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Physico-chemical typology of the quality of waters of the Oued Moulouya river and its tributary Oued Sebra *(Lower Moulouya Morocco North Oriental)*

A. Brahimi*, A. Chafi and M. Mouzouri

Laboratory of Water Sciences, Environment and Ecology, Department of Biology, Faculty of Science, University Mohammed 1er, Oujda, Morocco

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ABSTRACT

This research is to evaluate the physicochemical quality of surface waters Oued Moulouya relationship with his tributary Oued Sebra. These waters are threatened by the extent of urban and industrial discharges from the city of Zaio. Water samples were taken from five stations on the lower part of the Moulouya and a station on the left bank tributary of the Oued Sebra. This study focused on the distinction of physic-chemical water parameters (temperature, pH, CE, MES, turbidity, O_2, DBO_5, DCO, PO_4^{3-} , Pt, NH_4 +, NTK). In order to establish a relationship between these parameters and to better assess the impact of human activities on the quality of surface water, a statistical analysis PCA (Principal Component Analysis) was applied to all of these parameters in the wet season and dry season. The Explanatory Analysis by Principal Component Analysis (PCA) of data physicochemical, allowed us to identify correlations between the different parameters and differentiate a typology of water quality in the study area. The results show an alarming situation of the quality of the waters, especially of the Oued Sebra, that receives industrial waste from the city of Zaio. We are witnessing an increase in levels of DBO_5, DCO, MES ... NTK, and a decrease in dissolved oxygen levels, especially in the summer period (period of sugar activity). The explanatory analysis (PCA) showed an inter-station variability and corroborated the results of the descriptive analysis.

Keywords: Lower Moulouya, Oued Sebra, physic-chemical parameters, PCA, industrial pollution.

INTRODUCTION

The growing population in the world and the reproduced type of development will inevitably lead to an explosion in the consumption of water, accompanied by a degradation of its quality [1].Anthropogenic activities, mobilizing natural resources, generate solid waste, liquid waste and gaseous effluents. Thus, they cause transfers of pollutants to the natural environment; therefore, they may affect the ecological balance of ecosystems [2]. These pressures on water resources are accompanied from the one hand by the increasing degradation and the severe impact on their quality [3].They reduce the potential of water resources of good quality [4]. These renewable water resources will decrease by 20% by 2050, and water availability per inhabitant will decrease to the half [1].

Industrial activity causes more and more important degradation to the quality of ecosystems. This degradation is caused by a massive and uncontrolled pollution, either by natural organic matters or by industrial synthetic products. This pollution affects the ecosystem compartments (water, sediment, etc.). Indeed, the continuous release of chemicals in aquatic ecosystems can cause changes in the structure and functioning of the biotic community, in other words on the biotic integrity [5]. Depending on their bioavailability, pollutants which are in the effluent cause many adverse effects on the biodiversity of aquatic environments [6].

The impact of industrial discharges into the aquatic environment is mostly local in nature and depends on the flow of the water, instead of discharging to sensitive areas. The local industry is a big consumer of natural resources and is one of the main sources of environmental pollution. It puts pressure on water resources (taken massively and directly from the groundwater and rivers), on the land or on the quarry materials [7]. Food industries induce significant discharges of organic matters that are causing the proliferation of bacteria and other organisms, resulting in a decrease and in loss of aquatic oxygen and species extinction that needs significant oxygen.

In Morocco, pollution of water resources by industrial effluents is increasingly important. The total volume of waste water discharged by the Moroccan industries was estimated in 1993 at about 965 million m^3. These releases are usually organic and toxic. Three types of industries pose serious problems for producers of drinking water, namely: oil mills, sugar mills and tanneries. Their impact on water resources in Morocco was strongly felt in recent years and the production of drinking water from water point’s located downstream discharges of these industries has been seriously compromised [8]. The main industries that are causing degradation of water resources for the production of drinking water are among other “sugar refineries”, their wastewaters are rejected at a temperature between 40 and 57 ° C. They are heavily loaded with organic matters. The rejected stream pollution varies from 0.2 to 6.3 kg DBO_5 /t of treated cane and 0.57 à 2.07 kg DBO_5 /t of treated cane. Both Basins of Sebou and Oum Er-Rbia are most affected by this pollution in Morocco [8]. With an area of 54.500 km ² watershed, Moulouya is considered as the largest watershed in Morocco and also as the largest non Saharan river of North Africa. Its climate is semiarid Mediterranean kind with a marked irregularity of rainfall. Basin Moulouya experiences a situation of structural water deficit. The development of urban and industrial activities, generating wastewater and solid waste, as well as the intensive use of fertilizers and pesticides in agriculture , have inevitably led to a deterioration of the quality of water resources[9].

The North-Eastern Morocco is mainly the lower basin Moulouya and extends over a set of small Mediterranean basins adjacent to it: Oued Kert west and Oued kiss the east to the Algerian-Moroccan borders. The downstream part of this river receives some tributaries of the two banks; the main one is Oued Cherraâ that drains the massive Bni Snassen, followed by Oued Sebra which drains the plain Zebra [10]. The Oriental sugar Refinery is located in the municipality of Zaio which is under Nador province, about thirty kilometers south-west of this city (Figure 1). It is part of the agricultural development of the irrigation of the Lower Moulouya, and was located on the edge of the irrigated area in circle of Zaio to reduce distances to the transport of the used materials.

According to the latest census of 2004, the total population of Zaio is currently 29 851 inhabitants in 6067 households. Population growth of this center is 1.4% between 1994 and 2004. The drinking water is supplied from surface water of Moulouya sent from Machraâ Hammadi dam, through the irrigation canal Sebra[11].Zaio City knows a multiple daily aggressions caused by industrial pollution. Industrial and domestic wastewater is discharged directly into receiving aquatic areas (case of Oued Sebra) in a precarious way and without any prior treatment. In a few kilometers Oued Sebra is joined to Oued Moulouya.

To contribute to the assessment of water quality on our environment and to consider reliable and sustainable solutions, we have chosen to study the site of the lower part of the Oued Moulouya and its tributary Oued Sebra; this is due to several reasons: At the downstream of the estuary, it borders several human settlements and industrial unit "Sugar Refinery Oriental." This plant's main activity is the beet processing and treatment. Sugar activity period typically takes 90 days, from May to August. Despite the short duration of its activity, this unit handles about 240 000 ton of beets per year, producing about 73000 ton per year, with a rate of production of (25% pulp, 5% of discharges and 40% of water, 30% of the finished product and by-product for 100 tons of beets) [12]. The studied area receives domestic and industrial discharges. The risk of the contamination of surface water and groundwater that feeds the entire region is potentially drinking water. Thus, there is a need to assess the physic-chemical characteristics of the Oued Moulouya and its tributary Oued Sebra waters.

Moulouya river has attracted the interest of many researches, as the study of the quality of these waters [13-16] also study the longitudinal distribution of macro invertebrates [17- 18].

EXPERIMENTAL SECTION

1. Study area and sampling stations:
The basin of the Moulouya is about 450 km length. Take these sources to about 1800 m in the junction area of the High Atlas and the Middle Atlas, the general direction is South-West North-East[17].Oued Sebra is temporary tributary of the left bank of Oued Moulouya ,in the downstream Machraâ Hammadi dam. Its general direction is West East and joined the Moulouya to Oulad ben Quadour Issa, downstream from the town of Zaio (Figure 1). It is

part of glaze sector Moulouyeens [19], limited to the North -west by the small chain Kebdana, at the east end by Keker chain, and in both South and South-West by the chain of Bni Snassen.

Given the overall objective of this study, we selected six stations including five on the lower reaches of the Oued Moulouya, and its tributary Oued Sebra (Figure 1). These were chosen based on their accessibility and proximity to potential sources of pollution.

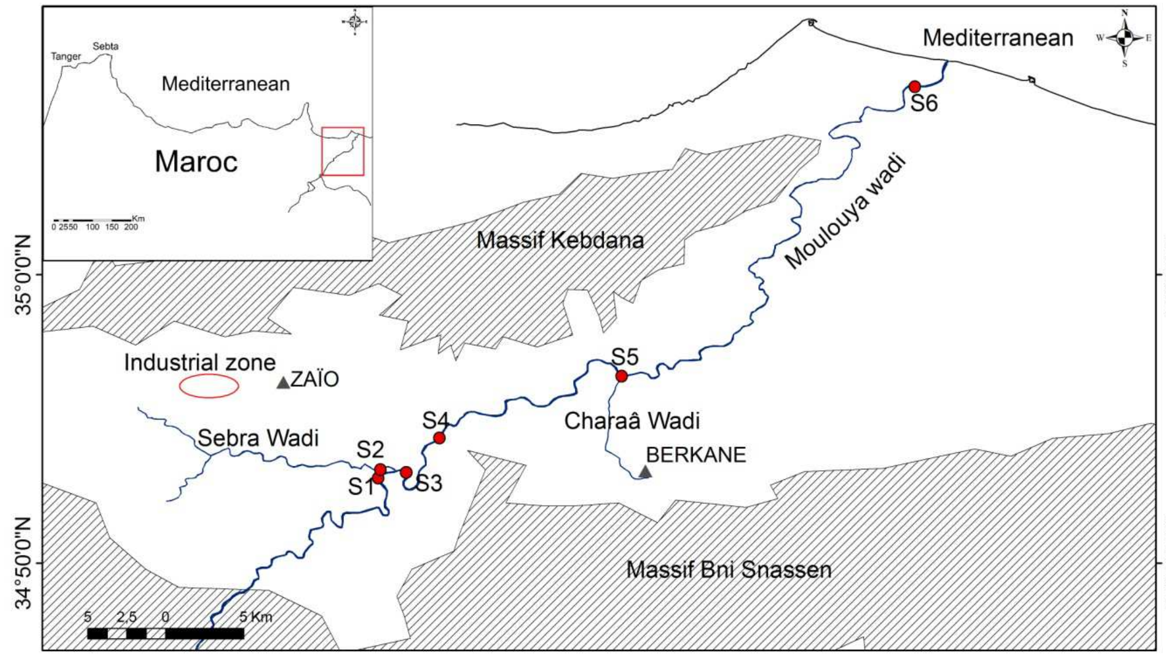

Figure1: Localization map of the study area and location of sampling stations area

• **Station1**: Chosen as reference station (control), located away from human disturbances, downstream the dam of Machraâ Hammadi, and upstream of the confluence of Oued Moulouya and Oued Sebra. It is located about 55 km from the mouth of the Moulouya River. The width of the river is about 5 to 7m, and its maximum depth is estimated to 160cm.

• **Station 2**: is located downstream of Oued Sebra, it was chosen to estimate the impact of inflows Release of the industrial area which is located in the south of the town of Zaio on Oued Sebra, its distance from the industrial unit is 10 km, and from S1 about 2 km. the river is very dark, troubling, and with a bad smell. Reddish sediment of the organic matter and proliferation of filamentous algae on the left bank of the river was observed.

• **Station 3**: is located near the confluence of Wadi Sebra with Oued Moulouya. This station is 1.5 km far from the two stations 1 and 2. It is chosen to evaluate the impact of inflows of Oued Sebra on Oued Moulouya. At this station we notice the mixture of clear waters of Oued Moulouya and those very dark of Oued Sebra.

• **Station 4**: is located near the bridge Hassan II, at "Machraâ Sâf-Sâf", 5 km from S3. It is located in an area for agricultural vocation, with very dense riparian vegetation consisting mainly of Tamarix and Laurel, whereas the bottom is made of the clayey sand. The watercourse is very wide.

• **Station 5**: located in the downstream of the meeting of the Oued Charaâ with Oued Moulouya at a distance of 13 Km from S4. It is chosen to estimate the impact of discharges from Berkane city, drained by Wadi Charaâ. The width of the watercourses is from 5 to 6m, the waters are agitated and the flow is important. The riparian vegetation is made of Tamarix.

• **Station 6**: is located at the bridge of the Mediterranean ring road, 3km from the mouth of the Moulouya River. It was chosen to assess the global burden of pollution drained by Oued Moulouya to the marine area.

EXPERIMENTAL SECTION

The field sampling was carried out during a dry period (July) and during floods (December) during a sugar activity period year (2011). The main objective of this study is to assess the potential contamination of water examined during industrial activity.

Twelve parameters were measured; each period is taken in polyethylene bottles water volume for physicochemical analysis. Transport to the laboratory, flasks sample was taken in a cooler at low temperature (4 ° C). At each station, three samples were taken in order to determine the average results for each parameter. At the same time the collection of water samples, some physic-chemical water measurements have been performed in situ: water temperature, electrical conductivity (CE), pH, dissolved oxygen (O_2). The remaining assessments were made by volumetric dosing, colorimetric or spectroscopic assays, according to the proposed analytical methods and techniques cited by Rowdier [20] and according to the standards of Afnor [21].

2. Statistical analysis

To better assess the impact of wastewater on water quality of the Moulouya river and its tributary Oued Sebra, and in order to visualize and analyze existing between the different variables through their structuring and guidance correlations and to identify the main factors responsible for the water quality of the surveyed environment, we statistically treated all data by Principal Component Analysis (PCA). This theory has been widely applied to various fields. PCA had been applied to physicochemical characteristics of inland waters by several authors [22; 23; 24]. It transforms complex variables into some principal components by using dimensionality reduction technique, of which principal components are orthogonal and reflect main information of original variables [25].

The principal component analysis is a method based on the study of correlations between samples and or variables [26; 27].Multivariate statistical treatment is widely used to characterize and evaluate the quality of surface water and freshwater, it is useful to testify spatiotemporal variations caused by seasonal natural and human factors [28-34]. It is a widely used methodology for interpreting hydro chemical data [35-42]. Principal component analysis is a kind of statistical analysis method that converts original multiple variables into minor few comprehensive indicators [43].This method has also found associations between variables, thus reducing the dimensions of the table data. This is accomplished by the diagonalization of the correlation matrix of data that transform a large number of variables to a smaller number of underlying factors (principal components (PCs) without losing much information [44; 45; 46].

PCA was performed on a data matrix consisting of 6 samples (6 stations x 1 wet season) and 6 samples (6 stations x 1 dry season). These results of this analysis are shown in Table 1, 2, 3, 4 and Figure 2 and 3.

RESULTS AND DISCUSSION

2.1. Description of data matrix:

This analysis was performed on a data table of six individuals (stations) and twelve variables: water temperature (T ° water), pH, Turbidity (Tub), conductivity (CE), Suspended Solids(MES), ammonia nitrogen (NH_4^+), kjeldahl Nitrogen (NTK), orthophosphates (PO_4^{3-}), Total Phosphorus (PT), chemical oxygen demand (DCO), biological oxygen demand (DBO_5), dissolved oxygen (O_2).

Table 1: Dates and codes of samples taken.

Sampling Dates	July 2011	December 2011
Station 1	J1	D1
Station 2	J2	D2
Station 3	J3	D3
Station 4	J4	D4
Station 5	J5	D5
Station 6	J6	D6

Table 2: Matrix data grouping estimated 12 physicochemical variables studied in 12 Samples

Record number	T°	pH	CE	Tub	NH4+	NTK	PO4	PT	O2	DBO5	DCO	MES
J1	28	7.5	1964	20	0.01	0.12	0.01	0.05	9.2	0.8	14	13.5
J2	35	6.5	8315	225	5.65	30.4	5.65	17.5	0.0	3650	6182	1350
J3	31	9.5	3300	84	3.95	12.56	2.18	10.53	1.2	280	658	548
J4	29	8.2	2800	57	0.15	1.53	0.18	1.65	1.5	35	76	165
J5	27.5	7.95	3275	76	4.35	6.12	1.96	0.95	1.76	56	127	273
J6	28.5	8	5320	36	0.13	1.86	0.15	0.43	1.78	42	90	145
D1	14	7	1290	45	0.01	0.11	0.01	0.02	9.5	2	12	35
D2	13	8	3450	36	0.05	0.28	3.45	13.6	6.5	70	156	95
D3	13.5	7.5	2075	55	0.06	0.31	1.2	8.9	8.5	41	86	165
D4	13	7.4	2420	24	0.029	0.42	0.09	1.02	8.64	15	33	243
D5	12.5	7.8	2950	46	2.54	3.54	1.66	0.7	6.45	45	110	277
D6	13.5	7.9	3270	28	1.83	2.56	0.1	0.5	8.75	25	68	125

The codes of the six Stations during two periods of studies (July and December 2011) are illustrated in Table 1. For the twelve physicochemical parameters evaluated, all the results are illustrated in Table 2. The same table also contains the matrix data statistically processed by the PCA. It is a matrix of data consisting of a double entry table"1 variable time 12 samples."

The codes of twelve physicochemical parameters and the numbers of samples taken during one year used in PCA are reported in Table 2.

2.2. Choice of Eigen values (selectable number of factors):
The Eigen value analysis is used to choose the number of factors, and therefore the number of axis to be considered in the analysis in order to minimize the loss of information.
Table 3 shows the variances of the different factors.

Table 3. Eigen values (contributions and percentage)

	F1	F2
Eigen values	**8.31**	**1.70**
Variance (%)	**69.28**	**14.19**
Cumulative (%)	**69.28**	**83.47**

The analysis of results shows that the majority of information is explained by the first two factorial axes (Tables 3, 4 and Figures 2, 3). The contributions of different parameters in the expression of the first two factorial axes F1 and F2 are respectively 69.28% and 14.19 % or a total of 83.47 % of the information explained. The maximum of the total inertia is accumulated by the plan formed by the factorial axis F1 × F2.Thus, the significance of physicochemical factor axis F1 and F2 is necessary.

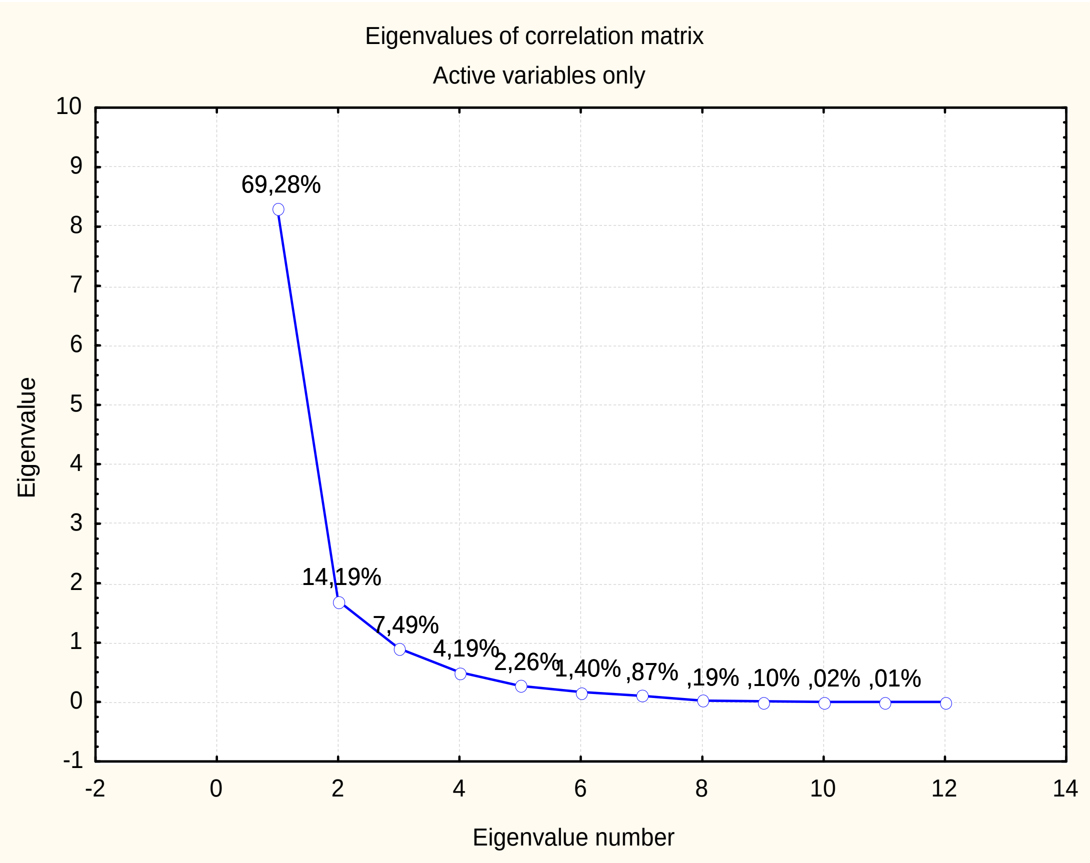

Figure 2: Eigen values of correlation matrix

3.3. Analysis of the distribution physic-chemical parameters in the plan F1xF2:
The matrix shows a high correlation between T° and CE, Turb, NH_4^+, NTK, DBO_5, DCO, MES. With the exception of the dissolved oxygen, all other parameters are well correlated. But the pH is negatively correlated with all other elements and positively with NH_4^+ (Table 4). This is well illustrated by projecting the variables on the factorial plan F1xF2 (Figure 3).

Table 4: correlation matrix of physic-chemical parameters

Variable	Matrix correlations of variables											
	T °C	pH	CE	Turb	NH4+	NTK	PO4	PT	O2	DBO5	DCO	MES
T °C	**1,000**											
pH	0,159	**1,000**										
CE	0,574	-0,239	**1,000**									
Turb	0,583	-0,328	0,803	**1,000**								
NH4+	0,508	0,049	0,619	0,778	**1,000**							
NTK	0,616	-0,208	0,833	0,965	0,846	**1,000**						
PO4	0,322	-0,176	0,722	0,825	0,698	0,808	**1,000**					
PT	0,246	-0,054	0,582	0,700	0,435	0,675	0,881	**1,000**				
O2	-0,805	-0,304	-0,692	-0,637	-0,627	-0,641	-0,511	-0,379	**1,000**			
DBO5	0,502	-0,495	0,850	0,950	0,655	0,936	0,791	0,680	-0,483	**1,000**		
DCO	0,511	-0,473	0,851	0,954	0,667	0,944	0,797	0,690	-0,494	1,000	**1,000**	
MES	0,545	-0,253	0,831	0,961	0,800	0,984	0,811	0,694	-0,614	0,943	0,950	**1,000**

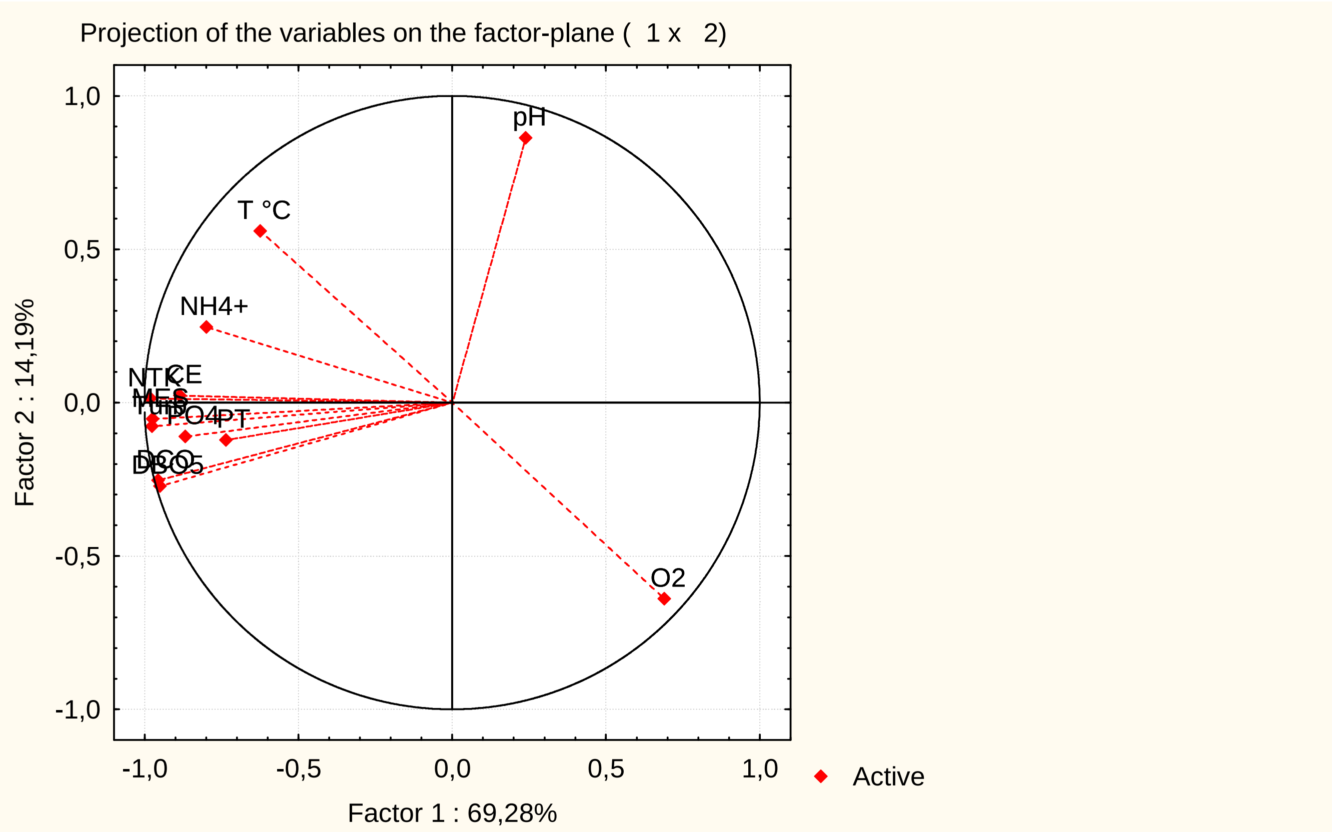

Figure 3: Projection of physic-chemical parameters in the factorial F1xF2

The correlation circle formed by the axis F1 and F2 (Fig. 3) shows 83.47% of the total information, indicated the existence of two kinds of water according to axis F1 69.28%. From the one hand, in the positive part of the F1axis, the well-oxygenated water and less charged slightly mineralized organic material, and on the other hand, in its negative side characterized in turbid and strongly mineralized waters presenting a very high conductivity, loaded into ammonia nitrogen and relatively high temperatures, associated with variables such as DBO_5, DCO and PO_4^{3-}, PT which are indicators of domestic pollution. This axis F1 defines a gradient of the mineralization from right to left. The Position of dissolved oxygen on the positive part of the component F1 could be justified by the fact that the waters of Moulouya are more oxygenated in the upstream part (D1 and J1), away from the impact of urban and industrial effluents, and in the downstream part during the wet season located in the downstream of the discharge points (D2, D3, D4, D5, D6) (Figure 4). This is in agreement with previous studies, suggesting that cold water contains a large amount of dissolved oxygen than warm water [47].

The axis F 2 (14.19%) is associated with variables such as suspended solids (MES) and turbidity. These two parameters evolve at the same time. This axis defines pollution by natural organically and mineral particles carried by the river during the flood period. The transport by runoff, of soil particles towards rivers causes an increase in suspended solids and turbidity. An increase in suspended solids is usually accompanied by an increase in turbidity [47].

Parameters: DBO_5, DCO, PO_4^{3-} and PT are negatively correlated with F2. Therefore, this pole includes the majority of parameters that determine the degree of organic pollution. This axis defines a gradient of organic pollution from the pole positive to the negative pole.

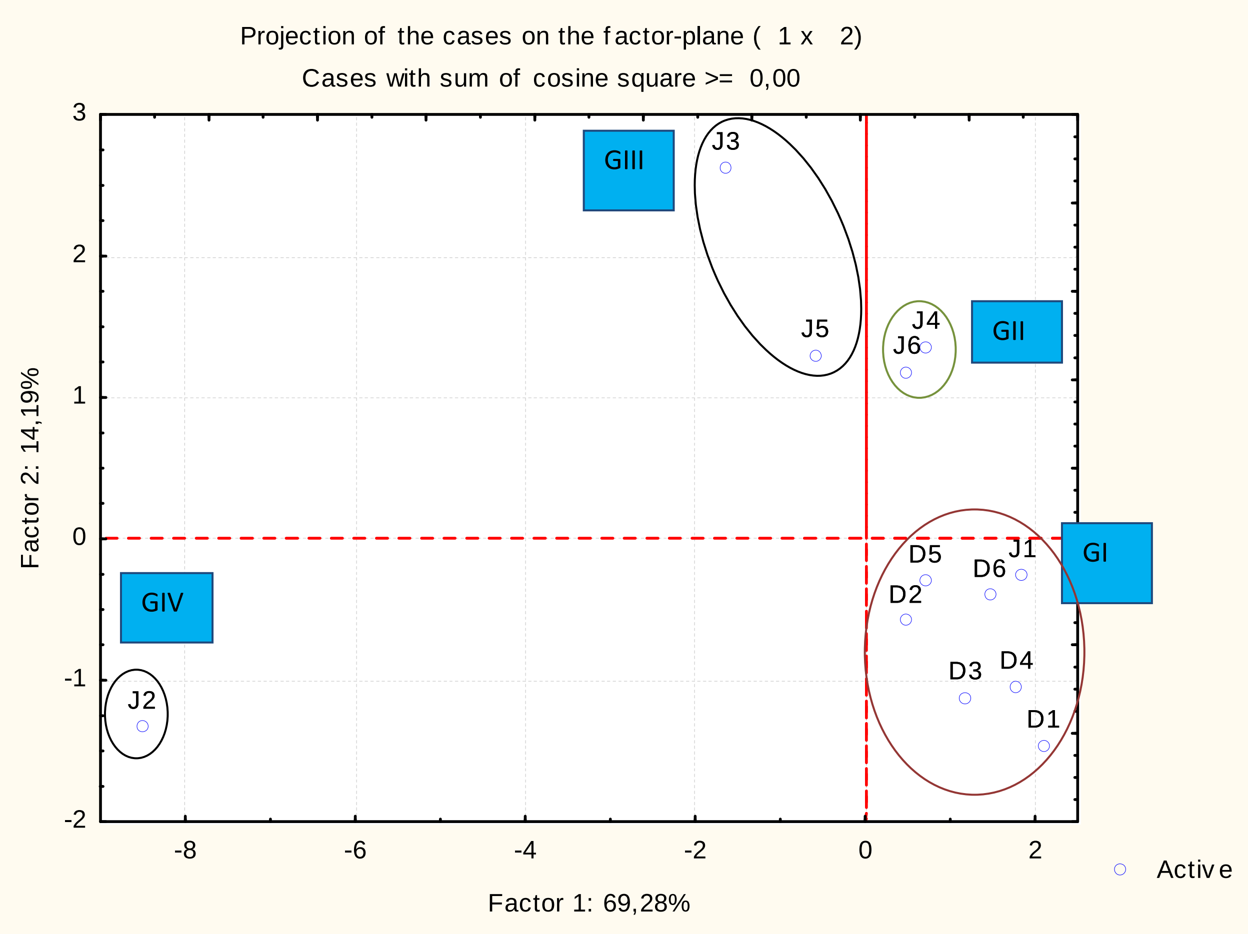

Figure 4: representation of stations of the map factor F1 × F2

PCA is a technique which, quite literally, takes a different viewpoint of multivariate data [43].

The analysis of the projection of individuals on the factorial plan F1-F2 allowed us to define a typology dominated by the individualization of four groups of stations. (Figure 4), we observed that the inclusion of mineral and organic variables is basically translated into the following observations:

Indeed, the spatial profiles of the DCO and DBO_5 are opposite to that of the dissolved oxygen. The values recorded in the study area show a large load of organic matter. J2 station on the river Sebra submitted periodically to industrial releases of sugar refinery of the Oriental and permanently to urban waste of the Zaio city, the situation is very critical. At that level we notice deoxygenating in the middle and lower dissolved oxygen values are also recorded respectively at stations (J3, J4, J5, J6) downstream of the Oued Moulouya (1.2, 1.5, 1.76, 1.78 mg $O_2.l^{-1}$) at the time of low water, where excessive amounts of organic matter leads to a significant decrease in dissolved oxygen as a result of its use in the phenomenon of biodegradation. In the wet period, we are witnessing a re-oxygenation of the medium part by increasing values of recorded dissolved oxygen. This re-oxygenation could be due to the assimilative phenomenon and brewing water. The evolution of nitrogen and phosphate forms reflects the chemical imbalance due to large domestic and organic pollution. Indeed, the evolution of ammonium, Kjeldahl nitrogen and orthophosphate in the different stations shows relatively high spatial variations, especially at stations J2, J3 and J5, influenced by industrial and urban waste respectively Zaio and Berkane cities.

The analysis of the projection of individuals on the factorial plan F1-F2 has enabled us to define a distribution of stations according to sampling month dominated by the individualization of four groups of stations GI, GII, GIII and GIV (Figure 4).

✓**The GI**: includes the station upstream of the study area and downstream of the Machraâ Hammadi dam, during summer and wet periods J1 and D1, and all stations downstream of the Oued Moulouya during the wet period (D2, D3, D4, D5, D6), positively correlated with the F1 component, characterized by the absence of sugar industrial activity and denoting well-oxygenated surface waters and excellent qualities [49].
✓**The GII**: is represented by the stations downstream of the Moulouya during summer periods J4 and J6 characterized by average water quality, following their remote distances of the points of discharge.
✓**The GIII**: is represented by the J5 and J3 stations located downstream of the study area, we note a very alkaline pH at these stations, characterized by large industrial and domestic pollution especially during the dry season, when the stations are more loaded with organic pollutants leading to low concentrations dissolved oxygen.
✓**The GIV:** is represented by the J2 station loaded with organic and mineral pollutants. It determines water of very low quality [49]. This resort is influenced by industrial discharges during the sugar activity period. This unit discharges the waste without any treatment in the receiving environment (Oued Sebra), and results in the training of pollutants that affect the quality of water resources in the lower Moulouya.

CONCLUSION

- Our study provided a good example of a high pollution Influenced by industrial discharges heavily laden with minerals and organic pollutants.
- Except pH, all the other parameters physicochemical have participated in the typology of Sebra and Moulouya rivers.
- All of the results proved that area waters are showing signs of deterioration Moulouya, since the majority of values recorded revealed that they exceed the Moroccan standards.
- This has a major risk deriving their degradation of this vital aquatic environment, the ecological balance and socio-economic development of the whole area of Eastern.
- The results obtained in this study indicate an alarming situation of Oued Moulouya and its tributary Sebra's water quality; which could have adverse effects on the fauna and flora of Wadi, on the soils irrigated by these waters and also the health of the surrounding populations.

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