International Journal of Latest Engineering and Management Research (IJLEMR)
ISSN: 2455-4847
www.ijlemr.com || Volume 03 - Issue 01 || January 2018 || PP. 19-26

Characterization of the origin of pollutants in groundwater using biostatistical tests: Case of the region of Daoukro, Central-East of Côte d'Ivoire

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Abstract: The objective of this study is to obtain the origin of groundwater pollution in the Daoukro region. The data collected during a measurement campaign on thirty pieces collected throughout the region were analyzed and compared to those of the WHO standards. Correlations between the physico-chemical parameters were highlighted using Kohonen's self-organizing map (SOM). The results of the presence of pollutants (nitrates and chloride ions) in foods were sampled with rates up to 85 mg / l for chloride ions and 39 mg / l for nitrates. The analysis of data from the SOM method reveals a correlation between nitrate, chloride ions and conductivity. There is also a correlation between bicarbonate, calcium and magnesium. These high levels of chlorides have their origin in the shale formations that constitute the substrate of the aquifer in this region, and the use of pesticides in rubber plantations for nitrates. To validate these results, a land cover map was developed to identify sources of pollutants in the production functions of different activities in the field of study.

Key words: Biostatistical tests, Côte d'Ivoire, Daoukro, Groundwater, pollution.

1. Introduction

Water is much more than just a human need. It represents an essential and irreplaceable element to ensure the continuity of life. However, it can also be a source of disease [1]. However, this resource is threatened by the excessive use of fertilizers and pesticides in large plantations and the increase of agro-industrial farms [2]. Combined with farming and animal breeding, the use of synthetic fertilizers and manure is often the root cause of nitrates in the water. Similarly, septic systems that do not exist or are deficient, as well as the natural decomposition of plant and animal matter, are also a source of nitrates in drinking water [3]. Several studies have identified the impact of agro-industrial farms on water resources in general and particularly on groundwater [4-5]. Thus, Daoukro, which was the first region in the production of coffee and cocoa, turned to rubber growing and oil palm production. There are vast agro-industrial plantations. These anthropogenic influences generate a significant risk of contamination of underground water naps. Determining the potential sources of this pollution and quantifying their impact on drinking water is therefore an approach conducted in this study to maintain the health and well-being of the populations of the Iffou region.

2. Material and methods

2.1. Presentation of the study area

The District of Daoukro is located in the Iffou region in central east of Côte d'Ivoire (Fig. 1). It is between longitudes 3° 29' and 4° 34' west and latitudes 6° 55' and 7° 32' north. The district has an area of 3745 km^2 and includes 4 cities (Daoukro, Ouéllé, Ettrokro and Ananda).

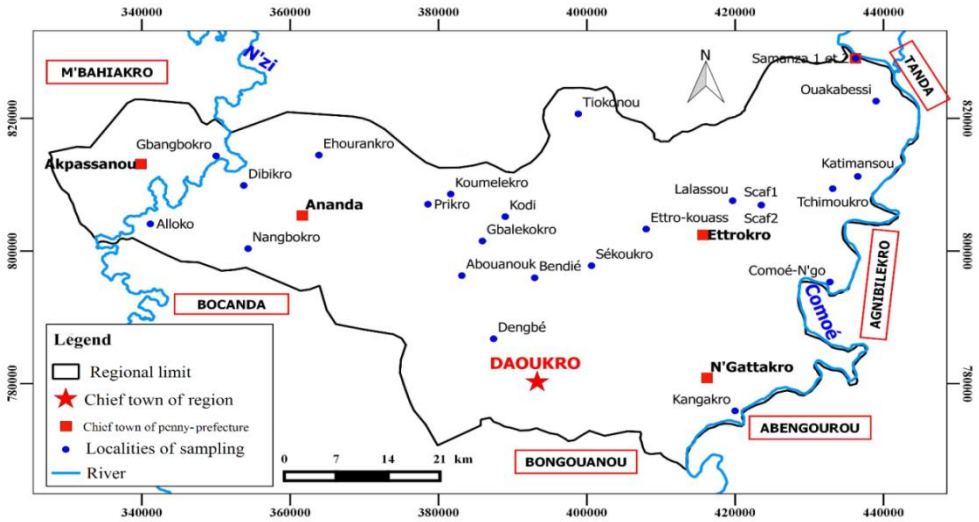

Figure 1: Location of the district of Daoukro.

It have an equatorial mitigated transition climate including 4 seasons: A great rainy season from March to June, a small dry season from July to August, a small rainy season from September to October and a big dry season from November to February. The months of December and February are the driest months with respectively 10.76 mm and 20 mm of rain. The average annual temperature of the area is around 27° C. The district of Daoukro belongs to the mesophilic sector covered by the mesophilic or semi-deciduous forest. Vegetation and soil are favourable for export crops, as well as for food crops **[6]**. (DCGTX, 1995). The study area is located in the N'zi-Comoé interfluve. It is dominated by a monotonous succession of low plateaux whose altitude decreases from 350 m in the north to 200 m in the south. The soil characteristics are dominated by ferralitic soils essentially. There are also hydromorphic soils. These soils are found along watercourses and in areas of depression. The population of the district is estimated at 159085 inhabitants **[7]**. This predominantly agricultural population consists of Agni, Baoulé and a minority of allogens. From a geological point of view, the region is composed of antebirimian formations (migmatites), volcano-sedimentary series, and intrusive assemblies (Fig. 2).

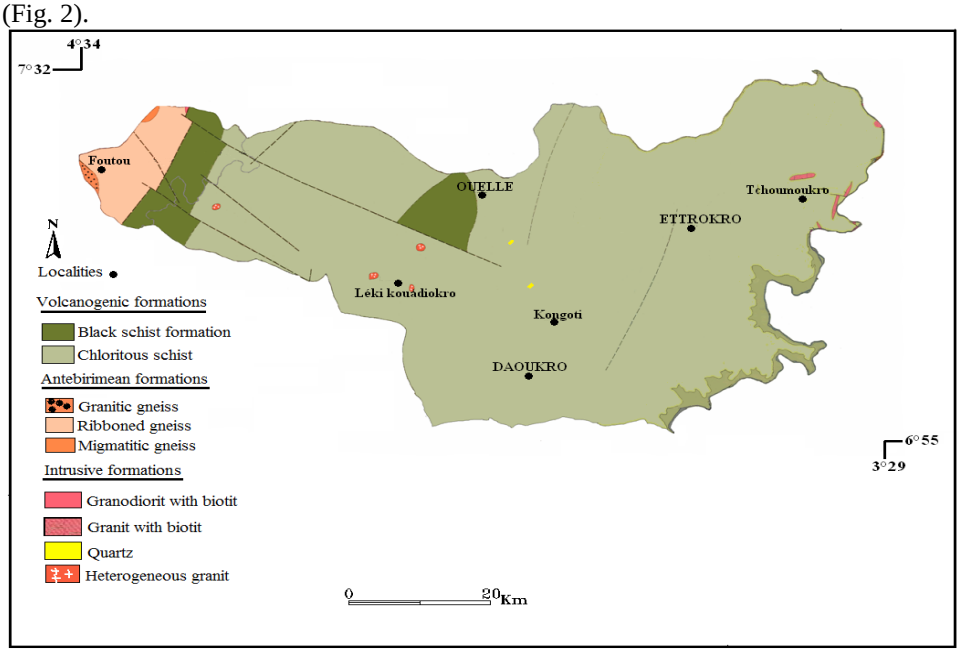

Figure 2: Geological map of Daoukro

The sukle of the region consists mainly of chloritic shale (80%) and black shale (about 5%) [8].Phyllic outcrops are found in some streams of the area. Phyllades are crystalline shales, laminated in appearance. They include slate, sericite and talcschist. Phyllades are more or less lustrous metamorphic rocks, such as slate shales

and sericiteschists. The region has two types of aquifers, namely the aquifer of alterites and the aquifers of the fissured sukle. However, this sukle is covered with thick layers of alterites (more than 100 m in some places) which considerably reduces the success rate of drilling **[9]** (Kanohin, 2010).

2.2. Study data

This study required the use of technicalindex card of 27 drillings distributed over the entire study area. A YSI brand multi-parameter was used to measure conductivity, pH, salinity, dissolved oxygen and temperature in situ. Turbidity was measured using a turbidimeter. Drill water samples were collected in 1-liter polyethylene bottles and sent to the Abengourou Analytical Laboratory. On the chemical analysis card of these drillings, our study relied on a number of chemical elements that are bicarbonate, calcium, chlorine, iron, magnesium, manganese and nitrate. The data used for this study come from the local agricultural development project of the district of Daoukro.

2.3. Statistical analyses

Statistical tests were performed to determine the correlations between the mineral elements of the groundwater. First a simplified analysis of the studied parameters in comparison with the standards of the WHO was made. Then the data processing was done by the SOM method (Self-Organizing Method) still called self-organizing maps of Kohonen [10; 11]. SOM is a type of Artificial Neural Network (ANN) characterized by unsupervised learning [12]. **[]** (Nguyen et al, 2014). The resulting maps are mathematical models that share with conventional ordination algorithms the idea of representing multidimensional data in a lower dimensional space **[13]** (Ohou-Yao et al., 2014). The objective of this study was to determine the presumed sources of pollution of the water supply sources (wells, springs and drillings) of the four study areas with regard to Kohonen self-organizing maps. These cards, which are actually matrix, were made with the Matlab 6.1 software. The number of cells to use and the size of the matrix (number of lines and number of columns) are two very important elements in the application of the SOM method. The number of theoretical cells is determined by the following formula:

$$m = 5\sqrt{n}$$

Where *m* is the cell number and *n* is the input parameter number **[12]** (Nguyen et al., 2014). As for the size of the matrix, its choice is made during the "learning" phase for which different sizes of cards are tested on the basis of the theoretical number of cells. The size used is the one with the lowest quantification errors (QE) and topography (TE) **[14]** (Kamagaté et al., 2010). The quantification (QE) and topography (TE) errors for the different cell sizes are presented in Table 1.

Table 1: Quantification and topography error of different matrix sizes

Card size	Quantification error	Topography error
5 X 5	0.460	0.000
4 X 6	0.495	0.000
6 X 4	0.475	0.000

Based on the values of QE and TE, a Kohonen map of 25 cells of size 5 X 5 was obtained for the projection of the 27 samples (Fig. 3).

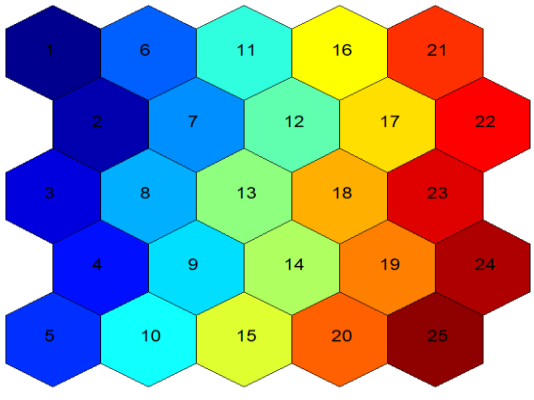

Figure 3: Self-organizing map of Kohonen size 5 X 5

The development of the land cover map required the use of satellite images. For this study, we used the Landsat 7 ETM + 196-55 scene of January 29, 2002. With the different bands of this scene we applied principal component analysis (PCA), color compositions and vegetation index standardized (NDVI). The training plots were then chosen to determine the different types of land use. The resulting map will then be subject to the validation of the results of the confusion matrix and the control graphs.

3. Results and discussion

3.1. Results

3.1.1. Physico-chemical parameter

Physical and chemical parameters include pH, conductivity, dissolved oxygen, nitrates, nitrites, calcium, magnesium, ferrous iron, manganese, chloride ions, bicarbonate, turbidity and color. The pH of the waters is close to 7. It varies between 6,11 and 7,10 with an average of 6,80. The conductivity is between 195 µS / cm and 860 µS / cm with an average of 445.6 µS / cm. 73PC of the sampled drillings have an electrical conductivity higher than the guideline value of WHO which is 300 µS / cm. Some drillings are weakly mineralized with a conductivity of between 195 µS / cm and 198 µS / cm. These water points represent 7.69PC of the water points analyzed. The high conductivity values ranging from 592 µS / cm to 840 µS / cm were found with 19.23PC of the drillings. The dissolved oxygen level is between 6.6 mg / l and 7.2 mg / l with an average of 6.72 mg / l. The analysis of dissolved iron (Fe^{2+}) levels in drillings shows a variation between 0.01 mg / l and 0.65 mg / l with an average of 0.04 mg / l. The basic statistics on the variables are given in Table 2.

Table 2: Basic Statistics of the Variables Studied

Variables	Number	Average	Standard deviation	Minimum	Maximum
pH	26	6,81	0,13	6,11	7,01
Cond	26	441,45	185,64	195	840,00
Cl-	26	39,01	27,47	7,09	85,10
fe	26	0,04	0,07	0	0,65
O2 dis	26	6,73	0,10	6,6	7,20
NO3-	26	27,38	18,02	7,5	65
Mn2+	26	0,01	0,03	0	0,50
Ca2+	26	24,85	15,84	8,016	78,76
Mg2+	26	5,35	0,89	1,45	13,61
HCO3-	26	198,25	67,28	73,2	469,70
turb	26	0,56	0,42	0,3	2,43
Coul	26	7,89	4,24	5	25,00

Overall, this table shows a small variation in levels with standard deviations that are often small compared to the average. However, the chlorine and nitrate contents are characterized by a large variation of the contents with a standard deviation in the same order as the average, which is 39.01 (± 27) mg / l for the chloride ions and 27.38 (± 18.02) mg / l for the nitrate. The analysis in Table 1 shows that bicarbonate and calcium with respective averages of 198.25 mg / l and 24.85 mg / l are the essential elements of the total mineralization of groundwater in the region. The presence of chlorine and nitrates is also noted in all sampled drillings with rates up to 85 mg / l for chlorine and 65 mg / l for nitrate. These high levels of chloride ions originate in the shale formations that constitute the substratum of the aquifer in this region but also wastewater discharges. These high levels of nitrate can come from the intensive use of fertilizers in the rubber and palm oil plantations of the region. The other ions present have low concentrations. The waters of the region thus have a chemical heterogeneity as a whole.

3.1.2. Mineralization and source of groundwater pollution

To determine the origin of the mineralization, the physicochemical parameters of the different samples were processed with the self-organizing map of Kohonen (SOM). The ascending hierarchical classification used is that of Ward (or of the k-mean type). It allowed to have the dendrogram (fig. 4).

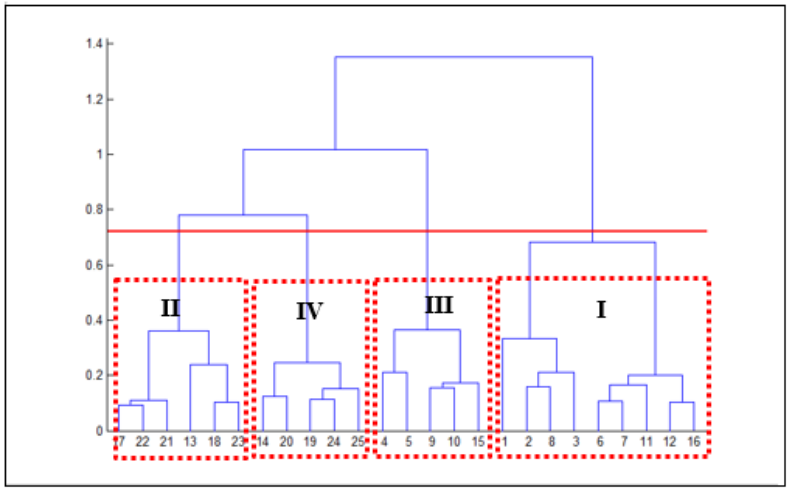

Figure 4: Kohonen's Map Classification Dendrogram

The matrix and ascending hierarchical classification of Ward then allowed the cells of the Kohonen map to be grouped into 4 groups corresponding to an Euclidean distance of 0.75 (Fig. 5).

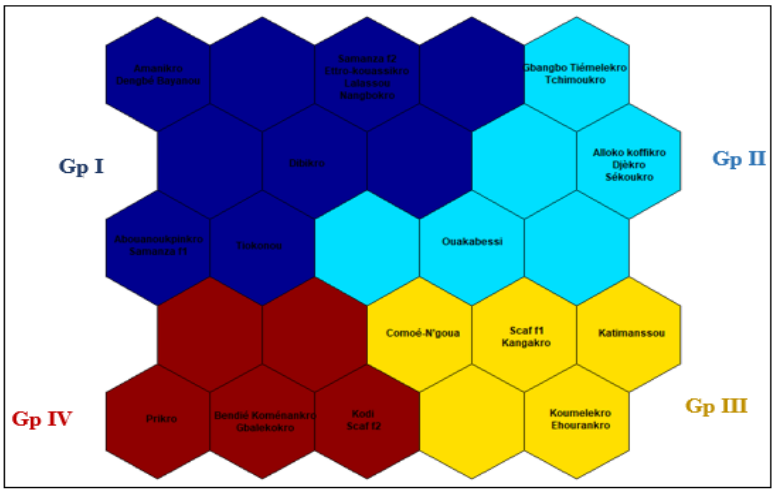

Figure 5: Distribution of samples by group of similarities on the Kohonen map

The interpretation of the Kohonen map coupled with the individual maps of the parameters (fig. 6) indicates the chemical elements that best discriminate the groups

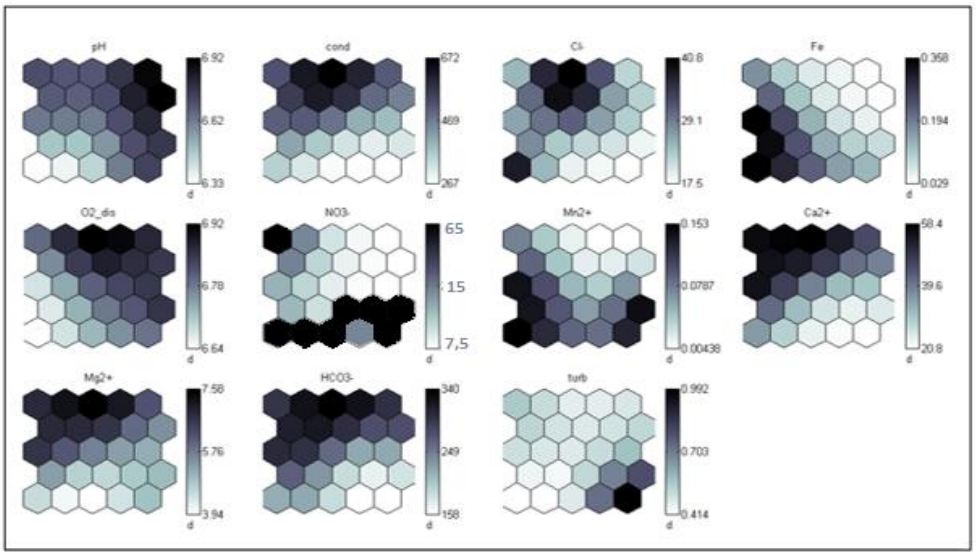

Figure 6: Individual Kohonen map of the different physicochemical parameters

This map represents the weight of the different physicochemical parameters taken into account in the grouping of each unit defined by the hierarchical cluster analysis used. The four groups obtained are as follows:
Group 1 comprises water samples (10) taken from the localities of DengbeBayanou, Samanza (f_2), Ettrokouassikro, Lalassou, Nangbokro, Dibikro, Abouanoukpinkro, Samanfa (f_1), Tiokonou and Amanikro. This group highlights the correlation between conductivity, bicarbonate, calcium and magnesium. It reveals the phenomenon of dissolution of rocks related to the time of stays. This group is marked by deep drillings that capture the fractured suckle and characterized by low thicknesses of alterites (thickness of alterites between 8 m and 20 m). The water from these drillings is rich in bicarbonates with contents ranging from 290 mg / l to 469 mg / l. The mineral salt concentrations are high (Ca^{2+}, Mg^{2+}, and cl^{-}). The conductivity values vary between 470 µS / cm and 672 µS / cm,
Group 2 includes six samples taken from the localities of Gbangbo-Tiemelekro, Chimoukro, Allokokoffikro, Djekro, Sekoukro and Ouakabessi. The parameters that best discriminate this group are: pH, iron, nitrate and dissolved oxygen. The pH values are the highest. The waters of this class are almost completely free of iron and highly oxygenated. Nitrate values range from 7.5 mg / l to 15 mg / l. Drillings in this group also captures the fractured suckles with total depths (between 50 m and 70 m) less than that of the first group. The waters of this group are also rich in bicarbonate
Group 3 comprises 6 samples taken from the localities of scaf (f1), koumelekro, Ehourankro, Katimansou, Kangakro, and ComoéN'goua. The waters of this class are weakly mineralized and poor in bicarbonates. High nitrate values of up to 65 mg / l are observed. It is also in this group that turbidity values are high (2.43). Drilling in this class has a high thickness of alterites (80 m - 103.5 m) with total depths ranging from 80 m to 106 m. This class shows mineralization influenced by rainfall intrusion into aquifers with high chloride ion content (63.32 mg / - 85.01 mg / l)
Group 4 includes the last 5 samples. It consists of very little turbid water and there is a strong presence of iron and Mn^{2+}. The pH values of this class are relatively low. This group includes low mineralized (7.5PC) drillings, low in bicarbonate and calcium. These water points exploit the aquifer of alterite. The levels of nitrate and chlorine are also high.
To confirm these results, the Daoukro land cover map was developed from Landsat ETM+ images (Figure 7).

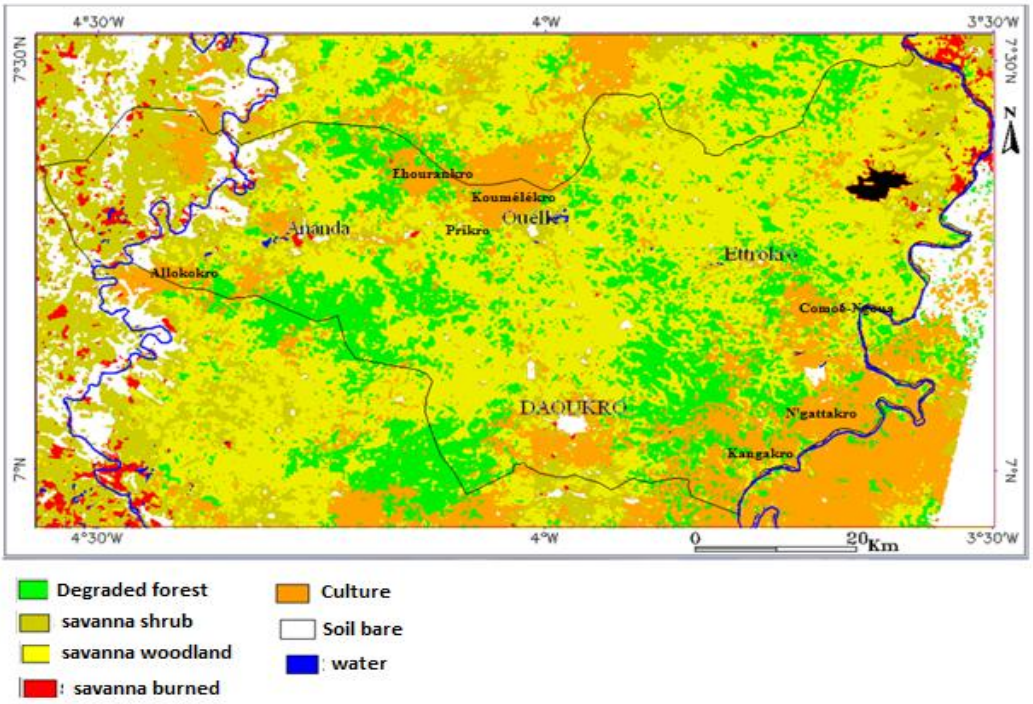

Figure 7: Map of Daoukro Land Cover

The confusion matrix (Table 3) of the different land cover classes indicates that the overall accuracy of the mapping is 96.98PC. This value makes it possible to conclude that the different formations are well discriminated. The map and the confusion matrix highlight the following classes: degraded forest, wooded savannah, shrub savanna, burned savannah, crops and naked soil. The naked soils are generally the dwellings and farms of the villagers. The growing areas are large plantations of rubber trees, teak, palm trees and coffee-cocoa. The superposition of the map obtained with that of the localities with a high concentration of culture

indicates the places of intensive use of pesticides (Ehourankro, N'gattakro, koumelekro). In these localities the nitrate level is around 65 mg / l.

Table 3: 2002 Landsat ETM + Image Classification Confusion Matrix

Classes	Forest	Savannah 1	Savannah 2	Savannah 3	Culture	Soilbare	water	Total
Forest	**97,55**	0,08	0,00	0,00	0,86	0,00	0,00	**100,00**
Savannah 1	1,53	**97,63**	0,10	0,70	0,10	0,02	0,61	**100,00**
Savannah 2	0,03	1,69	**94,48**	1,77	1,07	2,63	1,35	**100,00**
Savannah 3	0,08	0,43	2,87	**96,99**	0,00	0,04	1,60	**100,00**
Culture	0,72	0,09	0,00	0,01	**97,92**	0,00	0,37	**100,00**
Soilbare	0,00	0,05	2,53	0,19	0,04	**97,28**	0,61	**100,00**
water	0,08	0,03	0,02	0,34	0,01	0,02	**95,46**	**100,00**
Total	**100,00**	**100,00**	**100,00**	**100,00**	**100,00**	**100,00**	**100,00**	**100,00**

3.2. Discussion

The analysis of the physicochemical parameters of the Daoukro waters using the SOM (Self-Organizing Method) method, also called self-organizing Kohonen maps, made it possible to highlight four water classes. All samples have acidic pH values between 6.33 and 6.92. These pH are fairly close to neutrality and meet WHO standards. The waters studied show a presence of nitrate, which is an indicator of groundwater pollution. This observation could be explained by the fact that nitrates (NO_3^-) and nitrites (NO_2^-) are naturally occurring ions in the environment. They are the result of nitrification of the ammonium ion (NH_4^+), present in water and soil, which is oxidized to nitrites by bacteria of the genus *Nitrosomonas*, then nitrates by bacteria of the genus *Nitrobacter***[15]** (Degbey et al. al., 2010). The nitrate concentrations observed in this study may be related to the infiltration of wastewater or the use of chemical fertilizers near water points **[16]** (Mpakam, 2009). We noticed large plantations of rubber and palm oil on very large surfaces. Nitrate levels in the collected samples highlight the impact of agro-industrial operations on groundwater resources. This study also made it possible to know the origin of the ions present in the waters of Daoukro. Thus class 1 reveals a correlation between the conductivity and the major ions (calcium, magnesium, bicarbonate). The origin of these ions in groundwater is largely attributed to the chemical and mineralogical constitution of the lands crossed. And this mineralization of groundwater is controlled by water-rock contact **[17]** (Kanohin et al, 2017, Ahoussi et al, 2010). The suckle of the region consists mainly of chloritic shale (80%). These shale formations, which form the subsoil of the studied aquifer, are the main source of high concentrations of Cl^- in groundwater. The presence of chlorine in these waters can also be justified by the intrusion of wastewater and rainwater. This is the case of the water samples taken at Ehourankro and Koumélekro (drillings dug only in the alterites). The land cover map highlights potential sources of pollution such as large rubber and palm plantations. Statistical analysis using the SOM method revealed four classes that can be grouped into two main classes. A class of superficial origin contains pollutants from anthropogenic activities (nitrate and chlorine) and those whose origin is related to the dissolution of rocks (bicarbonate, calcium, magnesium, iron and manganese) **[18]**.

4. Conclusion

The study of the physicochemical parameters of the Daoukro waters shows the following results: the pH of the water is close to 7. It varies between 6.11 and 7.10 with an average of 6.80. The conductivity is between 195 µS / cm and 860 µS / cm with an average of 445.6 µS / cm. The dissolved oxygen level is between 6.6 mg / l and 7.2 mg / l with an average of 6.72. The mineralization of groundwater is controlled by the nature of the geological formations present in the area. Thus, the main ions come from the alteration of rocks and the hydrolysis of silicate minerals. The use of self-organizing maps of Kohonen revealed the sources of groundwater pollution at Daoukro, which are mainly the use of fertilizers and pesticides in the vast plantations of rubber, oil palm and teak. It should also be noted that the absence of sanitation structures in rural areas is also a source of pollution of groundwater.

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