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Physicochemical typology of the water in the watershed of Sebou river (Morocco)

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ABSTRACT

The Sebou river watershed covers a surface of about 40 000 km^2. Its water resources are estimated at 5600 billions of m^3 representing almost 27% of the whole country superficial waters. However, by an important anthropological influence, this water is exposed to several agricultural, industrial and urban constraints. Thus, it is necessary to monitor water quality of this watershed. So; the present work gives a physicochemical typology of waters of this watershed by using the physicochemical evaluation of fifteen environmental parameters. For this purpose, sixteen stations were chosen in order to be representative as much as possible of the various sectors that constitute the prospected zone.

The results have shown four groups of samples differing by the concentrations in magnesium, sulphates, carbonates, chlorides, sodium, potassium, nitrates and nitrites, and by the values of the conductivity and temperature. The value of the chemical oxygen demand and the concentrations in ammonium and in Calcium allows discriminating two categories of samples. Also, several zones of the studied environment were polluted, and the origin of this pollution was multiple: agricultural, industrial and urban. Also, certain physicochemical variations were linked to the "season" factor and to the anthropological activities connected to this change.

KEYWORDS

Clays;
Adsorption;
Heavy metal;
Landfill leachate;
Tunisia.

INTRODUCTION

Sebou river watershed (figure 1) is situated in the Northwest of Morocco and it is included between parallels 33° and 35° North and meridians 4 and 7 degrees West. Its surface covers about 40.000 km^2. It is integrated into the morphogenetic domain of alpine age. It drains the South hillside of the mountain range of Rif Mountains, the Northwest hillside of the Middle Atlas, and crosses the western part of the south corridor of the Rif. The climate is Mediterranean; the precipitations inter and intra-annually are

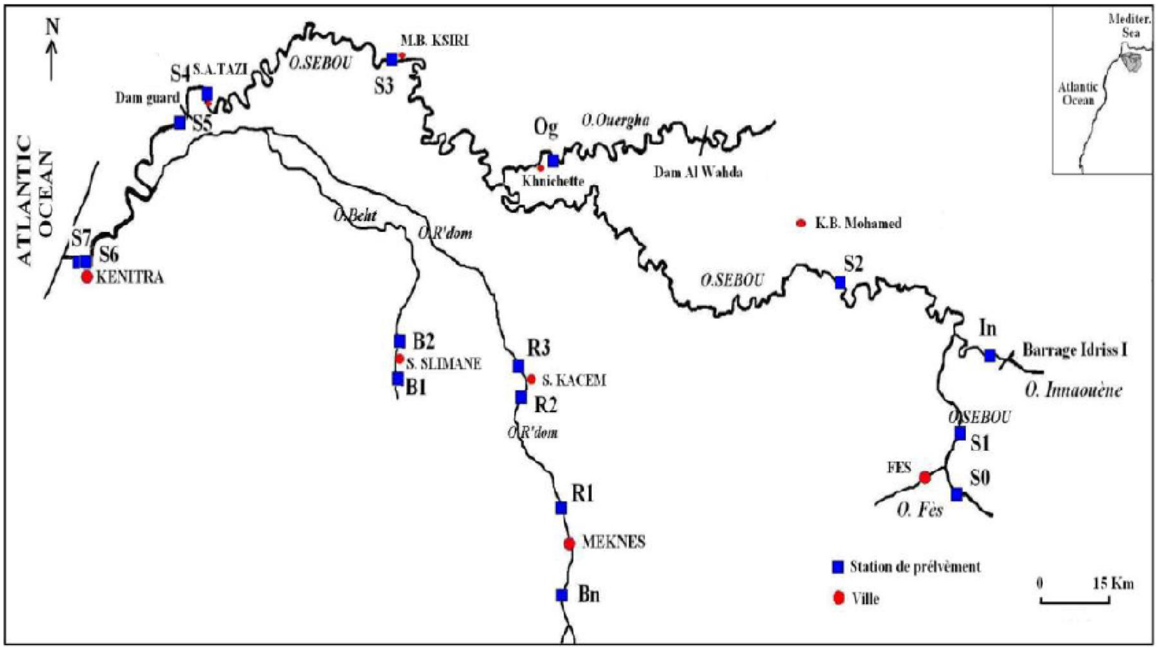

Figure 1 : Hydrologic map of Sebou watershed and localization of the studied stations

irregular. The temperatures are characterized by high seasonal differences.

Sebou river, which is the main watercourse of the watershed, takes its sources from the Middle Atlas mountain range and it crosses the grounds with a lithology dominated by carbonated formations of the Lias[1-4]. Only the rare Paleozoic buttonholes and a limited covering by effusions of quaternary basalts interrupt this dullness[5,7].

The water resources of the watershed are estimated at 5 600 billions of m^3 representing almost 27% of the contributions in superficial waters of the whole country, but the quantity of these water of surface is strictly linked to the characteristics of the climatic elements of the environment, so it is inter and intra-annual irregular.

In the watershed, the use of the water is multiple such as a drinking or irrigation water. Also, Sebou watershed is one of the most populated geographical zones in Morocco. In 1994, its population was estimated about 5.155.686 inhabitants among whom 22% live in rural areas that constitute 17% of the national population. Besides, the Sebou watershed is endowed with an important human activity. It constitutes one of the most important agricultural regions of the country, and it has a great useful agricultural surface that covers 191.000 hectares of farmlands[7]. Also, this watershed is equipped in various industries. This last activity is largely localized around or in many cities such as Fes and Kenitra. Two hundred units are installed on the watershed and are mainly represented by oil factories (65% of the national production), sugar factories (50% of the national production), tanneries (60% of the national production), a paper factory, textile units and an oil refinery. From the nature of these anthropogenic activities, we deduce that the degradation factors of the aquatic environment are varied and the watercourses of this environment are potentially subjected to physical, chemical and biotic constraints. Thus; it is necessary to estimate and to evaluate the physico-chemical superficial waters quality of this watershed.

So, the present work gives an outline about the characteristics of the main watercourses of this watershed in particular of the main watercourse, Sebou river

MATERIAL AND METHODS

The stations choice

The aim is to estimate the physical and chemical characteristics of superficial waters of the watershed. To this objective, sixteen stations were chosen in order to be representative, as much as possible, of the various sectors which constitute the prospected zone. In this choice, we took into consideration the following observations:

Before and after each rejection susceptible to be a source of pollution that can impair water quality, we have taken a sampling station. Other stations were situated far from any visible influences; so these stations were considered as reference sites. Also, some sites were set near the rural or urban human towns. The easiness of access and taking samples were also considered. Totally, a set of 16 stations, where the localization and the characteristics are indicated in the TABLE 1 and in the figure 1, were prospected.

Studied physico-chemical paramèters

To estimate the physico-chemical characteristics of the studied environment, we have estimated 18 parameters (TABLE 3). These evaluating were seasonally performed. Some parameters were measured in situ such as the temperature, the pH and the conductivity. Other measures were made in laboratory by volumetric or by spectrophotometer according to the methods indicated by Rodier (1996)[8].

TABLE 1: Situation, altitude and geographical coordinates of the prospected stations

Station	Situation	Altitude (m)	Geographical Coordinates
B1	In Dar Bel Amri located at 10 km upstream from the wastes of the city of Sidi Slimane	47	N: 34°11'-21.6'' W: 005°58'-0.3''
B2	In Sidi Slimane downstream of the domestical wastewaters	46	N: 34°15'-33.3'' W: 005°55'-15.7''
In	Near the main road Fes–El Houcima located at roughly 35 km downstream of the confluence point between oued Sebou and oued Fes	151	N : 34°11'-52.3'' W : 004°47'-49.7''
Og	In Ourgha at 10 km upstream of Khnichat	47	N : 34°27'-36.1'' W : 005°30'-29.1''
S0	In douar Mkhalef located at roughly 20 Km upstream from the city of Fes	245	N : 34°01'-48.8'' W : 004°49'-46.8''
S1	In Khmiss Hamria located at 1.5 Km downstream from the confluence point between oued Sebou and oued Fes.	245	N : 34°06'-56.7'' W : 004°53'-27.6''
S2	At 8 Km upstream from Kariat Ba Med.	84	N : 34°18'-33.5'' W : 005°08'-48.9''
S3	At 3 Km downstream from the urban wastes of Mchrae Bel Ksiri	16	N : 34°34'-04.3'' W : 005°57'-43.2''
S4	Downstream from the wastes of Sidi Allal Tazi	24	N : 34°31'-09.5'' W : 006°19'-33.1''
S5	At the impoundmen of the guard dam	16	N : 34°29'-21.1'' W : 006°24'-46.2''
S6	In Kenitra upstream discharges of sewage	5	N : 34°16'-33.7'' W : 006°35'-22.3''
S7	In Kenitra downstream from the Ouled Oujh. domestic wastewaters	5	N : 34°16'-33.7'' W : 006°35'-22.3''
Bn	In Oued Rdom at 5 km downstream from the Boufekrane city	550	N : 34°11'-42.3'' W : 005°14'-07.1''
R1	In Oued Rdom at 8 km downstream from the Meknes city	580	N : 33°911'-09.2'' W : 34°16'-33.6''
R2	In Oued Rdom at 5 km downstream from the Boufekrane city	550	N : 34°11'-52.3'' W : 005°14'-07.3''
R3	In Oued Rdom at 5 km downstream from the Boufekrane city	535	N : 34°11'-52.32'' W : 006°14'-22.3''

To elaborate a physico-chemical typology of the stations and samples, all obtained data were grouped in a matrix of '18 variables x 64 samples' which was handled by a multivariate statistical analysis, the P.C.A.

Let us remind that the P.C.A. is a factorial method that allows simplifying the description of a table grouping a lot of measures coming from a time space observation plan[9,10]. It is very used in chemistry and biology fields.

RESULTS AND DISCUSSION

As it is shown in TABLE 2, the first axis (C1) contributes by 24.4% in the explained inertia, the second

(C2) 18.8% and the third axis (C3) 13.5%, i.e. a total of 56.7%. This rate is highly enough to allow the interpretation of the projection plans of the variables and samples «C1xC2» and «C1xC3».

TABLE 2 : Eigenvalues and contribution percentages of the variables in the three axis

-	C1	C2	C3
Eigenvalues	4.4001	3.3839	2.4347
% variance	24.4	18.8	13.5
% cumulative variance	24.4	43.2	55.7

Interpretation of C1, C2 and C3 axes

The contributions of the variables in the constitution of the first three axes, illustrated in the TABLE 3, allow the determining of the physico-chemical meaning of every axis:

Constituent C1

Mainly, five variables contribute significantly in the constitution of C1: the conductivity (Cd), the concentrations of sodium (Na+), potassium (K+), chlorine (Cl^-) and carbonates (CaCO3-). From the negative side to the positive side of this first axis, we have noted an increasing gradient of concentration of five variables (figure 2). Thus, C1 is an axis representing a concentration gradient of salinity (K+, Na+ and Cl-), of content in CaCO3-, and of conductivity.

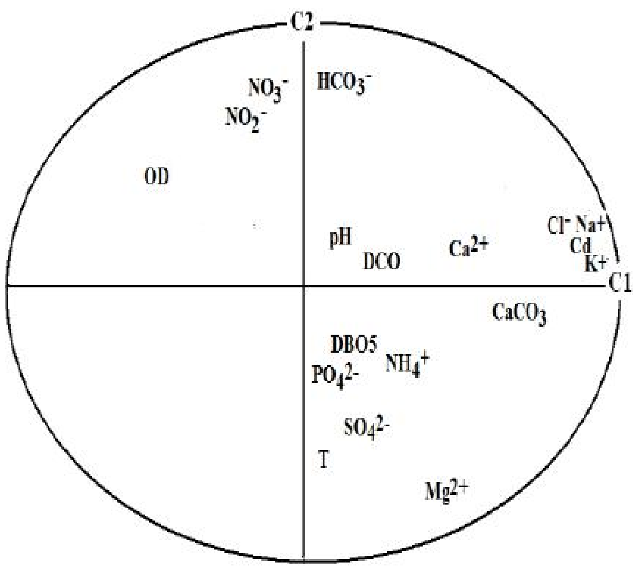

Figure 2 : Projection of physico-chemical variables on the factorial plan C1xC2

To facilitate this interpretation, we codified the samples in the following way; every sample is noted by a symbol indicating the station followed by one of the four alphabetical letters A, H, P or E. Each letter indicates the season when the levy was made with A = Fall, H= Winter, P= Spring, E= Summer. The sample symbolized OgA; for example, means that the sample was taken in autumn in the station symbolized Og.

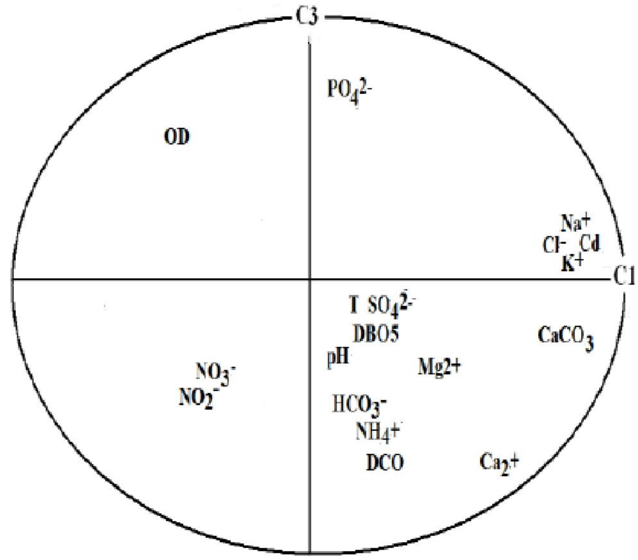

Figure 3 : Projection of physico-chemical variables on the factorial plan C1xC3

TABLE 3 : Contribution percentage of the 18 physico-chemical variables in the constitution of C1, C2 and C3 (In bold, the contribution rates retained as significant)

Variables	C_1	C_2	C_3
Disolved oxygen (OD)	-0.445	0.384	0.473
DCO	0.238	0.073	-0.623
DBO_5	0.102	-0.332	-0.104
HCO_3^-	0.122	0.687	0.293
$CaCO_3^-$	0.720	-0.156	-0.337
Ca^{2+}	0.558	0.138	-0.569
Mg^{2+}	0.361	-0.649	-0.269
Conductivity (Cd)	0.907	0.205	0.312
Chlorides (Cl^-)	0.848	0.197	0.359
Na^+	0.865	0.233	0.398
K^+	0.862	0.206	0.192
Sulfates (SO_4^{2-})	0.144	-0.540	-0.098
Phosphates (PO_4^-)	0.074	-0.391	0.587
Nitrates ($NO3^-$)	-0.108	0.728	-0.289
Nitrates ($NO2^-$)	-0.108	0.725	-0.289
Ammonium (NH_4^+)	0.221	-0.310	-0.505
Temperature (T)	0.075	-0.617	-0.101
pH	0.128	0.154	-0.056

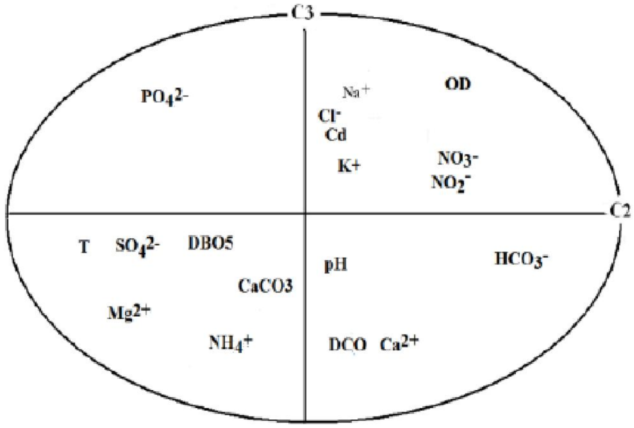

Figure 4 : Projection of the physico-chemical variables on the factorial plan C2xC3

Besides, the projection of the points representing the sampling on the C1xC2 plan (figure 5) does not showed the presence of the well defined groups of samples. But, in moving from the negative to the positive side of C1, the physico-chemical characteristics of the samples becomes gradually different towards the conductivity value and towards the contents in Na+, K+, Cl- and CaCO3-. The phenomenon is the same when we move gradually from the negative to the positive side of the C2 axis: the water temperature values and the water concentrations in nitrates, nitrites, sulfates and magnesium becoming higher.

So, by dividing the factorial plan C1xC2 into four compartments A, B, C and D separated between them by the axes C1 and C2, we can see four groups of samples. The physicochemical characteristics of these groups are as follows:

Group A

The concentrations of Mg^{2+}, $SO4^{2-}$, $CaCO^{3-}$, Cl^-, Na^+, K^+ were low; the conductivity and the temperature were also low, but the concentrations of nitrates and nitrites are high.

Group B

As opposed to the samples of group A, the concentrations of $CaCO^{3-}$, Cl^-, Na^+, K+ and the conductivity are high. The other characteristics were the same as those in group A.

Group C

The physic-chemical characteristics of the samples were the opposite of those the samples of the group B.

Constituent C3

Five variables correlate significantly to C3 axis: the concentrations of Ca^{2+}, $NH4^+$ (Ammonium), $PO4^{2-}$ (Phosphates), dissolved oxygen (OD), and the DCO value. Except Ca^{2+} concentration, these variables participate in the determination of the eutrophication and microbial pollution degree in the environment[11].

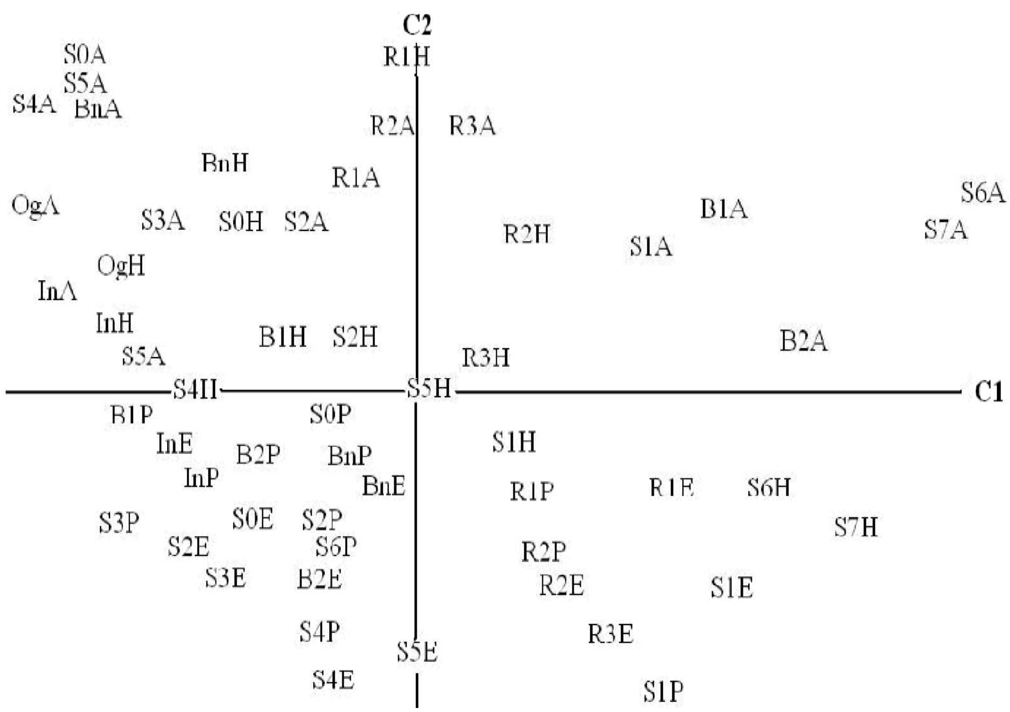

Figure 5 : Projection of the samples in the factorial plan C1 x C2

Group D

Physicochemical characteristics of the samples are opposite of those the samples of the group A.

Besides, in the C1xC3 plan (figure 6), from the negative side to the positive side of C3 axis, the samples shows a progressive change in their DCO values and their concentrations in Ca^{2+}, dissolved oxygen and phosphates. Also, if we share this factorial plan in four compartments A', B', C' and D' separated by the axes C1 and C3, two physico-chemical categories of samples could be distinguished:

Category 1

Formed by samples belonging to compartment A' or B', having some physico-chemical characteristics that were respectively the same as the samples of A and B (figure 5), but all of them have a low DCO and low concentrations of ammonium and Ca^{2+} while the concentration of dissolved oxygen and phosphates are high.

Category 2

Formed by samples belonging to compartments C' or D' and having certain physico-chemical characteristics that are respectively the same as the samples of C and D, but having all high DCO and concentrations of ammonium and Ca^{2+} while the concentration of the dissolved oxygen and phosphates are low.

In the factorial plan C2xC3 (figure 7) we distinguish a clear differentiation between two sets of samples separated by the axis C3 :

- a set situated on the negative side of the axis C2 constituted of samples taken in summer or in spring;
- a set of samples situated on the positive side of this axis, constituted of samples taken in autumn or winter.

Besides, the plan C2xC3 has showed that for a given station x, the positions of the points representing the seasonal samples do not change their position a lot according to C3 axis. It means that in this station, the values of the DCO, and the concentrations of dissolved oxygen, ammonium and phosphates remain relatively stable during the seasons. On the opposite, from the projection of these points along the C2 axis, we can deduct that the values of the temperature, the concentrations of nitrates, sulfates and magnesium vary according the seasons. So; for certain stations, we notice an antagonism between the values illustrated in summer and those illustrated in autumn.

Also; the results have showed that 16 among the 18 studied variables participate in the determination of the physico-chemical typology of the studied environment. Only the contribution of the pH and the DBO5 were not significant. Besides, the influence of the 'sea-

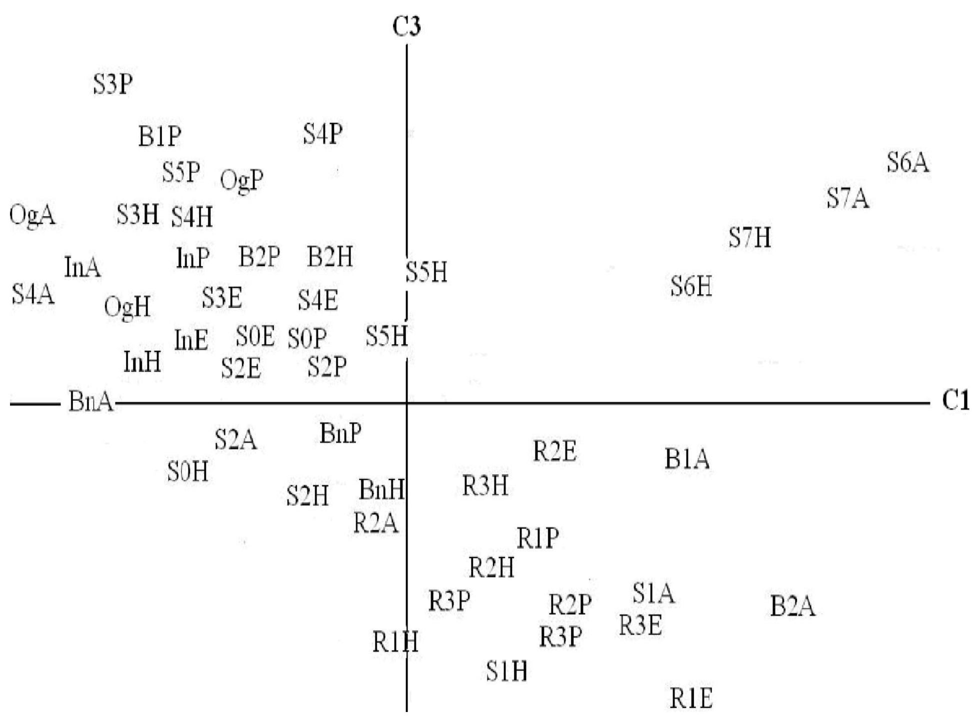

Figure 6 : Projection of the samples in factorial plan C1x C3

son' factor was not the same to all the variables. The concentrations of nitrates, nitrites, sulfates, magnesium and the value of the temperature were the most influenced by this factor.

The analysis of the three factorial plans C1xC2, C1xC3, C2xC3 and the results illustrated in the TABLE 4 shows that the physico-chemical characteristics of some studied stations change according to seasons. The model of the variation followed by this change was not the same in all the stations. The TABLE 4 has showed the existence of three types of categories of seasonal physico-chemical variations. Each of these categories is influenced by a seasonal variation of a group limited of physico-chemical variables that contribute significantly to C1, C2 or C3

- The factorial plan C1xC2 shows that the taken samples during the four seasons in the station called Og are all situated on the negative part of the axis C3. Thus, these samples are characterized by low concentrations of Na^+, Cl^-, K+and $CaCO^{3-}$, and the low conductivity. In the opposite, all the samples taken in the station S1, were situated on the positive part of the axis C3. So, the satations both Og and S1 were stable during the four seasons but with different physico-chemical characteristics.- Concerning the nitrates and nitrites, the plan C1xC2 (figure 5) has showed that in the samples taken in the stations called In, B1 and B2 the concentrations do not vary according to seasons. On the other side, those made in S4 and R2 has showed clear seasonal variations. This variation could be due to the presence of a diffuse pollution. Indeed, the presence of nitrates can have a multiple origin: agricultural, urban or industrial. Let us note that the presence of nitrites indicates a pollution of bacterial or organic origin.
- The station called Bn has presented a seasonal variation reflecting a pollution of multiple origins: agricultural, urban and industrial. This variation concerns several physicochemical charac-teristics in particular the concentrations of nitrites, nitrates, sulfates, $CaCO^{3-}$, Cl^-, Na^+ and K^+ (TABLE 4).

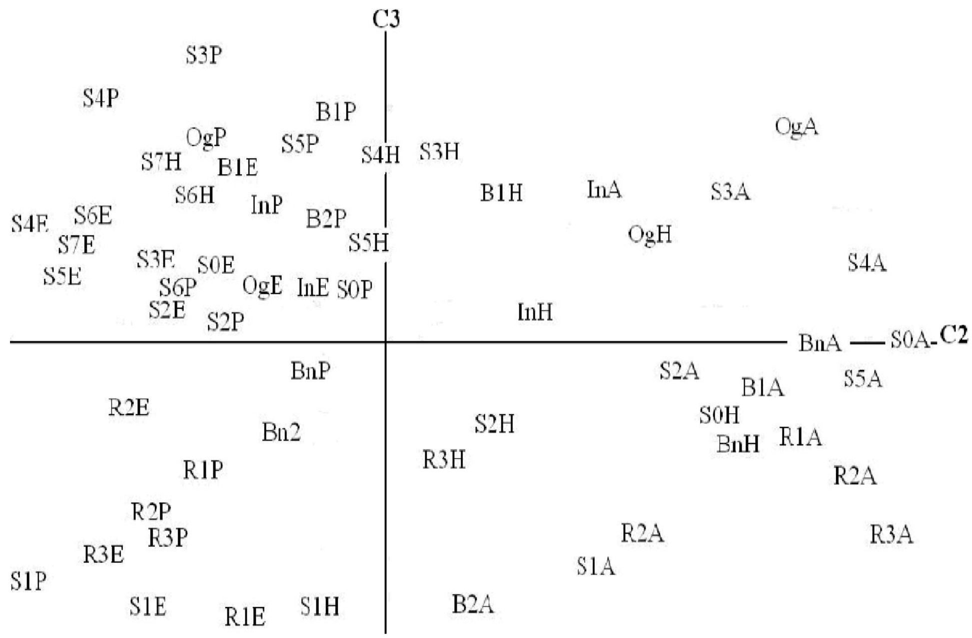

Figure 7 : Projection of the samples in factorial plan C2x C3

- The factorial plan C1xC3 (figure 6) indicates that the samples taken during the four seasons in the stations R2 and R3 are all situated on the negative part of the axis C3; on the opposite, those of the S3 and S4 are all situated on the positive part of the same axis. So; these two stations have seasonal physico-chemical stability. Let us note that station R2 and R3 were characterized by a high ammonium concentration, a high DCO value and a low rate of oxygen. Thus, these stations have an industrial pollution indicating an incomplete degradation of the organic matter and a decomposition of organic matters of animal or vegetable origin.

The plans C1xC2, C1xC3 and C2xC3 (figures 5, 6, 7) show that the stations S6 and S7 were the most touched by seasonal physico-chemical variations. The daily and seasonal flooding of these stations by waters of the low and the high tides are the main cause.

Besides, in a big part of sub-Saharan Africa, the lack of water creates serious problems[13,14]. In watershed of Sebou, the biggest hydrological network of Morocco, our study has showed that for several studied physico-chemical variables, the observed values indicate that pollutions of diverse origins (agricultural, domestic and industrial) threatens the quality of water. Consequently, these pollutions have important adverse effects on the environment and constitute many risks to the human and to other species health[15]. Three types of pollution are noticed in the studied watershed:

Pollution of agricultural origine

For several developing countries, agriculture consumes the largest part of available water. The Moroccan country is a case[11,4].

In this country, the Sebou watershed constitutes one of the most important agricultural zones. It includes a superficial important hydrological network: rivers, lakes and dams.

Moreover, in order to compensate the climatic changes, the irrigation is very used and the use of the artificial fertilizers, the pesticides products and the natural or artificial manures became usual. So, the infiltration of the agricultural water and the wastewater into the underground waters or into the watercourses cause an accumulation of these substances in the aquatic environment. The polluting loads of the aquatic environment of the Sebou watershed are essentially constituted by nitrates and phosphates. Indeed, during a period of four years (1989/1993), the National Office of Drinking Water[11] has estimated the annual amounts of wastes as following:

- 37330 tones of DBO5 per year ;
- 97330 tones of DCO per year ;
- 8300 tones of nitrogen per year;
- 1890 tones of phosphor per year.

The typological analysis showed that the C2 axis reflects an agricultural pollution. It represents a set of a concentration gradient of Mg^{2+}, nitrites, nitrates and sulfates. Concerning the origin of these chemical elements, let us remind that the magnesium is essential for the formation of the leaf and it is an essential chemical element for a good agricultural production. So, it is used in agriculture as a fertilizer. The main used form of this product is the magnesium sulfate more or less hydrated (MgSO4).

TABLE 4 : Seasonal physico-chemical variations recorded in prospected stations (+) : variation, (-) : no variation

Stations	Studied physico-chemical variables		
	Category 1	Category 2	Category 3
	Cd, Na^{2+}, Na^{2+}, K^+, Cl^-, $CaCO_3^-$	Nitrates, Nitrites, Sulfates, Mg^{2+},Temperatures	Ca^{2+}, NH_4^+, PO_4^{2-}, Dissolved Oxygen and DCO.
R1	-	+	-
R2	-	+	-
R3	-	+	-
R0	-	+	-
S1	-	+	-
S2	-	+	-
Og	-	+	-
S4	-	+	-
S5	-	+	-
Bn	±	+	-
S6	+	+	+
S7	+	+	+
In	-	-	-
B1	-	-	-
B2	-	-	-
S3	+	+	-

Besides, the fertilizers necessary to crops growth are physico-chemically various : nitrogen, phosphor, potassium, etc. But; these chemical products, spread on the ground or pulverized on the cultivated plant, then solubilized by the rain and carried by runoff or infiltration causes an increase in the water concentrations of Mg^{2+}, $SO4^{2-}$, nitrites, nitrates. Then, an agricultural pollution is established in the environment. The water which returns to rivers after being used for irrigation is often strongly degraded by excess of nutrients, salinity, pathogenic agents and some sediment which often make this water unsuitable for any usage unless it cleaned in water treatment plants[16]. For example, sulfate anions SO42- brought to the soil by the magnesium sulfate can be an acidifying agent in the environment; the nitrates and nitrites contribute to the eutrophication of water-courses or the water accumulations.

In 1993, for example, the pollution generated by the use of fertilizers and pesticides in Moroccan agriculture was estimated at 8500 tons of nitrogen and 15 tons of pesticides. 8 to 10% of the nitrogen used as fertilizer is leached into ground waters or into watercourses and 0.5 to 1% of the pesticides products join watercourses[17]. Thus, this type of pollution is very threatening.

Pollution of domestic origin

In 1993, the volume of wastewaters produced in urban zones is estimated at 500 billions of m^3. The part collected by the sewer networks represents a volume of 370 millions of m^3. The half of this quantity is rejected into the sea. The rest is rejected into river systems or spread on the ground[18]. For the same period, the main polluting materials conveyed by domestic wastewaters (infiltrated or discharged to the soil surface) are estimated as shown below: 260000 tones of oxidizing matter: 50%, 4800 tones of nitrogen: 54% and 7300 tones of phosphor: 53%.

Currently, the increasing size of the Moroccan population and its concentration in some geographic zones, the industrial production of new phyto-chemical quality and the increasing quantity of wastewater according to the various human activities have become worrisome. In addition, the studied basin is demographically very populated and the majority of its rural and urban concentrations discharged their wastewater without any treatment. Then, the aquatic environment of the basin is very exposed to various types of pollution from domestic sources[11]. Thus, this pollution is responsible for a much polluted environment by nitrogen and phosphorus[11].

According to the ONEP, in 1994 (Anonymous 2, 1994) among the impacts generated by direct discharges of wastewater into rivers:

- An eutrophisation of dams located downstream from the discharge centers;
- A reuse of raw wastewater in irrigation immediately downstream of the cities with all the health risks that may arise for farmers and consumer.

Similarly, the ONEP (Anonymous 2, 1994) indicated that these areas of rivers, located immediately downstream of discharges from towns and villages in the watershed of Sebou, have poor or very poor water quality. Large pollution loads of wastewater discharged into domestic and industrial waters are responsible for this pollution. The best examples are downstream of Fez, Meknes, Sidi Kacem and Sidi Slimane cities. According to the same resource, in the studied watershed, the main physicochemical parameters degrading the water quality relate to the organic matter and total phosphorus concentration.

Pollution of industrial origin

In Morocco, the branch of industry generates an organic and an important toxic pollution. In 1993, the volume of residual waters was estimated at 964 millions of m^3, that is 89% of the total used volume[18]. In 1996, it was already considered that between 200 and 400 chemicals contaminate watercourses in the world[19]. Today, because of the industrial development, these figures are widely exceeded.

In Sebou watershed, the industry sector is very diverse: food-processing industry (sweets, oil-works, dairies, and canning factories), paper industries, tanneries, textile industry, oil refineries, yeast production plants, alcohol production, etc. The total loads of organic pollution of industrial origin is estimated to 2 750 000 equivalents-inhabitants, among whom about 70 % result from sugar factories, paper factories and oil-work plants. The industrial pollution is responsible for 40 % of the organic pollution, 20 % of the nitrogenous and phosphorous pollution, 100 % of reject in heavy metals. In 1994, the ONEP has estimated this type of pollution at 2 million equivalents-inhabitants[11].

In the studies zone, the largest part of the organic industrial releases is spread directly in the Sebou watershed and indirectement in the Atlantic Ocean. So, the Sebou watershed concentrates an organic pollution[12] and a contamination by the chromium; the important part of this last type of pollution is caused by tanneries[7]. Food-processing industries reject about 22 millions of m^3 of water residual, constituting 90% of the using water in this sector. They contribute to the pollution by important loads in organic matters (80% in COD and 66% in BOD5) and by almost the totality of the pollution by nitrates and phosphors.

CONCLUSION

The results have showed that this environment was physico-chemically heterogeneous and several of its zones were polluted. The origin of this pollution is multiple (agricultural, industrial or urban) ; So, four groups of samples were distinguished and characterized by:

A first group (A)

The concentrations in Mg^{2+}, SO_4^{2-}, $CaCO_3^-$, Cl^-, Na^+, K^+ were low; the conductivity and the temperature were also low, but the concentrations in nitrates and nitrites were high.

A second group (B)

Trained by samples having high concentrations in $CaCO_3^-$, Cl^-, Na^+, K^+ and high value of conductivity; but other characteristics were the same as those of the samples in the group A.

A third group (C)

Constituted by samples having physico-chemical characteristics opposed to those of the group B samples.

A fourth and last group (D)

With physico-chemical properties which oppose to those of the samples of the group A.

Besides, the results have showed a distinction of two physico-chemical categories of samples:

- A first category where all the samples have low DCO and low concentrations in ammonium and in Ca^{2+} while the concentration in dissolved oxygen and phosphates were high.
- A second category constituted by the samples having physco-chemical characteristics that were opposed to those of the samples of the other category regarding the DCO and the concentrations in ammonium, Ca^{2+} high, dissolved oxygen and phosphates.

We have also noted that certain physico-chemical variations are linked to seasonal climate change and to human activities that were connected to this change.

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