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Multivariate Statistical Analysis of Groundwater Mineralization in Daloa and Zoukougbeu, Central West, Côte d'Ivoire

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ABSTRACT: This study aims to determine the mechanisms of groundwater mineralization in the departments of Daloa and Zoukougbeu (Central West, Côte d'Ivoire). In order to achieve this, a hydrochemical study was carried out from seventeen (17) water samples (wells and sources) collected in March 2018. It was based on the multivariate statistical analysis techniques: The Principal Component Analysis (PCA) and the Hierarchical Cluster Analysis (HCA) were applied to physicochemical parameters. Thus, the average values of temperature, pH, electrical conductivity, Total Dissolved Solids (TDS) and Turbidity measured *in situ* in source waters are respectively 27.63°C; 4.81; 84.6 µS / cm; 38.45 mg. L^{-1} and 40.78 NTU and in well water 27.90°C; 4.78; 81.85µS/cm; 36.61 mg. L^{-1} and 27.22 NTU. The average concentrations of the major cations Ca^{2+}, Mg^{2}, Na^{+} and K^{+} of well water are respectively 2.26; 1.01; 4.58; 1.41 mg. L^{-1} and those of spring waters 2.18; 1.03; 5.50 and 2.07 mg.L^{-1}. The major anions HCO_3^-, Cl^-, SO_4^{2-} and NO_3^- respectively amount to 8.81; 8.28; 5.33 and 7.67 mg.L^{-1} for well water and 11.77; 8.5; 5.27 and 8.25 mg.L^{-1} for spring waters. The PCA results show that three phenomena govern the mineralization of these waters. These are the phenomena of *mineralization-residence time of water* which is acquired by *acid hydrolysis of the host rocks, spatial origin of lower quality of water and the grounds throughfall*. These phenomena are confirmed by the Hierarchical Cluster Analysis (HCA). This work is therefore a tool for supporting groundwater management.

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Groundwater are the main source of drinking water supply due to scarcity and / or exposure to surface water pollution. They are exploited from various works: wells, boreholes, etc. (De Marsily et *al*., 2017). They were by far the least exposed resource to pollution. Unfortunately, nowadays, they are threatened with more and more contamination. On the other hand, in Africa, the difficulties of people's access to drinking water further complicate the achievement of the millennium goals for sustainable development. Like most Ivorian regions, the Central West is not spared despite the good rainfall (Adjiri et *al*., 2019). In the departments of Daloa and Zoukougbeu, surface water is in quantity, but the problems of quality, portability and continuity of service occur (Koukougnon, 2013). The only alternative to supply population with drinking water, especially in rural areas, is the exploitation of groundwater. In urban areas, it will provide good quality of water and less expensive. To do this, the knowledge of the functioning of aquifers is undeniable. This operation can be perceived by studying the mechanisms that govern waters mineralization contained in these aquifers. Indeed, the study of the hydrogeochemical processes is of capital interest to appreciate the quality of a region's groundwater. In fact, the variation and / or the presence of certain chemical parameters can reveal the interactions between water and its environment and can guide on the management methods to be implemented (Li et *al*., 2018). In addition, multivariate statistical analysis techniques have been used successfully in several hydrochemical studies. Montcoudiol et al. (2015), used these techniques in the Outaouais region, southwestern Quebec, to identify the processes that govern groundwater chemistry. In the Amacuzac River basin in central Mexico, Eric et *al*. (2016) used multivariate statistical analysis to search for geochemical evolution of groundwater. Benadela and Bekoussa (2017) also used multivariate statistical methods to study groundwater mineralization of the Ghriss plain in northwestern Algeria. It is in this context that the

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present study fits. It plans to investigate groundwater mineralization mechanisms in the departments of Daloa and Zoukougbeu, using multivariate statistical analysis tools such as Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA). Recall that various authors (Everitt and Hothorn, 2010, Eric et *al*., 2016) have indicated in their work that Principal Component Analysis (PCA) is generally used as a diagnostic tool to identify trends in geochemical data.

Study Area: The study area includes the departments of Daloa and Zoukougbeu, located in Côte d'Ivoire's central west. It lies between longitudes 6° and 7°West and latitudes 6° and 7° North (Figure 1).

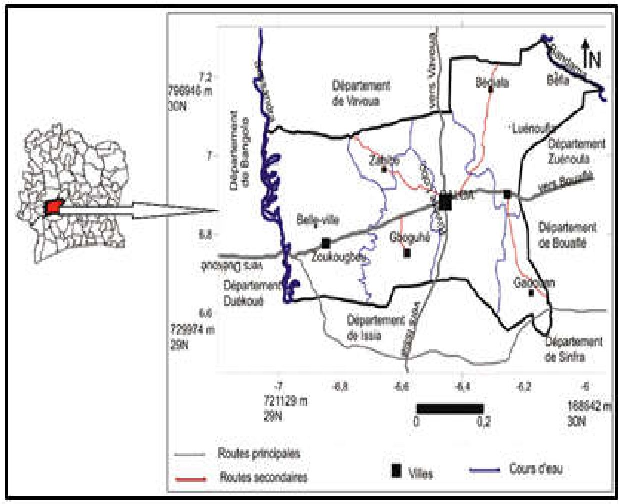

Fig 1: Location of the study area

It therefore belongs to the region of Haut Sassandra with chief town of region, Daloa. The city of Daloa is located at 383 km from Abidjan, the economic capital of the country. It is a forest area that is now degraded due to agricultural activities and logging. Soils are remodeled and hydromorphic types (Tahoux, 1995). The formers occupy more than 90% of the area and are generally derived from the granites' alteration. They are characterized by gravels in the upper part (Tahoux, 1995). The weathering patterns of these soils are mainly of the ferrallitic type with persistence of iron and aluminum in the form of oxides and hydroxides. This type of soil is favorable for many crops such as cocoa and coffee. As for the hydromorphic soils, these are observed along the rivers and in the shallows. These are soils that have a high capacity for water conservation and are generally used for rice growing and market gardening (Ligban, 2009). The departments of Daloa and Zoukougbeu belong to the West African climate regime characterized by the action of two air masses of different natures. It is the harmattan marked by warm and dry air, brought by the boreal trade winds that blow from the north-east to the south and the monsoon characterized by the cold and humid air coming from the Atlantic Ocean under the effect of the Southern trade wind and circulating from the South to the northeast. With annual rains dropped from 1868.5 mm in 1968 to 1120.4 mm in 2005, the region is experiencing a 40% drop in rainfall (Ligban, 2009). The average annual temperature recorded at Daloa station is 25.8°C with monthly variations generally below 3°C. The hydrographic system is dense with the Sassandra River which is the main river that regulates the hydrography of the zone. The river system attached to its bed is dominated by the Lobo and Davo rivers, which are respectively in the central and southeastern parts. Regional drainage occurs in north-south direction. Geologically, the main formations encountered are granitoids, dioritoids and shales. At the hydrogeological level, there are two types of aquifers: the aquifer of regolith and the aquifers of cracks.

MATERIAL AND METHODS

Material: The field equipment for the measurement of physicochemical parameters *in situ* consists of a HACH HQ40d multiparameter, a distilled water bottle, distilled water and nitric acid. For water sampling, we used 1-liter bottles of polyethylene and three coolers for sample retention. Garmin GPS was used for geolocation of water points.

Sampling methodology: Two water sampling campaigns were carried out in March 2018. They covered 17 water points including 11 sources and 6 large-diameter wells with an average depth of 8 m. During sampling, the following procedures were followed: the bottles, previously rinsed with distilled water, are rinsed 3 times with the water to be analyzed, then filled to the brim and tightly closed without leaving any bubbles. Once the bottles are filled, they are kept in a cooler to maintain a low temperature of 4°C. That avoids the degassing of water and the precipitation of certain chemical elements. Two samples were taken for each source, one for anion dosage and another for cation dosage. The analyses were performed 48 hours after taking samples. The contents of major ions (cations and anions) were determined using a colorimeter and a HACH-type digital titrator for anions and an atomic emission spectrometer (ICP-AES) whose source is plasma generated by inductive coupling for cations. To this end, we used various reagents and laboratory accessories. The turbidities were measured by a turbidimeter brand HACH 21000.

Data processing method: multivariate statistical analysis: Multivariate statistical analysis is a quantitative and independent approach to groundwaters classification to group samples and correlate chemical parameters with water samples. In this study, two methods of multivariate statistical analysis were used from the Statistica software 7.1: Principal Component Analysis (PCA) and Hierarchical Cluster Analysis (HCA).

RESULTS AND DISCUSSION

Basic statistics of physical parameters: Table 1 presents the results of basic statistics of the physical parameters measured *in situ* in the groundwater of the departments of Daloa and Zoukougbeu. The analysis of the results in table 1 shows that for spring waters, the TDS values are between 15.33 and 100.2 mg. L^{-1} for an average of 38.45 mg. L^{-1} and a standard deviation of 25.01. The minimum temperature is 26.2°C against 29.3°C for its maximum value with an average of 27.63°C. The pH is between 4.38 and 5.91 for an average of 4.81.

Table 1: Summary of basic statistics of physical parameters measured *in situ*

Parameters	Units	VG	Min	Max	Avg	Standard Deviation
Source Water						
TDS	mg L^{-1}		15.33	100.2	38.45	25.01
T	°C	22-25	26.2	29.3	27.63	1.3
pH		6.5 à 9.5	4.38	5.91	4.81	0.46
CE	µS/cm	1400	33.7	218.9	84.6	54.46
Turbidity	NTU	5	1.24	146	40.78	47.70
Well Water						
TDS	mg L^{-1}		25	48.8	36.61	7.98
T	°C	22-25	26.8	28.7	27.90	0.68
pH		6.5 à 9.5	4.02	5.14	4.78	0.42
CE	µS/cm	400	57.6	111.2	81.85	18.05
Turbidity	NTU	5	1.37	67.8	27.22	28.13

VG = WHO guideline values (2011); Min= minimum; Max= maximum; Avg = average

The electrical conductivity values range from 33.7 to 218.9 µS/cm for an average of 84.6 µS/cm. As for the turbidity values, they are between 1.24 and 146 NTU for an average of 37.78. For well waters, the TDS values are between 25 and 48.8 mg. L^{-1} for an average of 36.61 mg. L^{-1}. As for the temperature values, they range from 26.8°C to 28.7°C with an average of 27.90°C. The minimum pH is 4.02 for a maximum value of 5.14 and an average of 4.78. The minimum electrical conductivity is 57.6 µS/cm against a maximum value of 111.2 µS/cm for an average of 81.85 µS/cm. The minimum turbidity is 1.37 NTU against a maximum value of 67.8 NTU and an average of 27.22 NTU. With the exception of turbidity, these values are for the most part lower than the WHO guideline values (2011). These values indicate that waters are mostly acidic, weakly mineralized. The strong turbidities observed in some places are probably related to the lithological nature of aquifers and/or the presence of organic materials. Turbidity is one of the parameters used to characterize water quality. According to the definition given by standard NF EN ISO 7027 of March 2000, it is defined as the reduction of the transparency of a liquid due to the presence of undissolved materials.

Basic statistics of chemical parameters: Table 2 presents the results of the basic statistics of the chemical parameters dosed in laboratory. The minimum and maximum concentrations of hydrogen carbonate ions, chlorides, nitrates and sulphates are respectively 0.73 and 36.6 mg/L; 2.4 and 16 mg/L; 0.5 and 38.07 mg/L; <LD and 14 mg/L. The average contents are respectively 10.30; 8.41; 7.86; ≈5.29 mg/L. At cations level, the minimum and maximum concentrations of calcium, magnesium, potassium and sodium ions are respectively 0.4 and 9.2; <LD and 3.17; 0.41 and 6.67; 1.33 and 12.5. The average

contents are respectively 2.18; ≈1.01; 1.89 and 5.14 mg/L. These concentrations are all below the WHO guideline values (2011). However, bicarbonate seems to be the most concentrated, with contents in spring waters, about twice that of well water. The latter is followed by nitrate, relatively in the same proportions in the two resources. In terms of the other ions, the levels are relatively similar, both in spring water and in wells.

Results of multivariate statistical analysis: Principal Component Analysis (PCA): Analysis of eigenvalues and percentages expressed: The results of eigenvalues and percentages of expressed variance for the first four factors are shown in Table 3.

The table analysis shows that the first four factors account for 86.67% of the total variance. The first three factors alone account for more than 70% of the expressed variance. The factor F1 alone accounts for 44.59% of the variance, followed by the factor F2 with 18.71% and F3 with 14.46%. In view of these expressed percentages, we can say that the mechanisms that control the chemical evolution of waters in the region are largely contained in these three factors. As a result, our analysis will focus solely on these three factors. The eigenvectors that make it possible to define each of these three factors in relation to the variables are reported in Table 4.

Table 2: Summary of basic statistics of the measured chemical parameters

Parameters	Ca^{2+} (mg/L)	Mg^{2+} (mg/L)	Na^{+} (mg/L)	K^{+} (mg/L)	HCO_3^- (mg/l)	Cl^- (mg/L)	SO_4^{-2} (mg/L)	NO_3^- (mg/L)
Source Water								
Minimum	0.8	0.24	2.43	0.75	5.12	4.4	1	0.5
Maximum	9.2	3.17	12.5	3.31	36.6	16	14	38.07
Average	2.36	1.08	5.36	1.62	12.71	8.45	5.3	8.91
Well Water								
Minimum	0.4	<LD	1.33	0.41	0.73	2.4	<LD	1.7
Maximum	5.6	2.93	7.46	6.67	19.89	13.5	9	14.61
Average	2.00	≈0.94	4.92	2.16	7.89	8.38	≈5.28	6.82
WHO guideline values*	**70**	**50**	**200**	**12**	**200**	**250**	**250**	**50**

LD: detection limit

Table 3: Eigen values and percentage expressed

	F1	**F2**	**F3**	**F4**
Eigen value	5.80	2.43	1.88	1.16
% Expressed variance	44.59	18.71	14.46	8.91
% Cumulative expressed variance	44.59	63.31	77.76	86.67

Factorial plan analysis F1-F2: The correlation circle of the factorial plan F1-F2 (Figure 2) shows that the factor F1 with 44.59% variance is determined in its positive part by the group of variables Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, electrical conductivity (CE) and TDS. Sulphates (SO_4^{2-}) are opposed to these variables in the negative part. Variables such as Ca^{2+}, Mg^{2+} are generally derived from rock alteration and acid hydrolysis of silicate minerals. This phenomenon is a slow process, especially in fissure aquifers where water flow velocities are low due to a poorly developed fracture network in the basement region.

The factor F1 accounts for the mineralization acquisition conditions. It expresses the phenomenon of mineralization-residence time of waters in the aquifer. The F2 factor with 18.71% variance is expressed in its positive part by the nitrates (NO_3^-) and the pH and T°C variables in its negative part.

The variable NO_3^-reflects the nitrogen pollution of water. Its presence in groundwater is an indicator of the impact of anthropogenic activities such as the use of fertilizers in agriculture, wild garbage dumps and often litter. They reach the water table by infiltration per descendant.

Table 4: Coordinates of variables according to factorial axes

	Fact. 1	Fact. 2	Fact. 3
TDS	0.961845	0.199141	0.003940
T°C	0.089105	-0.724996	0.362815
pH	0.259594	-0.709261	-0.485332
CE	0.960708	0.216929	0.016317
Turb	-0.454350	0.307444	-0.664276
Ca^{2+}	0.809508	0.277862	-0.295396
Mg^{2+}	0.836179	-0.150294	-0.360831
Na^{+}	0.778750	-0.383183	-0.020309
K^{+}	0.453646	-0.374702	0.259995
HCO_3^-	0.159292	-0.470407	-0.774384
Cl^-	0.817413	0.195310	0.155805
SO_4^{2-}	-0.617853	0.296159	-0.397001
NO_3^-	0.652244	0.698898	-0.058561

On the other hand, the relative opposition of the Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, CE and TDS variables to pH and temperature would reflect the influence of the latter respectively on the acquirement of mineralization and water degradation. In total, the factor F2 expresses the phenomenon spatial origin of water quality degradation.

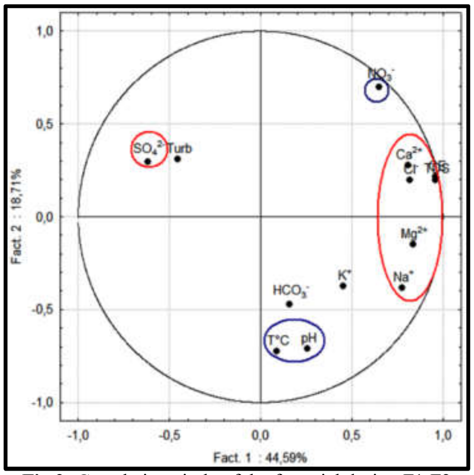

Fig 2: Correlation circle of the factorial design F1-F2

Analysis of the factorial design F1-F3: The correlation circle of the factorial design F1-F3 (Figure 3) reveals that F1 factor is controlled in its positive side by the group of variables such as Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{-}, NO_3^{-}, the electrical conductivity (CE) and TDS which is always in opposition with the SO_4^{2-} variable.

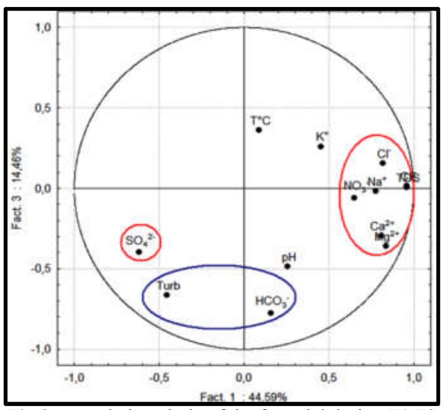

Fig 3: Correlation circle of the factorial design F1-F3

F1 expresses the phenomenon *residence time mineralization* in the aquifer waters. With 14.46% of variance, the F3 fact is determined in its negative side by the group of Turbidity variable (Turb) and content in HCO_3^{-}. This fact reveals that the turbidity of groundwater will be generally inorganic (limon, silt, clay and natural chemical components) and therefore caused by natural geological factors. This design then highlights superficial exchanges which occurred between groundwater and runoff waters coming from precipitation and soil drainage. These exchanges bring to light the throughfall of soils that contribute to the increase of the number of particles in the water bodies. The F3 fact therefore expresses a phenomenon of *soils'* throughfall surrounding water points.

Hierarchical Cluster Analysis (HCA): The dendrogram coming from the ascending hierarchical classification helps to define three major groups of variables. The first one is formed by the following variables: pH, Na^{+}, Ca^{2+}, Mg^{2+}, K^{+}, Cl^{-}, SO_4^{2-}, NO_3^{-} and HCO_3^{-}. This group of variables shows the *residence time mineralization* or *the hydrolysis of carbonate or silicate minerals* after an extension of water residence times in the aquifer. The second one is comprised of temperature and the TDS reveals the influence of temperature in the process of acquisition and mineralization. The third and last one includes the CE and the turbidity. This group highlights the phenomenon of soils' throughfall. In fact, as already explained at the level of PCA, the groundwater turbidity will generally be inorganic and caused by natural geological factors. This group of variables confirms that finding and effectively reflects the soils' throughfall.

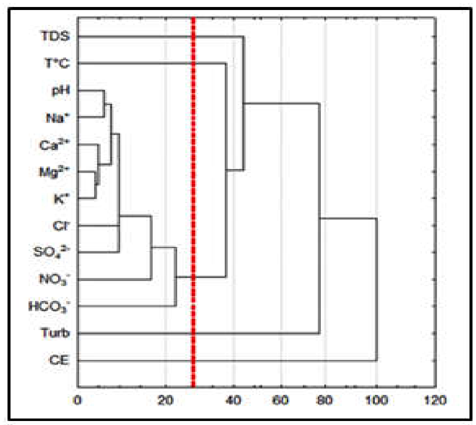

Fig 4: Horizontal dendrogram of waters study area

The results of basic statistics demonstrate that the average pH of well and spring waters are respectively 4.78 and 4.81. The pH value interval recommended by WHO (2011) is 6.5-9.5. The value of the obtained average pH are in total below 6.5. These waters are then acids. The acid nature of these waters is may be the result of an anthropogenic and biogeochemical process. This process is governed by the soil CO_2 generated through the breathing of plant roots and the decomposition of organic plant material. (Kortatsi, 2006; Kortatsi, 2007; Kortatsi et *al*., 2008, Matini et *al*., 2009). In fact, the presence of forests and a rainfall relatively abundant in the Ivorian Central West area causes the decomposition of organic material. According to Prasad and Narayana (2004), the decomposition of organic material inside soil in aerobic environment emits carbon dioxide. This latter dissolves in water in order to form a carbonic oxide following this chemical reaction $CH_2O + O_2 \rightleftarrows CO_2 +$

$H_2 0 \rightleftarrows H^+ + HCO_3^-$. According to these authors, this reaction illustrates the origin of the acid nature of waters. Ligban et *al*. (2009) and Adjiri et *al*. (2018) noted that acid nature of groundwater in the Haut-Sassandra area.

On the other hand, turbidity is one of the parameters which allows the characterization of water quality. According to the statistical analysis undertaken (PCA), the high turbidity measured in the spring as well as in well waters are linked to the geological nature of aquifers. Indeed, the identified wells and springs mostly came from shallow aquifers. (Adjiri et *al*., 2018). These aquifers are all regolith aquifers rich in clay. The run-off of this clay materials by rainwater would contribute to increase the fine particles load. In addition, some water points are located in shallows and cultivation area. The degradation of organic material and its run-off by rainwater also contributes to increase the turbidity of waters.

Furthermore, through the multivariate statistical analysis (PCA and HCA), the study of the origin of mineralization allowed to highlight three phenomena that will be responsible of water mineralization mechanism. These are the *waters residence time mineralization,* the *spatial origin of water quality degradation*, and *soils' throughfall*. The first one mainly the mineralization of groundwater according to the spent residence times in the aquifer has been revealed by Biémi (1992), Savané and Soro (2001) and Amadou et *al*. (2014). This has been possible through different works made on different river basins coming from the Precambrian basement of West Africa. According to these authors, the ions of the groundwater of the area concerned by their works come not only from alteration but also from the hydrolysis of silicate minerals such as biotite, silicate feldspars after a more or less longer contact time. Redwan and Moneim (2016) also make that remark in Egypt.

The second phenomenon demonstrates that the origin of the degradation of groundwater are caused by anthropic activities. In other words, waters seepage and/or of run-off coming from the washout of agricultural land are at the basis of the identified well and spring waters quality. This degradation is explained by the presence of nitrate in water. This phenomenon of mineralization by soils' throughfall has been undertaken by Hussein (2004) during his works on Blue Nil Basin's groundwater in Sudan. Concerning turbidity, it is the third phenomenon namely the soils' throughfall which may cause it.

*Conclusion***:** This study aimed at determine the origin of groundwater mineralization in the areas of Daloa and Zoukougbeu (Central West area of Côte d'Ivoire). It focuses on the multivariate statistical tools such as PCA and HCA. The result of the basic statistics demonstrates that groundwater (well and springs) are acids with an average pH of 4.78 and 4.81. These waters have low mineral content and are therefore in accordance with the chemical characteristic well recognized for groundwater in the area of base in Côte d'Ivoire. The principal component analysis (PCA) and the Hierarchical Cluster Analysis (HCA) revealed three phenomena which control groundwater mineralization. The first one was the *waters residence time mineralization*. The second one was the *spatial origin of water quality degradation*. The last one was *soils' throughfall*. These results represent an important database for the management and planning of groundwater resources in the areas of Côte d'Ivoire.

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