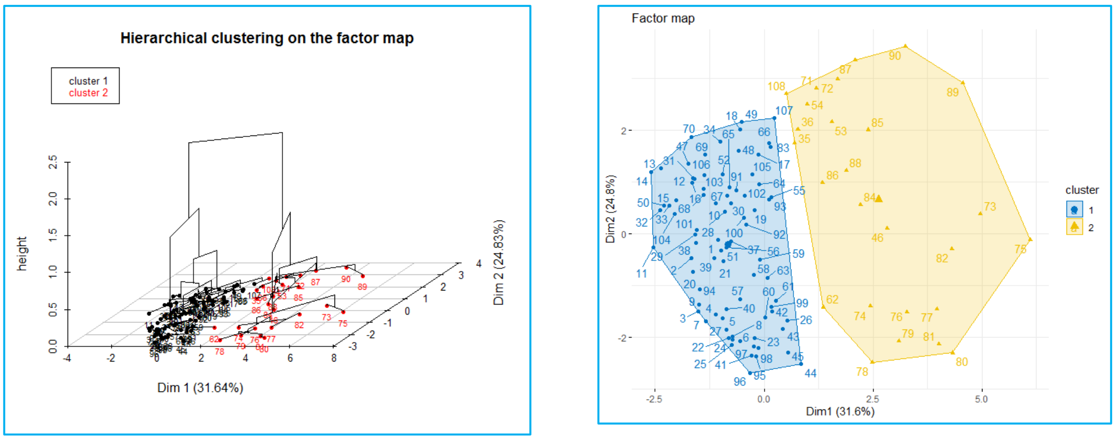

Fig.6. Hierarchical classification of individuals

The first group represents waters having a very high mineralization with very high values of Na^+ and Cl^-, taken from the Trouch and Cherf watercourses (low water period). They are the most loaded with dissolved mineralization and reflect a pollutant load contained in the clean water of Sédrata station and the leaching of salt rock in the watershed.

The second group is marked by high levels of Ca^{2+}. This is the water taken from the Cherf, Crab and Hamimine wadis. These waters are characterized by strong mineralization. These stations reflect discharges of purified and wastewater and leaching of carbonate rocks.

In order to test the spatial effect and temporal effect, the application of the Kruskal-Wallis test for the comparison of the physic-chemical parameters of the waters of the Cherf wadi watershed showed that there were very significant inter-site differences for pH, Conductivity, HCO_3^-, Cl^- and Na^+; as well as significant differences between dates for all variables (table 2).

Table 2. Comparison of the parameters according to the two factors "site" and "time"

Parameters	FACTORS			
	Site (ddl= 5)		Time (ddl= 17)	
	Value of P	Meaning	Value of P	Meaning
pH	0.000	***	0.000	***
T°	0.923	ns	0.000	***
Cond	0.000	***	0.032	*
HCO_3^-	0.000	***	0.000	***
SO_4^{2-}	0.924	ns	0.000	***
Ca^{2+}	0.069	ns	0.000	***
Mg^{2+}	0.045	*	0.000	***
Cl^-	0.000	***	0.007	**
K^+	0.011	**	0.004	**
Na^+	0.000	***	0.000	***
NB: * (P ≤0,05), ** (P ≤0,01), *** (P ≤0,001), ns (P >0,05)				

The typology highlighted by the PCA and the AHC is related to the contributions of mineral elements by the anthropic activities of variable intensity according to the sites in addition to a natural process of mineralization related to the contact water-rock and to the phenomena of rain -leaching. Indeed, the stations under strong anthropic and geological influence record the highest values of conductivity and major ion contents. These are stations of Cherf, Crab and Hammine wadis. Moreover, the anthropogenic effect on these stations is noted by their high levels of the descriptors of anthropization (Cl^-, HCO_3^-, Ca^{2+} and Na^+) as emphasized by Mary [12] and Gouiadia [13] respectively in New Caledonia and in Algeria. Conversely, the stations which record very high values of conductivity and very high concentrations of Cl^- and Na^+ are explained by the geology of the region and the low-water period of the wadis.

The variation of the temperature of the surface waters follows those of the variations of the atmospheric temperatures. We observed strong seasonal fluctuations in the surface waters. Summer peak maxima are recorded at site 6 (27.6 °C), while the winter minimum is observed at site 1 (6.8 °C). The standard deviation of temperatures, for all data, is greater in August than in January, which is related to hydrology within the wadis. In January, the arrival of water causes a mixing of water in the wadis, which explains the homogeneity of the temperatures. In August, the mixing of the water decreases following the reduction in contributions (fig. 7).

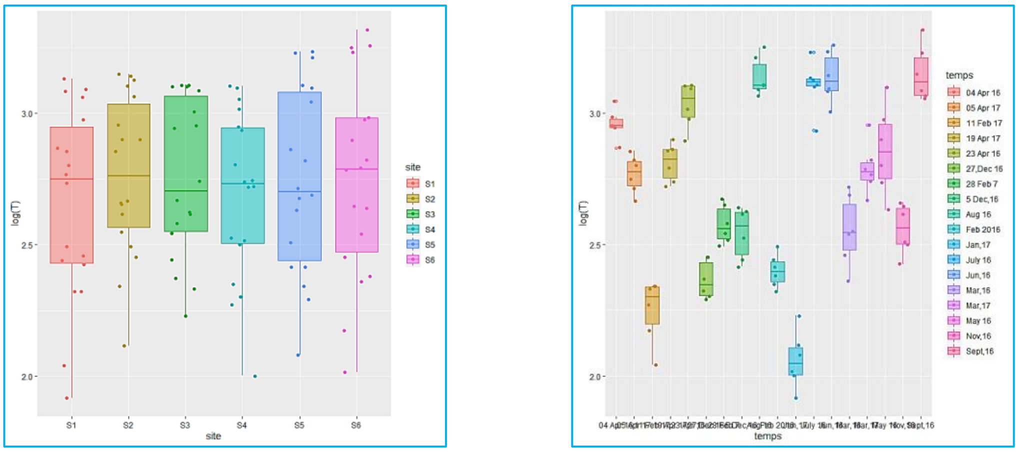

Fig. 7. Temperature evolution in time and space

Hydrogen potential is a limiting factor in aquatic ecosystems: if the pH is below 4.5 or above 10, it becomes toxic to living organisms. The observed values reveal that the pH of the waters of the watershed is alkaline in all the sites, both during the rain period and the dry one. The pH value varies between 7.56 and 8.06 (fig. 8). The high pH value is recorded at site 6.

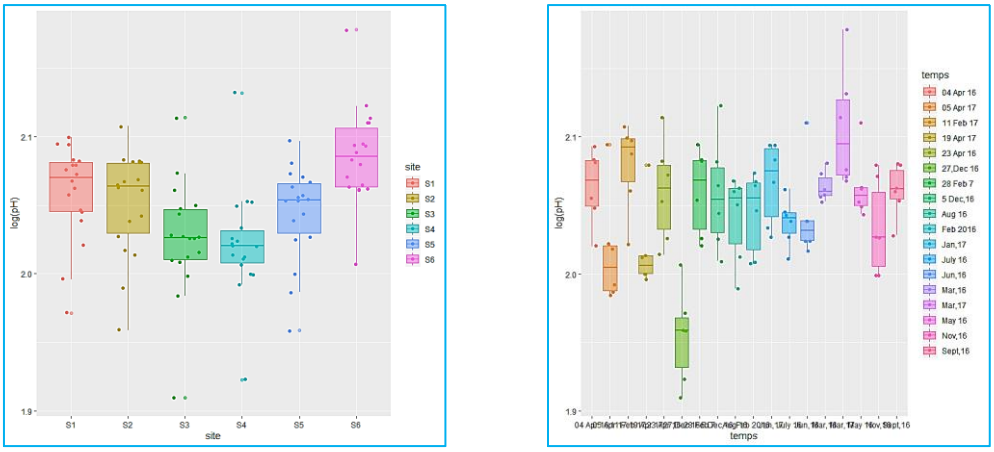

Fig.8. Evolution of pH over time and space

Conductivity allows to quantify the sum of dissolved salts present in water. Figure 9 represents the spatio-temporal evolution of the conductivity in the surface waters of the Cherf wadi watershed. It can be noted that the conductivity is not homogeneous throughout the water mass. The average values recorded show significant variations. They oscillate between 1311 us/cm and 5467 us/cm. The highest conductivity is observed at site 5, however, the lowest one is recorded at site 1. The temporal distribution of the conductivity shows a high value during the month of April (2017) and a decrease in the concentration during the winter period. This decrease is explained by the dilution of the water via the rainfall.

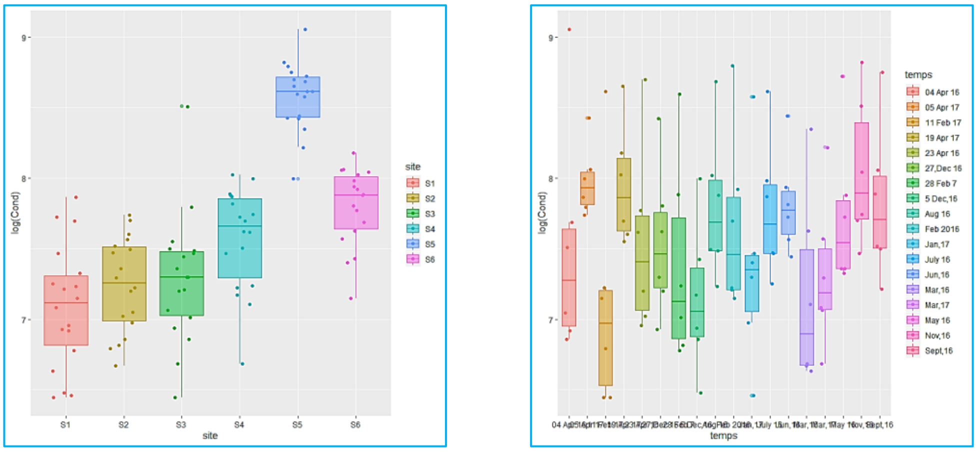

Fig.9. Evolution of conductivity in time and space

The clays and alluvia of the Mio-Plio-Quaternary filling deposit and the salt deposits, resulting from erosion, constitute the origin of these chlorides. They represent the highest concentration of anions in the majority of sites.

The highest average concentration (966 mg/l) is observed at site 5 and the lowest at site 1 (214 mg/l). High chloride values are observed during the summer period and decrease during the rainy season (fig. 10).

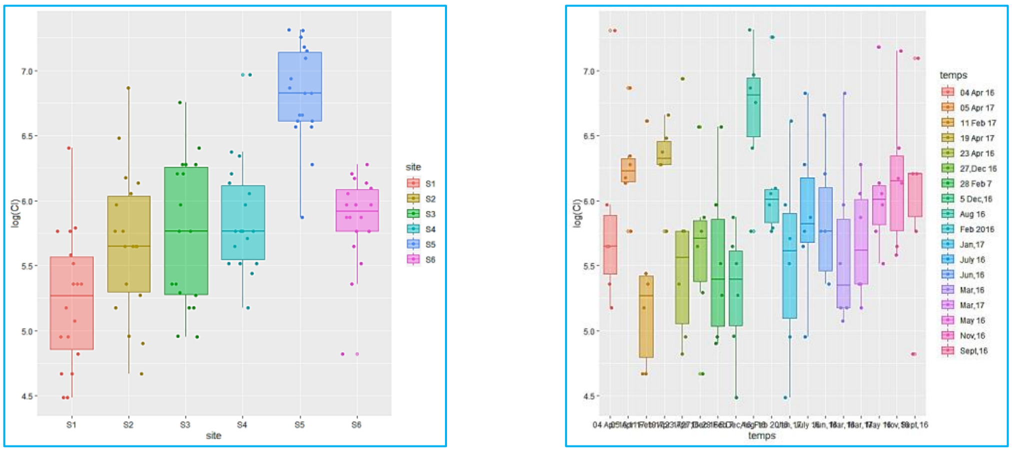

Fig. 10. Evolution of chlorides in time and space

The presence of bicarbonates in water is due to the dissolution of carbonated formations by water charged with carbon dioxide. They are in second position in all wadis from the point of view of concentration. The high average concentration (412 mg/l) is observed at site 5, and the lowest (256 mg/l) at site 6. The highest concentrations are observed during the spring period and the lowest during the winter period (fig. 11).

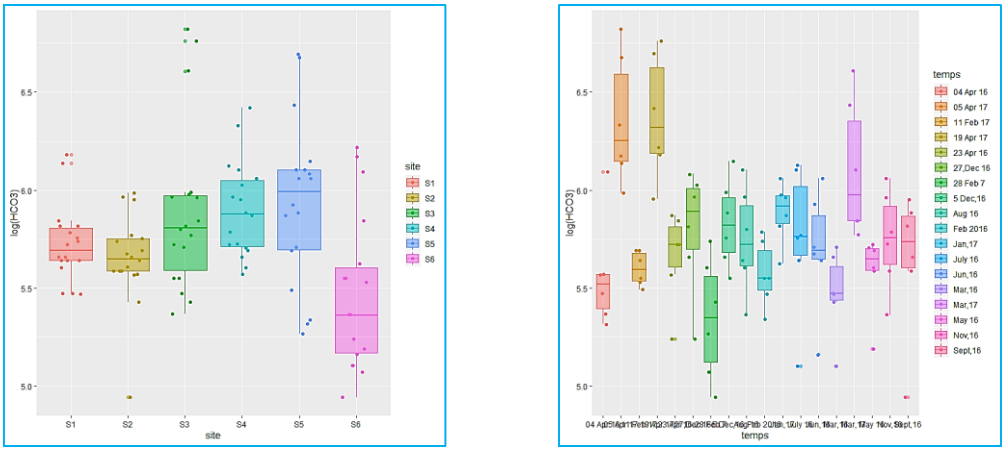

Fig. 11. Evolution of bicarbonates in time and space

Sulphates come from the dissolution of sulfur-containing minerals (triassic gypsum formations, or more recent formations such as the Miocene and Quaternary clays and marl), as they can be of anthropogenic origin through the use of fertilizers or phytosanitary products, in agriculture.

They are also indicators of pollution by wastewater. The average concentration of sulphates does not exceed 50 mg/l (fig. 12).

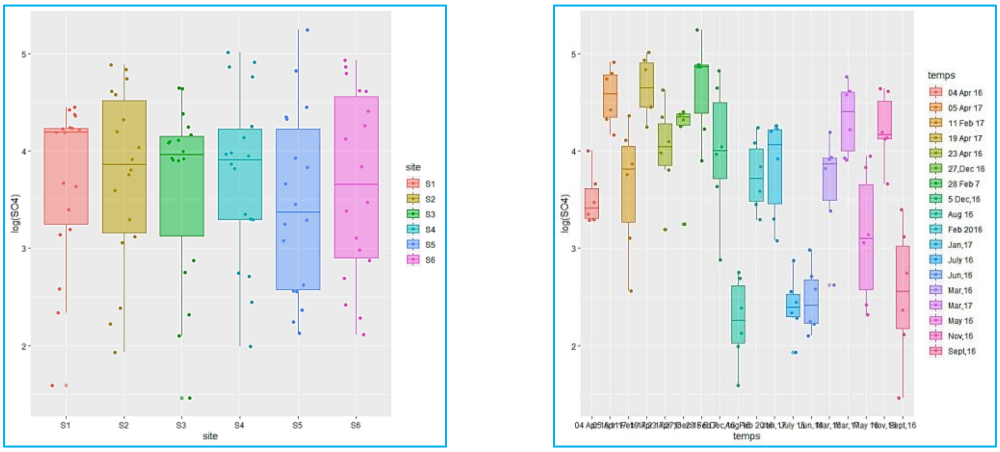

Fig.12. Evolution of sulphates in time and space

The evolution of sodium concentration is proportional to that of chloride. This similarity with chloride indicates that both elements have the same origin. It is very exchangeable in clay environments. The high average sodium content is observed at site 5 (449.5 mg/l) and the lowest at site 1 (81.33 mg/l). The maximum seasonal average values are recorded in spring and the lowest average values are recorded in winter (fig. 13).

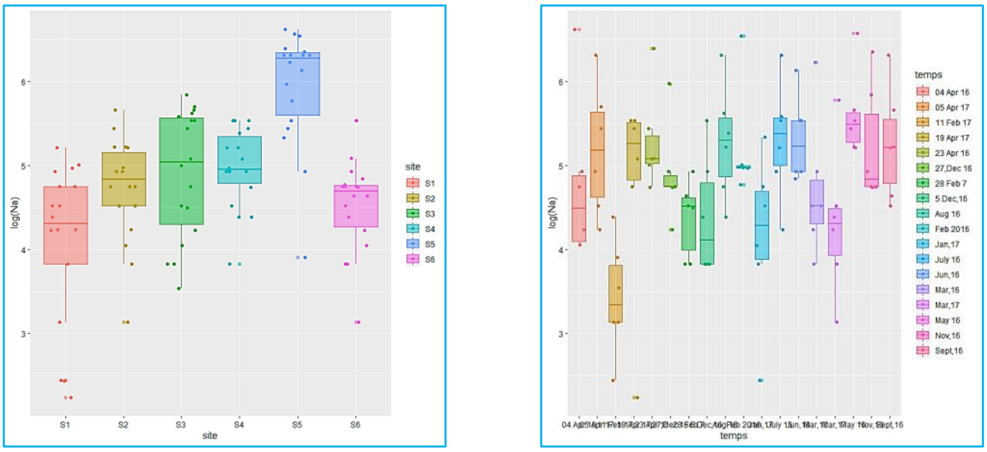

Fig.13. Evolution of sodium in time and space

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dissolution of carbonate formations ($CaCO_3$), or the dissolution of gypsum formations. It has the same behavior as sodium vis-à-vis clay media. Calcium comes in second position from the point of view of concentration. Site 5 has the highest average concentration (159.1 mg/l) and the lowest (79.16 mg/l) at site 1. The summer period is characterized by the lowest concentrations at the site level, while the highest values are observed in the spring (fig. 14).

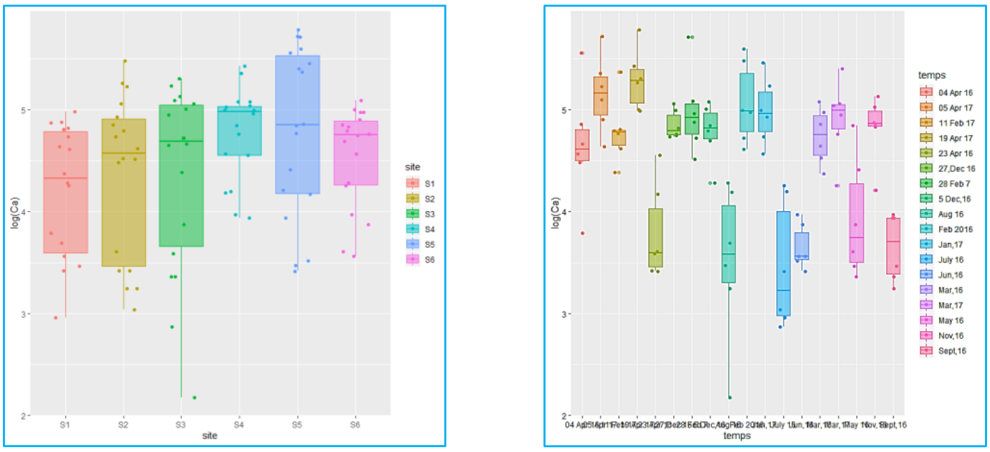

Fig.14. Evolution of calcium in time and space

Its origins are comparable to those of calcium, because it comes from the dissolution of carbonate formations with high levels of magnesium (dolomite). Magnesium comes in third position from the point of view of concentration. The contents are less important than those of sodium. The high average concentration is observed at site 6 (79 mg/l) and the lowest at sites 2 and 3 (42 mg/l) (fig. 15).

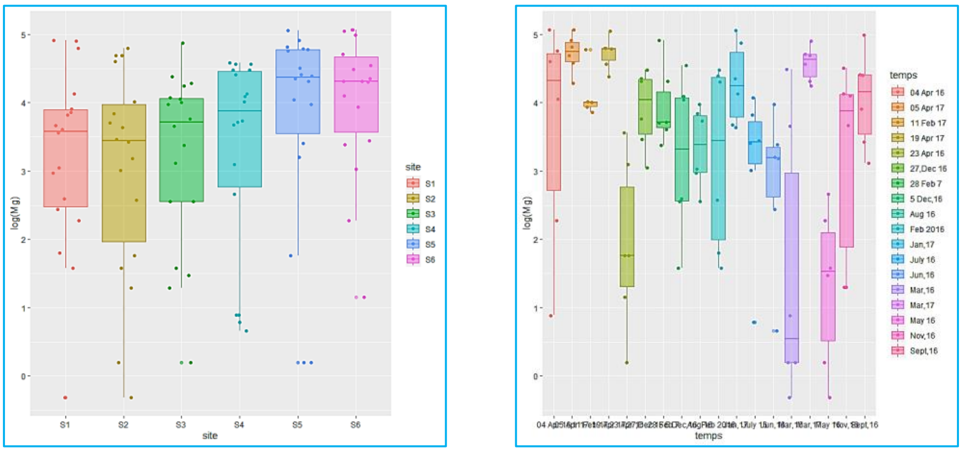

Fig. 15. Evolution of magnesium in time and space

Potassium comes from the alteration of silicate formations (gneiss, shale), potash clays and dissolution of chemical fertilizers (NPK). Potassium is very stable, can migrate and be exchanged in clay minerals and organic matter. Concentrations are virtually negligible compared to other elements. Site 5 has the highest average concentration (14.7 mg/l) and the lowest site 1 (7.6 mg/l) (fig. 16).

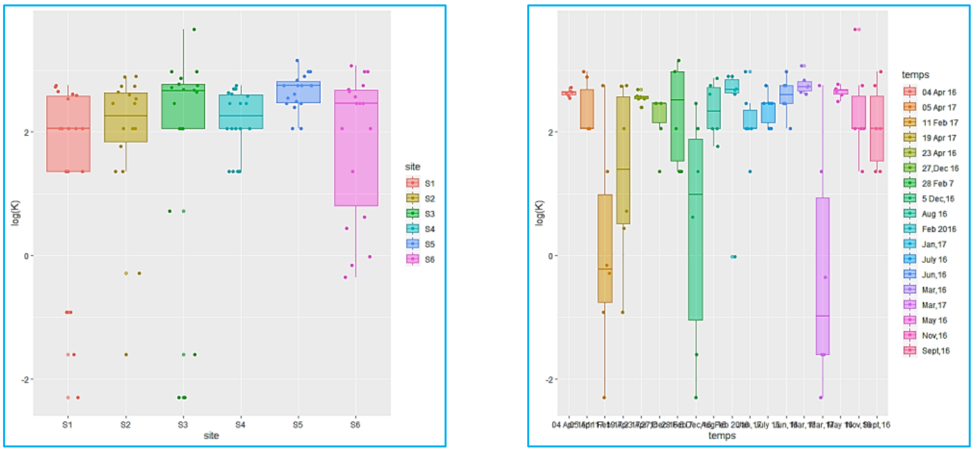

Fig.16. Evolution of potassium in time and space

4. CONCLUSION

This study allowed us to highlight the spatio-temporal evolution of the physico-chemical parameters of the waters of the Cherf wadi and its affluents as well as the natural and anthropogenic origin of these chemical species.

The statistical treatment allowed us as well to highlight two types of waters. The first type represents waters having very high mineralization with very high values of Na^+ and Cl^- characterizing the waters of the site 5. The second type is marked by strong mineralization with high levels of Ca^{2+}. It characterizes the sites receiving discharges coming respectively from certain agglomerations that are not connected to the sanitation network and the treatment plant. The methods of statistical analysis have also disclosed that the spatio-temporal evolution of physic-chemical parameters is governed by three major phenomena: anthropic activities, the rain-leaching of soils and the hydrolysis of minerals.

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How to cite this article:
Bellazi MA, Zenati N, Belahcene N, Berredjem Y, Gheid AE. Application of statistical methods to the study of the spatio-temporal evolution of the physico-chemical parameters of the surface waters of the cherf wadi basin. Algeria. J. Fundam. Appl. Sci., 2021, *13(2), 1132-1147.*