Multidimensional Analysis for the Assessment of the Physicochemical Quality of Waters in the Chaillu Massif (Republic of Congo)

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ABSTRACT
The supply of drinking water to rural populations is ensured by spring water and rivers in the Chaillu massif in the southwest of the Republic of Congo. The objective of this study is to evaluate the different physicochemical parameters that govern the hydrochemistry of these waters. Principal Component Analysis (PCA) and Ascending Hierarchical Classification (CAH) were applied to the chemical data of 13 sampled water points. The average water temperature is 24, 20 °C with an average pH of 6.72. The average electrical conductivity is 41, 28 μS/cm with extreme values between 26, 00 and 81, 00 μS/cm. These waters are suitable for consumption outside certain water points whose lead concentrations are higher than WHO standards. Three principal components accumulate a total variance of 63.168% of the 17 variables. PCA and CAH highlight three hydrogeochemical processes in the hydrochemical evolution of groundwater. Acid hydrolysis of silicates produces Ca²⁺, Mg²⁺ and SO₄²⁻ ions in water. Redox appears to be the source of iron and manganese. The concentrations of NO₃⁻ and Cl⁻ are related to the decomposition of organic matter. The hydrochemistry of the water in this massif is governed by natural factors.

Keywords: Congo, Chaillu massif, Hydrochemistry, Surface water, Groundwater.

INTRODUCTION
Water is an essential element for the life and development of territories. Unevenly distributed over the earth and sometimes present in limited quantities, it constitutes a major environmental issue.
The importance of water and in particular groundwater is not to be demonstrated. Groundwater is an invaluable supply of drinking water for humanity in domestic, industrial and agricultural sectors in many countries. Groundwater has become the main source of freshwater supply for rural communities (Ghislain et al., 2012). Groundwater is also a freshwater resource for rural communities. However, the captured water may contain elements that can have adverse health effects, such as pathogenic microorganisms, unwanted substances or even toxic substances (Yapo et al., 2010; & Jang et al., 2012). These substances can come either from the physical environment in which the water has evolved, or from discharges of certain human activities for which water has become the receptacle. The Republic of Congo, which is one of the wettest countries in Africa, is experiencing major water supply problems. Nearly 60% of the Congolese population use more or less protected and uncontrolled water collection facilities. Only large urban agglomerations have access to drinking water supplied by the National Water Distribution Company in the acronym SNDE (Moukolo, 2001). In the Chaillu massif, the difficulties linked to the management of the water supplying the various localities of this massif, constitute a major problem which these localities must face. Indeed, the use of this untreated water is dangerous and has serious consequences on their health. The objective of this work is to assess the physico-chemical quality and to determine the processes at the origin of the mineralization of the waters of this massif.

Geographic setting of the study

The Chaillu massif is a geomorphological region shared by Gabon and Congo. In Congo, it occupies the southwestern part of the republic, between latitudes 2°00 and 3°30 south and longitudes 11 ° 00 to 14 ° 50 East and extends over the administrative departments of Lékoumou and Niari (Figure 1). This massif covers an area of around 40000 km² (Novikoff, 1974). From a geological point of view, the Chaillu massif is entirely made up of Precambrian formations with several series, namely: the Inkisi series, the Mpioka series, schisto-limestone series, and the Louila series (Atlas, 2001). Its soils are classified in the category of yellow, reworked soils where the three ferrallitic soils, hydromorphic and modal soils clearly appear (Dadet, 1969). The Chaillu massif is dominated by the forest which covers its whole. Its climate is of the humid tropical type characterized by an alternation of two seasons: a hot and rainy season which extends from November to April and a dry and cool season from June to September (Samba-Kimbata, 2002).
MATERIALS AND METHODS

SAMPLING METHOD

In order to achieve the target, a total of 52 samples were collected, during the entire sampling period (November 2019 & May 2020), and this in two types of structures (sources and rivers). Water sampling has always been carried out after complete renewal of the water column in order to guarantee the representativeness of the samples. The water intended for the chemical analyses was taken in 500 ml flasks. The physical parameters (temperature, pH and electrical conductivity) were measured in the field, the chemical analyzes of the major ions (Na⁺, Ca²⁺, Mg²⁺, K⁺, Cl⁻, SO₄²⁻ and HCO₃⁻), were carried out in the laboratory of the IRSEN. These analyzes were carried out using a spectrophotometer using conventional methods recommended by French AFNOR standards. The potability of water is defined by physical, chemical and even biological parameters, but above all according to its use (Lallahem, 2002). A comparison of the levels of physical and chemical elements in the water at different points with the standards of the World Health Organization (WHO, Geneva, 2004) was carried out. The hydrochemical analysis was then carried out to characterize the geochemical facies of the waters of this contact zone. This diagram is very frequently used and gives very good results (Yermani et al., 2003; Alayat & Lamouroux, 2007; Kouassi et al., 2010; Ahoussi et al., 2011; Ahoussi et al., 2012; & Ahoussi et al., 2013). The statistical analysis was carried out on 13 samples and 17 variables using the XLSTAT 2016 software. These different analyzes make it possible to characterize the physicochemical aspects of the waters of the Chaillu massif. The different methods used in this study will make it possible to know on the one hand the mechanism of water mineralization of the studied sites and on the other hand the relationships that exist between the water resources of the study area. The quality of the analyzes was checked by ion balance for the reliability of the results.

HYDROCHEMICAL DATA PROCESSING

STATISTIC STUDY

For any geochemical study, the separate study of each of the variables is an important phase in the analysis of chemical behavior, but it is often insufficient. It is therefore necessary to analyze the data taking into account their multidimensional nature. To study the sources of water salinization, a statistical method was used: Principal Component Analysis (PCA).

THE MAIN COMPONENT ANALYSIS

Principal component analysis is a descriptive method whose objective is to present in graphical form the maximum amount of information contained in a database. This base is made up, in rows, of “individuals (sources and rivers)” on which “quantitative variables (major elements and trace elements)” are measured, arranged in columns. It makes it possible to reduce the number of variables in order to project the point cloud in a two-dimensional subspace generated by pairs of factor axes or factors (Cloutier et al., 2008; & Ahoussi et al., 2012).

RESULTS

Results of physico-chemical measurements of water

The results of the various physico-chemical analyzes carried out on the waters of the Chaillu massif are shown in Table 1.
Table I. Physico-chemical results of the laboratory

| Paramètres | R1  | R2  | R3  | R4  | R5  | R6  | R7  | R8  | S1  | S2  | S3  | S4  | S5  |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| pH         | 6.2 | 6.5 | 6.7 | 6.6 | 6.7 | 6.7 | 6.8 | 6.8 | 6.28| 7.13| 6.6 | 6.83|
| T°C        | 25  | 24  | 24  | 24  | 24  | 24  | 25  | 24  | 24  | 24  | 24  | 24  | 24  |
| CE         | 40  | 73  | 27.7| 35  | 28  | 43  | 37.2| 26  | 81  | 43  | 27.7| 29  |
| Mg²⁺       | 12  | 14  | 16  | 9   | 11  | 13  | 12  | 10  | 14  | 15  | 13  | 11  | 12  |
| K⁺         | 6.2 | 4.1 | 5.5 | 7.2 | 5.2 | 9.5 | 11.7| 8.2 | 6.6 | 5.9 | 4   | 6.1 | 12  |
| Ca²⁺       | 0.01| 0.11| 0.16| 0.12| 0.06| 0.10| 0.09| 0.13| 0.10| 0.14| 0.12| 0.07|
| Mg²⁺       | 0.13| 0.16| 0.20| 0.12| 0.14| 0.15| 0.13| 0.11| 0.12| 0.13| 0.15| 0.13| 0.10|
| Fe³⁺       | 0.03| 0.03| 0.07| 0.04| 0.07| 0.08| 0.07| 0.06| 0.06| 0.08| 0.06| 0.09|
| Pb²⁺       | 0.18| 0.21| 0.16| 0.10| 0.14| 0.20| 0.22| 0.20| 0.19| 0.18| 0.15| 0.12| 0.11|
| Cr³⁺       | 0.25| 0.18| 0.14| 0.26| 0.22| 0.20| 0.17| 0.28| 0.19| 0.30| 0.20| 0.31| 0.13|
| Mn²⁺       | 0.018| 0.016| 0.02| 0.03| 0.04| 0.03| 0.02| 0.02| 0.01| 0.03| 0.02| 0.02| 0.015|
| Cl⁻        | 2.3 | 1.22| 0.75| 1.01| 1.40| 1.22| 4.7 | 9.5 | 7.1 | 7.7 | 1.32| 0.99| 2.33|
| SO₄²⁻      | 9.00| 8.00| 6.00| 12  | 10.00| 13   | 8.00 | 13.00| 10.00| 16.00| 14.00| 14.00| 13.00|
| NH₄⁺       | 0.01| 0.02| 0.18| 0.14| 0.15| 0.17| 0.15| 0.14| 0.12| 0.16| 0.2 | 0.16| 0.13|
| NO₃⁻       | 0.012| 0.15| 0.17| 0.08| 0.07| 0.15| 0.17| 0.15| 0.08| 0.07| 0.04| 0.15| 0.13|

Analysis of this table shows that the waters of the Chaillu massif are acidic, with a pH varying from 6.2 to 7.13, for an average of 6.64. The electrical conductivity of water varies from 26.00 to 81.00 μS / cm, with an average of 42.17 μS / cm. These waters are generally weakly mineralized.

Hydrochemical classification of water

La classification hydrochimique des eaux dans le diagramme de Piper montre une prédominance des ions chlorures sur les ions sulfatés. Le calcium (Ca²⁺) constitue le cation le plus important, puis vient ensuite le potassium (K⁺) (Figure 2).

Figure 2: Classification of the waters of the rivers of the Chaillu massif from the Piper diagram
The Stabler diagram (Figure 3) makes it possible to represent the chemical facies of several waters. Each sample is represented by a broken line. The concentration of each chemical element is shown by a vertical line on a logarithmic scale. The broken line is formed by connecting all the dots representing the different chemical elements. When the lines intersect, a change in chemical facies is evident.

Figure 3: Classification of ions from the stabler Diagram

Figure 4: Stiff Diagram
The predominance of the chlorinated and sulphated calcium and magnesian facies is shown through the Stiff diagram (Figure 4). Through these representations, the surface waters of the Chaillu massif present a chlorinated and sulphated calcium and magnesian facies. According to the Schöeller-Berkaloff diagram (Figure 5), the dominant ions are chlorides for anions and calcium for cations. The concentrations are ordered as follows:

\[ \text{Cl} \rightarrow \text{SO}_4 \rightarrow \text{Ca} \rightarrow \text{Mg} \rightarrow \text{Na} + \text{K} \]

![Image of Stiff diagram](image_url)

Figure 5: Schöeller Berkaloff diagram

The Wilcox diagram (Figure 6) shows that the surface water of the Chaillu massif is excellent.

![Image of Wilcox diagram](image_url)

Figure 6: Wilcox Diagram
Results of the multivariate statistical study: Principal Component Analysis (PCA)

The eigenvalues of the factors are presented in Table II. The first two factors represent 63.17% of the expressed variance (Table II).

The correlation matrix which presents the different correlations between the variables necessary for understanding the phenomena studied is presented in Table III.

Table II. Specific values of the ACP

|       | F1    | F2    | F3    | F4    |
|-------|-------|-------|-------|-------|
| Valeur propre | 6.60  | 4.14  | 3.9007| 2.36  |
| Variabilité (%) | 38,81 | 24,36 | 22,944| 13,89 |
| % cumulé | 38,81 | 63,17 | 86,11 | 100,00|

The correlation matrix between variables

|       | pH    | CE    | T     | Ca²⁺ | Mg²⁺ | K⁺   | Al³⁺ | NH₄⁺ | Ce³⁺ | Cr³⁺ | Fe³⁺ | Pb²⁺ | Mn²⁺ | Cl⁻ | SO₄²⁻ | PO₄³⁻ | NO₃⁻ |
|-------|-------|-------|-------|------|------|------|------|------|------|------|------|------|------|-----|-------|-------|------|
| pH    | 1     |       |       |      |      |      |      |      |      |      |      |      |      |     |       |       |      |
| CE    | -0.606| 1     |       |      |      |      |      |      |      |      |      |      |      |     |       |       |      |
| T     | 0.182 | -0.296| 1     |      |      |      |      |      |      |      |      |      |      |     |       |       |      |
| Ca²⁺  | 0.295 | -0.733| 0.466 | 1    |      |      |      |      |      |      |      |      |      |     |       |       |      |
| Mg²⁺  | 0.147 | 0.488 | 0.280 | -0.043| 1    |      |      |      |      |      |      |      |      |     |       |       |      |
| K⁺    | -0.031| -0.328| 0.945 | 0.443| 0.000| 1    |      |      |      |      |      |      |      |     |       |       |      |
| Al³⁺  | -0.143| 0.617 | -0.146| -0.935| 0.109| -0.150| 1    |      |      |      |      |      |      |     |       |       |      |
| NH₄⁺  | -0.149| 0.854 | -0.049| -0.594| 0.822| -0.241| 0.591| 1    |      |      |      |      |      |     |       |       |      |
| Cu²⁺  | 0.187 | 0.329 | -0.800| -0.325| 0.275| -0.950| 0.072| 0.386| 1    |      |      |      |      |     |       |       |      |
| Cr³⁺  | -0.690| 0.483 | -0.697| -0.156| -0.081| -0.588| -0.181| 0.105| 0.486| 1    |      |      |      |     |       |       |      |
| Fe³⁺  | 0.503 | -0.119| 0.748 | 0.401| 0.761| 0.492| -0.159| 0.347| -0.201| -0.601| 1    |      |      |     |       |       |      |
| Pb²⁺  | -0.243| 0.453 | -0.632| -0.908| -0.354| -0.522| 0.799| 0.217| 0.311| 0.193| -0.689| 1    |      |     |       |       |      |
| Mn²⁺  | 0.512 | -0.076| -0.073| 0.399| 0.650| -0.347| -0.466| 0.271| 0.602| 0.072| 0.547| -0.536| 1    |     |       |       |      |
| Cl⁻   | -0.563| 0.521 | -0.268| -0.825| -0.370| -0.076| 0.801| 0.191| -0.156| 0.139| -0.609| 0.853| -0.839| 1    |     |       |       |      |
| SO₄²⁻ | -0.901| 0.696 | -0.395| -0.245| 0.088| -0.276| 0.000| 0.310| 0.195| 0.895| -0.430| 0.150| -0.115| 0.307| 1    |     |       |       |      |
| PO₄³⁻ | 0.248 | -0.461| -0.215| 0.733 | 0.000| -0.277| -0.899| -0.403| 0.370| 0.354| 0.058| -0.601| 0.695| -0.819| 0.048| 1    |     |       |       |      |
| NO₃⁻  | -0.724| -0.009| -0.293| -0.051| -0.779| 0.031| -0.100| -0.525| -0.307| 0.524| -0.818| 0.301| -0.707| 0.514| 0.522| -0.049| 1    |     |       |       |      |

This matrix shows an important correlation between T-K⁺ (0.945); Cr³⁺ - SO₄²⁻ (0.895); CE - NH₄⁺ (0.854); Pb²⁺ - Cl⁻ (0.853); Mg²⁺ - NH₄⁺ (0.822) and Al³⁺ - Cl⁻ (0.801). There is also to a lesser degree a correlation between variables such as Al³⁺ - Pb²⁺ (0.799); Mg²⁺ - Fe³⁺ (0.761); T-Fe³⁺ (0.748); Ca²⁺ - PO₄³⁻ (0.733); CE-SO₄²⁻ (0.696); Mn²⁺ - PO₄³⁻ (0.695); Mg²⁺ - Mn²⁺ (0.650); CE-Al³⁺ (0.617); Cu²⁺ - Mn²⁺ (0.602); Al³⁺ - NH₄⁺ (0.591); Fe³⁺ - Mn²⁺ (0.547); Cr³⁺ - NO₃⁻ (0.524); SO₄²⁻ - NO₃⁻ (0.522); CE-Cl⁻ (0.521); Cl⁻ NO₃⁻ (0.514); pH-Fe³⁺ (0.503); pH-Mn²⁺ (0.512). These different correlations reflect the influence of each parameter in the mineralization of the waters of the Chaillu massif. The Principal Component Analysis (Figure 7) carried out on the water family of the Chaillu massif shows, always taking into account the same parameters (17) as the two axes make it possible to explain 63.16% of all the variances which is quite significant. The first axis represents 38.812% of the variance. This percentage is an indicator of geochemical heterogeneity in the acquisition of mineralization. It is related to the...
mineralization of water between the ground and to surface pressures. The F1 axis groups together electrical conductivity, copper, ammonium, chromium, sulphates, aluminum, lead, chlorides and nitrate. In this group, the association of chloride, lead, aluminum, ammonium, nitrates and sulphate ions corresponds to the environmental pole of water mineralization. The remainder, conductivity, copper and chromium are indicators of the environment influenced by recent waters subjected to a mechanism of rapid acquisition of mineralization or anthropogenic pollution. On F1 the electrical conductivity, chromium, sulfate, ammonium, lead and aluminum are well correlated. The F2 axis pits manganese, magnesium, iron and phosphate against calcium, temperature and potassium. It is linked to the mineralization of water between the ground and the various geological formations. We also notice on this axis F2 the grouping of temperature, calcium and potassium. These associations (temperature and potassium-iron; magnesium-iron; calcium-phosphate; manganese-phosphate; pH and iron-manganese; magnesium-manganese) are characteristics of the alteration minerality in a semi-captive environment in a context of Precambrian. As a first approximation, the F2 axis has two roles: it first indicates the residence time of water (calcium, magnesium); then it opposes the recent waters nitrates and nitrates to sulfates and pH and to a lesser extent to chlorides. It explains the nitrification process occurring in effluents. The assessment of the quality of the groundwater studied was also made by grouping the water points sampled (sources and rivers) into heterogeneous zones. This classification makes it possible to reduce the number of sampling sites in the case of a temporal monitoring program. **Figure 8** shows the results of the classification of sampling points into heterogeneous areas. Three classes stand out in this classification: C1, C2 and C3. In these associations between sources and rivers are evident. This is the case for S1, S2, R6, R7 and R8 in class C1; from source and rivers S3, R2 and R3 in class C2; S4, S5 and R1, R4 and R5 in class C3. The associations in classes C1 and C3 are at approximately the same significant level.

![Variables (axes F1 et F2: 63.17 %)](image)

**Figure 7:** Analysis in the F1-F2 factorial plane
**Water quality compared to WHO standards**

The comparison of the physico-chemical characteristics of the waters of the Chaillu massif region with the WHO guideline values (WHO, 2008) are presented in the table below (Table IV). This comparison shows that with the exception of lead, the waters of this area have mineral element contents well below the WHO guideline values. These waters are of good quality and can be used for human consumption. The results of the physico-chemical parameters of the sampled water are reported in Table IV. The average values of pH, temperature and electrical conductivity are respectively 6.28 ± 6.20; 25 ± 24 °C and 73 ± 26 μS.cm⁻¹ for river water and 7.13 ± 6.6; 25 ± 24 °C and 81 ± 26 μS.cm⁻¹ for spring water. The average values of the contents of magnesium, potassium and sulphate do not show any significant difference in the waters of rivers and that of springs. Ammonium and calcium, on the other hand, show a significant difference between the waters of rivers and springs with respective average contents of 0.16 ± 0.01 and 0.15 ± 0.10 mg.L⁻¹ for ammonium and 18.00 ± 10.00 and 18.00 ± 11.00 mg.L⁻¹ for calcium. Spring water is therefore more loaded with ammonium, unlike that of the richest in calcium. Spatially, the high values for electrical conductivity are observed in the source (S2) (Figure 7) and in rivers (R2 and R5) with maximum levels greater than 50 μS.cm⁻¹ (Figure 8). The maximum levels of chlorides (Cl⁻), although below the WHO guideline, show high concentrations in the R8 Lelali river (9, 50 mg.L⁻¹), as well as in the S1 sources of Tembelé (7,1 mg.L⁻¹) and S2 from Aloumou (7,70 mg.L⁻¹) (Figure 7 and 8). Orthophosphates (PO₄³⁻) record low concentrations in both rivers and springs. The nitrate (NO₃⁻) concentrations recorded in rivers and springs are very low compared to the value recommended by the WHO directive, which is 50 mg.L⁻¹ (Table IV). The trace metallic elements Iron (Fe²⁺), Manganese (Mn²⁺) and Aluminum (Al³⁺) have heterogeneous concentrations.
Table IV. Summary of the measurements of the physico-chemical parameters of the waters of the Chaillu massif region

| Paramètres Physico-chimiques | Valeur Guide OMS | Mini | Maxi | Moyenne | Ecart-type |
|------------------------------|------------------|------|------|---------|------------|
| pH                           | 6,5 - 9,00       | 6,28 | 7,13 | 6,72    | 0,31       |
| CE (µS/cm)                   | 300,0            | 26,00| 81,00| 41,28   | 23,23      |
| T°C                          | 12 – 30          | 24,00| 25,00| 24,20   | 0,45       |
| Ca²⁺ (mg/L)                  | 75,0             | 11,00| 18,00| 14,60   | 2,88       |
| Mg²⁺ (mg/L)                  | 50               | 10,00| 15,00| 13,00   | 2,00       |
| K⁺ (mg/L)                    | 12               | 4,00 | 12,00| 6,92    | 3,01       |
| Al³⁺ (mg/L)                  | 0,1              | 0,01 | 0,07 | 0,04    | 0,02       |
| NH₄⁺ (mg/L)                  | 0,5              | 0,10 | 0,15 | 0,12    | 0,02       |
| Cu²⁺ (mg/L)                  | 1,00             | 0,10 | 0,15 | 0,12    | 0,02       |
| Fe³⁺ (mg/L)                  | -                | 0,13 | 0,31 | 0,22    | 0,08       |
| Pb²⁺ (mg/L)                  | 0,01             | 0,11 | 0,19 | 0,15    | 0,04       |
| Mn²⁺ (mg/L)                  | 0,5              | 0,01 | 0,02 | 0,01    | 0,01       |
| Cl⁻ (mg/L)                   | 200              | 0,99 | 7,70 | 3,88    | 3,25       |
| SO₄²⁻ (mg/L)                 | 250              | 10,00| 16,00| 12,000  | 2,828      |
| PO₄³⁻ (mg/L)                 | 5                | 0,110| 0,200| 0,144   | 0,036      |
| NO₃⁻ (mg/L)                  | 50               | 0,100| 0,800| 0,560   | 0,305      |

**Pollution parameters**

The mineral elements that we have classified among the pollution parameters were monitored for each water (surface and groundwater) sampled. Their concentrations are shown in Figure 9.

**CONCLUSION**

The objective of this study was to evaluate the various physicochemical parameters which control the hydrochemistry of the waters of the Chaillu massif using multivariate statistical analysis techniques (PCA and CAH). In terms of the physical parameters measured in the laboratory, the average water temperature of springs and rivers is 24, 20°C. The waters throughout this region are acidic with an average pH of 6,72. The average electrical conductivity is 41, 28 µS / cm with extreme values between 26, 00 and 81, 00 µS / cm. Overall, the waters are weakly mineralized and suitable for drinking. However, some water points have critical lead values and have
concentrations above the WHO standard. Water from these points must be treated before consumption because of the health risks it presents. Principal Component Analysis showed that the first three factors add up to 63.168% of the total variance expressed by the 17 variables. Furthermore, the combined analysis of PCA and CAH suggests that the hydrogeochemical characteristics of spring and river waters are mainly controlled by processes, the main one being the acid hydrolysis of silicate minerals. Specifically, in the region of the Chaillu massif, minerals such as biotite and micas produce most of the chemical elements in water such as Ca$^{2+}$, Mg$^{2+}$, SO$_4^{2-}$. Concentrations of nitrates and chlorides in water are attributed to the impact of the biogeochemical cycle (destruction of vegetation, decomposition of organic matter). In addition, the high concentrations of lead in water is linked to the oxidation-reduction phenomenon. This study has shed light on the processes that govern the hydrochemistry of the waters of this region. These results could help the authorities in charge of water supply to the populations for better planning and rational use of water resources in this forest region.

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