Pak. j. life soc. Sci. (2024), 22(2): 12071-12080 E-ISSN: 2221-7630;P-ISSN: 1727-4915

Pakistan Journal of Life and Social Sciences
www.pjlss.edu.pk

https://doi.org/10.57239/PJLSS-2024-22.2.00861

RESEARCH ARTICLE

Seasonal Variations in the Physico-Chemical Characteristics Of Lite-Bala Gold Site In The DRC

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ARTICLE INFO

Received: Sep 17, 2024

Accepted: Nov 3, 2024

Keywords

Trace elements
Characteristics
Mobility
Season
Test

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ABSTRACT

The physicochemical characteristics determine the mobility and distribution of trace elements on the Lite-Bala site. They vary with the climatic weather of the site, particularly with the season. The methodology of this study consisted of sampling in two seasons, in situ and laboratory analyses of the physicochemical parameters. Descriptive statistics were used to visualize the distribution of variables and to test the significance of the differences over the year. Principal component analysis made it possible to identify the most correlated variables and the similarities between compartments. The variations are from 4.92 to 5.46 for pH, 390 to 340 mV for Eh, 99.65 to 56.47 µS/cm for CE, 0.31 to 0.28% for Corg, 31.49 to 30.11% for clay contents and 26.12 to 28.02 °C for temperature respectively for the dry season and the rainy season for the entire site. Acidity, electron exchange capacity and electrical conductivity are more marked in the dry season than in the rainy season. The Mann-Whitney test attests that there are significant differences between the variables pH, Eh, EC and T for the two seasons. Fe contents are high in soils (2349.55 to 1683 mg/kg) and those of Ca (1346.47 mg/kg) in plants. The cation exchange capacity of soils and sediments is low (< 25 meq/100 g) facilitating the mobility of ETMs in soils and sediments. Season influences the quality of variables in different compartments of the Lite-Bala gold site. The behavior (mobility, availability, speciation) of trace metal elements on the site is impacted by the season.

1. INTRODUCTION

The distribution of trace elements naturally present in the different environmental compartments is determined by the biogeochemical cycle specific to each element. This cycle depends on the characteristics (physicochemical, biological, geological, climatic, etc.) of the site (Roux, 2024; Hullot, 2023; Brandely, 2022) . However, disturbances of the site characteristics lead to an accumulation of trace elements (TE) on the site, or even to an increase in risks to human health and the environment (Brandely, 2022; Vualu, 2020) .

In the Democratic Republic of Congo (DRC), studies conducted in the artisanal and small-scale mining (ASM) gold sector have focused more on socio-economic, anthropological and developmental, and theological domains in the eastern block of the country (Mangambu, 2023; Bikubanya et al., 2022) . This study is a seasonal physicochemical characterization of soils, sediments and waters of the Lite-Bala site in the northwest of the country.

II. METHODOLOGY

II.1 PRESENTATION OF THE STUDY AREA

The study site is the Lite-Bala gold site, in the North-East of the Nord-Ubangi province between 3°48'0'' – 3°44'3'' in the Northern Hemisphere and 23°6'30'' – 23°9'0'' East of the Meridian (fig.1).

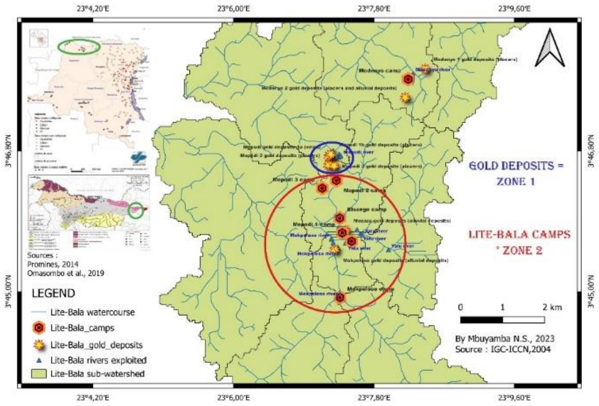


Figure 1 Location map of the Lite-Bala gold site

The Lite-Bala site is full of 8 (eight) gold deposits (2 non-active and 6 active) and 6 (six) camps. The site is located in a humid and hot tropical zone with high temperature ranges (10 - 20 °C), a rainy season from March to October, and a dry season from November to February. It is covered with dense forest and the annual precipitation accumulations vary between 800 mm and 1600 mm of water. The landscape is made up of plateaus and low altitude hills characteristic of the central basin (<700 m). The schistose and sandstone rocks with little or no metamorphosis are the main constituents of the site. The soils are associated with the Ferralsols group, mineral soils from highly weathered materials and rich in kaolinites and iron sesquioxides. The hydrography of the gold site is dense like that of the central Congo basin (Mantel et al., 2023; Omasombo et al., 2019; Ngongo et al., 2009) **.**

The population of the site, estimated at 6,000 inhabitants, fluctuates with the seasons, productivity and the economic situation of the province. It practices subsistence crops (cassava and corn) outside the site and rarely on the site, and small trade inside the site. The health situation of the Lite-Bala site is precarious with a range of diseases (malaria, gastrointestinal diseases, high blood pressure, dermatitis, kidney diseases, anorexia, sexually transmitted diseases, urinary infections, etc. (WHO, 2017) .

II.2 Sampling strategy

sampling was used during the sampling campaigns. The number of samples to be collected is determined by the surface area of the sampling area ($\sqrt{A}$ +1 where A is the surface area in hectares) (ADEME, 2018) and the length of the river (Casado et al., 2021) . Twenty-eight (28) soil samples were collected at the surface (0 – 25 cm) in zones 1 and 2 (SS) and at depth (40 - 65 cm) noted DS in zone 2. Ten surface water (RW) samples, ten interstitial water (IW) samples taken from the sediments after a 24-hour rest and two spring water (WS) samples were also collected on the site. Samples were packaged in plastic bags and polyethylene (PE) bottles, after drying of soils and sediments under shade or acidification of surface and interstitial waters (IUSS Working Group WRB, 2022) .

II.3 Physicochemical analyses

Physicochemical analyses concerned the variables influencing the mobility of ET in soils and sediments as well as the transfer of ET to plants (pH, Eh, organic carbon (Corg), granulometry, O_2 dissolved) (Roux, 2024; Hullot, 2023; Brandely, 2022; Bataillard et al., 2012) . These variables were determined in the field using a multiparameter Oyster Meter probe, Model 341350A are pH (NF T 90 008) and Eh by potentiometry with an electrode in $Ag/AgCl$, KCl saturated (E_0 = 0.199mV) on a soil or sediment solution (1:5 v/v), and O_2 dissolved using a HANNA HI 9146 brand Oximeter. In the laboratory, organic carbon (Corg) was determined by the Walkley and Black method (not standardized) and the particle size (NF P 94-057) by the sedimentation method. (IUSS Working Group WRB, 2022; Casado et al., 2021) .

II.4Statistical processing

Descriptive statistics were used to visualize the results (boxplots) while principal component analysis (PCA) was used to reduce the explanatory variables of the mobility and transfer of trace elements to plants (Husson et al., 2018) .

III. RESULTS

III.1 Analyses of the physicochemical variables of the soils and sediments of the Lite-Bala gold site.

Figure 2 reveals seasonal variations in pH at the site.

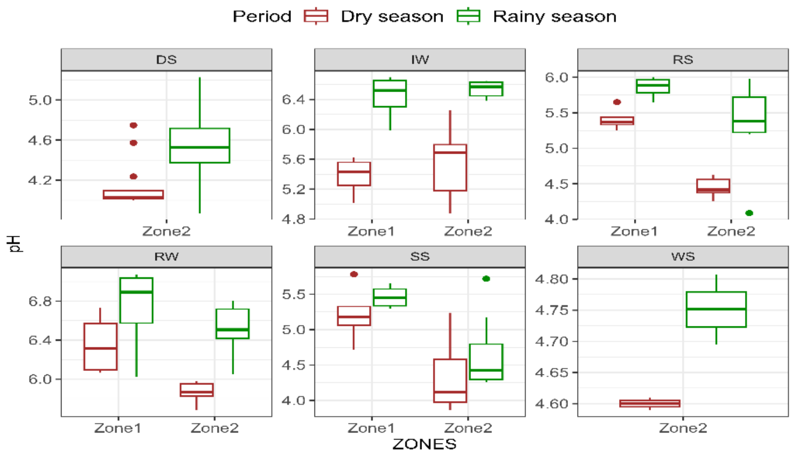


Figure 2 Seasonal variation of pH

It is clear from this figure that the pH values are below 7, and the most acidic compartments are SS, DS, WS, slightly acidic (RS) and less acidic (RW and IW). The average pH of the soils at the Lite-Bala gold site changes from 5.46 in zone 1 and 4.62 in zone 2 during the rainy season to 5.21 in zone 1 and 4.32 in zone 2 during the dry season . Figure 3 shows the seasonal evolution of the redox power (Eh) at the gold site.

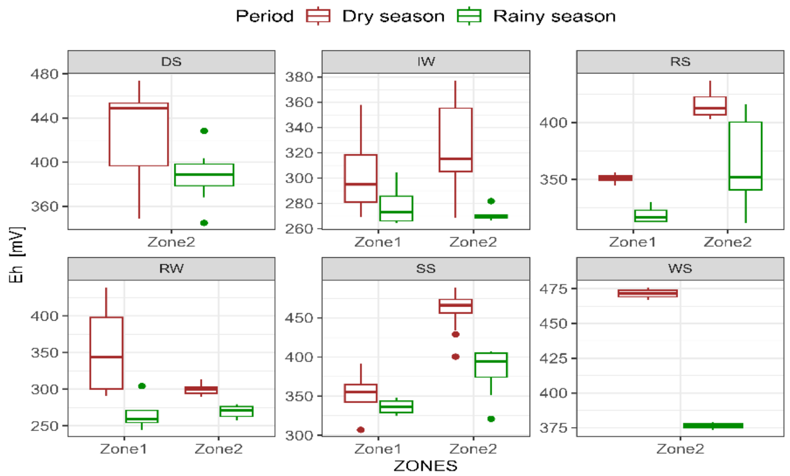


Figure 3 Seasonal variation of redox power (Eh)

It is clear from this figure that the SS, DS, WS and RS compartments exalt more oxidizing conditions than RW and IW. The values of the redox power (Eh) are high (390 mV) in the dry season than in the rainy season (340 mV) . Figure 4 illustrates the evolution of the electrical conductivity with the season.

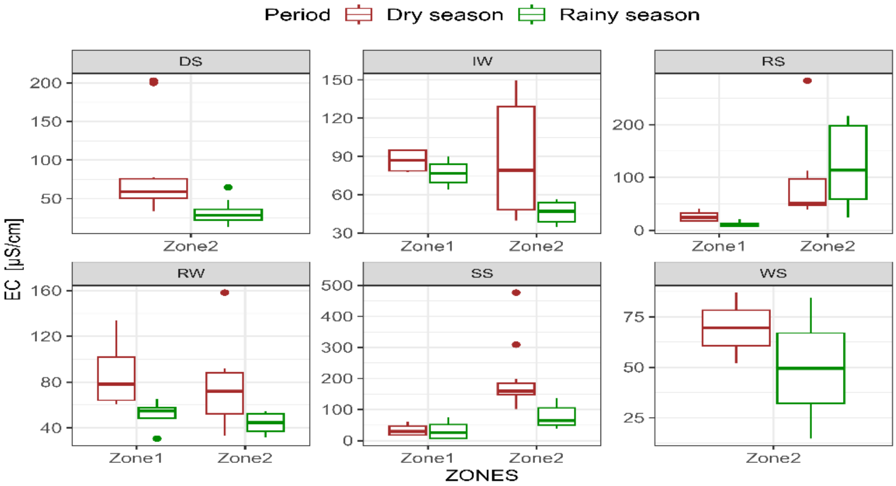


Figure 4 Seasonal variation of electrical conductivity

This figure shows that EC values are higher in the dry season (± 99.65 µS/cm) than in the rainy season (± 56.47 µS/cm). Figure 5 displays the seasonal variations in organic carbon (Corg) contents of soils and sediments of Lite-Bala.

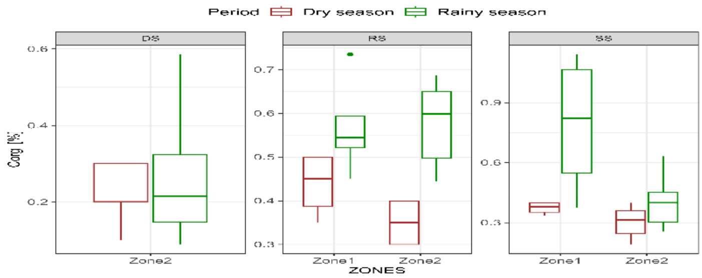


Figure 5 Seasonal variation of Corg

This figure shows low Corg contents (<1%) and fluctuations are less significant (0.31% in dry season and 0.28% in wet season). Figure 6 displays the seasonal variation of clay contents in soils and sediments at the Lite-Bala gold site.

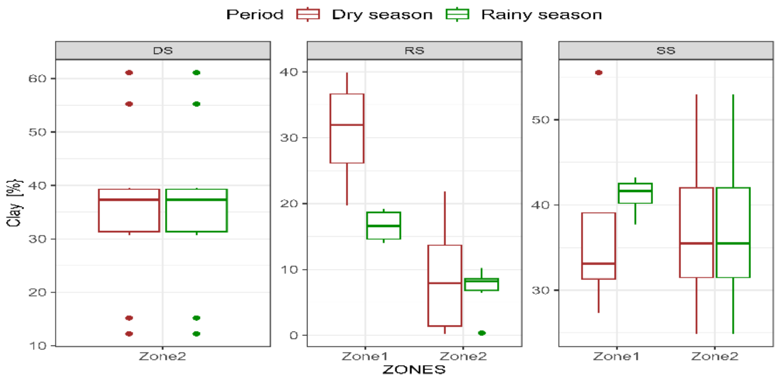
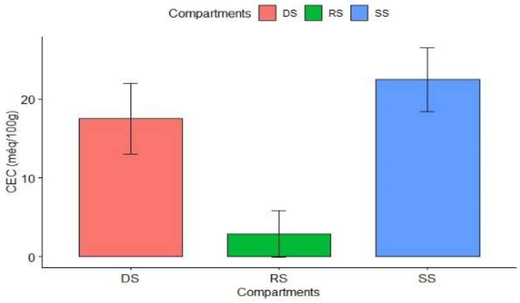


Figure 6 Seasonal variation in clay contents

This table shows that deep soils experience fewer fluctuations than surface soils and sediments. Fluctuations in clay content are very marked in zone 1 (RS: 16.63 - 7.01%) than in zone 2 (34.27 - 41.07%). Figure 7 provides information on the cation exchange capacity of soils and sediments according to their clay content.



This figure shows that the CEC values of deep soils (DS) (17.52 meq/kg) and surface soils (SS) (22.5 meq/kg) are higher than those of sediments (2.86 meq/kg). Figure 8 provides information on temperature fluctuations in the rainy and dry seasons.

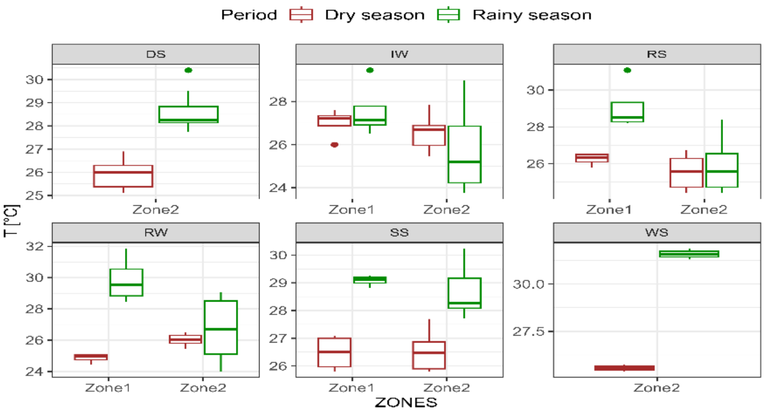


Figure 8 Seasonal temperature fluctuations

This figure shows temperature differences between the wet and dry seasons for most compartments. Figure 9 displays major element contents of soils and sediments at the gold site.

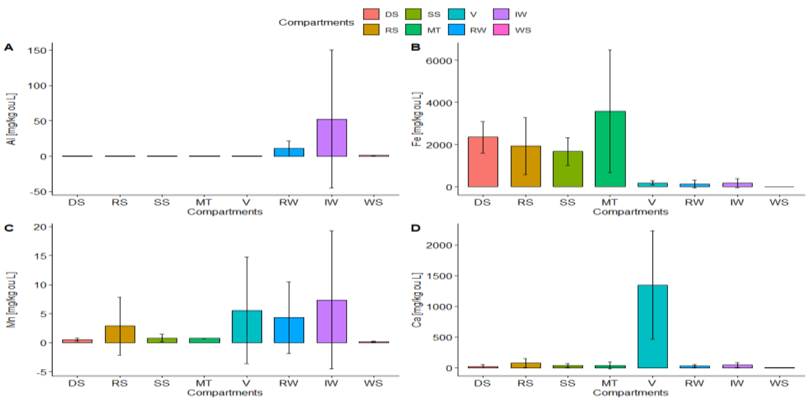


Figure 9 Major element contents in soils and sediments

It is clear from this figure that iron contents are high in residues (MT) 3582.65 ± 2910.76 mg/kg and deep soils (DS) 2349.55 ± 731.48 mg/kg. Ca contents are high in plants (V) 1346.47 ± 883.97 mg/kg those of aluminum and Mn in interstitial waters (IW) for respectively 52.56 ± 97.60 and 7.36 ± 11.90 mg/kg. Surface and spring waters show values of 10.633 ± 10.87 and 0.97 ± 0.46 mg/L in Al, 0.108 ± 0.23 and 0 mg/L in Fe, 4.30 ± 6.23 and 0.18 ± 0.09 mg/L, respectively.

III.3 Statistical analysis

III.3.1 Significance test of deviations

Table 1 provides information on the significance of seasonal variations.

Table Mann-Whitney significance test by season

Mann-Whitney test	Settings (rainy season and dry season)						
	pH	Hey	EC	Corg	Sand	Clay	T
W	2412.5	1036	1088	999.5	783	706	2957
p-value	0.001317**	6.139e-05**	0.0001881**	0.3045*	0.5296*	0.872*	1.275e-09**

* p-value > 0.05: there is no significant difference ** p-value < 0.05: there are significant differences

This table reveals that the pH variables Eh, EC and T experience significant variations with the seasons.

III.3.2 Principal component analysis (PCA): biplots

Figures 9 and 10 respectively represent the correlation circle between the physicochemical variables and the biplot of the best projected individuals and variables of soils and sediments.

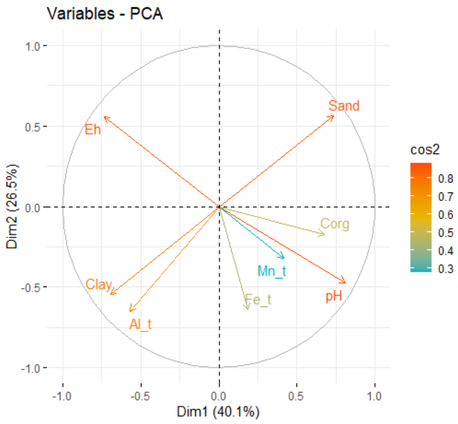


Figure 9 Correlation circle between physicochemical variables

This circle shows that the best projected variables are Eh, clay and sand contents, pH and aluminum (Al) contents with a total inertia of 66.6%. A strong correlation between clay contents and aluminum contents but also between pH and Eh. Fe, Corg and Mn contents are not well projected.

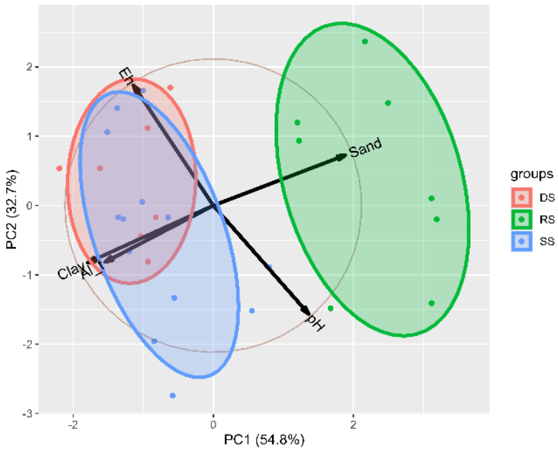


Figure 10 Biplot of individuals and soil and sediment variables

This figure shows that the variables contributing significantly to explaining certain phenomena in soils and sediments are the sand and clay contents (PC1 54.8%) and the pH and the redox potential (PC2 32.7%) for a total inertia of 87.5%. This figure also shows that the pH is highly correlated in the opposite direction to Eh (- 0.86) and the sand content to the clay contents (- 0.75) while the total extractable aluminum content is highly correlated to clay.

IV. DISCUSION

Several authors claim that the dynamics of ETMs are based on several mechanisms linked to the physicochemical characteristics of the soils, sediments and waters of the site. Indeed, the main agents of the degradation or alteration process of rocks and minerals of superficial formations are temperature, water, wind and living organisms, and the latter differ from one point of the globe to another (Roux, 2024; Brandely, 2022; Quimeby et al., 2022; Caurel, 2019) .

Furthermore, the parameters affect the physicochemical characteristics of the compartments of a site in different ways. Thus, the weathering phenomena of rocks, in cold and hot environments, differ and lead to the formation of very different and varied primary and secondary minerals, including clays, aluminum and iron oxides and hydroxides, and carbonates (Gasser et al., 2023; IUSS Working Group WRB, 2022; Caurel, 2019) . The nature of these compounds in the compartments of the Lite-Bala site determine the acidity, the redox power, the sorption or desorption capacity, etc. of soils, sediments, and waters.

Other authors still maintain that the soil and climate conditions of the site (temperature, humidity, rainfall), human activities (cultivation practices, use of phytosanitary products and chemical fertilizers, etc.) as well as biological activities impact the pH of soils, sediments and water. These impacts are manifested by variations in pH over time, or even during the year. The magnitude of these impacts is determined by the various factors mentioned above (Brandely, 2022; Quimeby et al., 2022) .

Previous studies show that over time, leaching by rainwater containing sulfur or nitrogen-based acid anhydrides and carbon dioxide from the decomposition of organic matter or industrial waste acidify soils (Quimeby et al., 2022; Assad, 2017) . The Lite-Bala gold site, located in a humid tropical zone with significant thermal and water amplitudes, can only present fluctuations in variables during the year and in the long term. The high pH values of surface soils in the rainy season and in the dry season are due to rainwater whose pH is 5.60, but overall the pH of the soils varies between 4 - 8 (Caurel, 2019; Pedro et al., 2007) .

Several scientific studies have demonstrated that the redox capacity (Eh) conditions the chemical and biological processes involving electronic exchanges. In addition, the redox capacity modifies the oxidation state of ions in solution and influences the formation and dissolution of trap particles. For water, Eh provides information on the oxidative or reducing nature of water and consequently on the mobility of ETMs in water (rain oxidation state) (Roux, 2024; Caurel, 2019; Hayzoun, 2014) .

The redox potential of soils and sediments allows to define the redoxymorphic characteristics (oxymorphic and reductimorphic) of soils and sediments. Otherwise, it informs whether soils and sediments can contain substances in the oxidized state exalt a redder tint while unlike substances in the reduced state manifesting a dark tint (IUSS Working Group WRB, 2022) . The Eh values of Lite-Bala soils and sediments indicate that they have oxymorphic characteristics and a red coloration. As for the mobility of ETM on the Lite-Bala gold site in relation to the redox potential, it varies with the seasons as indicated by the results obtained, Eh is high in the dry season and Eh low in the rainy season.

Some authors, however, have indicated that the high number of processes and redox couples involved make its interpretation less easy in the field. Furthermore, high concentrations of ETM in soils can affect the electron exchange capacity (Eh) but also the biological processes modifying the pH and Eh of soils (Roux, 2024; Caurel, 2019) . As for watercourses, studies show that the parameters (pH, Eh) are defined by the calco-carbonic balance and therefore change with the seasons. The Eh of water is also modulated by the oxygen content and seasonal changes in Eh in the water column affect the mobility of ETM but also the presence of organic and inorganic complexing agents (chlorides, sulfates, etc.) (Vualu, 2020; Hayzoun, 2014) .

Several authors claim that the electrical conductivity of soil and sediment solutions as well as water provides information on the soluble salt content and is determined by the geochemical nature of the site and the concentration of ions in solutions but also by the calco-carbonic balance (Amlan et al., 2023; Hayzoun, 2014)

As for organic matter, studies have shown that it plays an important role in the migration of ETMs. Indeed, the carbon cycle is determined by natural processes and human activities, and therefore experiences seasonal fluctuations (Feix & Tremel- Schaub, 2020) . In the case of Lite-Bala soils and sediments, the low Corg contents make these variations barely perceptible.

The CEC of soils and sediments is a function of the type of soil and sediment composition (Corg, clays, pH) (Casado et al., 2021; Amel, 2020, 2020; Caurel, 2019) . The CEC values obtained are close to the CEC values of kaolinites, the most abundant clay minerals in humid tropical areas (Amel, 2020) . In sediments, CEC varies between 2 and 200 cmol(+)/kg depending on its clay composition (type and quantity). The soils and sediments of Lite-Bala display CEC values close to the lower limit.

Regarding the temperature of soils, sediments and waters, several researchers report that it is an important parameter influencing chemical and biological processes, and changes with daily and seasonal variations in ambient temperature. The drop in temperature promotes physical adsorption while the increase in temperature promotes chemical adsorption. The temperature difference between the two seasons will affect the behavior of ETMs (Casado et al., 2021; Amel, 2020; Caurel, 2019; Hayzoun, 2014) .

As for the granulometry, a function of the parent rock, the climate and physical, chemical and biological alterations, it displays a diversity of composition in clay minerals. Several studies reveal that in hot tropical zones, kaolinite is preferentially formed and the number of charges that can be fixed by this clay is low (CEC < 35 cmol(+)/kg (Amel, 2020; Ngongo et al., 2009) . In Lite-Bala soils, the yellowish color resulting from the mixture of red ferric compounds with white kaolinite is an indication of the presence of this clay.

Several authors also claim that high contents of major elements such as Fe and Mn can lead to oxidation of ETMs allowing their stabilization by adsorption on clay particles (Amel, 2020; Caurel, 2019) . Concerning iron, the form Fe^{3+} is insoluble at pH > 4 while Fe^{2+} remains soluble up to pH 6. Variations in pH and Eh in soils, sediments and waters with the seasons affect iron contents in these compartments (Roux, 2024; Brandely, 2022; Pedro et al., 2007) . The water quality criteria values for Al, iron and Mn, for consumption and preservation of aquatic organisms in surface waters, being respectively 0.1, 0.3 and 0.05 mg/L, the contents found in the surface and spring waters of Lite-Bala in Al suggest a degradation of their quality. However, compared to the tolerable daily doses in ETM, which for a 60 kg individual are 60 mg/kg for Al, 30 mg/kg for Fe and 10 mg/kg for Mn, they do not present a health risk (Roux, 2024; Beaulieu, 2021; Vualu, 2020) .

The variability of physicochemical variables is attested by the Mann-Whitney significance test for which several variables have a p-value less than 0.05 (Husson et al., 2018) while the strong correlation between Al and clay contents is due to the fact that the latter is a component of clays (Amel, 2020) . The difference in resemblance between soils and sediments is due to the fact that the latter are formed by accumulation and deposition of particles suspended in the water column (Hayzoun, 2014) .

CONCLUSION

The season impacts the physicochemical characteristics (Eh, pH, CEC, ETM contents) as well as the biological processes of soils, sediments and watercourses of the Lite-Bala gold site, in other words the mobility of ETMs. The impact evolves not in the direction of modifying the pH, Eh and CE values but rather in the direction of amplifying them. The behavior of ETMs (mobility, availability, bioavailability) evolves in one direction or another. The high Fe contents are responsible for the red coloring of soils and sediments which is influenced by the presence of kaolinite, a white clay. The high Al and Fe contents also reflect the state of degradation of the rivers exploited on the Lite-Bala gold site. The strong correlation between Al and clay contents indicates that the latter is a component of clays.

DEDICATION AND ACKNOWLEDGEMENT

This study was possible with the partnership of the National Water Institute of the University of Abomey-Calavi of Benin and the University of Kinshasa of DRC. Our thanks to the academic authorities of these two institutions.

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