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PHYSICO-CHEMICAL CHARACTERIZATION, POLLUTION AND TYPOLOGY OF WATER SEBOU RIVER ESTUARY

Samiha Kaioua[1], Ghizlane Houzi[2], Hefdhallah Alaizari[4]*, Latifa El Harrak[3], Hanae El Harche[1], Mohamed Fadli[1]

[1]Laboratory of Plant, Animal and Agro-Industry Productions, Faculty of Sciences Kenitra, Ibn Tofail University, Kenitra, Morocco.
[2]Laboratory of Biology and Health, Faculty of Sciences Kenitra, Ibn Tofail University, Morocco.
[3]Laboratory of Human Biology and population Health, Department of Biology Ibn Tofail University, Kenitra, Morocco.
[4]Department of Chemistry, Faculty of Education, University of Dhamar, Yemen.

Correspondent authors: Alaizari2@gmail.com

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ABSTRACT

The present study focuses on the Physico-chemical analysis of water samples collected seasonally from five sites longitudinally distributed along the Sebou River (North West Morocco). The objective of the study is to characterize and assess the degree of global pollution and to develop a Physico-chemical typology of the estuary. Sampling and analysis of Physico-chemical parameters were seasonal during the year 2019. The results show that the values of the Physico-chemical parameters vary according to the seasons, the distance of the site from the mother, and the discharge points of urban and industrial wastewater. Likewise, for various sites, the degree of pollution changes over the year and the qualitative and quantitative change in the discharge of wastewater discharged into the estuary. It should also be noted that the results showed that in all the prospected sites and for all the seasons, the waters of the estuary are severely polluted. For the typology of the waters of the estuary, the projection of the water readings in two factorial planes C1xC2 and C1xC3 showed the differentiation of several Physico-chemical groups according to the axes C1 and C2, and C3 with: C1 is a gradient of pollution of the estuary which results from both urban wastewater discharges and industrial wastewater. C2 is an axis representing an increasing gradient of mineral pollution and continentally about the sea. C3 axis represents a gradient of increasing pollution of multiple origins: agricultural, urban, and industrial.

INTRODUCTION

An estuary is the portion of the mouth of a river where the effect of the sea or the ocean into which it flows is perceptible. It is a wetland that constitutes a transition zone between the continental and the marine environment. In ecological balance, the estuary is an area of great biodiversity, however, often this balance is disturbed mainly because of the human gravity that this hydro system presents. Indeed, as indicated by **Khan *et al.* (2014**), because estuaries offer many economic and ecological interests to humans and a diversity of habitats for many species of great interest to humans, these ecosystems are subject to many constraints of human origin. However, as an ecosystem, estuaries are very fragile. Thus, most estuaries face a range of stresses so much that estuarine degradation is a common problem in developing countries (**Kennish, 2002; Zambrano-Monserrate and Ruano, 2021**). And, almost on a global scale, estuarine ecosystems are degrading and human action is the main cause (**Lotze *et al*. 2006; de Juan *et al.* 2014**). In fact, estuaries often constitute a receiving environment, direct or indirect, of substances contaminated by pollutants, of untreated urban or industrial wastewater discharges, and of leaching water from the river basin supplying the estuary (**Borrego *et al.* 2013**). Another type of degradation that disrupts the physicochemical quality of the estuary environment is poorly studied development or the dredging of sand from the estuary (**Hughes *et al*. 2014).** Moreover, among the consequences of anthropogenic interventions on estuaries is the gradual loss of ecological balance which often begins with a change in the physico-chemical conditions of the water in the estuary resulting in a subsequent biological modification of the water in The hydro system. Thus, to develop any preventive control strategy against an evolution of the degradation of an estuary, it is necessary, first of all, to estimate the physicochemical characteristics of the biotope.

MATERIALS AND METHODS

Study site: Sebou River

The estuary, site of our study, is the final part of the Sebou River, a stream in the northwestern part of the Moroccan Atlantic coast. This river originates in the mountains of the Middle Atlas, stretches over 614 km with a watershed covering a large area.. The lower part of Sebou crosses the plain of Gharb. The climate of the estuary and Mediterranean area has an oceanic influence, but inside the basin the climate becomes more continental. Moreover, according to **El Blidi and Fekhaoui (2003**) the hydrology of the lower part of Sebou is linked to seasonal variations in the climate and reflects that of precipitation. The water regime of the river is also confronted with the tidal dynamic which conditions the various parameters of the environment, in particular its hydrology (Figure. 1). Note that the Sebou basin has a number of industrial activities on the banks of its main river, including sugar factories, paper mills, oil mills, tanneries, cement factories, the textile industry and the oil refinery. Similarly, several human agglomerations have developed on the edge, the two cities of Rabat and Fes are the main ones. Moreover, the Sebou wadi is considered one of the most polluted Moroccan rivers. The origin of its pollution is multiple: urban and / or agricultural wastewater discharges, agricultural activities, drainage water from the watershed, etc.

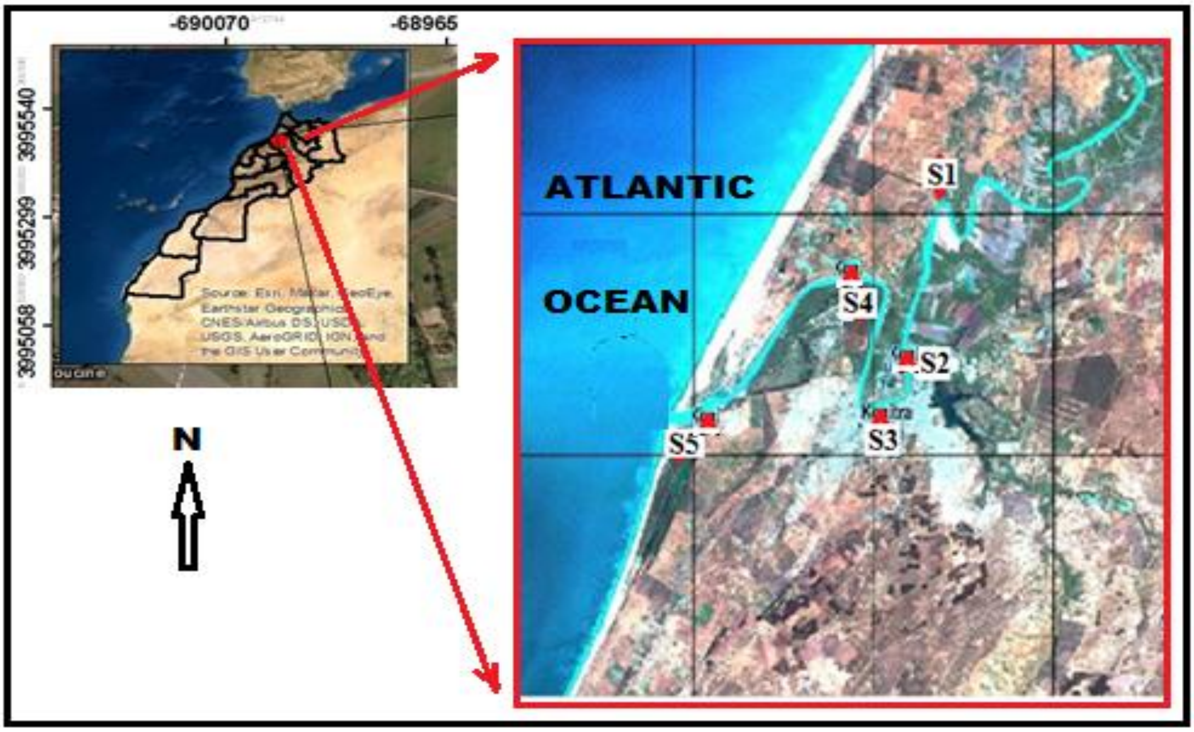

Figure 1: Study area

Samples collection

The physicochemical characterization of the collected water, via the measurement of fourteen physicochemical parameters, of which the temperature, the pH and the conductivity were measured in situ by a digital electronic equipment, and other parameters which were measured by chemical volumetry. In our choice of the stations to prospect (Figure. 1), we took into consideration the distance of the station from the mouth of the estuary and, consequently, the importance of the influence of the action of the sea on the physico-chemical conditions of the water at station level. Likewise, we took into account the position of the station in relation to the nearest source of pollution. Thus the five selected stations are characterized by:

S1: located most upstream of the studied part of the estuary it is at 10 km upstream from the industrial waste collector of the paper factory (CMCP). It is the least exposed to the discharge of wastewater from the city of Kenitra and the most influenced by continental waters and conditions.

S2: Located with the Cherifienne Petroleum Company and the wastewater collector of the CMCP company;

S3: Located downstream from the port of Kenitra and receiving domestic waste from the city of Kenitra.

S4: Located between the mineral port and the fishing port of the city of Kenitra

S5: located 500 m from the mouth; it is the area most exposed to maritime influences.

In addition, the sampling of the water to be analyzed was carried out seasonally and at low tide. The collected water was stored at 4°C until processing and physicochemical analyzes within 48 hours of collection.

Statistical analysis of the results

The physico-chemical characterization of water data set was subjected to four types of statistical analysis: univariate, bivariate and multivariate (principal component analysis, PCA), and to an evaluation of the degree of pollution by water global pollution index (P) whose formula is:

$$P=\frac{1}{n}\sum_{i=1}^{n} Ci/Si$$

Where Ci is the measured concentration of the pollutant or chemical parameters (in mg / l); Si represents the limits authorized by the Moroccan government for the control of the quality of surface water (**Meyer-Reil and Köster, 2000**), it is the number of pollutants selected. As has been reported by Mishra *et al.* (2016) and Zhao *et al.* (2020), this index qualifies the water as clean if P <0.20, as sub-clean if 0.20 <P≤ 0.40, as slightly polluted if 0.4 <P ≤ 1.00, as moderately polluted if 1.01 <P≤2.0) and highly polluted if P> 2.0 (**Mishra *et al.* 2016; Zhao *et al*. 2020**).

RESULTS AND DISCUSSION

Estimation of the physical parameters of the environment:

The results of this estimation are grouped in Table1.

Water temperature ranged from 16.6 to 27.5 °C, the lowest temperature was in station 2 in winter, and the high temperature was in station S1 in autumn. The pH values fluctuate between 7.5 (station 1 in spring) and 8.7 (station 3 in winter). The electrical conductivity (CE) and salinity (TDS) respectively vary from 2836 to 14847 µs / cm and from 1815 to 9502 mg /l. The highest values were shown in the fall at station 5 and the lowest values at station 1 in the spring. The BOD5 and COD concentrations varied respectively from 158.6 to 542.4 mg / l and from 127.3 to 824. The lowest value of BOD5 was measured in a station 4 in summer, the highest value was noted at station 3 in the fall similarly the lowest value of COD was shown at station 3 in the fall, the highest values were at station 2 in the spring and at station 3 in a summer. The concentration of suspended matter (SEM) varies between 187 and 521 mg / l. The lowest value was in station 1 in summer and the highest value was in station 3 in spring. Respectively, the concentrations of NH_4^+ and NO_3^- vary from 7,200 to 19.6 mg / l and from 11.1 to 18.3 mg / l. The low values were measured in Station 5 in autumn and in station 4 in autumn, while the highest values were measured in station 3 in spring and in station 2 in spring. Respectively, the concentration of NO_2^- and O-PO4 vary between 0.46-0.10 mg / l and 0.25 - 1.61 mg / l respectively. The lowest values were in station 1 in spring and in station 3 in autumn, the highest concentrations were in station 2 in spring and in station 2 in summer. Respectively, the concentrations of HCO_3^- and SO_4^{--} vary between 16.5-5.31 mg / l and 191.792 mg / l and respectively the lowest concentrations in summer in station 1 in winter and in station 1 in autumn. While, the highest concentrations were measured in station 1 in autumn and station 5 in spring and autumn.

Table 1: Values of the physico-chemical parameters

STATION	Temperature (T)	pH	Electrical Condictivity (EC)	Dessolved Oxygen (DO)	HCO3	Suspended matter (SPM)	Biological oxygen Demand (BOD5)	Chemical oxygen Demand (COD)	Salinity (TDS)	NH4	NO3	NO2	O-PO4	SO4
S1Wi	24	7.6	3215	2.1	5.31	284	329	570.6	2057.6	11.3	12.7	0.2	0.44	364.2
S1Sp	22.8	7.5	2836	2.3	13	281	227.2	454.2	1815.04	11.5	13.2	0.1	0.38	392
S1Su	26	7.8	2952	3.45	12.5	294	198	324	1889.28	14.4	14	0.15	1.5	486
S1Au	27.5	7.7	2837	2.7	16.5	187	396.15	498.5	1815.68	12.7	15.8	0.13	0.46	191
S2Wi	16.6	8.17	7810	1.3	8.1	498	541.7	605.1	4998.4	15.9	16.6	0.15	1.58	346
S2Sp	23	8.29	6122	1.9	10.2	520	442	824	3918.08	15.3	18.3	0.46	1.51	412
S2Su	26.7	7.9	8756	2.34	13	312	225.4	502.6	5603.84	14,6	17	0.37	1.61	464.6
S2Au	24	7.59	7512	2.19	12	310	428.7	626	4807,68	17,8	15,24	0.37	0.45	245.54
S3Wi	16.7	8.7	9122	2.6	6.3	462	532.7	824	5838.08	16.4	14,9	0.35	1.45	223
S3Sp	22	8.5	9134	5.1	8	521	423.2	735.4	5845.76	19.6	14,2	0.37	0.42	398
S3Su	26.2	7.8	10961	3.2	10.3	373	259	805	7015.04	15.3	15,6	0.42	1.56	411
S3Au	19	0.53	11965	3.32	9	330	542.4	127.3	7657.6	15.7	12,8	0.41	0.25	505.7
S4Wi	19	7.6	9706	5.56	7.9	327	425	429.2	6211.84	13.4	11,5	0.27	0.37	372
S4Sp	22.9	7.6	12500	5.6	8.5	354	319.3	324	8000	15,5	12,9	0.26	0.92	456
S4Su	23	7.7	12509	2.43	13	381	158.6	423.4	8005.76	13.6	13,3	0.22	1.42	498
S4Au	20	7.53	11697	3.91	6	500	487.9	523	7486.08	12.9	11,2	0,25	0.35	403
S5Wi	19.5	7.87	12150	4.84	14.6	324	227	324	7776	10.1	11,9	0,32	0.38	325
S5Sp	20.7	7.96	13164	5,9	15	365	226.6	23.4	8424.96	12.6	13,2	0,17	0,42	792
S5Su	21	7.6	14765	4,6	12.3	388	168,2	275	9449,6	11.8	14,5	0.22	1.39	622.6
S5Au	20	7.7	14847	5.1	12	401	479.9	342.4	9502.08	7.2	11.1	0.25	0.48	792

Assessment of the physico-chemical pollution of the environment

The physico-chemical parameters concerned by this type of assessment must have the same units of measurement. Thus, eight parameters are affected because they are all expressed in milligrams per liter. The results are grouped in Table 2.

Table 2: values of the global pollution index (P)

Statio	**S1Wi**	**S1Sp**	**S1Su**	**S1Au**	**S2Wi**	**S2Sp**	**S2Su**	**S2Au**	**S3Wi**	**S3Sp**	**S3Su**	**S3Au**	**S4Wi**	**S4Sp**	**S4Su**	**S4Au**	**S5Wi**	**S5Sp**	**S5Su**	**S5Au**
P	6.95	5.34	4.97	7.58	10.1	9.60	5.87	**8.73**	**10.7**	**9.29**	**7.27**	**8.59**	**7.93**	6.53	4.72	**8.97**	4.88	5.03	4.38	**8.18**
Severely polluted																				

As shown in Table 2, all values found for the global pollution index are greater than 2 which, according to Mishra *et al.* (2016) and Zhao *et al.* (2020) indicate that, in general, the waters of the estuary are severely polluted (**Mishra *et al.* 2016; Zhao *et al.* 2020**). The values are even greater than 7 in the waters of the S1Au, S2Wi, S2Sp, S2Au, S3Wi, S3Sp, S3Au, S3Su, S4Au, S4Wi, and S5Au survey waters. Thus, according to this list of water sample reading, stations S2 and S3 are the most polluted, in other words, it is the satiations most exposed to wastewater discharges (urban and industrial) from the city of Kenitra which are the most polluted. It should also be noted that this significant pollution concerns stations S4 and S5, both of which are downstream from stations S2 and S3; thus their position explains the importance of their degree of pollution. Also, the results show that even the waters of S1, which is a station located upstream of the wastewater discharges from the city of Kenitra, are polluted. Pollution of the estuary therefore even affects the upstream part of the wastewater discharges from the city of Kenitra.

Moreover, the results show that in the same station, the degree of water pollution can change from one season to the next. The S4 station could be an example. Indeed, the degree of water pollution at this station is lower in summer than in autumn, and the waters of the S2 are less polluted in summer than during other seasons. The quantitative and qualitative variation in the flow of the Sebou wadi and the wastewater discharged into the estuary could be the main cause.

Physico-chemical typology of estuary waters

Principal Component Analysis: multivariate analysis factor analysis was carried out on 14 variables and 5 sampling stations to identify the variation in the quality of the water in the estuary. The values of the factor loads and the explained variance of the water quality parameters of this analysis are expressed in Table 3 and the graphic representation of the factor loads of the principal components is given by figure 2&3. The respective inertia percentages at three axes (C1, C2 and C3) are 32%, 25% and 14%, for a total of 71%.

Table 3: Factor load values and explained variance of water quality parameters

Variable	PC1	PC2	PC3
T °C	0.077	**-0.391**	-0.250
pH	**0.285**	0.249	-0.146
CE	-0.274	**0.366**	-0.239
DO	**-0.336**	0.184	-0.016
HCO_3^-	-0.156	-0.295	**-0.354**
SPM	0.143	**0.442**	-0.081
BOD5	0.163	0.278	**0.423**
COD	**0.402**	0.093	-0.006
TDS	-0.274	**0.366**	-0.239
NH4	**0.320**	0.137	-0.045
NO_3^-	**0.364**	-0.078	-0.354
NO_2^-	0.168	**0.274**	-0.159
O-PO_4	0.223	0.025	**-0.501**
SO_4^{--}	**-0.323**	0.117	-0.296
Eigenvalue	4.50	3.51	1.95
Proportion	0.32	0.25	0.14
Cumulative	0.32	0.57	0.71

Three components of the multivariate analysis group together 71% of the total variance. Component 1, representing 32% of the total variance, is positively correlated with the parameters pH, COD, NH_4^+ and NO_3^-, and is negatively correlated with the concentrations of dissolved oxygen (DO) and those of SO_4^{--}. From the negative side to the positive side, the axis C1 therefore corresponds to a concentration gradient (or values) increasing for the first group of variables and decreasing for the second group of variables. For the C2 axis, it represents 25% of the total variance, it is positively correlated with values of EC, SPM, TDS and NO_2, and is negatively correlated with temperature. The C2 axis therefore corresponds to a gradient of concentrations (or values) increasing for the first four variables and decreasing for temperature.

Concerning the C3 axis, according to the results, it corresponds to an increasing gradient for the values of the BOD5 and decreasing for the orthophosphates (O-PO_4) and HCO_3^-.

Typological of the physicochemical characteristics of the sampled water readings:

The analysis of the projection of the readings on the planes C1xC2 (Figure 3) and C1xC3 (Figure 4) shows that:

a. Distribution of readings in the C1xC2 plane

As shown in Figure 2, three groups of readings (G1, G2 and G3) are distinguished by their characteristics relating to the physicochemical parameters which contribute significantly in the components C1 and C2:

With respect to the physicochemical significance of the C1 axis, group G1 consists of readings with low pH and concentrations of COD, NH_4^+ and NO_3^-, but the concentrations of dissolved oxygen and sulphates are high. Likewise, according to the physicochemical significance of component C2, these readings have low temperatures and high values of electrical conductivity (EC), suspended matter (SPM). This group is made up of the S3a readings (carried out in autumn in S3) and all the readings which were carried out in the different seasons in S4 and S5. Thus, for all seasons the water pollution of stations S4 and S5 and during the fall the water pollution is characterized by readings with pH and high concentrations of COD, NH4 and low NO3; but the concentrations of dissolved oxygen and sulphates are low.

- Related to the physico-chemical constitution of the C1 axis, the second group G2 is formed by water sample readings having physicochemical characteristics opposite to those of the readings of the G1 group, i.e. readings with low pH and COD concentrations, High NH4 and NO3. But as with the G1 readings, the G2 group water sample reading have low temperatures and high values of electrical conductivity, suspended matter (SPM). It should also be noted that this group includes the S3 water sample reading taken in winter, spring and summer and two readings taken in winter and spring in S2. Thus, during the period of our study, in S3 for the majority of the seasons and in winter and in spring for station S2, the pollution is a consequence of a mixture of discharges of the original wastewater.

Note that a pollution characterized by excessive concentrations or values of organic matter is a sign of eutrophication of the medium(**Meyer-Reil and Köster, 2000**).

- The third group G3 is made up of water sample readings having certain physico-chemical characteristics intermediate between those of the G1 group readings and the characteristics of the G2 group readings, namely high concentrations of COD, NH_4^+ and NO_3^-, and low concentrations of dissolved oxygen and sulphate. But, vis-à-vis the characteristics relating to the signification of the axis C2, unlike the water sample readings of groups G1 and G2, water is characterized by higher temperatures and lower values of electrical conductivity (EC), suspended matter (SPM), salt (TDS) and nitrite (NO_2^-). Also of note, the G3 group brings together the readings of all seasons from station S1 and the summer and autumn readings of S2. All these readings show a lower degree of mineralization than those of the G1 and G2 groups.

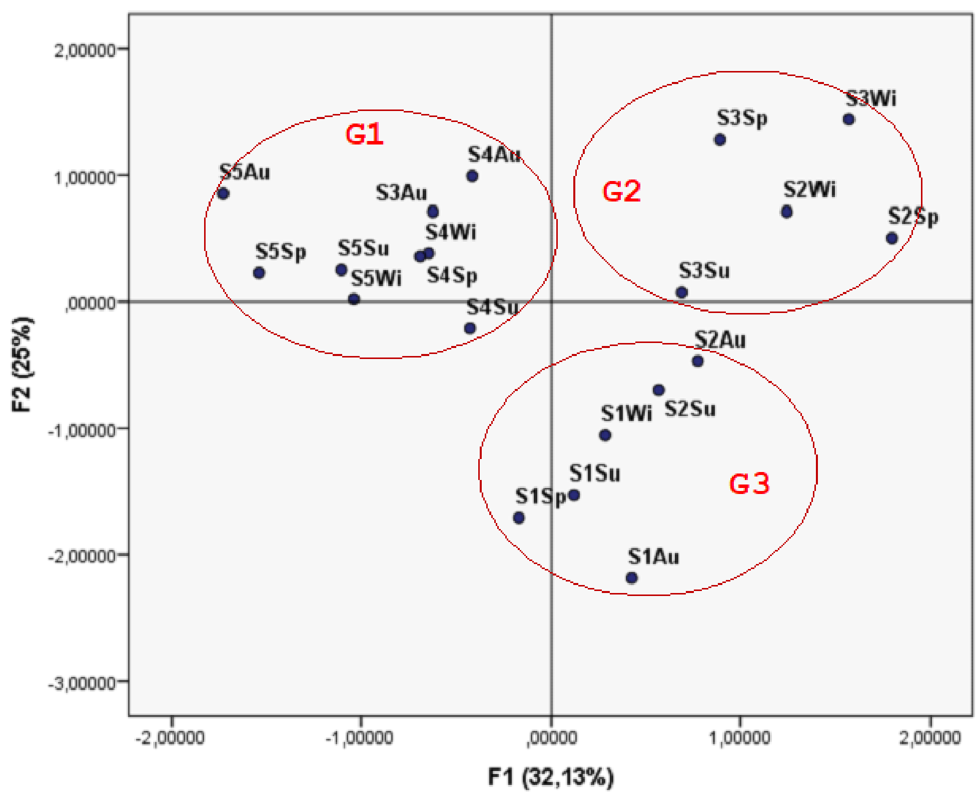

Figure 2: Projection of the readings in the factorial plane C1xC2

b. Distribution of readings in the C1XC3 plan

As shown in Figure 3, three groups of water sample reading (G'1, G'2 and G'3) are distinguished by the characteristics relating to the physicochemical parameters which contribute significantly in the constitution of the C3 component. The G'1 group is reassuring in the readings characterized by higher BOD5 and lower concentrations of O-PO4 and HP3 than those of the readings that make up the G'3 group while the readings of the G'2 group are characterized by concentrations of BOD5, alkalinity and orthophosphates intermediate between those noted in the readings of the group of G'1 readings and those of the water sample reading constituting the G'3 group. Note that, for all the stations surveyed, the distribution of water sample readings according to groups G'1, G'2 and G'3 shows that in the concentrations of BOD5, the alkalinity and orthophosphates which change in importance d 'one season to another. The qualitative and quantitative change in the physico-chemical characteristics of wastewater and leaching water from the catchment area could be the main causes.

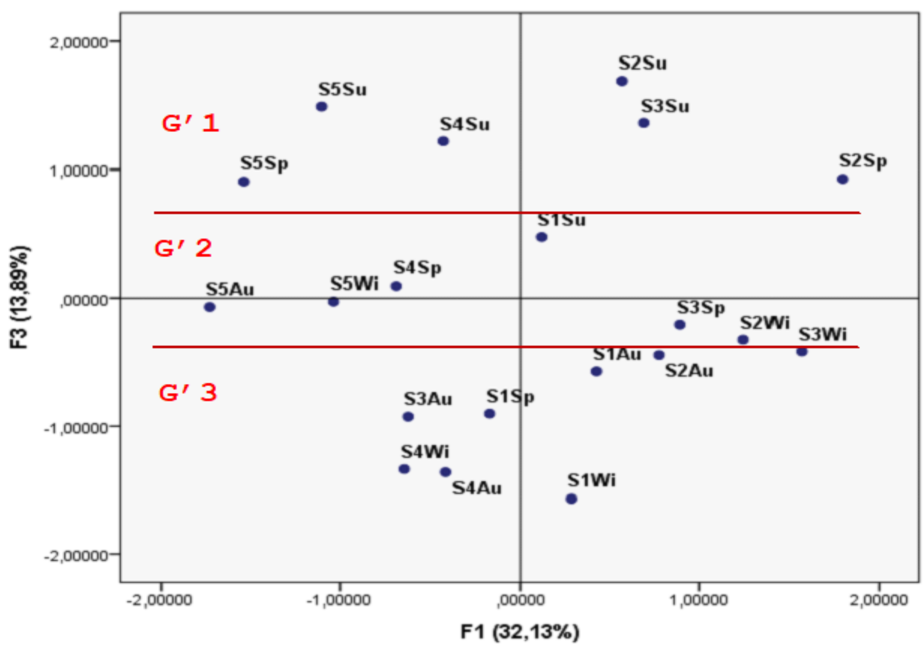

Figure 3: Projection of the readings in the factorial plane C1xC3

Furthermore, the C1 axis, from the negative side of this axis to its positive side, is a pollution gradient of the estuary which results from both urban wastewater discharges and industrial wastewater. Indeed, a richness of the environment by nitrogenous matter and a factor of eutrophication (**Kän-man and Jönsson, 2001**), and indicates an organic pollution of the environment, the decrease in the level of dissolved oxygen in the water can be due to a degradation of this organic matter, and high pH and COD characterize biotope pollution by industrial wastewater (**Jing *et al.* 2020**). It should also be noted that the highest concentrations of sulphates in wastewater can have an anthropogenic origin, and be present in the water via industrial effluents and atmospheric deposits (**Quinn *et al.* 2007**). Axis 2, by its physic-chemical characteristics, can be interpreted as an axis representing an increasing gradient (from the negative side to the positive side of the axis) of mineral pollution and the degree of continentally in relation to the sea in fact, mineral pollution can be characterized by high values of conductivity (**Totsche *et al.* 2007**), suspended solids content (**Petersen *et al.* 2004**), and high salinity of water (**Pawlowicz, 2008**).

For the distribution of the readings made with respect to the levels of BOD5, orthophosphates and alkalinity, the main axis of this distribution (C3), from its negative side to its positive side, can be considered as the axis representing an increasing gradient of increasing pollution of multiple origins: agricultural, urban and industrial. Indeed, the presence of orthophosphates in water can come from the leaching water of agricultural fertilizers and the degradation of organic matter of urban or agricultural origin (**Nest *et al*. 2016**), urban or industrial discharges for polyphosphates (**Hussain *et al.* 2011**). Thus, it is the readings of group G'3 that are the most affected by this mixture of different types of pollution, namely the majority of the readings carried out in S1, S2 and S3.

For the meaning of the C3 component, three chemical variables are significantly involved in its constitution. On the positive side of this axis are the readings with high BOD5 and low alkalinity and concentrations of orthophosphates. However, the high values of BOD5 indicate significant bacterial activity in the medium. Likewise, an alkalinity and a low concentration of orthophosphate indicate a low degree of mineralization of the water (**Adande *et al.* 2017**). Thus, for the readings located on the negative side of the C3 axis, the BOD5 are lower and the alkalinity and the concentrations of orthophosphates higher than those noted in the readings on the positive side of the C3 axis. Consequently, the fact of noting that, for the same station, the concentrations of BOD5, on one side and the concentrations of alkalinity and orthophosphates on the other side, change according to the seasons, this indicates that the importance of the activity and the degree of mineralization of the waters of this station change according to the seasons, and the quality and / or the quantity of polluting substances also change according to the seasons.

CONCULSION

The results show that the physico-chemical characteristics vary with the seasons, in other words the quantity of fresh water brought by the river to the estuary. Indeed, the variables whose concentration depends on the degree of dilution of the water of the estuary by the fresh water (water from the wadi Sbou and runoff water) showed low values in winters or in spring and high values in summer or fall. For example, electrical conductivity. On the contrary, other variables recorded high values during the rainy seasons such as the content of substances brought to the estuary by the water which comes from the leaching of the watershed feeding the river. For example, suspended matter and SO4 (polluting substance very present in fertilizers). It should also be noted that, for some stations, the variations in the physico-chemical characteristics of the water noted over time seem to be linked to the qualitative and quantitative variations in the wastewater discharges discharged into the estuary. Moreover, the analysis of the water quality of the estuary by the global pollution index showed that, for all the water readings analyzed, classifies the estuary as a spatio-temporally severely polluted hydro system. Likewise, the typological analysis of the waters of the estuary differentiated three groups of readings G1, G2 and G3 according to the values of pH, dissolved oxygen, chemical demand for oxygen, NH4, NO3 and SO4, and in two groups G1-G2 and G3 according to temperature, electrical conductivity, suspended matter, salinity, and in three groups of readings G'1, G'2 and G'3 according to the content of the BOD5, alkalinity and sulfates readings.

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