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Study of the chemical and bacteriological quality of water resources in Hozin, district of the commune of Dangbo in Benin

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Abstract

This study was conducted on the watershed of the Ouémé river in the farming area of Hozin. It focused on the monitoring of the physico-chemical and bacteriological contents of the surface and underground water. For this purpose two campaigns were carried out on thirteen sites over the sampling of water from different sources (water drilling, devices-ordinary wells and river water). The two sampling operations match with the beginning and the end of the rice cultivation period in area study. The results obtained show that ammonium and iron concentrations exceed the regulatory limits set by WHO. Similarly, the values of BOD₅ and COD were out of the ordinary. It should also be noted that the P₂ well has higher levels than the average for several parameters studied. Surface waters were more polluted than groundwater excepted well P₂. The microbiological parameters indicate a water contamination by faecal streptococci, faecal and total coliforms.

Keywords: chemical, microbiological, water resources, pollution, Hozin

1. Introduction

Water is of vital biological and economic importance. It is the foundation of life and ecological balances. It is at the same time a food, possibly a drug, an industrial raw material, energy, agricultural, and a means of transport and / or leisure including bathing and fishing (Festy *et al.*, 2003). The degree of quality required of the waters depend on each of the uses. Its use for drinking water purposes requires excellent physicochemical and microbiological quality (Wissem and Mohamed, 2016) [36]. The increase in populations, the development of agglomerations, industrial units and cultivated lands, as well as the search for raw materials, have resulted in a deterioration of the quality of water resources and a very significant reduction in water reserves, sometimes represent the only water resources for the drinking water of the populations especially in the developing countries (Baali *et al.*, 2007) [4]. This degradation of water resources has become today one of the major problems that threaten the health of populations, undermine the stability of ecosystems and consequently affect the renewal of natural and even biological mineral resources (Ramade, 2006) [32]. According to the World Health Organization (WHO) 2.6 billion people in the world do not have access to drinking water and 1.8 million of whom 90% of children under five die each year especially in developing countries where hygiene and basic sanitation are inadequate or non-existent (Dovonon, 2011) [15]. According to the same institution, 80% of diseases in developing countries are water-related (Drouart and Vouillamoz, 1999) [16]. In a region where the main activity revolves around agriculture and livestock breeding and scarce sanitation facilities, the risk of pollution by chemical agricultural inputs and microbial germs threatens water resources (Zenati, 1993) [37]. Thus, the Ouémé river basin, the first river in Benin, is under the influence of several industrial, agricultural and livestock activities likely to generate industrial, agricultural and / or microbiological pollution (Pazou, 2005) [31]. In recent years, a large activity of rice and cattle breeding has developed in the Ouémé Valley, leading to an increase in water needs and a degradation of the quality of the resource. The present work aims at studying the physicochemical and microbiological quality of the surface and underground waters of an agricultural area in the catchment area of the Ouémé River.

2. Material and Methods

2.1 Area study

The present study was carried out in the municipality of Dangbo located in the department of Ouémé. It covers an area of 149 km² with a density of 443 inhabitants / km². It is limited to the North by Adjohoun Commune, Aguégues Commune to the South, Akpro-Misséréte Commune to the East and So-Ava Commune to the West (Atlantic Department). With a humid subequatorial climate, the Commune has two (02) rainy seasons and two (2) dry seasons (Akomagni and Guidibi, 2006) [3]. The average annual rainfall at Dangbo is 197.83 mm. This average varies from year to year between 818, 93 and 1376.73 mm of rain per year. The months of June and October are the most watered. The

average annual temperature is 28.06 °C and the monthly average temperatures vary between 25.91 and 29.00. Two different ecological zones define the relief offered by the municipality of Dangbo. This is the lower valley " Wodji " and the plateau " Aguédji " (CeCPA, 2009) [6].

2.2 Identification of sample sites collection

The identified sampling sites are on agricultural perimeters located in Hozin in Dangbo Commune. Thirteen selected stations consist of surface and underground water distributed over the entire agricultural field. These sites were chosen because of their proximity to the cultural areas. Table 1 gives a list of the different sampling sites and Figure 1 gives a synoptic map of the study environment.

Table 1: Water sampling sites

| N° | Name of sites | Codes | Geographic coordinates |
|----|--------------------------|-----------------|--------------------------|
| 01 | Djigbé Tokpa Blihè | P ₁ | 31N0450653 UTM : 0721189 |
| 02 | Well Djigbé Tokpa Blihè | P ₂ | 31N0450829 UTM : 0721368 |
| 03 | Djigbé Tokpa | P ₃ | 31N0450631 UTM : 0721489 |
| 04 | Artesian well Djigbé | P ₄ | 31N0450711 UTM : 0721598 |
| 05 | Bembè bridge right side | P ₅ | 31N0449641 UTM : 0721788 |
| 06 | Bembè bridge left side | P ₆ | 31N0449868 UTM : 0722002 |
| 07 | Artesian well rice field | P ₇ | 31N0449979 UTM : 0722128 |
| 08 | Bridge avagbodji | P ₈ | 31N0449528 UTM : 0722429 |
| 09 | market Drilling Hozin | P ₉ | 31N0449817 UTM : 0722345 |
| 10 | Drilling BemBè | P ₁₀ | 31N0448971 UTM : 0722494 |
| 11 | Middle river | P ₁₁ | 31N0448921 UTM : 0721204 |
| 12 | Right bank river | P ₁₂ | 31N0448969 UTM : 0721359 |
| 13 | Left bank river | P ₁₃ | 31N0448869 UTM : 0721161 |

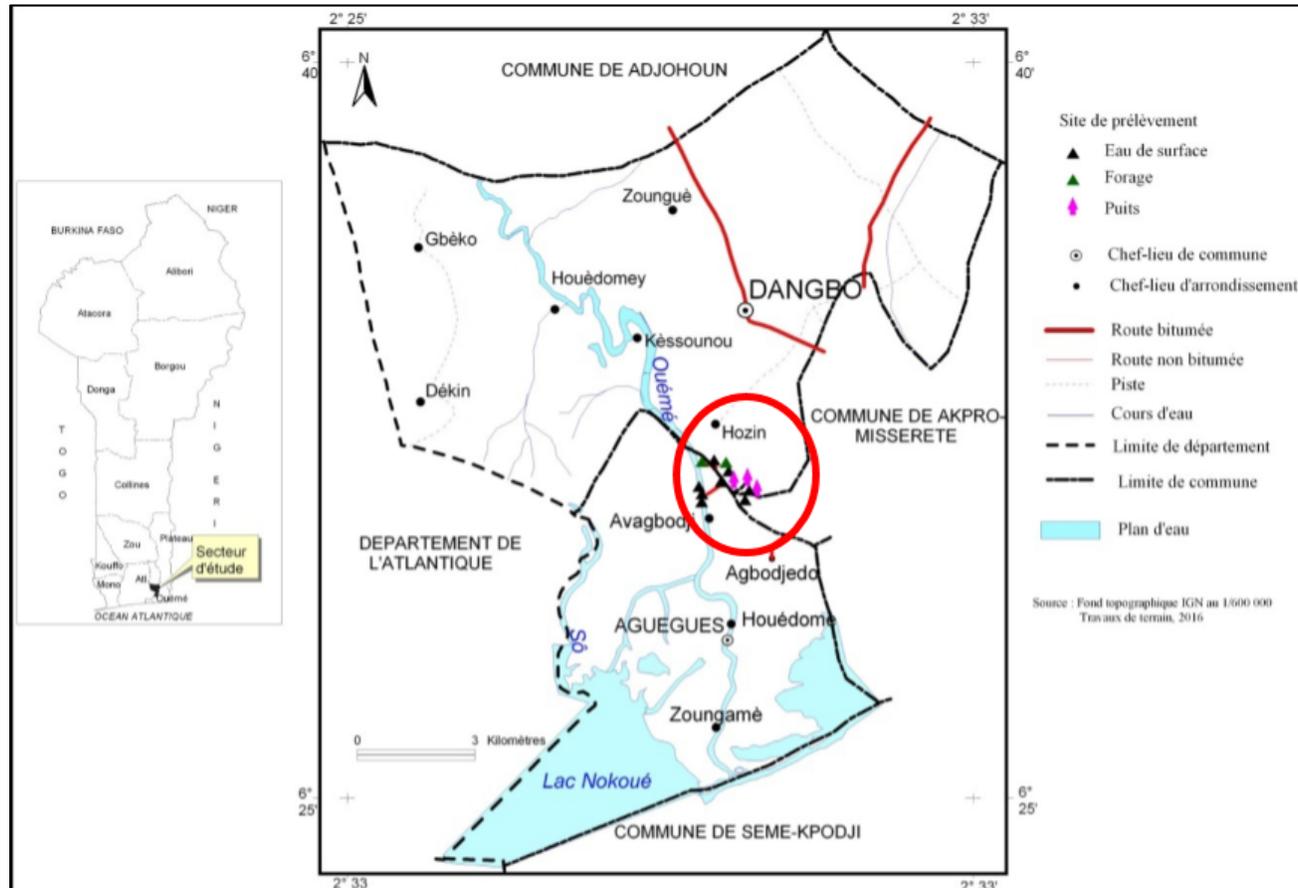


Fig 1: Synoptic map of the study environment

2.3 Sampling

This study was the subject of two sampling campaigns, the first of which took place at the end of September 2015 and the second at the beginning of July 2016. For Physico-chemical analysis, all water samples were recovered in plastic bottles of mineral water 1,5 L previously emptied, soaped without detergent and rinsed three times with bi-distilled water. Before any sampling, the vials thus conditioned were rereleased three times with the water to be sampled. The methods of collecting water samples varied depending on the water source. Thus, for surface water samples were recovered in the water column about 5cm from the surface. For well waters, well-cleaned plastic wells was used to collect samples. Finally, for boreholes equipped with a human-powered pump, a constant flow pump of 10 minutes was required before sampling. After sampling, the vials were labeled and stored in a cooler with a cold accumulator and sent to the laboratory for analysis.

2.4 Physico-chemical analysis methods

Parameters such as pH, temperature, electrical conductivity, Total Dissolved Solids (TDS), salinity and dissolved oxygen were measured in and / or on the basis of NF EN 25814 with the help of a multi parameter type Aqualyse Professional Plus YSI.

The standard methods in force used for the determination of certain physicochemical parameters in the laboratory are presented as follows: the NH_4^+ was determined according to the NFT 90-015-2 standard, the NO_2^- according to the NF EN 26777, the SO_4^{2-} according to the NF T 90-040, the total P according to NF EN ISO 6878 (T90-023), Cl^- according to NF ISO 9297, TH according to NF T90-003, TAC according to NF EN ISO 9963-1, COD according to NF T90-101, BOD_5 according to NF EN 1899-2, MES according to NF EN 872, turbidity according to NF EN ISO 7027, O_2 dissolved according to NF EN 25814 and total iron according to NF T90-017. The principles of the standard methods are given in Table 2. Parameters such as fluoride ions F^- , nitrate ions NO_3^- and color were determined as follows:

Ions F⁻: F-fluoride ions form with zirconium and in the presence of erochrome-cyanine R, a complex capable of an indirect spectrometric assay at 540 nm (Rodier *et al.*, 2009) [33].

Nitrate ions NO₃⁻: In the presence of sodium salicylate, nitrates give yellow-colored sodium parnitrosalicylate, which is capable of a colorimetric assay at 520 nm (Rodier *et al.*, 2009) [33].

Color: Staining of water samples is determined by comparison with a platinum-cobalt reference solution (Rodier *et al.*, 2009) [33].

Table 2: Methods for determining physico-chemical parameters

| Parameters | Principle of the method | Reference |
|------------------------|--|--------------------------|
| NH_4^+ | Formation in an alkaline medium of an indophenol compound by reaction of the NH_4^+ ions with phenol and ClO_3^- in the presence of nitroprusside $\text{Na}_2[\text{Fe}(\text{CN})_5\text{NO}] \cdot 2\text{H}_2\text{O}$ as catalyst gives a blue indophenol color. spectrophotometric measurement at $\lambda = 630$ nm | NFT90-015-2 |
| NO_2^- | The method is based on the reaction of NO_2^- ions with 4-aminobenzene sulfonamide at $\text{pH} = 1.9$ in the presence of H_3PO_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_3PO_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 reddish-colored 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 $\text{pH} = 5.4$ | NF EN ISO 9963-1 |
| COD | Acid Oxidation of Organic Matter by Excess $\text{K}_2\text{Cr}_2\text{O}_7$ in the Presence of AgSO_4 as Catalyst and HgSO_4 to Complex Cl^- and Determination of Excess Oxidant with Mohr Salt Solution ($\text{NH}_4\text{Fe}(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$) | 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 $20^\circ\text{C} \pm 2^\circ\text{C}$ for 5 days | NF EN 1899-2 |
| MES | Filtration of water on fiberglass filter and then dried at $105 \pm 2^\circ\text{C}$ and gravimetric determination by mass difference | NF EN 872 |
| Turbidity | Radiation emission of $\lambda = 860$ 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 $\text{CH}_3\text{COONH}_4\text{-CH}_3\text{COOH}$. 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 |

For all spectrophotometric methods, the Spectrometer Spectro II-4C of Lovibond mark has been used. For the DOB_5 , the respirometric method, with Oxitop BOXCALF WTW R in a thermostatic surrounding wall to 12 stations has been used. The Kit of Winkler and Aquamerck 1.11136.0001 served respectively for the measure of the oxygen dissolved and the dissolved iron

2.5 Microbiological analysis methods

The water samples taken were evaluated by standard microbiological parameters. These are total coliforms (NF EN ISO 9308-1 (T 90-414)), faecal coliforms (NF EN ISO 4832: 1991) and faecal streptococci (NF EN ISO 4832). It should be noted that sites P₁, P₃, P₄, P₆ and P₈ were not subjected to

microbiological analysis because of loss samples during transport.

The principles of the methods for determining the different microbiological parameters are given in Table 3.

Table 3: Method for determining microbiological parameters

| The different parameters | Principle of the method | Reference of the method |
|----------------------------|---|-----------------------------|
| Total coliforms /100mL | Membrane filtration Incubation at 37°C Enumeration of confirmed colonies | NF EN ISO 9308-1 (T 90-414) |
| Faecal coliforms /100mL | Membrane filtration; Incubation at 37°C; Enumeration of confirmed colonies | NF EN ISO 4832 : 1991 |
| Faecal streptococci /100mL | Inoculation of the broth by incorporation; Incubation at 37 °C. Enumeration of confirmed colonies | NF EN ISO 4832 |

2.6 Statistical analysis

The data has been tested for normality. In case of normality of the distributions of beginning and end of campaign on the one hand and homogeneity of the variances of these distributions, the comparison of the monitored parameters was carried out by the t-test of comparison of two paired samples. In case of non-satisfaction of one of these two conditions; the nonparametric Wilcoxon test was applied to compare the parameters. In case the normality was checked and not the equality of the variances, the t-test was applied with an approximation of the variance by Welch's method. The level of significance is set at $p < 0.05$.

3. Results and Discussions

3.1 Physico-chemical parameters

3.1.1 The temperature

Water temperature is an important factor in the aquatic environment because it governs almost all physical, chemical and biological reactions (Chapman and Kimstach, 1996) [7].

Figure 2 shows the change in temperature of the water at the sites sampled during the two seasons. The analysis of the graphs shows that the temperature varies from 26 °C to 28.9 °C during the first season, whereas this variation is between 26.1 and 29.4 °C during the second season. The minimum temperatures for both seasons are recorded at site P₁, with the maximum recorded at the P₄ sites during the first season and P₉ during the first season. Our minimum temperature values are higher than those found by Zinsou *et al.*, (2016) [39] who worked in the same study area, but on a wider range with a minimum of 22 °C. Maxima close to 30.5 °C are similar to those found by the same authors in the same area. On the other hand, its maxima are higher than those found by Wissem and Mohamed, in 2016 in well water in Algeria (24 °C). These observed variations in the measurement of the temperature would be related to several climatic parameters such as the sunshine, the rainy period and the time of the day when the measurement was made.

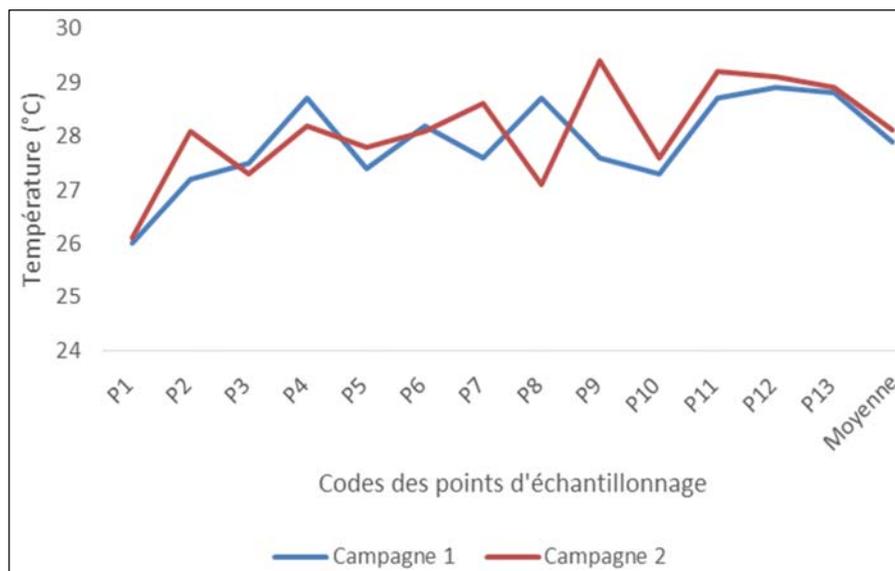


Fig 2: Spatiotemporal variation of temperature in the sampling area

3.1.2 The potential of hydrogen (pH)

Figure 3 shows the spatio-temporal variations of the pH. The analysis of the graphs in Figure 3 shows that the values taken by the pH range from 5.5 to 7.3 during the first season and from 5.3 to 7.4 during the second season. Recommended pH values for surface water range from 6.5 to 9 (Rodier *et al.*, 2009) [33]. No site has a pH greater than 9. But P₂, P₄, P₈, P₉ and P₁₀ sites have pH less than 6.5. Outside the P₈ site, which is surface water, all other sites with pH values below 6.5 are groundwater. In addition, the P₇ site is groundwater at a pH between 6.5 and 9. If our minima are slightly higher than 4.1 found by Zinsou *et al.*, (2016) [38]. our maxima are close to

their value that is 7.5. These low pH values in some groundwater reflect a high CO₂ content of these waters, mainly due to the microbial mineralization of organic matter contained in them. Indeed, the pH of the water decreases when its concentration of CO₂ increases and vice versa. On the other hand, water from the P₈ site, which is a surface water with a pH below 6.5, indicates pollution. The measurement of pH is essential, because its value conditions a large number of chemical equilibria including the formation, the alteration and the dissolution of the minerals as well as the ionic balance of the water

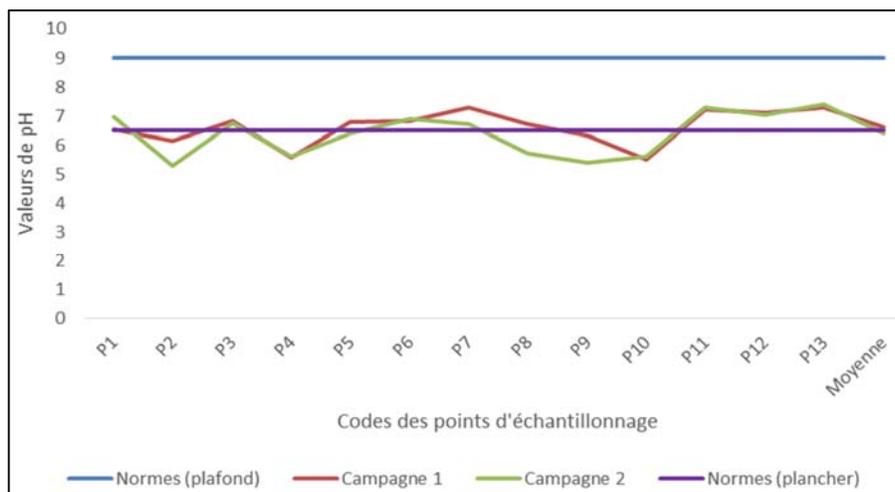


Fig 3: pH variation of water at sampling points

3.1.3 Electrical Conductivity and Total Dissolved Solids (TDS)

Electrical conductivity reflects the overall content of the ions in the water, makes it possible to quickly assess the degree of mineralization of a water (Mahamat *et al.*, 2015) [25], and to verify the existence of pollution in the water (Ghazali and Zaid, 2013) [20]. According to the histogram of figure 4, the values of the electrical conductivity oscillate between 47.3 $\mu\text{S}/\text{cm}$ and 363 $\mu\text{S}/\text{cm}$ during the first campaign. At the

second campaign, the conductivity extremes are respectively 46.5 $\mu\text{S}/\text{cm}$ and 617 $\mu\text{S}/\text{cm}$. Conductivity minima across all campaigns are recorded at site P₉ and maxima at site P₇. All recorded conductivity values are below the recommended limit value of 2000 $\mu\text{S}/\text{cm}$ for freshwater. TDSs move in the same direction as electrical conductivity and range from 34 to 258 mg/L with an average of 97.92 mg/L in the first season; while in the second season these extremes are respectively 46.7 and 617 mg/L with an average of 130.44 mg/L.

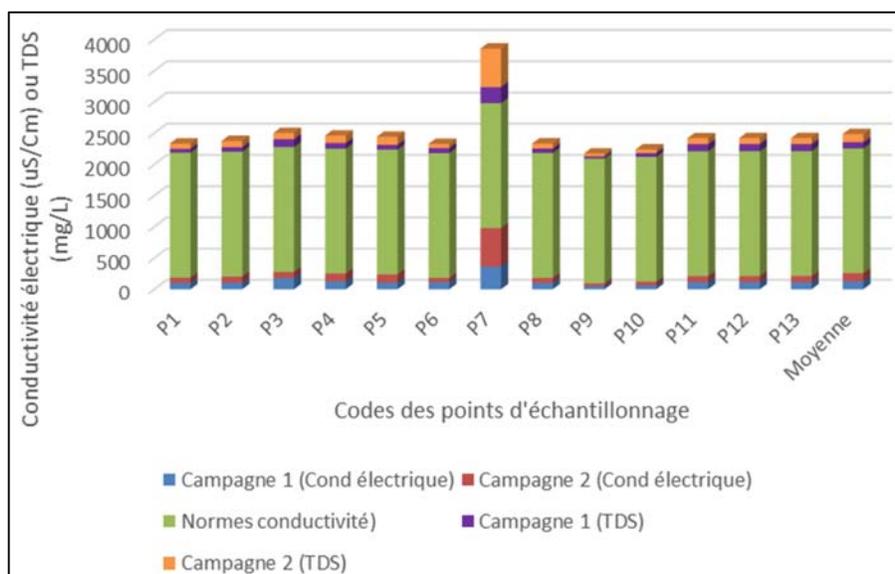


Fig 4: Spatio-temporal Variation in Electrical Conductivity and Dissolved Total Solids (TDS)

3.1.4 Color

The graphs of the variation of the true color of the waters according to the sampled sites are represented in figure 5. These graphs show a sawtooth evolution of the values taken by the color from one site to another. The extremes vary between 0 and 920 UCV during the first season, while these extremes range from 0 to 925 UCV during the second season. The minima for both seasons are recorded at the groundwater level of sites P₄, P₇, P₉ and P₁₀. The maximum value of the color for each campaign is recorded at site P₆. The guideline value recommended by WHO is 15 UCV for drinking water. We find that only drilling water meets the required standards. This can be explained not only by the depths of these waters,

but also by the appropriate facilities around these situations that protect them from degradation of the physical quality of the water. The distributions of water color indicators at the beginning ($W = 0.9083$, $p\text{-value} = 0.1736$) and end ($W = 0.901$, $p\text{-value} = 0.1379$) of campaigns follow the normal distribution but have variances that could be no reason to statistically be considered different at a level of confidence close to 80% ($F = 0.8554$, $\text{num df} = 12$, $\text{denominated df} = 12$, $p\text{-value} = 0.7911$). According to the results of Student's t-test, there is statistically no reason to reject the assumption that water color indicators at the beginning and end of the campaign are equal ($t = -0.0727$, $\text{df} = 12$, $p\text{-value} = 0.9432$)

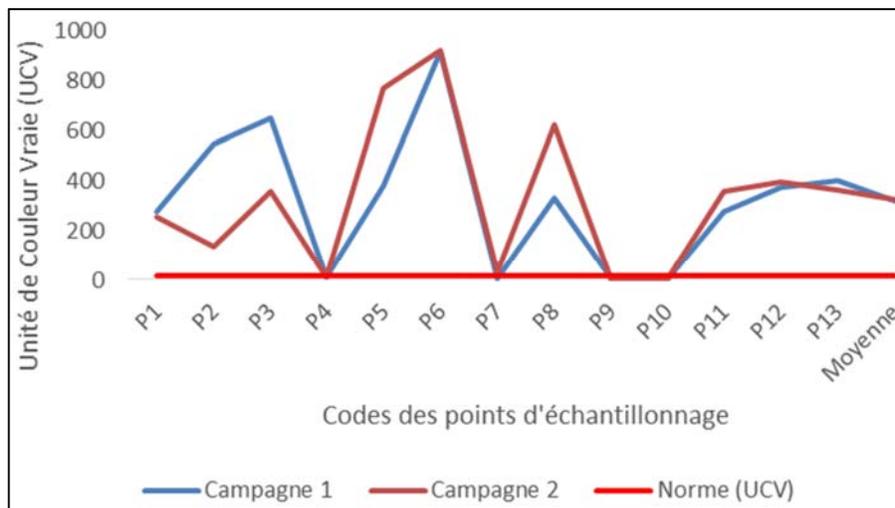


Fig 5: variation of the true color of the water according to the sampled sites

3.1.5 Turbidity

Turbidity is defined as the reduction of the transparency of a liquid due to the presence of undissolved materials (NF EN ISO 7027, 2000). Figure 6 shows the spatio-temporal evolution of the turbidity of the water samples during the study period. The turbidities during the second season are higher than those of the first season. The lowest turbidity levels are found in groundwater (P₇, P₉ and P₁₀). The maximum allowable value for WHO for drinking water is 5 NTU. Apart from P₇, P₉ and P₁₀ all other sites have turbidities higher than WHO requirements. If high levels of turbidity can be understood in surface waters because they are highly exposed to direct discharges and surface runoff, they cannot be accepted at the well water level as in P₄ where water is used for the needs, raw food without any treatment. The start of campaign (W = 0.9333, p-value = 0.3759) and end (W =

0.8968, p-value = 0.1209) distributions follow the normal distribution but have variances that could not be considered significantly different with risks of being wrong less than one tenth of a thousandth (F = 0.1229, num df = 12, denominated df = 12, p-value = 0.0009721). According to the results of the t-test with approximation of the variances by Welch's method, the turbidities at the beginning and the end of the season are significantly different with a risk of being erroneous of less than 1.5% (t = -2.867, df = 12, p-value = 0.01417). More specifically, the turbidity at the beginning of the season would be statistically lower than the end-of-season turbidity (t = -2.867, df = 12, p-value = 0.007084). This state of affairs is justified in surface water by the input of runoff water having carried portions of soil pickled, plant debris, faecal pellets and anthropogenic discharges.

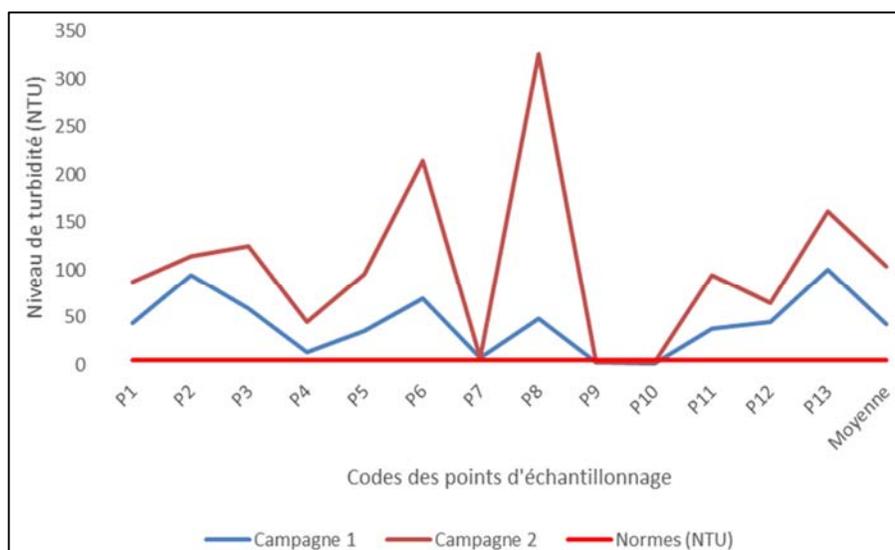


Fig 6: Variation in Turbidity of Water Samples in Time and Space

3.1.6 Suspended matter

The variation of the suspended matter content as a function of the sampling sites is shown in Figure 7. The analysis of the graphs shows that the suspended matter minimum is 0 mg/L regardless of the campaign. On the other hand the maxima are

respectively 65 mg/L during the 1st campaign and 198 mg/L during the 2nd. The maxima and minima are obtained respectively at the P₈ sites during the first campaign and at P₂ during the second campaign. The suspended matter levels in the second season are higher than in the first season. This

observation is already justified at the level of turbidity. The start of season (0.8996 , $p\text{-value} = 0.1319$) and end of season ($W = 0.9$, $p\text{-value} = 0.1336$) distributions follow the normal distribution but have variances that could not be considered to be significantly different. with risks of being wrong less than three thousandths ($F = 0.145$, num $df = 12$, denominat $df = 12$, $p\text{-value} = 0.002154$). According to the results of the $t\text{-test}$ with approximation of the variances by Welch's method, the

quantities of suspended matter at the beginning and at the end of the campaign are significantly different with a risk of being wrong less than 7 thousandths ($t = -3.2968$, $df = 12$, $p\text{-value} = 0.006378$). More specifically, the amount of suspended solids at the beginning of the campaign would be statistically lower than the amount of suspended solids at the end of the season ($t = -3.2968$, $df = 12$, $p\text{-value} = 0.003189$). This observation is already justified at the level of turbidity.

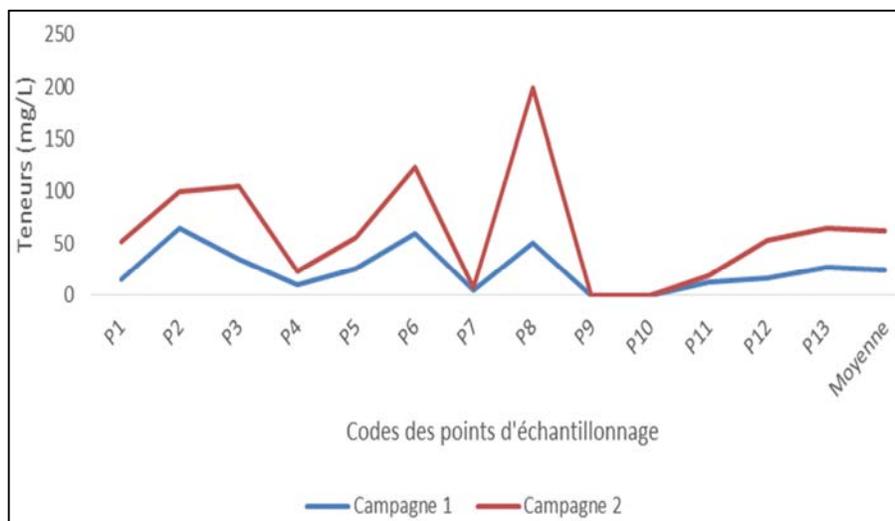


Fig 7: variation of the MES content according to the sampling sites

3.1.7 Dissolved Oxygen

Dissolved oxygen is a function of the origin of the water. Surface waters may contain relatively large amounts close to saturation. On the other hand, groundwater usually contains only a few milligrams per liter (Rodier *et al.*, 2009) ^[33]. Similarly, in surface waters, the respiration of aquatic species and the mineralization of organic matter are conditioned by the presence in the medium of dissolved oxygen and vice versa. It is therefore the most sensitive factor to organic pollution in natural waters. Our oxygen levels vary from 0.1 to 3.5 mg/L during the first campaign. During the 2nd season the content varies between 0.2 and 4.6 mg/L. The minimum

levels of dissolved oxygen are recorded in P_8 . The upper limit for surface water is 8 mg/L. All recorded oxygen levels are well below this limit. The relatively high levels recorded during the second season are either related to the turbulence of surface water during the rainy season that saturates dissolved oxygen in the water column, or the supply of groundwater reserves by water infiltration, runoff loaded with dissolved oxygen. Our minima are lower than those found by Wissem and Mohamed, (2016) ^[36]. However, our maxima are higher than those found by these same authors (1.8 to 2.72 mg/L). This global deficit in dissolved oxygen can compromise aerobic aquatic life, especially in surface water.

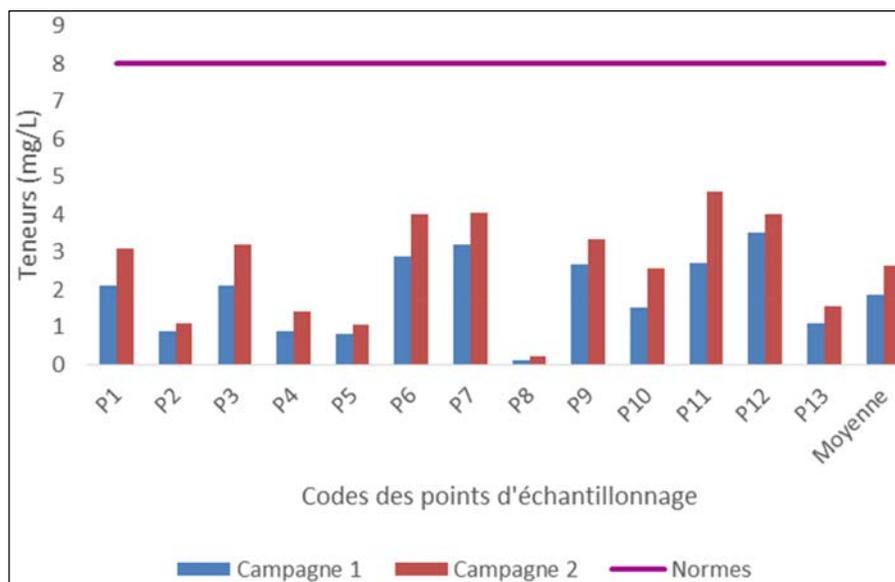


Fig 8: Water content of sites sampled in dissolved oxygen (mg/L)

3.1.8 Total iron

The graphs in Figure 9 give the spatio-temporal evolution of the total iron content in the analyzed water samples. The extremes during the first season range from 0.09 to 10 mg/L with a campaign average of 2.2 mg/L. Those in the 2nd season range from 0.04 to 9.12 mg/L with an average of 2.365 mg/L. The maximum allowable value is 0.3 mg/L according to WHO quality guidelines for drinking water. All samples collected at well and borehole water meet this standard, however, all surface water far exceeds this maximum value and indicates contamination of the iron resource. In fact a

contamination of iron water is not a bad thing in itself. The human body needs it as a hemoglobin heme. 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 sulphide SO_4^{2-} in sulfide H_2S odor source in anaerobic waters (Dohnalek and FitzPatrick, 1983; Chatelus 1987) [14, 8]. In addition, the presence of iron in the water causes visual pollution of the sanitary and kitchen facilities by creating reddish streaks on the porcelain walls.

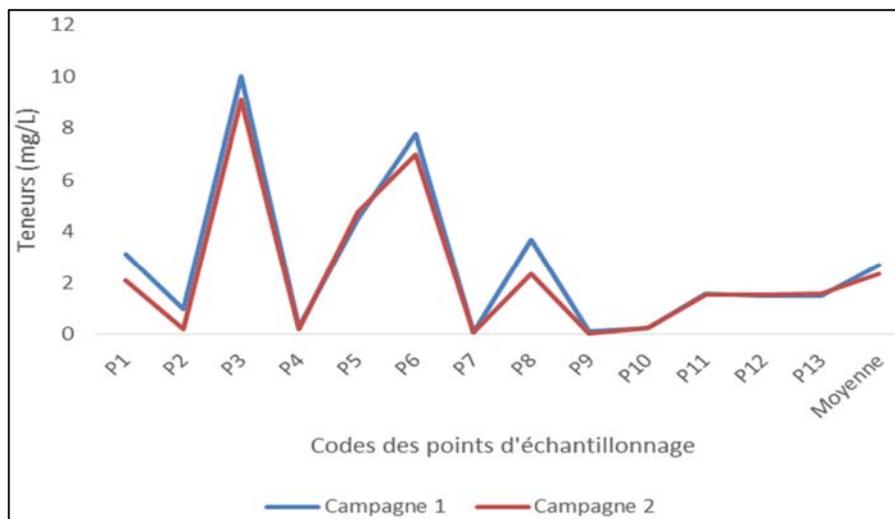


Fig 9: Total iron content in the sampled waters

3.1.9 Chloride in water

Chlorides are important inorganic anions contained in varying concentrations in natural waters, usually in the form of sodium (NaCl) and potassium (KCl) salts. They are often used as a pollution index. Chlorides exist in all waters at very different concentrations. The origin can be natural (Abdoulaye *et al.*, 2014) [1]. Figure 10 shows the spatio-

temporal variations in the chloride ion content of the analyzed water samples. The minima are respectively 24.85 mg/L and 14.2 mg/L at the P₉ site and the maxima are respectively 142 mg/L at the P₇ site (1st season) and 149.1 mg/L at the P₂ site (2nd campaign). Drinking water quality guidelines require a maximum value of 250 mg/L. All saved values are below this limit.

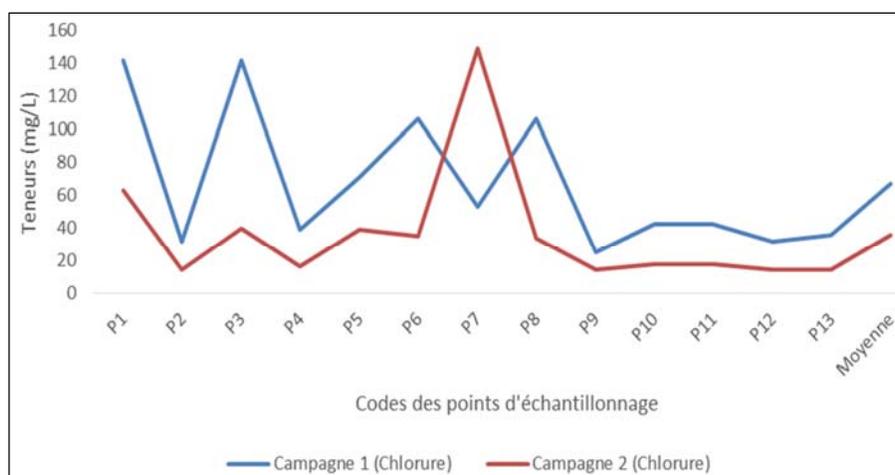


Fig 10: Variation in Chloride Levels of Water Samples in Two Campaigns

3.1.10 Hardness of water

The hydrotimetric titre TH varies from 10 to 110 mg of CaCO_3/L during the first campaign. During the 2nd season this variation is between 8 and 168 mg of CaCO_3/L . The maximum permissible value in the WHO guidelines for drinking water is

500 mg CaCO_3/L . No site has a TH value greater than this limit value. The lowest TH values are found at the groundwater level with the exception of the P₇ site where the maximum was recorded. The permanent hardness related to calcium ions Ca^{2+} (THCa^{2+}) varies between 1.52 and 41.06

mg of Ca^{2+}/L during the 1st campaign, whereas during the 2nd campaign it varies from 1.60 to 38.48 mg Ca^{2+}/L . The maximum allowable value is 100 mg Ca^{2+}/L . All recorded values are below this limit value. As for the permanent hardness related to magnesium ions (THMg²⁺), it varies between 0.86 and 18.24 mg of Mg^{2+}/L in the first campaign. During the 2nd campaign the recorded values oscillate between

0.97 and 17.51 mg of Mg^{2+}/L . The maximum allowable value is 50 mg Mg^{2+}/L . Our values are below this limit. At the level of the temporary hardness or hardness related to the bicarbonate ions it varies between 2.23 and 8.87 mg of CaCO_3/L during the first campaign. During the 2nd season the variations vary between 3.05 and 12.2 mg of CaCO_3/L .

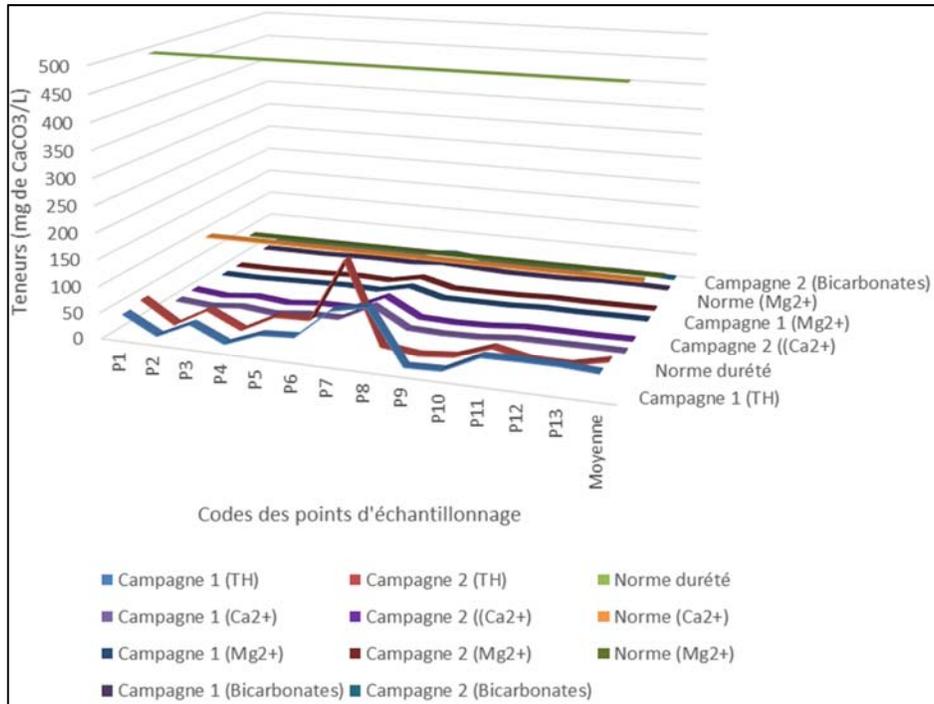


Fig 11: Spatio-temporal variation in the hardness of water samples

3.1.11 Alkalinity

The range of pH recorded during the campaigns being $5.3 \leq \text{pH} \leq 7.4$ so TA is zero and the alkalinity is reduced to the TAC (Table 4). The TAC ranges from 11 to 80 mg of CaCO_3/L with an average of 50.31 mg of CaCO_3/L during the first campaign, whereas it varies from 4 to 20 mg of CaCO_3/L during the 2nd campaign with an average of 9.69 mg CaCO_3/L .

Table 4: Alkalinity of the samples

| sites | P ₁ | P ₂ | P ₃ | P ₄ | P ₅ | P ₆ | P ₇ | P ₈ | P ₉ | P ₁₀ | P ₁₁ | P ₁₂ | P ₁₃ | Average |
|--------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|---------|
| Campaign (1) | 60 | 18 | 80 | 16 | 70 | 60 | 74 | 70 | 11 | 12 | 60 | 62 | 61 | 51,30 |
| Campaign (2) | 6 | 5 | 12 | 4 | 10 | 9 | 20 | 10 | 5 | 5 | 10 | 15 | 15 | 9,69 |

3.1.12 Nutrient contents

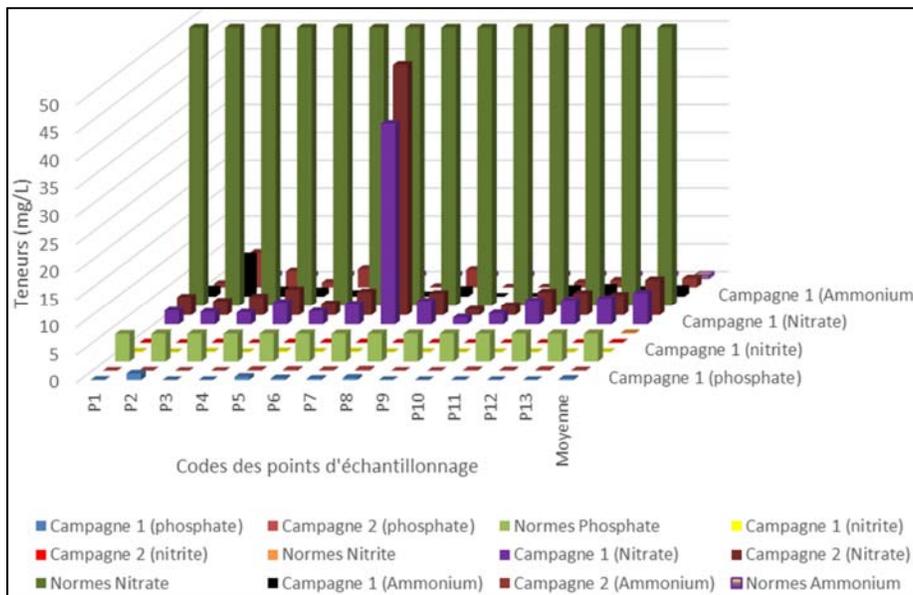
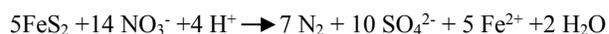


Fig 12: Spatio-temporal variation of nutrients in water samples

The histograms in Figure 12 show the spatio-temporal variation of nutrients in the water samples analyzed. From the analysis of the histograms the Ammonium NH_4^+ ion contents vary from 0.01 to 7.31 mg/L with an average of 1.44 mg/L during the first campaign and from 0.013 to 6.244 mg/L with a average of 1.64 mg/L during the 2nd. The minima and maxima are recorded respectively at sites P₉ and P₂. The maximum value allowed by the WHO guidelines for drinking water is 0.5 mg/L. values are much higher than those found by Zinsou *et al.*, (2016) [38] with extremes ranging from 0.016 to 0.978 mg/L. Outside the sites P₇, P₉ and P₁₀ where the limit value is not reached, all the other sites are contaminated with ammonium ions. The ammonium ion is the smallest form of nitrogen pollution. It is not toxic to aquatic fauna, but in basic medium the ammonium ions can be transformed into ammonia NH_3 and become toxic for the aquatic fauna. During our follow-up no recorded pH reached the pka of the $\text{NH}_4^+ / \text{NH}_3$ pair which is 9.2.

The intermediate form of nitrogen pollution is nitrite NO_2^- . The minimum levels of this ion in our samples during the two campaigns are 0 mg/L and are recorded respectively at sites P₂ and P₄ which are artisanal wells used by the populations to satisfy their water needs. The maximum levels recorded are 0.12 mg/L (at the P₅ 1st campaign site) and 0.099 mg/L (at the P₇ 2nd campaign site). The maximum allowable value is 0.1 mg/L. The most oxidized form of nitrogen pollution is NO_3^- nitrate. The extremes are 1.23 and 36.12 mg/L for the first campaign. During the 2nd season, there are 1.02 and 45.01 mg/L. Zinsou *et al.*, (2016) [33] found values between 0 and 6.94 mg/L. The maximum value allowed by the WHO guidelines for drinking water is 50 mg/L. No saved value has reached this limit. As a result, the waters studied are not subject to the risk of nitrate pollution. Our results are consistent with those found by Haissoufi *et al.*, (2011) [17] and Ghazali *et al.*, (2012) [19]. Nitrate ions constitute the assimilable form of nitrogen by many plants. Nitrate input into water resources can result from the leaching of agricultural nitrates by rain, especially in rainy weather and after significant thunderstorms soon after fertilizer application (Chapman and Kimstach, 1996) [7]. If runoff brings nitrate loads directly to water resources, aerobic decomposition of dead organic matter within waterbodies, especially by aeration of sediments accumulated and deposited at the bottom of water bodies, may also produce nitrates, but this source is, in general, very small compared to the agricultural origin mentioned above. A third source of nitrate in water bodies is: Cyanobacteria that directly use the abundant atmospheric nitrogen (80% of atmospheric gases) to produce nitrate via NH_4^+ ammonium ions (Bergstöm and Jansson, 2006). The major effect of nitrates on surface water is to lead to eutrophication. Nitrate levels that prevent eutrophication of streams are much lower than allowable levels for drinking water. Instead of 50 mg/L of NO_3^- for drinking water, it is as early as 1 mg/L in surface water that the risk of eutrophication can start, starting with stagnant water. This process is triggered when the waters are overloaded with nitrates and phosphates, these two nutrients allow the growth of algae. When they are both in large quantities in the water, phytoplankton and macrophytes develop excessively. The organic matter present in the body of water increases excessively, and when the algae die, this organic matter decomposes by consuming the oxygen of the water column, thus inducing anoxia, that is to say the absence of oxygen in the water, and thus the death of the aquatic fauna. This anoxia

does not generally occur in the fluvial network but in turbid estuaries where the transit of water is strongly slowed and where the decomposition outweighs the algal production. The phenomenon of fluvial eutrophication occurs mainly in the dry season, when the sun is strong, allowing photosynthesis by algae, and the high temperature. In the water column of surface waters, nitrates are not decomposed because the water is generally aerated, except under extreme circumstances. However, the flow of nitrates is not fully conserved. Indeed, important exchanges are made between the river and its alluvial layer, and the water of the river penetrates



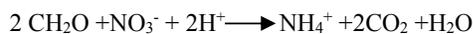
As long as there are nitrate ions in water the Fe^{2+} ferrous ion is unstable and oxidizes to Fe^{3+} ferric ion insoluble according to the reaction:



In addition, in sediments deposited at the bottom of the river, rich in organic matter, these materials can sometimes decompose by creating anaerobic conditions favorable to denitrification leading to gaseous species that are easily eliminated in water. According to Burns *et al.*, (2008), the mechanism of such a reaction is the reduction of nitrates coupled with the oxidation of Organic Matter (OM) in the presence of heterotrophic bacteria following the reaction:



Under reducing conditions, denitrification is not necessarily the only chemical process that takes place. On the contrary, under certain conditions, the reduction of nitrates does not necessarily lead to gaseous species, but to the production of NH_4^+ ammonium ions. This reduction coupled with the oxidation of the organic matter (MO) is written:



Apart from these natural processes of nitrate removal in water resources, it is very difficult to fight against nitrates of agricultural origin, except by reducing fertilizer inputs. To avoid eutrophication, failing to be able to act on agricultural practices, it is therefore better to work on phosphates, either by dephosphating industrial wastewater or by fighting against erosion in agricultural land, because phosphorus is in rivers in adsorbed form to solid particles that are eroded and carried away during floods. In our study, the levels of phosphate ions ranged from 0.01 mg/L to the P₁₀ site regardless of the campaign at 1.19 (P₂ site) and 0.23 mg/L (P₈ site) during the 1st and 2nd years respectively campaign with averages of 0.22 mg/L and 0.1 mg/L. The maximum value allowed by the WHO guidelines for drinking water is 5 mg/L. No site has reached this limit. Phosphorus is 90% of urban origin, and only 10% of agricultural origin (Dauvin *et al.*, 2008) [10]. Being in an exclusively rural zone, it is thought that the phosphorus contributions of our samples would be of agricultural origin. In general, the presence of phosphorus and nitrogen in bodies of water is an eutrophication factor. The ratio of Redfield or ratio between nitrates and phosphates measured in aquatic plants and which leads to the optimal development of algae is of the order of 7 by weight of N/P. Figure 13 is shown N/P ratios by site and by season.

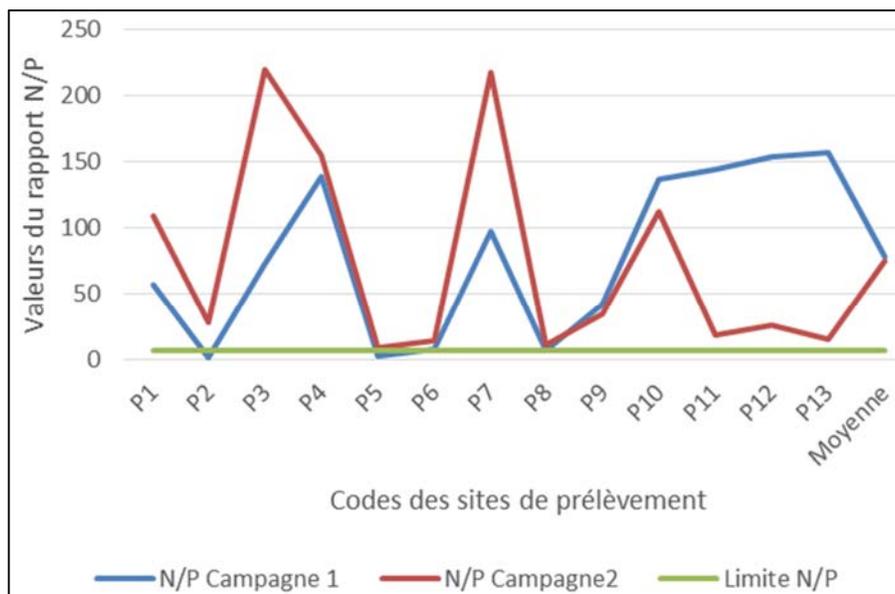


Fig 13: Spatio-temporal variation of the N / P ratio in the sampled waters

From the analysis of the curves in Figure 13, we see that during the first campaign all the N / P reports are greater than 7. During the 2nd campaign outside the P₂ and P₅ sites, all other sites have a N / P ratio greater than 7. This observation means that phosphorus is the limiting factor of eutrophication in our study area without forgetting the conditions of sunshine.

3.1.13 Variation of Chemical Oxygen Demand

COD is a global measure of organic matter and some oxidizable mineral salts (total organic pollution) present in water. The histograms in Figure 14 show the spatio-temporal variation of the COD. From the analysis of the histograms, it

appears that the measurements of COD carried out vary from 0 to 189 mg of O₂/L during the first campaign, then from 0 to 245 mg of O₂/L in the second campaign. With the exception of well P₂, all groundwater has zero values. Our values are similar than those found by Haissoufi *et al.*, (2011) [17] with extremes ranging from 24.5 to 263.3 mg/L in Morocco wells. The increase in COD in P₂ can be explained by the direct contact of runoff with the well which is unhedged and uncemented. It should be noted that the highest values are generally obtained on surface water. This can be explained by high organic loads carried by water by which the decomposition of macrophytes present in these waters can be indexed.

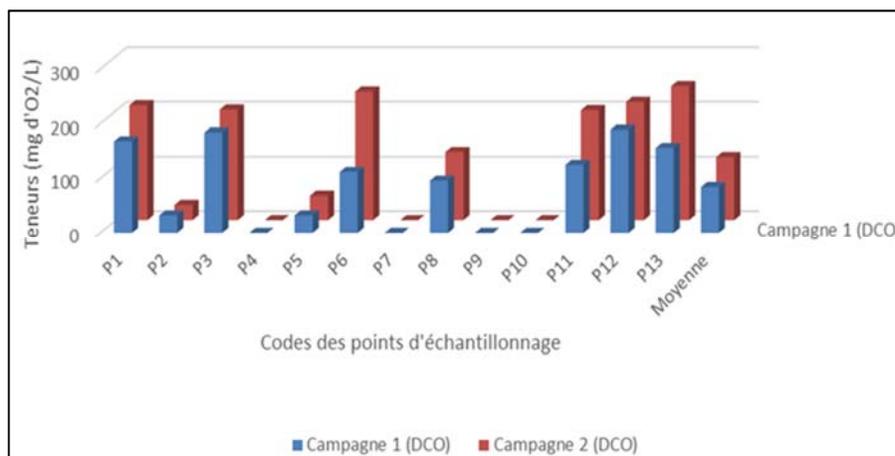


Fig 14: Spatio-temporal variation in COD of water samples

3.1.14 Variation in Biochemical Oxygen Demand in Water Samples

Figure 15 presents histograms showing the spatio-temporal variation in five-day biochemical oxygen demand (BOD₅) of the sampled waters. The BOD₅ concentrations recorded in the studied waters range between 0 and 28 mg of O₂/L in campaign 1 and between 0 and 39 mg of O₂/L in campaign 2. The measurements carried out for the first campaign are of value average of 12.846 mg O₂/L and 19.692 mg O₂/L in

second season. The BOD₅ of unpolluted surface water normally ranges from 2 to 20 mg/L. In addition to samples from well P₂, all groundwater sampled has zero BOD₅. The maximum value of BOD₅ is recorded during the second campaign at site P₁₃ which is nothing other than the bank of the Ouémé River near Hozin. The increase in BOD₅ values could be explained by organic pollution from anthropogenic activities (Ben-hida *et al.*, 2012) [5]. At this site, apart from the organic loads carried by the river, there are rejections of fish

remains from the evisceration activities of scalars and fishmongers. The difference between COD and BOD₅ is due

to non-biodegradable substances.

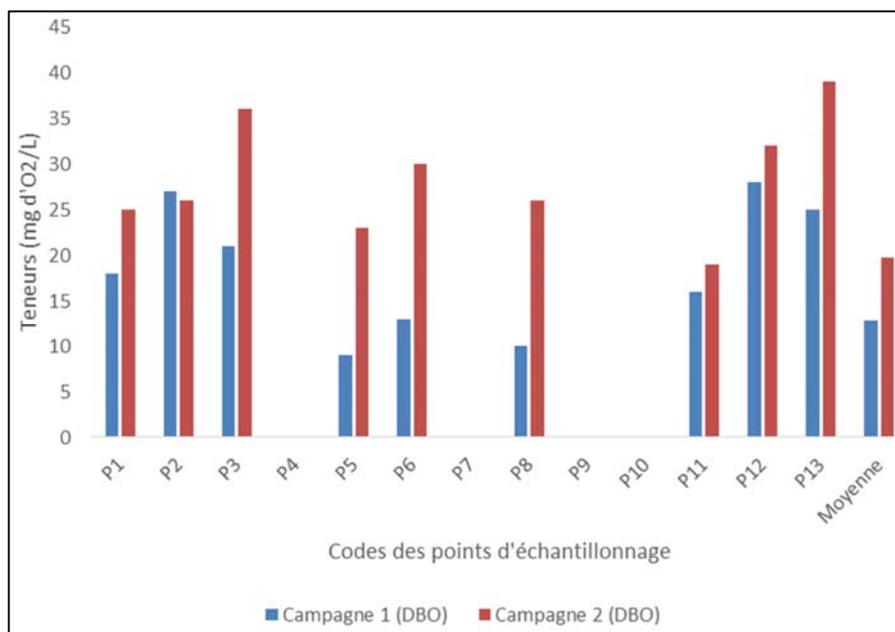


Fig 15: Biochemical oxygen demand (BOD)

3.1.15 COD / BOD₅ ratio

The ratio COD / BOD₅ gives an indication of the origin of the organic pollution. Table 5 gives us the result of this report.

Table 5: COD / BOD₅ values

| sites | P ₁ | P ₂ | P ₃ | P ₄ | P ₅ | P ₆ | P ₇ | P ₈ | P ₉ | P ₁₀ | P ₁₁ | P ₁₂ | P ₁₃ |
|----------------------------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|----------------|-----------------|-----------------|-----------------|-----------------|
| DCO/DBO ₅ (campaign1) | 9,33 | 1,18 | 8,76 | 0 | 3,55 | 8,61 | 0 | 9,6 | 0 | 0 | 7,81 | 6,75 | 6,24 |
| DCO/DBO ₅ (campaign2) | 8,4 | 1,07 | 5,61 | 0 | 1,95 | 7,83 | 0 | 4,81 | 0 | 0 | 10,57 | 6,75 | 6,28 |

The ratio COD / BOD₅ varies between 0 and 9.6 in the first season and from 0 to 10.57 in the campaign 2. The averages are respectively 4,759 and 4,097. Higher values are recorded at the P8 (surface water) sites during the 1st season and P11 (surface water) during the 2nd season. If the COD / BOD₅ ratio is less than 3, a biological treatment must be able to eliminate most of the organic pollution. All groundwater (P₂, P₄, P₉ and P₁₀) is self-polluting. On the other hand, not all surface waters are self-polluting because a large part of the organic matter that polluted these water bodies is not biodegradable. In fact, water bodies are the main receptacles for anthropogenic discharges, among which are synthetic organic pollutants such as pesticides, dyes, used motor vehicle oils, etc. Under these conditions, organic pollution threatens the stability of ecosystems and it is preferable to consider a physicochemical treatment of water to effectively eliminate organic pollution. At the same time, communication campaigns and sensitization of local residents are essential for an awareness of the state of pollution of the watercourse and the corrective measures envisaged.

3.2 Overall comparative analysis of sampling sites with regard to physico-chemical pollution monitoring parameters:

3.2.1 Start of Campaign

Figures 16 and 17 show the comparative analysis at the beginning of the campaign of the sampling sites using the scoring and double projection diagrams. From the analysis of the two diagrams, it appears that among the waters of the well, P₇ is distinguished from other well waters by higher

calcium, magnesium, nitrate and sulphate contents as well as by physical parameters in this case the conductivity electric and the TDS higher. In contrast, the water from well P₂ is closer to the characteristics of surface water to a lesser extent to site P₈. The content of iron and that in chloride evolve in the same direction. This state of affairs suggests that dissolved iron comes from iron chloride II (FeCl₂). The decrease in iron and chlorides would coincide with a decrease in pH, thus an increase in acidity, as well as a decrease in turbidity, a decrease in suspended solids and a drop in the water color indicator. The sources P₇ (well), P₃ (surface water) and P₆ (surface water) are marked by acidification of the water, a low value of the amounts of suspended matter, indicators of turbidity, and coloration, as well as low levels of iron and chlorides. In contrast, the sources P₁₀, P₉ and P₄ have characteristics contrary to those of the sources P₇, P₃ and P₆. The sources P₅, P₁₃, P₁₂, P₁₁ and P₁ do not seem to display values of the characteristics making it possible to discriminate them from the others; they seem to be a group that is difficult to classify from the point of view of the present characteristics. A decrease in ammonium and phosphate contents is coupled with an increase in COD. In addition, the high levels of nitrites, chlorides and fluorides are coupled with low values of the turbidity indicator of water. The description of the relationships between the physicochemical parameters and the characteristics of the sources by means of the principal components analysis makes it possible to collect 55.9% of the overall information of which 33.9% and 22% respectively for the first and second axis. The variables "calcium content", "magnesium content", "nitrate content",

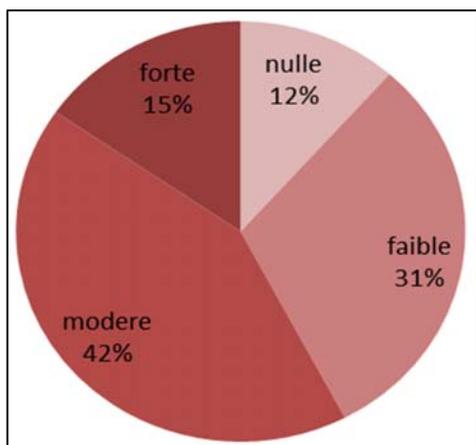


Fig 20: Classification of the study area in terms of organic pollution level according to the Leclerc and Maquet pollution index

3.3 Parameters for monitoring the microbiological status of sampling sites

Table 6 shows the different values obtained for the different microbiological parameters.

Table 6: Level of microbiological contamination of collected water samples

| Bacteria Sites | Total coliforms to 37°C (CFU/100mL) | faecal coliforms to 44,5°C (CFU/100mL) | Faecal streptococci to 44,5°C (CFU/100mL) |
|--------------------------|-------------------------------------|--|---|
| P2 | > 600 | 100 | 125 ± 10 |
| P5 | 1500 | 400 | > 600 |
| P7 | >700 | 40 ± 5 | 35 ± 10 |
| P9 | 25 + other colonies | < 1 | < 1 |
| P10 | < 1 + 05 banal colonies | < 1 | <1 |
| P11 | 1800 | 550 | 155 ± 10 |
| P12 | 1000 | 170 | 250 ± 10 |
| P13 | > 800 | 150 | 240 ± 10 |
| Maximum allowable values | 10 | 00 | 00 |

Cfu : Colonies Forming Unit

From the data analysis in Table 6, the water samples indicate contamination levels ranging from < 1 to 1800 cfu/100mL for total coliforms. Similarly, for faecal coliforms and faecal streptococci, the contamination levels vary between < 1 and 550 cfu/100mL respectively and between < 1 and 600 cfu/100mL. These values are extremely high in comparison with WHO standards (<10 cfu/100mL for total coliforms and 0 cfu/100mL for faecal coliforms and faecal streptococci) (WHO, 1994) except for the P₁₀ site which has values less than 1 for all microorganisms. The high rates of microorganisms at most sites are similar to those found by Nola *et al.*, (1998) [27] at the Yaoundé water table in Cameroon. These microbial contaminations could be attributed either to the lack of knowledge of elementary rules of hygiene leading to an inadequate sanitation system in the vicinity of the wells, or to an infiltration of polluted surface water into the well (Degbey *et al.*, 2010) [12]. In nature, especially surface water resources carry a considerable number of microorganisms, bacteria, viruses and protists of all kinds, which live there and develop there, as well as a number of parasites whose hosts are dependent on water resources (Chippaux *et al.*, 2002 ; Wissem and Mohamed,

2016) [9, 36]. But total coliforms are a heterogeneous group of faecal and environmental bacteria that include *E. coli* (Leclerc *et al.*, 2001; Tallon *et al.*, 2005) [23, 34]. Indeed, most species can be naturally found in soil and vegetation. Although bacteria in this group are more persistent in the environment than *E. coli*, their detection in water generally does not indicate faecal contamination or health risk, but rather vulnerability to contamination or recolonization bacterial and consequently a degradation of the bacterial quality of the water (Kaoruko *et al.*, 2008 ; Verhille, 2013) [22, 35]. The analysis of total coliforms thus provides information on the potential vulnerability of a well to surface pollution such as the P₂ well and the P₉ well. *E. coli* bacterium is a very abundant species in the human and animal intestinal flora, and it is also the only species that is strictly faecal (Degbey *et al.*, 2011; Maoudombaye *et al.*, 2016) [11, 26]. Although it has a disadvantage of being generally less persistent in the environment, it's considered the best indicator of faecal contamination (Wissem and Mohamed, 2016) [36]. Therefore, its presence in the water means that the latter is contaminated by faecal pollution and can therefore contain pathogenic microorganisms (Degbey *et al.*, 2010) [12].

As for faecal coliforms and faecal streptococci, they should remain without trace in drinking water as recommended by the WHO (WHO, 2011) [30], this is not the case for the P₂ site which is a well. The highest value of faecal coliforms is obtained at the P₁₁ site (550 cfu/100mL) and that found for faecal streptococci is greater than 600 cfu/100mL (site P₅). For these two germs, the values are zero at the level of drilling, which is obvious because of their depth and the perimeter of protection. The presence of these bacteria indicates a faecal danger. Gastroenteritis is the most common disease associated with the ingestion of faecally contaminated water (Degbey *et al.*, 2010; Diallo, 2010) [12, 13]. Although this disease is often benign, it can sometimes have very serious consequences on human health. Other more serious diseases such as cholera, typhoid fever, hepatitis or meningitis can also be caused by ingestion of contaminated water (Degbey *et al.*, 2010) [12].

4. Conclusion

At the end of our study, the analytical methods made it possible to follow and to understand the spatio-temporal evolution of the physicochemical and bacteriological characteristics of the surface and underground waters of the Ouémé watershed in the Hozin area. From our results, it is noted that the majority of monitored sites (with the exception of drilling water) have waters whose ammonium concentrations are above the maximum guideline value of the WHO Guidelines for Quality of Life drinking water. This pollution is linked to human activities, including the use of chemical fertilizers and nitrogen herbicides in agriculture such as NPK, urea ((NH₂)₂CO, NO₃NH₄, triazines and phenylureas. P₇ is distinguished from other well waters by higher levels of calcium, magnesium, nitrates and sulphates as well as by physical parameters, in this case the higher electrical conductivity and TDS is closer to the characteristics of surface water to a lesser extent at the P₈ site, whereas the water from the P₄ well is closer to that of the drilling water in the zone, and the decrease in ammonium and phosphate contents is coupled with increase in COD This leads to the conclusion that the nutrients detected in the water column do not come from the decomposition of aquatic plants that are subservient to the aquatic environment but these nutrients come from other sources, such as runoff from agricultural

areas treated with chemical fertilizers. Microbiologically, except for drilling water, all waters contain a total coliform level greater than the maximum allowable value of 10 cfu / 100mL recommended by the WHO drinking water guidelines. But the detection in well water of total coliforms does not usually indicate a faecal contamination or a health risk, but rather a degradation of the bacterial quality of the water. This degradation can be attributed inter alia to an infiltration of surface water into the well. The presence of faecal coliforms and faecal streptococci in well and even surface water signals a faecal danger. This type of pollution threatens the health of the consumers of these waters.

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