

## A chemometric method for contamination sources identification along the Oum Er Rbia river (Morocco)

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In the present work, a chemometric tool, namely, principal component analysis was used to understand the behavior of sampling stations, relationship between measured variables and to classify sampling locations into groups of similar water quality characteristics. The samples (24) were collected in the 8 sampling stations located along the Oum Er Rbia river, in three different campaigns from 2016 to 2017. The study area includes several sensible sampling points such as sources (S1), upstream and downstream of Khenifra (S2), Zawiat Cheikh (S3, S4), Kasbat Tadla (S5, S6) and Dar Oulad Zidouh (S7, S8) cities. Several physicochemical variables were measured such as temperature (of water and air), pH, electrical conductivity, total hardness, dissolved oxygen, complete alkalimetric title, oxidizability, turbidity, chlorides, sulfates, nitrates, nitrites, ammonium, Fe, Zn, Pb, Cu, Cd, Cr and Ni. Results revealed that principal component analysis applied to the data analysis as chemometric approach reduced the number of variables in the first two PCs that captured 65 and 19% of the variance for PC1 and PC2, respectively, with a total variance of 84%. The principal component analysis showed the similarity between the sampling locations according to their water characteristics, the possible correlations between the variables studied and finally classified the sampling points to three groups (GR1, GR2 and GR3), according to the water quality characteristics of each site. The result demonstrated that chemometric method used in this work is effective and often useful for analysis, interpretation and classification of this river water based on the physicochemical loading of each sampling point.

**Keywords:** Oum Er Rbia river, Chemometric, Principal component analysis, Scores plot, Loadings plot, Bi-plot.

### INTRODUCTION

Water is an important and precious natural resource for different uses (domestic, industrial and agricultural). It is an element basis for a healthy life and is directly attached to human survival. So, the consciousness of the limited amount of unpolluted water available to mankind is on the rise [1-6]. Water pollution, defined as physical, chemical, or biological degradations caused by human activity, disrupts living conditions and aquatic balances thereby compromising their multiple uses [7-11]. However, the quality of surface water is influenced by natural processes (soil erosion, precipitation, evaporation) as well as by human activity (agriculture, urban and industrial wastewater) [12, 13].

Rivers are considered as the net receivers of the different anthropogenic pollutants [14]. Rivers are systems that carry a significant load of dissolved and particulate matter from natural and anthropogenic origin in one direction [15]. Environmental control campaigns for rivers water, produce large amounts of analytical data that are

not always easy to interpret [16, 17]. In this context, chemometric techniques are important numerical methods and more appropriate tools that allow significant data reduction and interpretation, to extract useful information [18]. The use of different multivariate statistical techniques (principal component analysis (PCA)) for the interpretation of the analytical results seems an interesting solution for a better understanding of the water quality distribution and the ecological states of the investigated environments [19]. PCA is a mathematical procedure used widely in chemometric data analysis, representing a multivariate technique [20, 21]. Chemometric tools are usually chosen to uncover information hidden in the complex data sets [22]. PCA was realized by eigenvalue decomposition of the correlation matrix of the obtained data sets [23, 24]. It was applied to visualize the similarities between the samples analyzed, and also the trace element content [25-27]. The principal idea for utilizing this chemometric tool (PCA) was the reduction of the number of variables studied, called principal components (PCs).

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PCs explain the global variations within the data to let the components more interpretable [28]. It is a statistical tool that projects data from a large dimensional space over a two-dimensional space, covered by some uncorrelated factors. For the studied dataset, it allows revealing the relationship between the water samples collected over the investigated period and the parameters measured for the consecutive filtering units, and also it can elucidate the relationships among these parameters. In recent years, the PCA approach has gained a lot of attention in chemometrics, due to its computational efficiency [29]. PCA is primarily used to determine general relationships between data. It is a very widely applied method for the interpretation of analytical data, especially on water quality. Several investigations carried out on the application of chemometric tools for water data analysis were reported in the literature by many researchers [17, 30-35].

The objectives of the present work are to obtain more detailed information about the global changes of the monitored physicochemical parameters along the river in three sampling expeditions (2016 to 2017), to explain the variation, similarities between sampling locations, correlations between variables studied and finally to classify sampling locations according to their water quality characteristics and to apply chemometric tools such as PCA.

## MATERIAL AND METHODS

### Area description

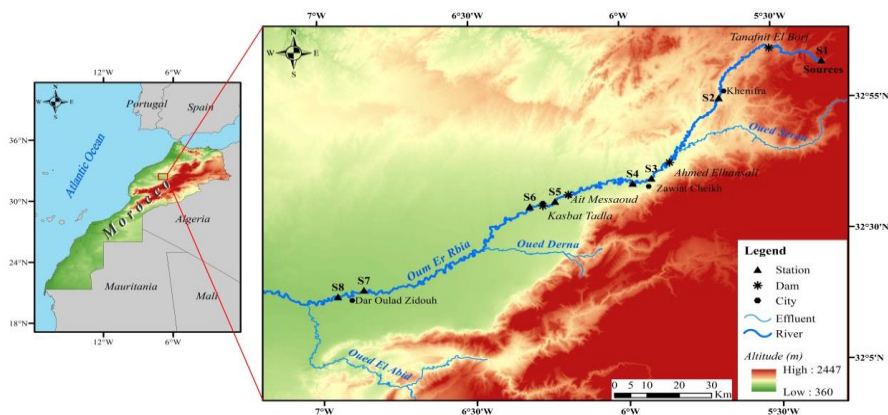
The system under study (Oum Er Rbia river) is located in the Oum Er Rbia basin. It is one of the most populated basins in Morocco, it is located in the center-west of Morocco (Fig. 1), at 31°19.33'-33° 22.21"N lat. and 5°8.55'-8° 22.53 W long and

covering an area of about 48,070 km<sup>2</sup> which represents nearly 7% of the country's surface area [36]. It is rich in renewable resources with more than 3,130 Mm<sup>3</sup>, a quarter of the resources of Morocco. The studied river is approximately 550 km long with a mean flow of 117 m<sup>3</sup>/s from the Middle Atlas to 1800 m, 40 km from the Khénifra city, and crosses the Tadla plain, the coastal plateau, and discharges in the Atlantic Ocean at Azemmour city. Serou, Derna, and El Abid (Fig. 1) rivers are its main tributaries. At the river level, several dams and reservoirs have been built whose objective is the supply of water for domestic, industrial and irrigation uses as well as the production of hydroelectrical energy. In addition, untreated municipal sewage ends up in the Oum Er Rbia river and its tributaries from neighboring cities.

### Analytical procedures

The temperature measurements were carried out using a mercury thermometer, the pH was measured using a pH meter INOLAB pH7110, the electrical conductivity (EC) was measured by a conductimeter INOLAB cond720 and the turbidity was determined by a turbidimeter HACH 2100N.

Ammonium, nitrite and nitrate ions were determined by the indophenol blue, sulfanilamide and sulfanilamide methods, respectively, after reduction in a column of cadmium. The oxidizability was measured by hot oxidation in an acid medium by potassium permanganate. The total hardness (TH) was determined by complex titration with EDTA with indicator Eriochrome Black T; chlorides were determined by volumetric determination with mercuric nitrate. The measurement of dissolved oxygen (DO) content was done by the iodometric method. Sulfates were measured using the nephelometric method with barium sulfate, and the complete alkalimetric title (CAT) was determined by titrimetry.



**Fig. 1.** Map of the study area and sampling stations along the Oum Er Rbia river.

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All analyses were carried out according to the Moroccan standard NM 03.7.001(N.M 03.7.001).

The metals concentrations (Pb, Cu, Ni, Cr, Fe, Cd, and Zn) were measured by inductively coupled plasma optical emission spectrometry (ICP-OES) using a Perkin Elmer Optima 8000 apparatus.

#### *Sampling stations*

Because of the various activities identified in the study area (liquid discharges from neighboring cities and agricultural activities in the Oum Er Rbia watershed), eight sampling stations (S1 to S8) distributed along the Oum Er Rbia river were used to represent the overall states of the stream according to the activities in its vicinity and to cover all possible pollution sources of the river. The exact sampling stations were: sources (S1), upstream and downstream of Khenifra (S2), Zawiat Cheikh (S3, S4), Kasbat Tadla (S5, S6) and Dar Oulad Zidouh (S7, S8) cities. A total of 24 water samples were collected along the river, all sites were sampled during three sampling expeditions, in April 2016, August 2016, and February 2017.

#### *Sampling procedures*

The river water samples were collected from the selected eight monitoring stations (S1-S8). The sampling was done at the sampling site approximately 30 cm below the water surface using a polyethylene bottle with a 1.5 L capacity previously rinsed 3 times with the water from the station. The collected samples were refrigerated ( $\pm 4$  °C) in isothermal boxes, and transported to the laboratory quickly after sampling for testing.

#### *Data analysis*

Data statistical treatments were performed using the IBM SPSS Statistics 25 software packages. Chemometric treatments were performed using the Unscrambler X software version 10.2 from CAMO (Computer-Aided Modeling, Trondheim, Norway).

## RESULTS AND DISCUSSION

### *Physicochemical parameters studied*

The obtained analytical results for each physicochemical parameter during the three sampling periods along Oum Er Rbia River are represented in box-whiskers plots as follows in Fig. 2.

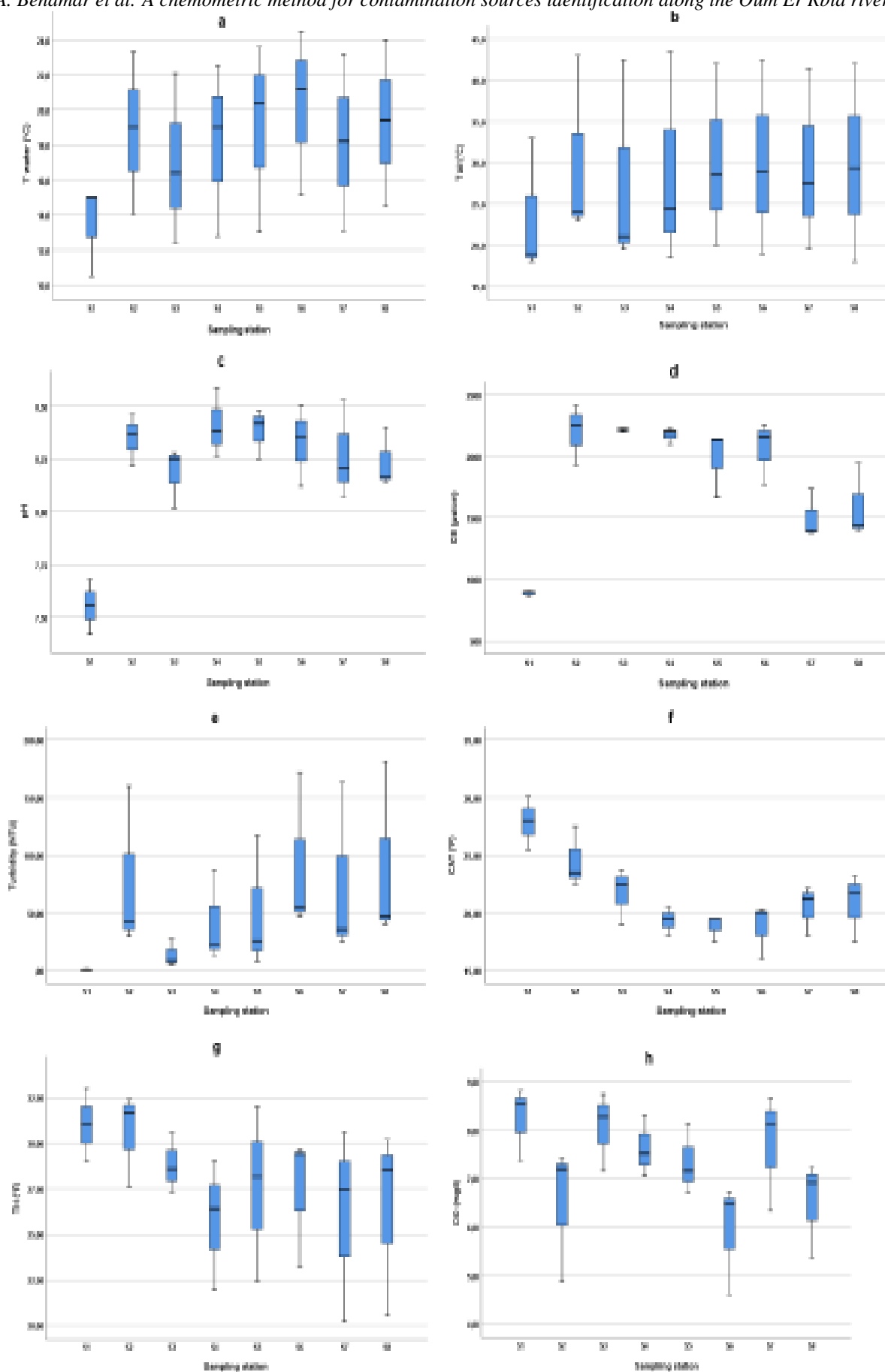
The variables are the temperature of the water, the temperature of the air, pH, EC, TH, DO, CAT, oxidizability, turbidity, chlorides ( $\text{Cl}^-$ ), sulfates ( $\text{SO}_4^{2-}$ ), nitrates ( $\text{NO}_3^-$ ), nitrites ( $\text{NO}_2^-$ ), ammonium ( $\text{NH}_4^+$ ), Fe, Zn, Pb, Cu, Cd, Cr and Ni. The spatiotemporal variation of the 21 variables studied

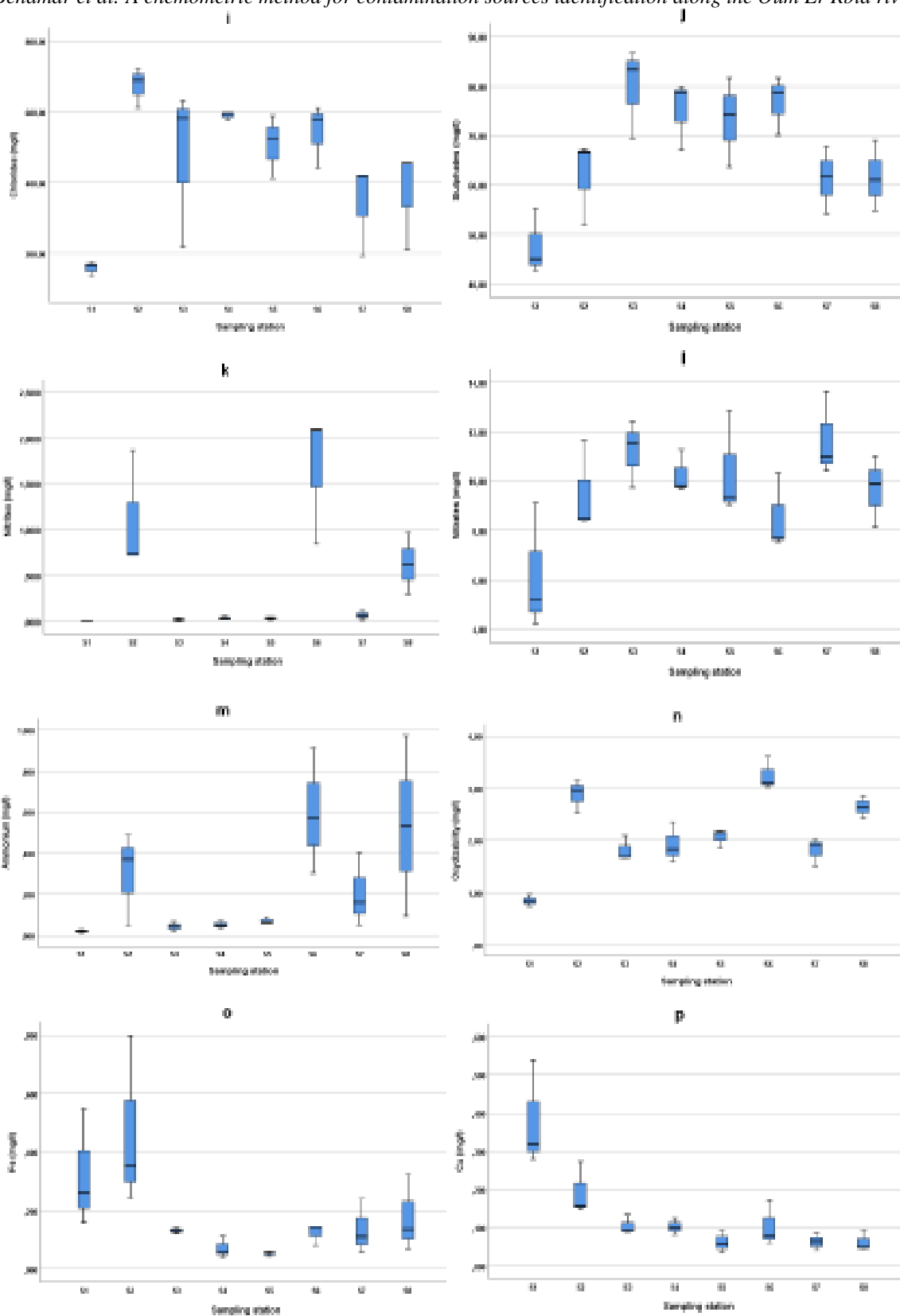
in three sampling expeditions at all locations (S1-S8) is shown in Fig. 2.

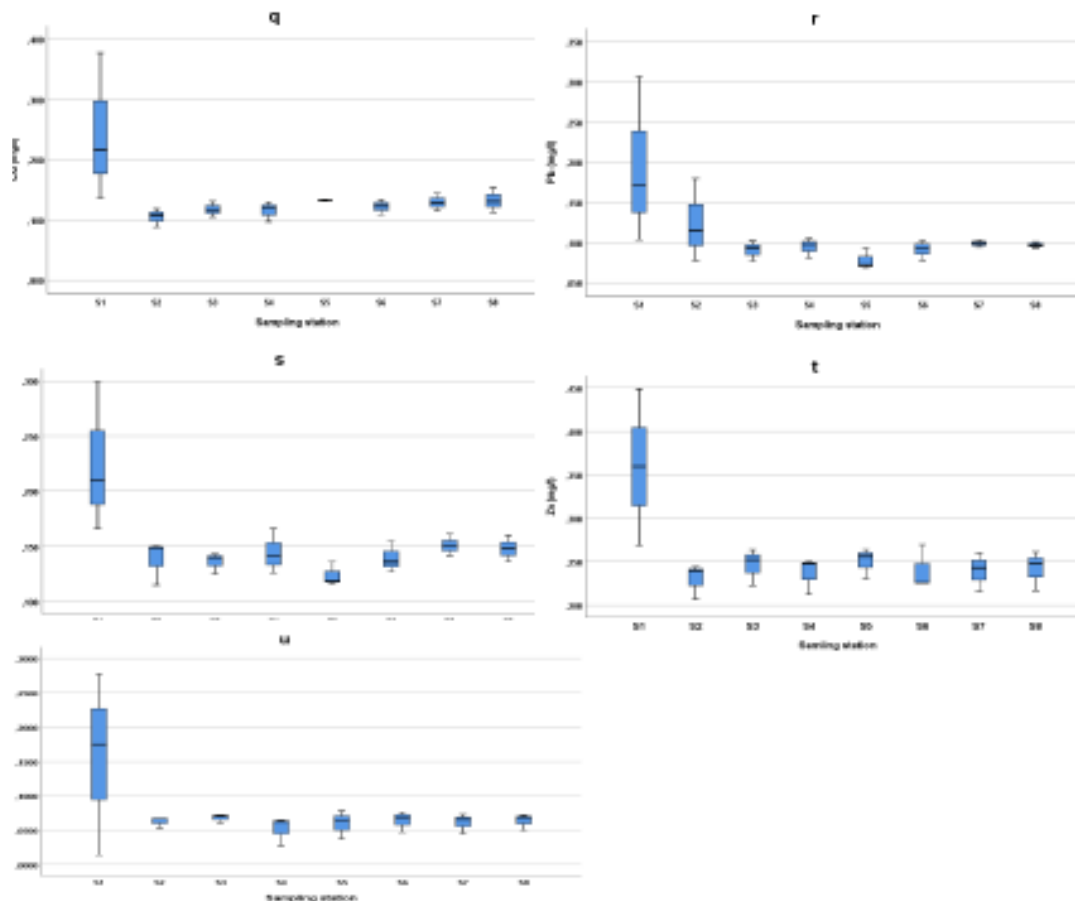
The water temperature of the different stations studied varies between 14 and 25 °C. The main reason for this difference in temperature values between all sites may be due to the large difference in altitude along the Oum Er Rbia river, the geographical characteristics of each station and the period of sampling. Nitrates present minimum values at S2, S6, and S8 stations, which can be related to the agricultural activity and excessive use of fertilizers. The maximum value of DO is observed at location S1 (sources) in all sampling periods and low values are observed at S2, S6, and S8 stations because of the discharging of wastewater from neighboring cities at S2, S6 and S8 stations. There are several variables (turbidity, oxidizability, ammonium and nitrites) at the S2, S6 and S8 locations that show maximum values mainly caused by the influence of the wastewater input in the river from Khenifra (S2), Kasbat Tadla (S6) and Dar Oulad Zidouh (S8) cities without treatment. The highest concentrations of total hardness, alkalinity, and heavy metals are recorded at the location S1, which is a result of the water's own characteristics. The lowest values of pH, chlorides, sulfates and EC are observed at station S1. The interpretation of the obtained results from the box-whiskers plots diagrams and the analysis of the correlations between the variables from one sampling site to another requires time, important verification and comparison between all the physicochemical parameters at the level of each diagram from one period to another and between all sampling locations. To distinguish and understand the relationship and variation between all physicochemical parameters investigated and the sampling locations along the Oum Er Rbia river, the application of chemometric methods is necessary.

### *Descriptive statistics*

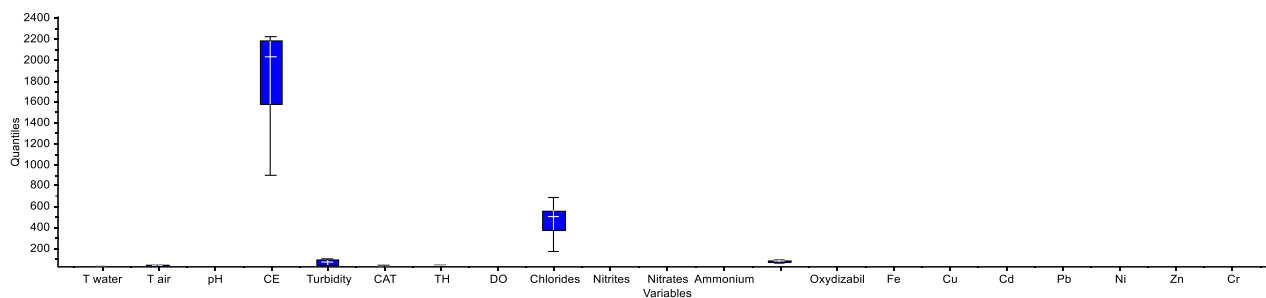
Preliminary exploratory data analysis was performed using univariate descriptive statistics. The descriptive statistics (minimum, maximum with mean and standard deviations) were computed for each physicochemical parameter during three sampling expeditions of the 21 water quality variables at the eight stations on the river, and are summarized in Table 1.



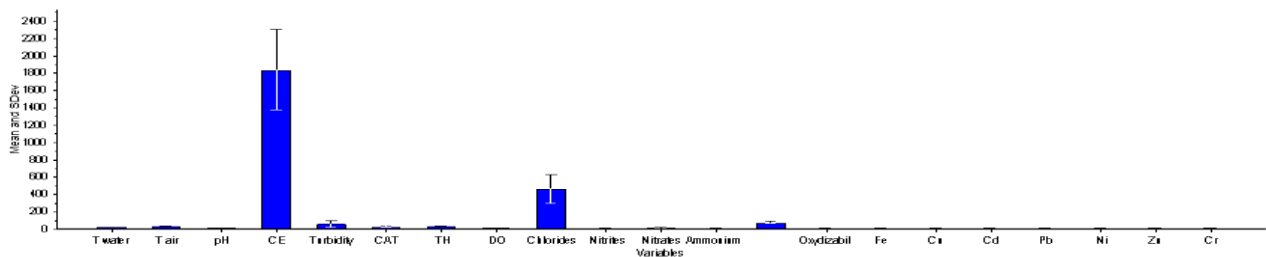




**Fig. 2.** Spatial and temporal distribution of (a) water temperature, (b) air temperature, (c) pH, (d) electrical conductivity, (e) turbidity, (f) complete alkalimetric title, (g) total hardness, (h) dissolved oxygen, (i) chlorides, (j) sulfates, (k) nitrites, (l) nitrates, (m) ammonium, (n) oxydizability, (o) iron, (p) copper, (q) cadmium, (r) lead, (s) nickel, (t) zinc and (u) chromium in the sampling stations along Oum Er Rbia river.



**Fig. 3.** Average and standard deviation graph of the different variables.



**Fig. 4.** Box-whiskers plot of the different variables.

**Table 1.** Global statistics of physicochemical parameters at the river level.

Parameter	Minimum	Maximum	Mean	Std. Deviation
Temperature of water (°C)	10	24.5	18.0083333	2.0622649
Temperature of air (°C)	18.0	43.5	28.6875000	2.3193800
pH	7.42	8.59	8.21416667	0.2775800
CE (µS/cm)	856	2420	1827.58333	468.50100
Turbidity (NTU)	0.43	182.00	54.8383333	34.405800
CAT (°F)	16.00	30.05	21.5395833	3.1679800
TH (°F)	20.18	33.00	27.9408333	2.0047000
DO (mg/L)	4.62	8.80	7.23708333	0.8296400
Chlorides (mg/L)	134.9	724.9	458.184167	162.67510
Nitrites (mg/L)	0.003	2.090	0.44646250	0.6375330
Nitrates (mg/L)	4.22	13.64	9.67541667	1.7311900
Ammonium (mg/L)	0.011	0.973	0.22737500	0.2291872
Sulfates (mg/L)	42.66	86.70	67.1666667	10.881905
Oxidizability (mg/L)	0.75	3.61	2.15708333	0.7510911
Fe (mg/L)	0.042	0.799	0.18525000	0.1395100
Cu (mg/L)	0.036	0.539	0.13458333	0.107850
Cd (mg/L)	0.088	0.378	0.13733333	0.044290
Pb (mg/L)	0.069	0.307	0.10875000	0.036820
Ni (mg/L)	0.115	0.300	0.15070833	0.031290
Zn (mg/L)	0.207	0.449	0.25562500	0.042340
Cr (mg/L)	0.0143	0.2780	0.07322083	0.033690

**Table 2.** Sampling stations projection in the space formed by PC1 and PC2.

Scores	PC1	PC2	Scores	PC1	PC2
S1	8.9227	0.5402	S5	-1.6504	-1.5890
S2	-0.9534	2.7306	S6	-2.8586	2.4601
S3	-0.1489	-2.2069	S7	-0.5592	-1.2333
S4	-1.4422	-1.9354	S8	-1.3101	1.2336

**Table 3.** Variables projection in PC1 and PC2 space.

X Loading	PC1	PC2	X Loading	PC1	PC2
Temperature of water	-0.2578	0.1236	Ammonium	-0.1288	0.3741
Temperature of air	-0.2602	0.0654	Sulfates	-0.2016	-0.1771
pH	-0.2626	-0.0425	Oxydizability	-0.2145	0.2996
CE	-0.2180	-0.0435	Fe	0.1168	0.3291
Turbidity	-0.1921	0.2757	Cu	0.2438	0.1526
CAT	0.2332	0.1488	Cd	0.2558	0.0229
TH	0.1729	0.1936	Pb	0.2526	0.1554
DO	0.1660	-0.3825	Ni	0.2575	0.0704
Chlorides	-0.2079	0.0660	Zn	0.2612	0.0150
Nitrites	-0.1114	0.4306	Cr	0.2632	0.0755
Nitrates	-0.1886	-0.2773			

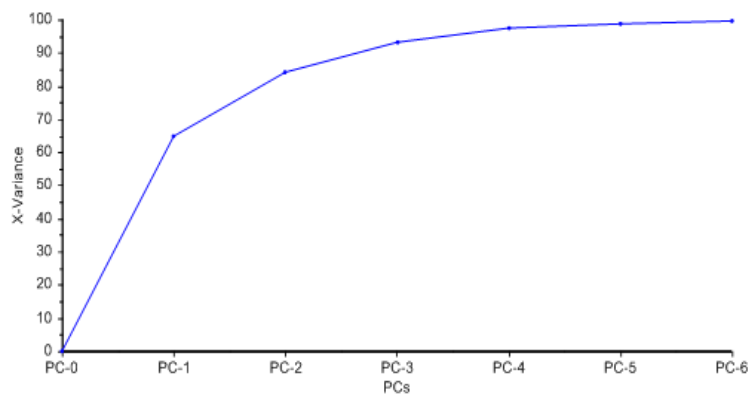


Fig. 5. Explained variance of each PC.

Mean and standard deviations were used for PCA pre-treatment. Prior to applying the principal components analysis to the data matrix, data sets were examined to visualize the weight and influence of each measured variable on the chemometric model by applying the descriptive statistics (mean, standard deviation, median, quintiles) as shown in Figs. 3 and 4.

From the original data of the raw results obtained, variation between all physicochemical parameters was observed. The descriptive statistics show a large difference in the statistical data of all variables studied in the 8 sampling stations along the river. In a first step, we compared the different variances of the 21 variables with each other. It is evident from this dataset that the variables differ considerably and show non-homogeneous dispersions. The unit of measurement and/or the measuring range changes according to the nature of the parameter.

Figs. 3 and 4 show that some variables (physicochemical parameters) like electrical conductivity, turbidity, chlorides and sulfates, are important values, therefore they will have a major influence on the chemometric model compared to other parameters. Consequently, pretreatment is necessary, which is performed by subtracting the corresponding column mean from each data element and dividing it by the corresponding column standard deviation. As a result, the variables have the unitary variances (scale) and consequently, they will have the same importance in the application and construction of the principal components analysis model.

#### Chemometric analysis

Like all chemometric tools, PCA treats all types of datasets, that is, tables containing many individuals and few variables (or *vice versa*), or many individuals and many variables. Chemometric data analysis methods such as PCA

provide powerful tools for the analysis and interpretation of large multivariate data of physicochemical analysis parameters. This approach can represent the total variability of the original data in a minimum number of principal components. Principal components analysis is a multivariate analysis method that is being increasingly utilized to visualize data because a large amount of information can be compared fluently in simple graphical form, which is very difficult to do using number tables or univariate statistics [37]. PCA is an exploratory data analysis that is primarily utilized to establish global relationships between data. Occasionally, more complex questions need to be answered. The objective of PCA is to determine underlying information from multivariate raw data.

The average values of each parameter at each station were grouped in a mathematical data matrix composed of  $21 \times 8$  elements. A total of 8 rows represent water samples formed by 21 variables. PCA was applied using The Unscrambler software. The principal components were obtained by the linear combination of the initial variables which are more or less correlated to them. These components, therefore, define a space of reduced dimension in which are projected the initial variables accounting for the maximum information.

According to Fig. 5, the PCA model obtained from the pretreated dataset is defined by 4 PCs with a total variance of 96% but the results can be interpreted by the first two PCs with a variance of 84%. The first two PCs were extracted and utilized in two-dimensional bivariate plots. The first principal component covers as much of the maximum variation in the dataset as possible. The second principal component is orthogonal to the first and usually covers remaining variation as possible but less than the first component, and so on [38]. Because the first and second principal components generally cover a big part of the total



variance, a regrouping of samples, according to the effect of all variables within the two-dimensional plane, is possible by plotting against each of the first two column vectors (the first two principal components: PC1 and PC2) of data matrix [39].

The loadings of variables, scores of sampling stations and bi-plot of the sampling stations and variables have been plotted. The analysis of the sampling locations distribution in the plan formed by the principal components PC1 and PC2 allows highlighting the similarities and dissimilarities existing between the sites according to their physicochemical composition. To investigate the eight sampling points along the Oum Er Rbia river, the scores for sampling sites computed and represented in the graph shown in Fig.6 indicate and identify the links between all studied sampling stations. The scores plot represents the dispersion of the different samples in the space formed by the first two principal components PC1 and PC2 to better understanding the distribution of locations and relationships between sampling stations. The distance between the samples indicates their similarity or dissimilarity. The first principal component represented 65% of information

whereas the second explained only 19% with a total variance of 84% in the dataset. From the scores plot (Fig. 6) and Table 2, it was observed that the samples S1, S5, S6 and S8 are well expressed by the first principal component, while the samples S2, S3, S4 and S7 are well represented by the second principal component in the PCA model obtained from the data matrix. According to the scores plot, we observed that the samples S2, S6 and S8 are close to each other which means that the three sampling stations have similar characteristics. The same explanation was applied for the group formed by the following samples, S3, S4, S5, and S7. The scores plot is used to show the relation between sampling locations based on their nearness or similarity. Sampling site S1 has different properties compared to the other sites (far from other samples in the scores plot diagram). This technique showed easily the sampling sites that have the same physicochemical characteristics and the same degree of pollution along the river. Several researchers have used the scores plot of principal components to elucidate the pattern of the distribution of sampling sites [40-42].

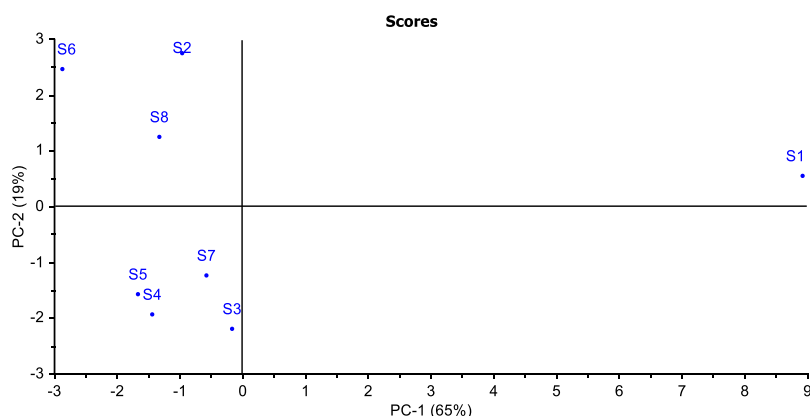


Fig. 6. Scores plot of the river water samples in each sampling station.

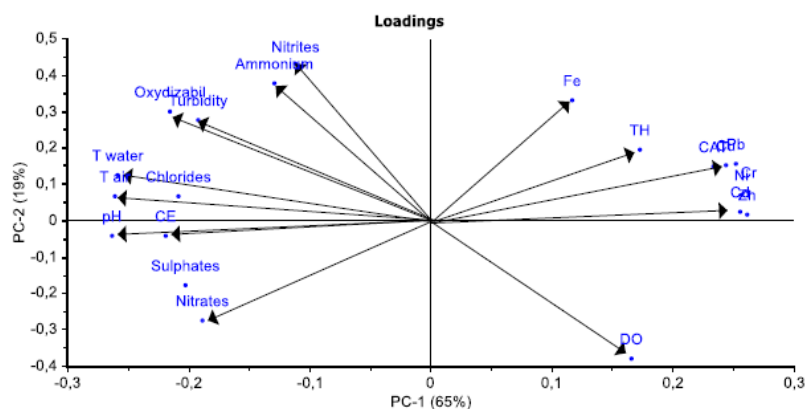


Fig. 7. Variables PCA loadings plot.

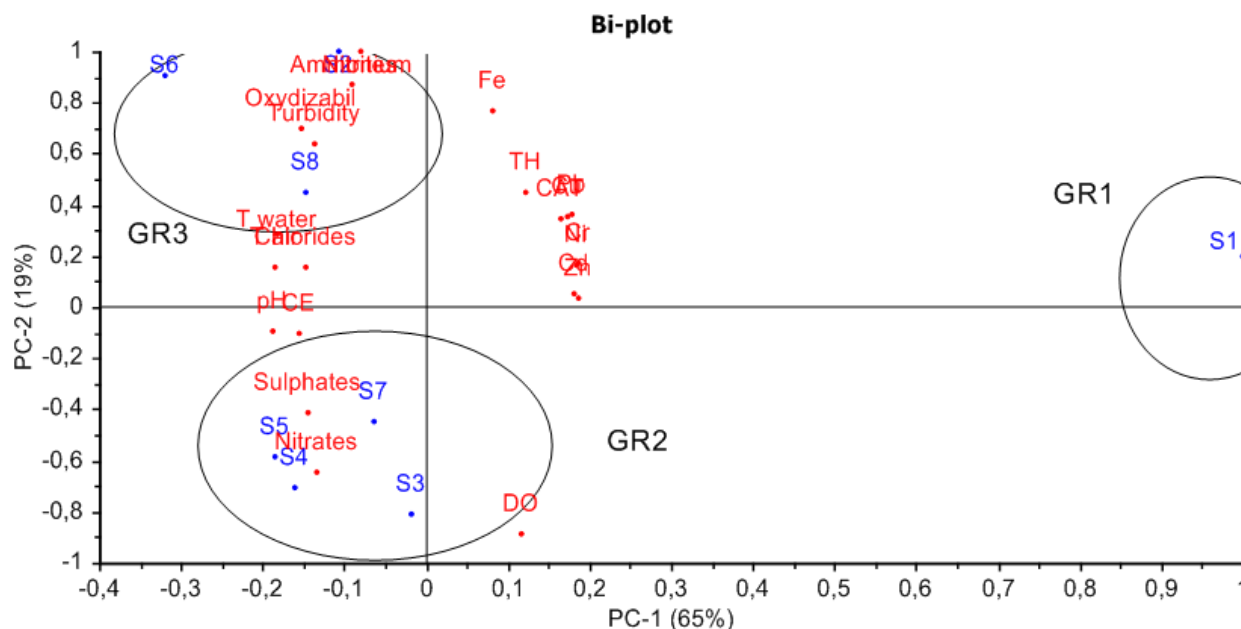
In this work, a bivariate correlation that is a statistical tool was used to understand the relationship between all physicochemical parameters investigated.

Fig. 7 shows PCA loadings plot which describes the distribution of the variables in the space formed by the first two principal components explaining 84% of the variance in the original experimental data. From the loadings plot (Fig. 7) and Table 3, all variables possessed higher loading and are well distributed on PC1–PC2 subspace, with no one being predominant, they are all very important and explain a lot of weight that helps to describe the dataset variation at the PCA model developed. PC1 (65% of the total variance) is mainly contributed and characterized by loadings of the variables: temperature of air, temperature of water, CE, Ni, Zn Pb, Cd, Cr, Cu, sulfates, CAT, chlorides and pH, whereas the variables: DO, TH, oxidizability, Fe, nitrites, nitrates, turbidity and ammonium are more important in the second principal component PC2 (19% of the variance). The study of the bivariate linear correlation between the investigated physical and chemical parameters gives information on the associations and relations between them. The correlation was calculated after mean centering and standardization of the raw data from the obtained results. The overall correlation between the

different physicochemical parameters is shown in Table 4 and the loadings plot (Fig. 7).

The analysis of the variables showed both positive and negative correlations between the different parameters studied. The positive correlation between the air temperature and the water temperature and the positive correlation between pH and temperature indicates that in most natural waters, pH is usually between 6 and 8.5, whereas in warm water it is between 5 and 9.

A positive correlation was observed between the EC and the chlorides which is due to the mineral character that could be related to the substrate. In addition, a high conductivity translates either abnormal pH, most often high salinity, which was observed along the river. Another positive correlation was observed between oxidizability and turbidity, because of the presence of various organic particles, clay of colloids, plankton, etc. Turbidity can be favored by rainfall. Positive correlations in river water samples of the study area are clearly present between HT and CAT; ammoniacal nitrogen and nitrites; between all heavy metals, etc. The significant positive correlation found between all heavy metals studied suggests that these elements are derived from a common source, mainly from parent rock and carbonate minerals [43].



**Fig. 8.** Bi-plot of scores and loadings on the plane defined by the first two principal components (PC1-PC2). There was a strong positive correlation between the following pairs of physicochemical parameters: temperature of air/temperature of water (0.972), oxidizability/turbidity (0.854), ammonium/nitrites (0.855), chlorides/CE (0.941), TH/CAT (0.851), temperature of water/pH (0.896) and between all heavy metals (0.256 to 0.989). Negative correlations were observed for the following pairs of parameters: DO/temperature of water (-0.800), oxidizability/DO (-0.950), ammonium/DO (-0.909), nitrates/DO (-0.916), temperature of water/heavy metals (-0.321 to 0.874).

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**Table 4.** Matrix of correlation between the variables on all stations studied.

	T water	T air	pH	CE	Turbidity	CAT	TH	DO	Chlorides	Nitrites	Nitrates	Ammonium	Sulfates	Oxidizability	Fe	Cu	Cd	Pb	Ni	Zn	Cr
T water	1	0.972**	0.896**	0.664	0.863**	-0.802*	-0.582	-0.800*	0.692	0.592	0.502	0.675	0.581	0.897**	-0.321	-0.817*	-0.837**	-0.828*	-0.857**	-0.880**	-0.874**
T air	0.972**	1	0.946**	0.691	0.823*	-0.782*	-0.577	-0.688	0.721*	0.454	0.643	0.537	0.558	0.819*	-0.293	-0.854**	-0.891**	-0.855**	-0.910**	-0.932**	-0.929**
pH	0.896**	0.946**	1	.833*	0.637	-0.821*	-0.614	-0.513	0.832*	0.296	0.732*	0.312	0.710*	0.703	-0.388	-0.859**	-0.952**	-0.899**	-0.949**	-0.963**	-0.983**
CE	0.664	0.691	0.833*	1	0.282	-0.586	-0.234	-0.380	0.941**	0.318	0.567	0.120	0.856**	0.621	-0.223	-0.591	-0.887**	-0.741*	-0.870**	-0.816*	-0.812*
Turbidity	0.863**	0.823*	0.637	0.282	1	-0.510	-0.461	-0.871**	0.412	0.701	0.258	0.857**	0.122	0.854**	-0.009	-0.574	-0.587	-0.495	-0.531	-0.672	-0.619
CAT	-0.802*	-0.782*	-0.821*	-0.586	-0.510	1	0.851**	0.369	-0.479	-0.145	-0.640	-0.302	-0.775*	-0.508	0.813*	0.914**	0.703	0.931**	0.794*	0.747*	0.827*
TH	-0.582	-0.577	-0.614	-0.234	-0.461	0.851**	1	0.161	-0.148	0.095	-0.602	-0.242	-0.446	-0.244	0.791*	0.818*	0.490	0.724*	0.494	0.580	0.665
DO	-0.800*	-0.688	-0.513	-0.380	-0.871**	0.369	0.161	1	-0.519	-0.916**	0.065	-0.909**	-0.200	0.950**	-0.135	0.342	0.487	0.357	0.459	0.523	0.456
Chlorides	0.692	0.721*	0.832*	0.941**	0.412	-0.479	-0.148	-0.519	1	0.451	0.419	0.199	0.669	0.700	-0.012	-0.465	-0.847**	-0.605	-0.798*	-0.787*	-0.767*
Nitrites	0.592	0.454	0.296	0.318	0.701	-0.145	0.095	-0.916**	0.451	1	-0.253	0.855**	0.145	0.863**	0.306	-0.075	-0.336	-0.126	-0.258	-0.337	-0.235
Nitrates	0.502	0.643	0.732*	0.567	0.258	-0.640	-0.602	0.065	0.419	-0.253	1	-0.094	0.570	0.196	-0.477	-0.837**	-0.772*	-0.806*	-0.769*	-0.785*	-0.813*
Ammonium	0.675	0.537	0.312	0.120	0.857**	-0.302	-0.242	-0.909**	0.199	0.855**	-0.094	1	0.056	0.831*	0.084	-0.319	-0.327	-0.262	-0.266	-0.395	-0.314
Sulfates	0.581	0.558	0.710*	0.856**	0.122	-0.775*	-0.446	-0.200	0.669	0.145	0.570	0.056	1	0.436	-0.639	-0.684	-0.725*	-0.828*	-0.792*	-0.672	-0.720*
Oxidizability	0.897**	0.819*	0.703	0.621	0.854**	-0.508	-0.244	-0.950**	0.700	0.863**	0.196	0.831*	0.436	1	0.033	-0.523	-0.720*	-0.564	-0.679	-0.735*	-0.668
Fe	-0.321	-0.293	-0.388	-0.223	-0.009	0.813*	0.791*	-0.135	-0.012	0.306	-0.477	0.084	-0.639	0.033	1	0.670	0.256	0.674	0.407	0.295	0.427
Cu	-0.817*	-0.854**	-0.859**	-0.591	-0.574	0.914**	0.818*	0.342	-0.465	-0.075	-0.837**	-0.319	-0.684	-0.523	0.670	1	0.814*	0.969**	0.871**	0.865**	0.911**
Cd	-0.837**	-0.891**	-0.952**	-0.887**	-0.587	0.703	0.490	0.487	-0.847**	-0.336	-0.772*	-0.327	-0.725*	-0.720*	0.256	0.814*	1	0.860**	0.942**	0.989**	0.969**
Pb	-0.828*	-0.855**	-0.899**	-0.741*	-0.495	0.931**	0.724*	0.357	-0.605	-0.126	-0.806*	-0.262	-0.828*	-0.564	0.674	0.969**	0.860**	1	0.939**	0.880**	0.930**
Ni	-0.857**	-0.910**	-0.949**	-0.870**	-0.531	0.794*	0.494	0.459	-0.798*	-0.258	-0.769*	-0.266	-0.792*	-0.679	0.407	0.871**	0.942**	0.939**	1	0.934**	0.950**
Zn	-0.880**	-0.932**	-0.963**	-0.816*	-0.672	0.747*	0.580	0.523	-0.787*	-0.337	-0.785*	-0.395	-0.672	-0.735*	0.295	0.865**	0.989**	0.880**	0.934**	1	0.985**
Cr	-0.874**	-0.929**	-0.983**	-0.812*	-0.619	0.827*	0.665	0.456	-0.767*	-0.235	-0.813*	-0.314	-0.720*	-0.668	0.427	0.911**	0.969**	0.930**	0.950**	0.985**	1

\*\*Correlation is significant at the 0.01 level (2-tailed)

\*Correlation is significant at the 0.05 level (2-tailed)

A high negative correlation is observed between water temperature and DO. DO concentrations have an inverse relationship with stream temperatures so that as temperatures increase, less DO is contained in the water [44, 45]. The concentration of DO in water is generally related to the effects of several factors such as temperature, salinity and eutrophication. Another negative correlation is marked between oxidizability and DO, it is due to the consumption of dissolved oxygen by microorganisms in order to degrade the organic matter (high oxidizability). Nitrite is also negatively correlated to DO. The loadings plot as a step in this chemometric analysis is an efficient method that fluently shows the relationship between all physicochemical parameters studied.

The distribution of samples on the bi-plot graph shows that it is possible to isolate different groups of samples more easily. The loadings of variables and scores of sampling stations were plotted and the obtained results are presented in Fig. 8. The bi-plot graph shows the interpretation of the relation between the samples and the behavior of the variables in the PCs space formed by the first two principal components. It was employed in this study to obtain groups of sampling stations based on the similarity of the water physicochemical composition and the water quality characteristics. The Oum Er Rbia water river reveals the presence of three groups (GR1, GR2 and GR3) of water. The first group (GR1) included the station S1, situated in the upstream of the river (the sources). It is characterized by water with low temperature; the pollutant parameters are low compared to the other groups, highly loaded in some parameters such as total hardness, CAT and heavy metals; this site is characterized by good quality water compared to the other stations. The second group of river water (GR2) essentially includes the stations S3, S4, S5 and S7, expressed by the two PCs and situated on the upstream and downstream (S3, S4) of Zawiat Cheikh, and upstream of Kasbat Tadla and Dar Oulad Zidouh cities, respectively. This group is characterized by the abundance of DO, nitrates, and sulfates, with significant chlorides and EC values comparable to those of the first group. The stations constituting the second group are affected by agricultural activities practiced in the study area and have moderate pollution. The third group (GR3) is constituted by the stations (S2, S6 and S8) located on the downstream of Khenifra, Kasbat Tadla and Dar Oulad Zidouh cities. This group indicated the presence of pollution indices which are: oxidizability, turbidity, nitrites, ammonium, and chlorides because of the discharging of wastewater from neighboring cities directly into the

river without any prior treatment. This group is characterized by higher values of temperature and lower water quality than the other two groups; the group includes stations having the highest pollution sources. This group corresponds to the zones with a higher urban influence.

## CONCLUSIONS

In this work, the surface water samples collected at different locations along the Oum Er Rbia river were analyzed for various physical and chemical parameters in three sampling times from 2016 to 2017. The application of a chemometric tool such as principal component analysis based on the analysis of data obtained offered the possibility to simplify the aquatic environment results analysis and interpretation. The principal component analysis model reduced the number of variables in the first two PCs with a total variance of 84% and showed the similarity between the sampling locations according to their water characteristics, the possible correlations between the variables studied. The chemometric technique applied to data analysis showed and successfully suggested the existence of three clearly separated groups of water: GR1 (S1), GR2 (S3, S4, S5 and S7) and GR3 (S2, S6 and S8). The anthropogenic activities mainly affecting the water quality along the river are urban, in particular at locations S2, S6 and S8, and agricultural activities, especially in all other zones except S1. This study demonstrated that the integration of chemometric approach can be used as a suitable and effective tool, while saving time, simplifying the study, to reduce the cost of monitoring river water and classify the locations according to the pollution state of each sampling station.

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