
Environmental Impacts of Industrial Liquid Discharges from the Food Alcohol Production Plant on the Waters of the Klou River of Logozohè in Benin

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Abstract: This study aims the evaluation of environmental impacts of dusty fluid on the production of nutriment alcohol at Logozohè through a physico-chemical settings of its components and an assessment of it impact on river Klou which is the fallen point. Then, twenty-two (22) skills were measured through the normative methods on eight (08) areas along the Klou river from the upstream to the downstream around the production land in 2017; August 25th to 28th. Data were submitted to descriptive and statistical analysis and a Main Components Analysis made with Minitab 14. Results reveal that the pH, turbidity, suspended matter (SS) and COD of the principal effluent and Klou river do not meet drinking and wastewater water quality standard for Republic of Benin. But nitrogen pollution is low and it's reduced to kjeldahl nitrogen (NTK). Organic pollution is very important and not biodegradable. This leads to suspicion of the use of synthetic organic solvents in the processes of the production unit. Conclusion: This massive organic pollution of the receiving environment on which local residents depend challenges more than one of the environmental impact of the food alcohol production plant on the future of the Klou river.

Keywords: Pollution, Water, Klou, Effluent, Industry, Agribusiness

1. Introduction

The first men, few in number and devoid of technical means, lived for a long time in harmony with their environment, like other animals [1]. The transition from the Paleolithic to the Neolithic with the sedentary lifestyle and the first agricultural

revolution profoundly disturbed this initial balance [2]. Subsequently, we have witnessed the population growth and industrial development, which have worsened the degradation of all environmental components [3]. Thus, the race to economic growth is engaged with a strong consumption of raw materials, the degradation of the living environment with rejections of all

kinds and many consequences on the nature, its resources and indirectly on the Man [4]. In addition, the industry has often favored sites near water bodies such as rivers, oceans and seas for the transportation of raw materials, for water supply and for discharges of industrial effluents [3, 5]. Thus, for decades, rivers and oceans have been the receptacle of industrial direct discharges, victims of accidental spills and/or polluted by runoff that leached from contaminated areas [6, 7]. This is the case in Benin of a Chinese food production plant based on cassava chips set up near the Klou river located in the district of Logozohè, commune of Savalou from where it draws a portion of its water needs and rejects its industrial effluents. After about ten years of activity, we are witnessing today an advanced and continuous degradation of a portion of the watercourse on which often depend the peasant riverside populations. The incessant aggravation of the pollution to the detriment of the populations (human, animal and vegetable) subservient to the watercourse pushed us to seek the environmental impacts of the liquid discharges of the food alcohol production plant on the waters of the Klou river of Logozohè.

2. Material and Methods

2.1. Presentation of the Study Area

The framework of our study is the Klou River, specifically the watershed from the Klou spring to the outlet of the Logozohè bridge located between 07°53,199'N and 002°05,995'E. It covers part of the communes of Savalou and Glazoué. Its altitude varies from 215 m from the source to 140 m at the outlet of Logozohè for an average altitude of

154.71 ± 21.96. The average elevation of the Klou catchment is 178.1 ± 19.9 m [7]. This region benefits from a humid tropical transition or Sudano-Guinean climate [8], belonging to a region subject to both equatorial influences and Guinean alternating regime influences. This region benefits from a humid tropical transition or Sudano-Guinean climate [8], belonging to a region subject to both equatorial influences and Guinean alternating regime influences. The average rainfall is 1150 mm, varying between 864 and 1637.3 mm between years. Temperatures are high all year round with minima ranging from 23 to 24°C and maxima ranging from 35 to 36°C [9]. Its relief is based on material Its rainfall pattern characterized by a distribution of rains marked by the appearance of two rainy seasons from March to July and from September to November; from two dry seasons from December to March and the month of August which corresponds to the decrease of precipitations precambrian granite-gneiss of the old base. These are metamorphic rocks marked by magmatic intrusions (granites). The relief culminates between 120 and 500 m with slopes varying between 3 and 10% in the agglomerated sites. The most common soils are tropical ferruginous soils with areas of concretion. There are also hydromorphic soils, vertisols [9].

2.2. Choice of Sampling Sites

The sites were selected from upstream to downstream of the plant according to a sampling plan (Table 1) in order to evaluate the quality of the water before and after the rejections of the plant.

Table 1. Sampling Sites and Geographic Coordinates.

N°	Denomination of the sites	Codes	Geographic coordinates
1	Site 1 "Source Klou" is located between the Aklampa village and Yagbo behind the village of Zoungoudo. It is here that the Klou river rises in the middle of rice and yam fields.	ST 1	08°07.209'N 002°08.012'E Alti : 215m
2	Site 2 located at the bridge between Ouèdèmè (common Glazoué) and Lahotan (common Savalou) as indicated by the name given to the site. Sampling was done on the left side under the bridge towards Lahotan.	ST 2	08°00.830'N 002°06.915'E Alti : 179 m
3	Site 3 or site of the Klou Dam. Sampling was done at the weir of the dam. It represents the receptacle of the waters of the river klou just before the mouth between the effluent of the plant and the river.	ST 3	07°53.270'N 002°06.098'E Alti : 159 m
4	Site 4 is located at the main liquid effluent of the plant. This is the place of the wastewater receptacle of the plant. Site 4 is used to evaluate the gross pollutant characteristics released by the plant before any contact with the waters of the Klou river.	ST 4	07°53.254'N 002°06.004'E Alti : 130 m
5	Site 5 is the point of contact between the Klou river and the effluent from the plant. Sampling was done in the sewage trench at the mouth of the liquid effluent and the Klou river.	ST 5	07°53.247'N 002°06.018'E Alti : 130 m
6	Site 6 is located in the Klou river at the mouth about 1 m after site 5	ST 6	07°53.240'N 002°06.016'E Alti : 131 m
7	Site 7 is located after the mouth of the effluent where the wastewater is mixed with water from the Klou river from the dam to the Klou Bridge	ST 7	07°53.199'N 002°05.995'E Alti : 140 m
8	Site 8 is located after the Logozohè bridge. It is another receptacle of Klou water and effluents from the alcohol production plant. This is one of the pockets of water in the dry season.	ST 8	

2.3. Sampling of Water

This study was the subject of a single campaign carried out

in the rainy season from 25 to 28 August 2017. All the water samples were recovered in plastic bottles of 1.5 L mineral water previously emptied, soaped without detergent and

rinsed three times with distilled water. Before any sampling. The vials thus conditioned are rerinsed three times with the water to be sampled. Samples are collected in the water column about 5 cm from the surface. After sampling, the vials are labeled and stored in a cooler equipped with a cold accumulator and sent to the laboratory at 4°C until analysis.

2.4. Physico-chemical Analysis Methods

Parameters such as pH, temperature, electrical

conductivity, dissolved total solids (TDS), salinity and dissolved oxygen were measured in situ according to standard NF EN 25814 using a multi parameter type Aqualyse Professional Plus YSI. The Winkler and Aquamerck Kit 1.11136.0001 were used respectively for the measurement of dissolved oxygen and total iron in situ by chemical means. Table 2 presents the standard methods used to determine the parameters for determining the physico-chemical characteristics of the water of the klou river.

Table 2. Standard Methods Used to Determine Laboratory Parameters.

Different parameters	Principle of the method	Reference of the method
NH ₄ ⁺	Formation in an alkaline medium of an indophenol compound by reaction of NH ₄ ⁺ with phenol and ClO ₃ ⁻ in the presence of nitroprusside Na ₂ [Fe(CN) ₅ NO].2H ₂ O as a catalyst gives a blue indophenol color. spectrophotometric measurement at λ = 630 nm	NFT90-015-2
NO ₂ ⁻	The method is based on the reaction of NO ₂ ⁻ ions with 4-aminobenzene sulfonamide at pH = 1.9 in the presence of de H ₃ PO ₄ to form a diazo salt which complexes with N- (Naphthyl-1) diamino dihydrochloride 1,2-ethane to give a pink color whose intensity is proportional to the NO ₂ ⁻ content and measurable at 540 nm	NF EN 26777
SO ₄ ²⁻	Precipitation of the sulphate ions by BaCl ₂ in a hydrochloric medium in the form of stabilized BaSO ₄ by a 25% solution of polyvinylpyrrolidone and nephelometric measurement at 650 nm.	NF T 90-040
P total	The method relies on the reaction of H ₃ PO ₄ ions with an acid solution containing molybdate and antimony ions to form an antimonyl phosphomolybdate complex which is reduced by ascorbic acid in bright-colored molybdenum blue measurable at 700 nm.	NF EN ISO 6878 (T90-023)
Cl ⁻	Reaction of Cl ⁻ ions with Ag ⁺ ions to form insoluble AgCl. Addition of a small excess of Ag ⁺ to give reddishcolored Agent Chromate in the presence of the chromate ions used as an indicator reaction pH of between 5 and 9.5.	NF ISO 9297
TH	Complexation of Ca ²⁺ and Mg ²⁺ ions using EDTA at pH 10. And assay in the presence of Eriochrome Black T as an indicator	NF T90-003
TAC	Titration of a sample of water to be analyzed by a 0.02 N acid solution at pH = 5.4	NF EN ISO 9963-1
COD	Acid Oxidation of Organic Matter by Excess K ₂ Cr ₂ O ₇ in the Presence of AgSO ₄ as Catalyst and HgSO ₄ to Complex Cl ⁻ and Determination of Excess Oxidant with Mohr Salt Solution (NH ₄ Fe (SO ₄) ₂ .6H ₂ O)	NF T90-101
BOD ₅	Oxidation of the biodegradable organic matter contained in a water sample by natural microorganisms in the dark in amber bottles saturated with O ₂ placed in a thermostatic incubator at 20°C ± 2°C for 5 days	NF EN 1899-2
MES	Filtration of water on fiberglass filter and then dried at 105 ± 2°C and gravimetric determination by mass difference	NF EN 872
Turbidity	Radiation emission of λ = 860 nm in a sample and measurement of scattered radiation transmitted by suspended particles	NF EN ISO 7027
O ₂ dissolved	Immersion of a probe consisting of a closed cell by a dissolved membrane permeable to O ₂ dissolved and containing the electrolyte and two metal electrodes in the water to be analyzed.	NF EN 25814
Total iron	Transform and / or maintain the iron contained in a Fe II water sample by acidification of the sample. The buffered medium at a pH of 4.5 with a solution of CH ₃ COONH ₄ -CH ₃ COOH. Complex the dissolved iron with hydroxylamine hydrochloride solution in the presence of 1,10-phenanthroline which develops a measurable orange-red color at 510 nm	NF T90-017

Determination of the ion Nitrate NO₃⁻

In the presence of sodium salicylate, the nitrates give the yellow-colored sodium paranitrosalicylate which is capable of a colorimetric determination at 520 nm [10]. For all spectrophotometric methods, the Lovibond Spectro II-4C Spectrometer was used. For BOD₅, the respirometric method with Oxitop BOX WTW R in a 12-station thermostatic chamber was used.

2.5. Statistical Analyzes

The data from the laboratory analysis as well as those taken or measured in the field were the subject of a descriptive statistic in which the means and standard deviations of the data of the different sites studied were calculated. The description of the links between the chemical characteristics of the pollutants of the river in the rainy season was made by a Principal Component Analysis. Excel

and Minitab 14 software were used.

3. Results and Discussion

3.1. Spatial Variations of Physicochemical Parameters

3.1.1. Temperature and Hydrogen Potential (pH)

Figure 1 shows the variation in water temperature at the sites sampled during the campaign. From the analysis of the graph, it appears that the temperature varies between 24.9 and 30.9°C with an average of 26.76 ± 0.90°C. The lowest value of the temperature is observed at the ST3 site while the highest value is observed at the ST4 site. The coefficient of variation (% CV) of the temperature is 9.54 lower than 10, showing that the temperature data are homogeneous. Despite this homogeneity of the temperature data, it should be noted

that the hottest points are at the main effluent and the confluence zone between the main effluent and the river water. Temperature differences between the Klou river water and the plant effluent are around 6°C. However, wastewater discharge standards in the Republic of Benin recommend variations of less than or equal to 5°C [11]. Our average temperature value is higher than that obtained by [12] who worked in the Ouémé Delta basin with temperature averages of 22 and 26.20 ± 0.47°C. Our maximum value is close to 30.5°C found by the same authors in this area (Ouémé Basin). On the other hand, these average values are lower than those obtained by [4] whose average values are 27.9 ± 0.86 and 28.1 ± 0.95°C, with maxima respectively 28.9 and 29.4°C in the same zone as [12]. These observed variations in the temperature measurement would be related to several climatic parameters such as sunshine, the rainy season and the time of day when the measurement was made. However, it should be noted that [12] worked exclusively on surface water, as did the present study, while the [4] studies focused on both surface water and groundwater.

Figure 2 shows the change in pH of the water at the sites sampled during the campaign. From the analysis of the graph, it appears that the pH varies between 5.32 and 7.52 with an average of 6.92 ± 0.27. The lowest pH value is observed at the ST4 site (main effluent) while the highest value is observed at the ST2 site (Ouèdèmè-Lahotan bridge site). The coefficient of variation (% CV) of the pH which is 11.1 (10 ≤ % CV ≤ 30) shows that the homogeneity of the pH data is acceptable. The average of our pH values is higher than those obtained by [12] and [4] whose values vary respectively between 6.62 ± 0.6 and 6.39 ± 0.8. Our maximum value is close to those obtained by these authors (respectively 7.5 and 7.3). The recommended pH values for surface water are between 6.5 and 9 [10]. No site has a pH greater than 9. However, the pH of the main effluent is less than 6, which is contrary to the normative requirements of Benin [11]. pH depends on carbon balance and photosynthetic activity of ecosystems. pH conditions bacterial growth. Nitrifying bacteria require pHs between 7.4 and 9 for Nitrosomonas, 8.5 and 9.1 for Nitrobacter; in contrast, the Acinetobacter dephosphating bacteria thrive further at more acidic pHs, ranging from 6.1 to 7.5 [4].

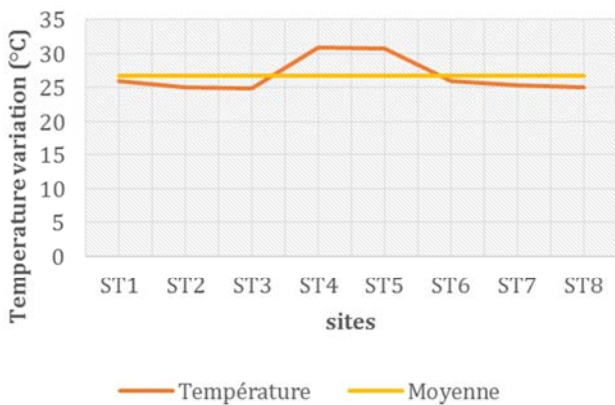


Figure 1. Spatial temperature variation in the sampling area.



Figure 2. Spatial variation of the pH of the water in the sampling area.

3.1.2. Electrical Conductivity and Turbidity of Water

Figure 3 shows the variation of the electrical conductivity of the water at the sites sampled during the campaign. From the analysis of the graph, it appears that the electrical conductivity varies between 51.4 and 470 µS/cm with an average of 185.23 ± 61.10 µS/cm. The lowest value of electrical conductivity is observed at the ST1 site while the highest value is observed at the ST4 site. The coefficient of variation (% CV) of the conductivity is 93.3 showing a disparity between the conductivity data. The disparity noted is mainly due to the high conductivities of the effluents of the plant which are more than 5 times the electrical conductivity of the waters of the receiving environment. Our extreme values (minimum and maximum) are respectively lower and higher than those obtained by [12] which are respectively 59.8 and 238 µS/cm. All these values obtained are lower than the recommended limit value for freshwaters of 2000 µS/cm [11].

Figure 4 shows the variation in turbidity of water at the sites sampled during the campaign. From the analysis of the graph, it appears that the turbidity varies between 134 and 1313 NTU with an average of 401.75 ± 136.46 NTU. The lowest value of turbidity is observed at the ST1 site while the highest value is observed at the ST5 site. The coefficient of variation (% CV) of the turbidity is 96.07. This % CV value shows a dispersion of the data. This dispersion is created by the high turbidity value recorded at the ST5 site, which is more than four times the turbidity recorded at the ST3 site located in the river before the confluence zone. This local observation of turbidity is due to a swirling of the water at the meeting point of the two water masses which resuspends the surface sediments. Our extreme values (minimum and maximum) and our average are much higher than those obtained by [4] which are respectively from 2 to 100 NTU for the first campaign with an average of 43.15 ± 32.1 NTU and 3 to 326 NTU for the 2nd season with an average of 103.54 ± 91.54 NTU. The maximum value recommended by the World Health Organization (WHO) for drinking water is 5 NTU [13]. All values obtained are above WHO allowable values, indicating that the waters of the sampled sites are unfit for consumption, except after adequate treatment that lowers its turbidity.

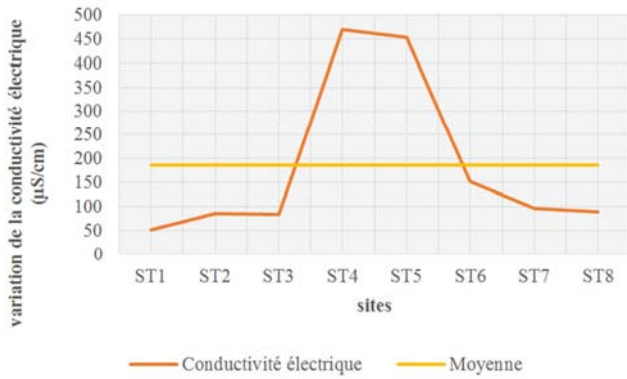


Figure 3. Spatial variation of electrical conductivity of water in the sampling area.

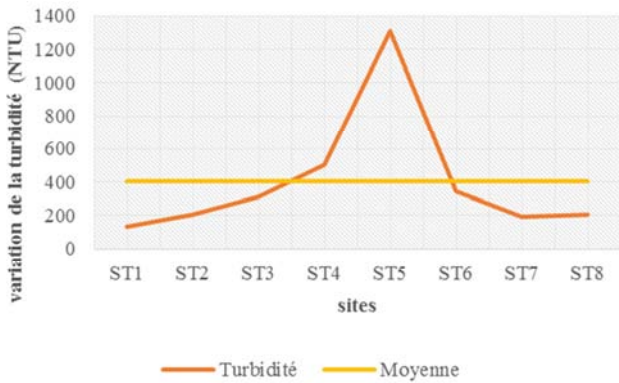


Figure 4. Spatial variation of water turbidity in the sampling area.

3.1.3. Suspended Matter and Salinity of the Samples

Figure 5 shows the variation of SS in the water at the sites sampled during the campaign. From the analysis of the graph, it appears that the shape of the curve of figure 5 is comparable to that of fig. 4. The contents of MES vary between 44.92 and 998.25 mg/L with an average of 276.81 ± 116.70 mg/L. The lowest value is observed at the ST1 site while the highest value is observed at the ST5 site. Our extreme (minimum and maximum) values obtained are higher than those obtained by [4] which is of zero mg/L for the minima then respectively 65 mg/L and 198mg/L for the maxima. From the superposition of the curves of Figures 4 and 5, it is tempting to deduce that the turbidity of the water is caused exclusively by the suspended matter (SS). These SS are not exclusively from industry releases, but also from runoff that has been stranded in the Klou river.

Figure 6 shows the variation of the salinity in the water at the sites sampled during the campaign. From the analysis of the graph, it appears that the salinity varies between 0.02 and 0.21 ppt with an average of 0.07 ± 0.02 ppt. The lowest value is observed at the ST1 site while the highest value is observed at the ST5 site. The coefficient of variation (% CV) of the salinity is 81.8. This value of the coefficient of variation shows that the salinity values recorded are not homogeneous. The non-homogeneity in all the salinity data is caused by the values taken by this parameter at the ST4 and ST5 sites which are 4 to 7 times the water salinity at the ST3 site. The salinity of the river water just after the mouth of the

plant effluent is higher than before the mouth. Therefore the effluents from the plant slightly disturb the physico-chemical balance of the Klou river without modifying it fundamentally because the salinity values return to normal at the ST8 site. Our extreme (minimum and maximum) values obtained are higher than those obtained by [4] which are of zero mg/L for the minima then 10 and 20 ppb respectively for the maxima. WHO recommends 1.5. ppm in drinking water. Our values are in every respect well below this limit.

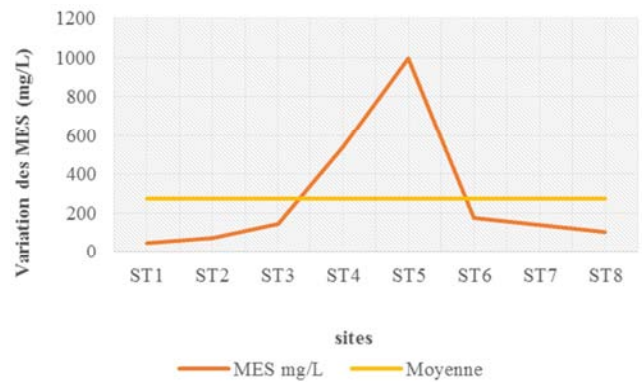


Figure 5. Variation of Suspended matter.

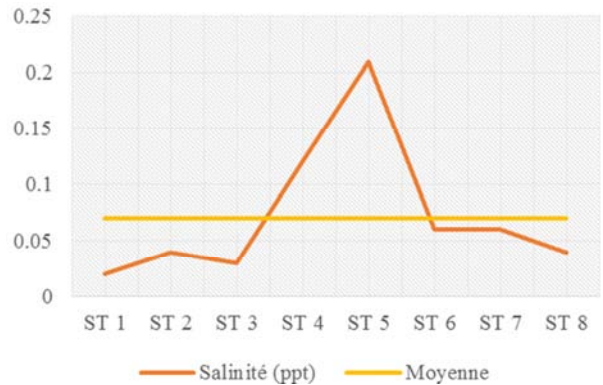


Figure 6. Spatial variation of water salinity.

3.1.4. Spatio-temporal variation of nutriments

i. Total Iron



Figure 7. Spatial variation of Total Iron.

Figure 7 shows the variation of total iron in water at the sites sampled during the campaign. From the analysis of the

graph, it appears that Total Iron varies between 0.5 and 7.5 mg/L with an average of 2.81 ± 1.05 mg/L. The lowest value of total iron is observed at the ST2 site while the highest value is observed at the ST4 and ST5 sites. The coefficient of variation (% CV) of Total Iron is 105.25, which allows us to state that the total Iron data are disparate. This disparity is due to the high total iron values recorded at the ST4 and ST5 sites. Our minimum value obtained is higher than those obtained by [4] which are respectively 0.09 and 0.04 mg/L and that of [14] on the dam of SONEB Okpara (0.15 mg/L). Our maximum value obtained is lower than those obtained by these same authors. Their values are respectively 10 and 9.12 mg/L for both campaigns with averages of 2.2 ± 3.11 mg/L and 2.36 ± 2.88 mg/L [4] and 38 mg/L [14]. [11] laying down quality standards for wastewater in the Republic of Benin does not formally regulate total iron, but recommends that other inorganic pollutants not formally regulated should individually contain daily contents not exceeding 5.0 mg/L. The maximum allowable value according to WHO guidelines for the quality of drinking water is 0.3 mg/L. In our case, we are beyond this limit for waste water discharged by Logozohè food alcohol production plant. In fact a contamination of iron water is not a bad thing in itself. The human body needs it as a source of hemoglobin improvement. But high levels of contamination of iron water promotes a proliferation of microorganisms especially sulphate reducer using iron as an oxidant. These chemical processes lead to the reduction of sulphates SO_4^{2-} into H_2S sulphide source of odor in anaerobic waters [15-16-4].

ii. Total Manganese

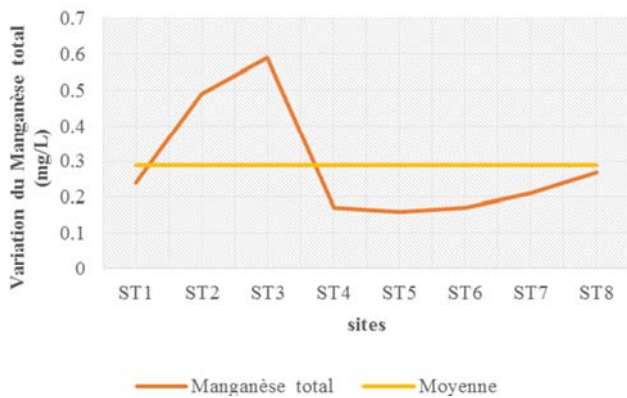


Figure 8. Spatial variation of total manganese.

Figure 8 shows the variation of total manganese in water at the sites sampled during the campaign. From the analysis of the graph, it appears that the total manganese varies between 0.16 and 0.59 mg/L with an average of 0.29 ± 0.06 mg/L. The lowest value is observed at the ST5 site while the highest value is observed at the ST3 site. Our values obtained are lower than those obtained by [14] at the Okpara dam with extreme values (minimum maximum) respectively 0.07 to 5.5 mg/L. The total iron (0.75 mg/L) and total manganese (0.59 mg/L) values at the ST3 site show that these values stand and reflect the telluric origin followed by a

phenomenon of accumulation of these parameters at the dam level [17-21].

iii. Chloride Ion Content

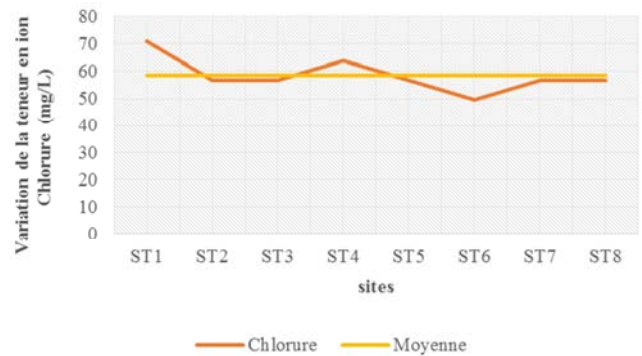


Figure 9. Spatial variation in chloride ion.

Figure 9 shows the variation of chloride ion in water at sites sampled during the campaign. From the analysis of the graph, it appears that the chloride ion concentrations vary between 49.7 and 71 mg/L with an average of 58.575 ± 2.23 mg/L. The lowest value is observed at the ST6 site while the highest value is observed at the ST1 site. Also, the coefficient of variation (% CV) of chloride ions at the sites sampled is 10.74. This value shows that the degree of homogeneity of the recorded values is acceptable. This homogeneity reflects a lack of unusual contribution of chloride ion to the receiving medium. Our minimum value obtained is higher than those obtained by [4] which are respectively 24.85 and 14.2 mg/L. Our maximum value obtained is lower than those obtained by these same authors who are respectively 142 and 149.1 mg/L for both campaigns. The drinking water quality guidelines require a maximum value of 250 mg/L [11]. All values obtained are below this limit.

3.1.5. Hardness of Water and Alkalinity of Samples

Figure 10 shows the spatial variations in water hardness. From the analysis of the curves, it appears that the calcium hardness varies between 1.78 and 5.35°f with an average of 2.45 ± 0.47 °f. The lowest value is observed at sites ST1, ST2, ST3, ST6, ST7 and ST8 while the highest value is observed at the level of the main effluent of the plant, that is to say at the ST4 site level. The magnesium hardness varies from "not determined" (ND) to 36.05°f with an average of 8.11 ± 4.18 °f. The lowest value is observed at the ST1 site while the highest value is observed at the ST3 or Logozohè dam site. Calcium and magnesium hardnesses are not regulated by the standards of rejections in Benin. On the other hand, the Benin standard on the quality of drinking water sets the limit of calcium and magnesium hardness respectively at 25°f (100 mg/L) and 23.83°f (50 mg/L). All levels of calcium hardness recorded are well below this threshold. On the other hand, at the level of the magnesium hardness, the value recorded at the ST3 site exceeds the threshold. The temporary hardness or bicarbonate hardness varies between 4 and 8°f with an average of 6.25 ± 0.6 °f. The lowest value is observed at sites ST1 and ST4 while the highest value is observed at sites ST5,

ST6 and ST7. The total hardness (TH) ranges from 1.78 to 37.83°F with an average of $10.56 \pm 4.22^\circ\text{f}$. The lowest value is observed at the ST1 site while the highest value is observed at the ST3 site as the magnesium hardness. The Beninese standard on the quality of drinking water requires a limit of 200 mg/L for the hardness is 20°f. The ST3 site alone has a hardness above this threshold. This jump in value of the magnesian and total hardness at the ST3 site would be related to a phenomenon of accumulation.

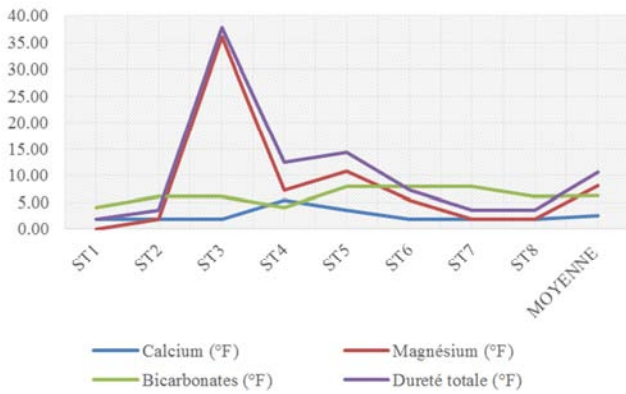


Figure 10. Spatial variation in water hardness.

Figure 11 shows the variation of alkalinity in water at the sites sampled during the campaign. From the analysis of the graph, it appears that the alkalinity varies between 4 and 8°f with an average of $6.25 \pm 0.6^\circ\text{f}$. The lowest value is observed

at sites ST1 and ST4 while the highest value is observed at sites ST5, ST6 and ST7. Our extreme (minimum and maximum) values obtained are higher than those obtained by [4] which are respectively 1.1 and 0.4°f for the minima and then 8 and 2°f respectively for the maxima. For a pH ranging between 5.32 and 7.52, the alkalinity is exclusively related to the bicarbonate ions.



Figure 11. Spatial variation of alkalinity of water in the sampling area.

3.1.6. Nitrogen Pollution and Orthophosphate

Table 3 presents the variations in nitrogen pollution in wastewater from the agri-food industry and the klou river.

Table 3. Variation of nitrogen pollution in the study area.

Site Settings	ST1	ST2	ST3	ST4	ST5	ST6	ST7	ST8	Average	Ecart-type
Nitrates N-NO ₃ ⁻ (mg/L)	< 1	6	< 1	2	2	< 1	< 1	< 1	1,25	0,81
Nitrites N-NO ₂ ⁻ (mg/L)	< 0.046	< 0.046	0.04	< 0.046	< 0.046	< 0.046	< 0.046	< 0.046	ND	ND
Ammonium N-NH ₄ ⁺ (mg/L)	0,6	1	0,8	3,5	3,7	1,9	0,4	1,2	1,6375	0,46
NTK (mg/L)	2,8	1	3	21,2	34,1	2,8	0,7	5,6	7,51	4,6

<: sign of inferiority; ND: Not Determined

Table 3 presents the variation of nitrogen pollution in the study area. From the analysis of the table data, it appears that the oxidized form of the nitrogen pollution (NO₂⁻ and NO₃⁻) is negligible as a whole, except at the ST2, ST4 and ST5 sites for the nitrate ions where the measured values are respectively 6 mg/L and 2 mg/L. For the nitrite ion outside the ST3 site where the measured value is 0.04 mg/L, all other sites have nitrite ion values of less than 0.04 mg/L. The Ammonium ion varies between 0.4 and 3.7 mg/L with an average of 1.64 ± 0.46 mg/L. The lowest value is observed at the ST7 site while the highest values are observed at the ST4 and ST5 sites. The coefficient of variation (% CV) of the ammonium ion contents is 79%, showing that the contents of this parameter change to sawtooth. The Beninese standard for waste water did not regulate ammonium ions. The variation of NTK in water at the sites sampled during the campaign ranged from 0.1 to 34.1 mg/L with an average of 7.51 ± 4.6 mg/L. The lowest value is observed at the ST2 sites while the high values are observed at the ST4 and ST5 sites. The Beninese standard for wastewater recommends 200 mg/L. Our values are well below this limit. These low values of the

NTK result from the fact that the current campaign was carried out at a time when the plant is idle and secondly that the majority of the pollution discharged was leached by rainwater. The measurement of NTK represents the sum of NH₄⁺ contents and organic nitrogen. From the data in Table 3 we find that the low nitrogen pollution is essentially organic. On the other hand, if NH₄⁺ is not directly toxic to aquatic fauna, its conjugate base NH₃ is very toxic for ichthyenne fauna. But our pH values ranging between 5.32 and 7.52 do not allow to glimpse a significant presence of NH₃ in the receiving medium.

Figure 12 shows the variation of orthophosphate in water at the sites sampled during the campaign. From the analysis of the graph, it appears that the orthophosphate varies between 0 and 2.7 mg/L of P with an average of 0.71 ± 0.43 mg/L. The lowest value is observed at the ST3 sites while the higher values are observed at the ST4 and ST5 sites. These values are much higher than those obtained by [12] which are very close to zero. The threshold for phosphorus release is 2 mg/L for sensitive media [11]. The total phosphorus input of effluents from the mill to the watercourse exceeds this limit.

This state of affairs exposes the receiving environment to eutrophication and, in the long term, to the death of the stream downstream from the point of discharge of the plant if no action is taken.

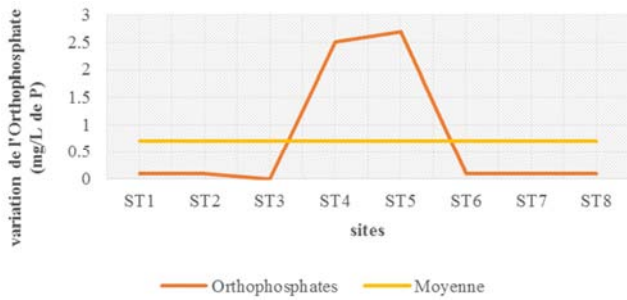


Figure 12. Spatial variation of Orthophosphate in samples.

3.1.7. Variation of the N/P ratio in the samples

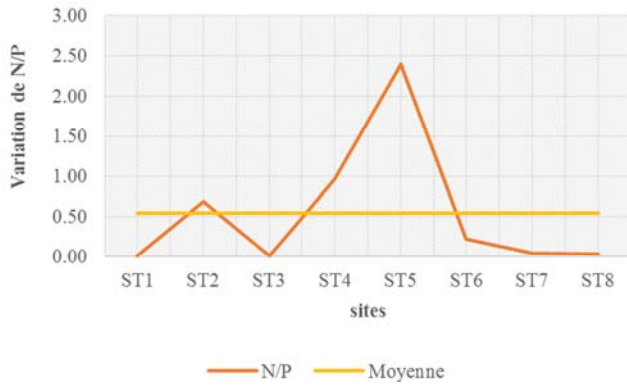


Figure 13. Spatial variation of the N/P ratio in the samples.

Figure 13 shows the variation of the N/P ratio in the water at the sites sampled during the campaign. From the analysis of the graph, it appears that the ratio N/P varies between 0.01 to 2.40 with an average of 0.55 ± 0.3 . The lowest value is observed at the ST1 site while the highest value is observed at the ST5 sites. All of these N/P ratios are below 7.2, indicating that nitrogen is the limiting factor for eutrophication [18]. This limiting nitrogen is very available. Depending on the organisms, it can be captured directly in the air and/or come from run-off water having leached agricultural areas chemically amended by agricultural fertilizers.

3.1.8. Biochemical Oxygen Demand (BOD) and Chemical Oxygen Demand (COD) in Water Samples

Figure 14 shows the variation of BOD₅ in the water at the sites sampled during the campaign. From the analysis of the graph, it appears that the BOD₅ varies in sawtooth from the ST1 site to the ST8 site. The values for BOD₅ range from 0 to 102 mg O₂/L with an average of 33.38 ± 13.54 mg O₂/L. The lowest value is observed at the ST4, ST6 and ST8 sites while the highest value is observed at the ST5 site. Our minimum value obtained is consistent with those obtained by [4] which is 0 mg O₂/L. Our maximum value obtained is higher than those obtained by these same authors who are

respectively 28 and 39 mg O₂/L for the two campaigns with average values of 12.846 mg and 19.692 mg of O₂/L. On the other hand, our minimum value is lower than that obtained by [20] which is 10 mg O₂/L for a maximum value of 29 mg O₂/L. BOD₅ expresses the amount of oxygen required for degradation of biodegradable organic matter in one liter of water by microorganisms at 20°C. It is a way of assessing the biodegradable organic matter content of a receiving medium through the cost of dissolved oxygen to pay for eliminating this pollution. The Beninese industrial wastewater discharge standard sets a limit of 0.11 kg of BOD/hL of products manufactured for the agrifood industries or just 100 mg of BOD/L of wastewater discharged. This value is reached only at the ST5 site probably due to the accumulation phenomenon. The ST4, ST6 and ST8 sites where the measured value of BOD₅ is zero are located on the penetration side of the main effluent from the mill into the watercourse. It is as if in each of these points, it is always the BOD₅ of the main effluent that is measured. This can be explained by the fact that the discharged effluent does not mix rapidly with the waters of the watercourse due to the difference in density (wastewater \approx river water \approx) and seems to be pushed along the river.

Figure 15 shows the variation of COD in water at the sites sampled during the campaign. From the analysis of the graph, it appears that the COD varies between 49.06 and 4612.11 mg O₂/L with an average of 1150.04 ± 577.43 mg O₂/L. The lowest value is observed at the ST1 site while the highest value is observed at the ST5 site. Our minimum value obtained is consistent with those obtained by [4] which is 0 mg O₂/L. Our maximum value obtained is greater than those obtained by these same authors who are respectively 189 and 245 mg O₂/L for the two campaigns with average values of 12.846 mg and 19.692 mg of O₂/L. This shows that there is a shortage of Oxygen in the river and raises many questions about the future of this river if nothing is done when we know that Oxygen is essential for life [20]. The Beninese standard did not specifically regulate the COD at the level of the rejects of the agro-food industries. On the other hand, at the level of other industries, the threshold of COD varies according to the type of industry. The threshold not to be exceeded is 30 kg of COD/tonne of finished product. The standard requires a maximum daily release of COD not exceeding 300 mg/L. This limit is exceeded at the ST4, ST5, ST6 and ST8 sites. Recall that in these points the BOD₅ is zero except at the site ST5. This observation suggests that the effluent discharged by the plant into the watercourse is mainly loaded with organic matter refractory to biodegradation. This type of pollution is very damaging to the receiving environment, which manifests itself in the loss of the river's biodiversity and the emission of foul odors that is harmful to local residents.

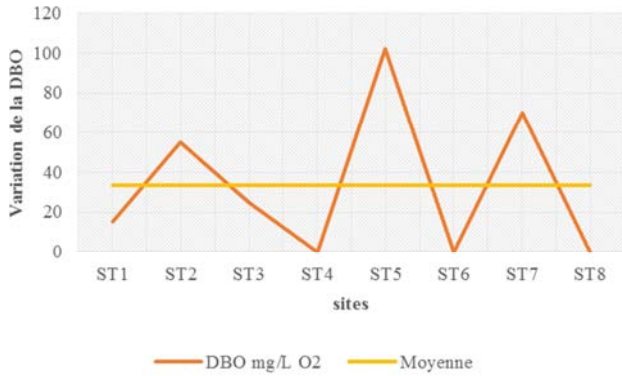


Figure 14. Spatial variation of BOD in water samples.



Figure 15. Change in COD in the water of the sampling area.

3.1.9. Variation in BOD/COD Ratio in Samples

Figure 16 shows the variation of the BOD/COD ratio in the water at the sites sampled during the campaign. From the



Figure 16. Spatial variation of the BOD/COD ratio in the samples.

3.2. Analysis of Sampling Sites

The different links between the pollution parameters monitored and the sampling sites are given in Tables 4 to 8 and Figures 17 and 18.

Table 4. Eigenvalues.

Eigenvalue	12.611	3.711	2.717	1.758	0.614	0.482	0.108	0	0
Proportion	0.573	0.169	0.123	0.08	0.028	0.022	0.005	0	0
Cumulative	0.573	0.742	0.865	0.945	0.973	0.995	1	1	1

analysis of the graph, it appears that the BOD/COD ratio varies between 0 and 0.38 with an average of 0.17 ± 0.06 . The lowest value is observed at the ST4, ST5 and ST6 sites while the highest values are observed at the ST1, ST2, ST3 and ST7 sites. According to [4], the BOD_5/COD ratio gives a first estimate of the biodegradability of the organic matter of an effluent at the intervals below:

- (1) $BOD_5/COD > 0.5$: the effluent is easily biodegradable.
- (2) $0.33 < BOD_5/COD < 0.5$ the effluent is biodegradable with selected strains.
- (3) $0 \leq BOD_5/COD < 0.33$ the effluent is not biodegradable.

Virtually all the water in the Klou river is not biodegradable except at the ST2 and ST3 sites where it is difficult to biodegrade with selected bacterial strains. This state of affairs may be justified by the fact that the Klou river is in a highly agricultural zone where the use of synthetic pesticides is widespread, the runoff having leached from freshly sprayed agricultural areas drained pesticide residues in the stream making it refractory to biodegradation. Also, this non-biodegradability of the water has been reinforced by the effluents of the plant. Thus, depending on the biological treatment sought and the bacterial populations to be favored, the following nutritional ratios should also be respected:

- (1) $10 < COD/N < 60$, to promote denitrification (conversion of nitrogen in the form of nitrates to nitrogen gas);
- (2) $30 < COD/P < 300$, to promote the dephosphatation (overaccumulation of phosphorus by bacteria).

The analysis of vectors and eigenvalues shows that the first three main components account for more than 86.5% of the information contained in the initial variables. We can therefore use the first three components to interpret the

relationships between the input variables since the share of information that these (03) components group together is greater than 50% (Table 4).

Table 5. Correlation Between Variables.

Variables	PC1	PC2	PC3
Turbidity	0.24	-0.251	-0.03
Temperature	0.275	0.05	-0.084
Potential Hydrogen	-0.139	-0.344	-0.026
Electrical conductivity	0.275	0.003	-0.064
Complete alkalinity	0.015	-0.396	0.32
Chloride	0.016	0.333	-0.82
Calcium	0.243	0.153	-0.155
Magnesium	-0.011	-0.229	-0.451
Total hardness	0.017	-0.21	-0.465
Dissolved oxygen	-0.273	-0.079	0.041
Ammonium	0.272	-0.01	0
Oxydability	0.278	-0.01	-0.019
Total iron	0.278	0.016	-0.039
Total manganese	-0.175	-0.183	-0.344
BOD	0.072	-0.383	0.009
COD	0.267	-0.113	0.005
MES	0.265	-0.162	-0.048
NTK	0.273	-0.096	-0.058
Pt	0.109	0.374	-0.269
N/P	0.258	-0.178	-0.016
DBO/DCO	-0.197	-0.107	-0.288
DBO/(DBO+DCO)	-0.196	-0.104	-0.28

Summarizing the different correlations in Table 6 we note that:

Table 6. Main Components and Types of Correlations with Starting Variables.

Sign	PC1	PC2	PC3
-	Dissolved Oxygen	Turbidity, Potential hydrogen, Complete Alkalinity, DBO	DBO/DCO, Magnesium, total hardness, total manganese
+	N/P, DCO, MES, NTK, Ammonium, oxydability, total iron, Calcium, electrical conductivity, Temperature	Chloride, Pt	Compleat alkalinity

- (1) On the first axis (principal component PC1), the MES are to a lesser extent positively correlated with the ammonium ions, the COD, and NTK appearing as well as the majority of the MES are organic that mineral corroborating the thesis according to which the non-biodegradability of The Klou river is caused by runoff from agricultural areas treated with refractory agricultural inputs such as organochlorine pesticides. On this first component, there is also a negative correlation between dissolved oxygen and SS, oxidability, COD, NTK, ammonium ions and total iron. This state of affairs can be explained by the fact that the main causes of the low dissolved oxygen content of Klou river water are the presence of iron and organic matter in the water column.
- (2) On the second axis (principal component PC2), the turbidity, the BOD, the pH and the total alkalinity on the one hand and on the other hand the Pt are negatively correlated. In other words, an increase in the Pt content promotes a microbial proliferation that accelerates the decomposition of the biodegradable

organic matter into CO₂ and H₂O according to the equation: $\{CH_2O\} + O_2 \leftrightarrow CO_2 + H_2O$. The production of CO₂ influences the pH and the production of bicarbonate (HCO₃⁻) according to the equation: $CO_2 + 2H_2O \leftrightarrow H_3O^+ + HCO_3^-$. On the third axis (component PC3), magnesium and total hardness are positively correlated. This observation shows that the total hardness is mainly magnesium. The negative correlation between the BOD/COD ratio and the total alkalinity is still justified by the biodegradation of the organic matter in favor of the production of bicarbonate.

Tables 7 and 8 show the sets of points that have similarities and the correlations between monitored parameters and sampling points.

Table 7. Main Components and Types of Site Correlations.

Sign	PC1	PC2	PC3
-		Site 1, site 3, site 5	Site 8
+	Site 2, site 4, site 7	Site 6	

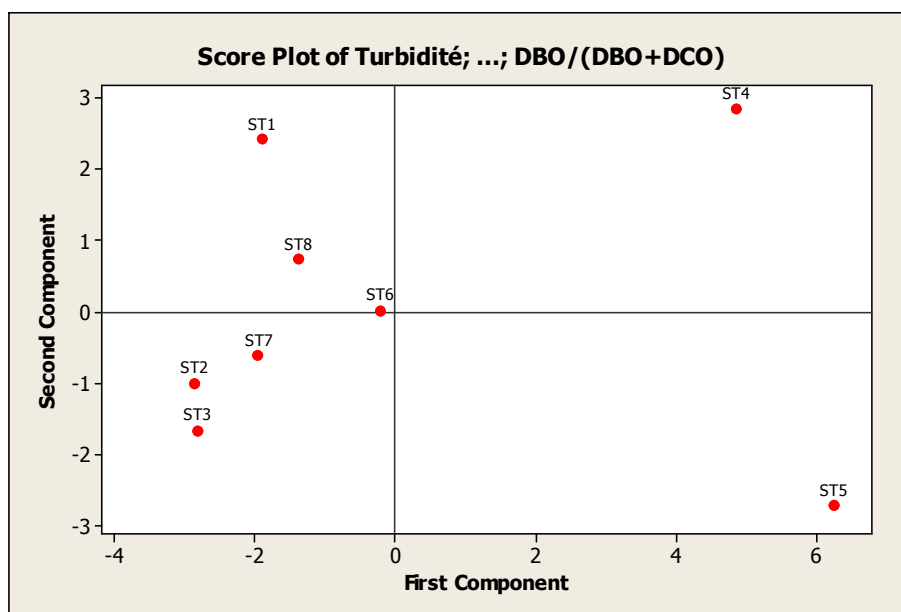


Figure 17. Score plot.

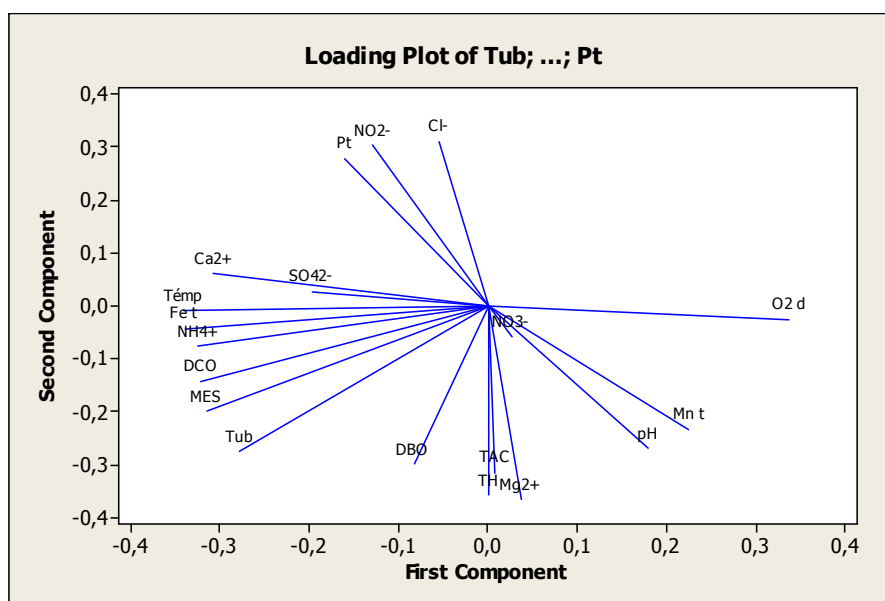


Figure 18. Loading plot.

Table 8. Analysis of relationships between pollutants and sites.

Signe	PC1	PC2	PC3
-	Dissolved Oxygen	Turbidity, Potential hydrogen, complete alkalinity, DBO, Site 1, Site 3, site 5	DBO/ (DCO+DCO), DBO/DCO, Site 8, Magnesium, total hardness, total manganese
+	N/P, DCO, MES, NTK, Ammonium, oxydability, total iron, Calcium, electrical conductivity, Temperature, Site 2, site 4, site 7	Site 6, Chloride, Pt	Complete alkalinity

It appears that :

(1) the sites 2, 4 and 7 have, to a small extent, a high electrical conductivity associated with a high temperature, a high ammonium content, a high level of calcium, a large amount of total iron, a high degree of oxidation, a high ratio of High N/P, a large COD, MES,

NTK but not associated to a small extent with a large amount of dissolved oxygen. This finding simply shows that the availability of Organic Matter (OM) in the water column is negatively correlated with the availability of dissolved oxygen. In other words, at sites 2, 4 and 7 the biodegradation of the organic

material is very active and generates other electrolytes such as NH_4^+ ions and the source heat of high temperatures recorded ;

- (2) sites 1, 3 and 5 have a high hydrogen potential which is associated with a high total alkalinity, a high biochemical oxygen demand (BOD) and, to a lesser extent, a high turbidity while the site 6 has a high rate of chloride associated with a high level of total phosphorus (Pt);
- (3) the site 8 has a high magnesium content which is associated with a high total hardness and a high total manganese content and, to a lesser extent, a high BOD/COD ratio, but is not associated with a high total alkalinity.

4. Conclusion

At the end of our study, the analytical methods made it possible to characterize the liquid effluents emitted by the alcohol factory of Logozohè and to evaluate the levels of contamination of the Klou river through the determination of the physicochemical parameters of water quality. From our results, the pH, turbidity, SS, and COD of water at the main effluent and Klou river do not meet the drinking water and wastewater quality standards in the Republic of Benin. The organic pollution of the effluent discharged by the plant into the watercourse is mainly loaded with organic matter refractory to biodegradation. This type of pollution is very damaging to the receiving environment, which manifests itself in the loss of the river's biodiversity and the emission of foul odors that is harmful to local residents. Similarly, the calculation of the BOD₅/COD ratio has also revealed that almost all the water in the Klou river is not biodegradable except at the ST2 and ST3 sites, where it is difficult to biodegrade with selected bacterial strains. This non-biodegradability of water has been reinforced by plant effluents that do not undergo adequate treatment.

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