

Phosphorus fractionation in sediment and agricultural soils surrounding Lake Toho in the rainy season

ABSTRACT

In recent years, land use related to anthropogenic activities has contributed to high surface water contamination. During the last decade, Lake Toho, in the Republic of Benin, has suffered anthropogenic pollution by the use of fertilizers from farmers around the lake. We assessed the mobility and bioavailability of phosphorus in cultivated soils around the lake to detect the extent of the contamination. The results showed that the cultivated soils around Lake Toho are weakly acidic or even basic with water pHs between 6.25 and 8.3. The humidity of cultivated soils varies from 1% to 38% on different horizons. The content of organic matter is ranged from 40.30% to 49.70%. The total phosphorus concentration ranged from 1049.74 $\mu\text{g}\cdot\text{g}^{-1}$ to 28436.52 $\mu\text{g}\cdot\text{g}^{-1}$ with a high rate of enrichment at the 30 cm horizon. The high contents of total phosphorus recorded at the superficial horizon were due to the use of fertilizers to amend the soil. All forms of phosphorus are represented (P-L, P-Fe, P-Ca, P-Al, and P-OM). The organic fraction predominates on the upper layer of the soil except for sites located outside crop fields. The strong correlation between the Total phosphorus (TP), the (Pr), mobile phosphorus (P-L), and the to organic matter-bound Phosphorus (P-OM) showed that the high phosphorus contents at the upper horizon of the soil were due not only to the anthropogenic contribution but also to the source rock. The remarkable presence of phosphorus in the P-L and P-MO fractions poses a risk of phosphorus transport to the lake. This can lead to eutrophication which can cause the death of fish and harmful toxins development.

Keywords: bioavailability, cultivated soils, Lake Toho, Mobility, phosphorus.

INTRODUCTION

Phosphorus is one of the essential elements for living. It is a building block of DNA, ATP, and phospholipids [1]. Calcium phosphates are major constituents of the skeleton. Thus, phosphorus is mainly found in bones, teeth, and nervous tissue.

Phosphorus is involved in plant growth [2, 3, 4, and 5]. Before agricultural industrialization, in the terrestrial biogeochemical cycle of phosphorus, plants assimilated phosphates present in the soil, while the heterotrophic processes of organic matter decomposition returned the mineral phosphorus to the soil. This complementarity of autotrophic and heterotrophic metabolisms constitutes the essence of the phosphorus cycle in pre-industrial agriculture. Phosphorus is one of the three major elements of fertilization, along with nitrogen and potassium. It plays an important role in root development and early cycle growth. The nitrogen and phosphorus contained in these chemical fertilizers cause environmental problems such as eutrophication and surface water toxicity⁶. Eutrophication can lead to surface water anoxia due to plant respiration and its degradation by aerobic bacteria [7, 8, and 9].

This phenomenon can lead to the elimination of the most demanding species and the development of invasive species, the development of algal biomass, and an increase in the turbidity of surface waters, inducing the appearance of bad odors, as well as a change in the water color [10].

In the soil, phosphorus is found in several soluble and mineral forms. However, the soluble fraction (PO_4^{3-}) is the only fraction that can easily be uptaken by plants and crops [11]. The other forms that cannot be assimilated by plants end their course in surface water, accumulate in the soil or seep into groundwater [6]. The study carried out [12] on the Porto-Novo lagoon revealed a strong presence of organic phosphorus in the sediments. They attributed the condition to the use of organic fertilizers in the lagoon catchment area, and the presence of living or degrading animal and plant organic matter.

Lake Toho, located in southern Benin, has experienced the death of fish on several occasions in 2012, 2018, and 2021. According to information from PNE-Benin, the 2012 drama occurred following a stormy rain that changed the turbidity of the water causing deoxygenation and deaths. In 2018 and 2021, the same drama happened on the same lake with a color change. The main cause mentioned for the past two years is the dumping of harmful substances from an unknown source¹³ which certainly led to the pollution of water and/or sediments. Studies have shown that Lake Toho is subjected to nitrogen, phosphorus, organic, and metallic pollution [14 and 15]. They contributed the case to the agricultural activities characterized by the use of chemical NPK fertilizers, herbicides, and pesticides. The phosphorus in these fertilizers and pesticides can end up in surface waters. The high phosphorus contents in these waters lead to the proliferation of blue-green algae, the degradation of which leads to toxin formation or eutrophication which results in water anoxia resulting in the loss of diversity.

The transfer of phosphorus contained in chemical NPK fertilizers applied in cultivated soils to water resources is a simple concept but difficult to assess, given the number of possible physicochemical and biological mechanisms involved and the types of soil. It is therefore preferable to study the mobility and bioavailability of phosphorus in cultivated soils to better understand and describe the dynamics of phosphorus transfer from soils to water resources.

MATERIALS AND METHODS

2.1 Study area

Located in the south of Benin between $6^{\circ}36'35''$ - $6^{\circ}40'00''$ N and $1^{\circ}45'00''$ - $1^{\circ}50'00''$ E, Lake Toho covers an area of 9.6 km² at low water and 15 km² during flooding with an average depth of 2.1 m¹⁶. It has an average length of 7 km; a southern width varying between 0.5 and 2.5 km and about 500 m in northern width. It is part of the Mono basin. The latter covers an area of 374 km² and is located in the western complex of wetlands in southern Benin¹⁴. Lake Toho straddles the municipalities of Athiémé, Lokossa, and Houéyogbé and crosses the villages of Vèha, Logbo (municipality of Lokossa), Tohonou, and Tokpa (municipality of Houéyogbé). The valley of the Sazué River serves as an outlet during the flood season through two channels. This valley also serves as a tributary during the Mono floods.

Due to its geographical location, the Lake Toho area is influenced by a subequatorial climate characterized by two dry seasons (mid-July to mid-September and mid-November to mid-March) and two rainy seasons (mid-March to mid-July and from mid-September to mid-November) dominated by continental winds and the harmattan¹⁷. The annual rainfall varies between 544 mm and 1376 mm while the temperature ranges between 20.6 and 33.5°C with an annual average of 28°C. The relative humidity varies from 65% in January to 80.6% in June¹⁵.

2.2 Sampling

The **sampling was** carried out in January 2022 at thirteen (13) sites. The sites were chosen according to the position of the cultivated **fields concerning the lake and the** water supply. The position of the different sites **concerning the lake is presented in Figure 1.**

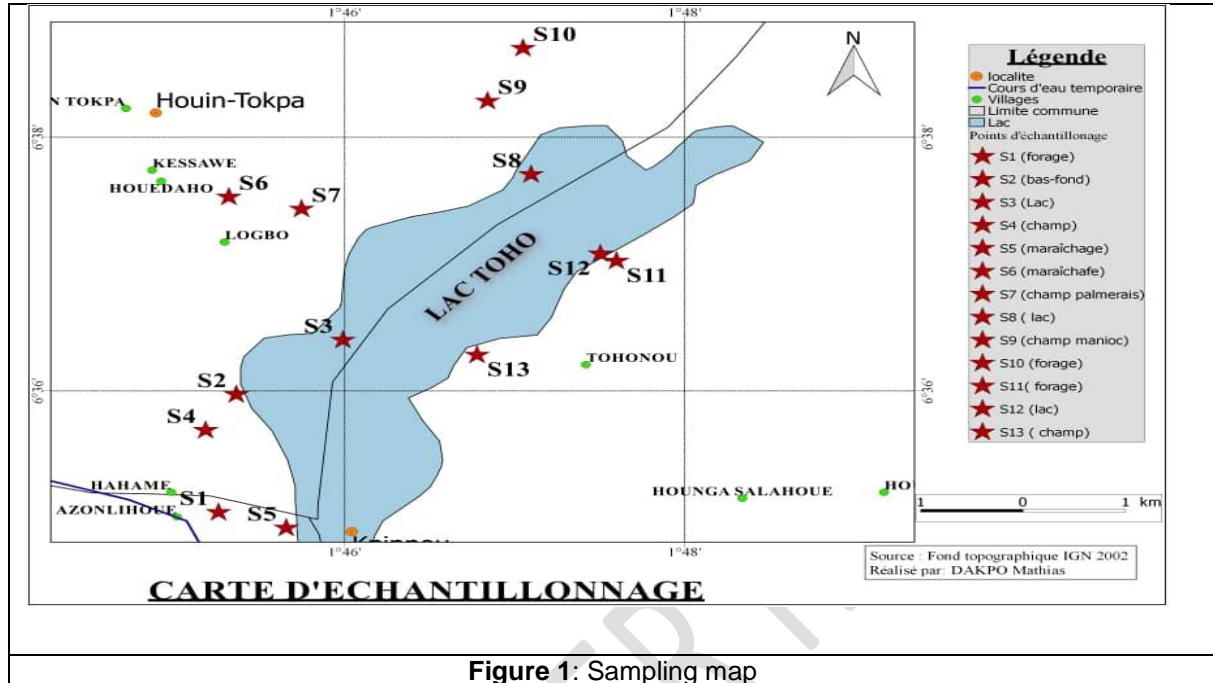


Figure 1: Sampling map

2.3 Analytical methods

Physicochemical parameters were analyzed. The pH of the sediments was measured according to standard NF X 31-103 1992 while the humidity was determined according to standard AFNOR X31-102, AFNOR 1994. As regards organic matter, the Walkley method-Black [18] was used. The phosphorus **content was determined** by mineralization with potassium persulfate in an acid medium (H_2SO_4) at $120^\circ C$ **for 2 h**. The fractionation of phosphorus was carried out following Rydin and Welch¹⁹ scheme.

2.4 Statistical analysis

The data relating to the physicochemical and fractionation parameters of phosphorus were subjected to a principal component analysis (PCA) and to the calculation of the correlations using the X-Lstat software

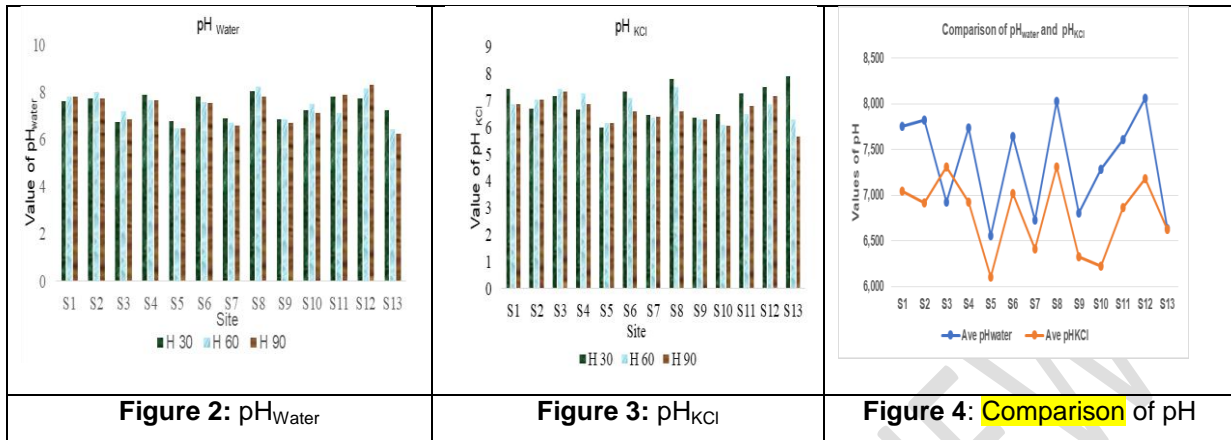
RESULTS AND DISCUSSION

3.1 Physicochemical parameters

pH and pH_{KCl} :

The water pH of the soils around Lake Toho ranges from 6.25 to 8.3 (Figure 2). The highest pH value **was recorded** at the site 12 to 90 cm deep and the **lowest at** the site 13 to 90 cm deep. At the same site, the pH varies very slightly passing from one horizon to an **other except for sites 12 and 13 which**

were located near Lake Tohonou. The pH_{KCl} ranges from 5.66 to 7.91 (Figure 3); the highest and lowest values were recorded at site 13. On 9/13 of the sites, the pH_{KCl} was inversely proportional to the depth. The average value of pH_{KCl} is lower than that of pH_{water} on almost all the sites (Figure 4).



Humidity and Organic matter

According to Figure 5, the water content in the soils around the lake varies from one horizon to another. This water content increases proportionally with depth on 9 of the 13 sites.

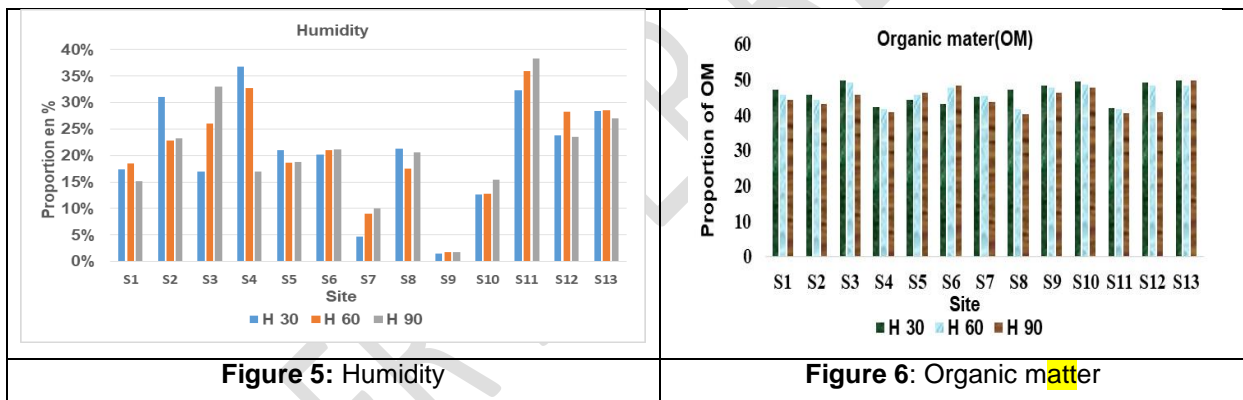


Figure 6 presented the variation of organic matter in soils. The highest levels of soil organic matter are recorded at sites 3 and 13. For the majority of sites, the organic matter content is higher in the upper horizon and decreases towards the bottom. This was explained by the fact that this part of the ground receives dead leaves, plant debris, and animal carcasses. Sites located outside the fields have low organic matter contents.

Total phosphorus (TP) and fractionation

According to Figure 7, the TP varies from $28436.52 \mu\text{g}\cdot\text{g}^{-1}$ to $1049.74 \mu\text{g}\cdot\text{g}^{-1}$. The highest value was observed at site 2 and the lowest at site 11. For the majority, phosphorus was mainly concentrated in the upper soil layer H30-H60.

The sites outside the fields (S1, S11) and the sites located in the unamended fields (S4, S9) have low phosphorus contents.

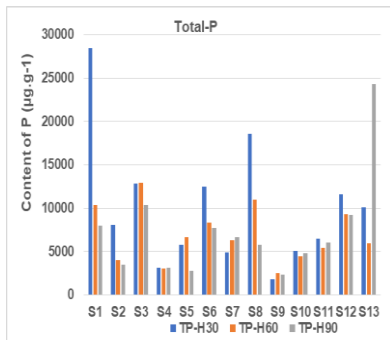


Figure 7: Total phosphorus

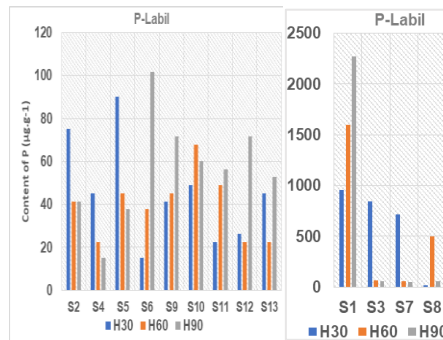


Figure 8: Mobile phosphorus

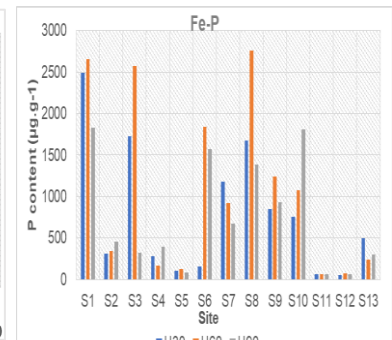


Figure 9: Phosphorus bound to iron

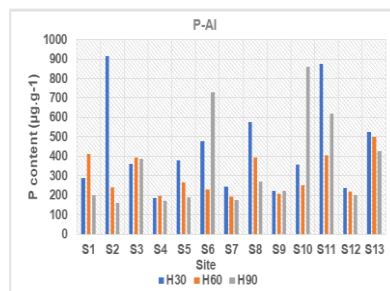


Figure 10: Phosphorus bound to aluminum hydroxides

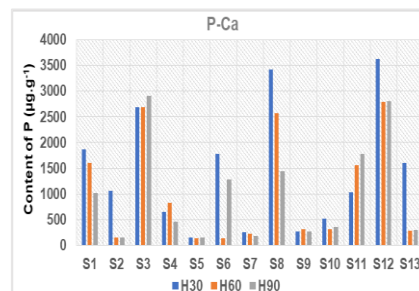


Figure 11: Phosphorus bound to calcium

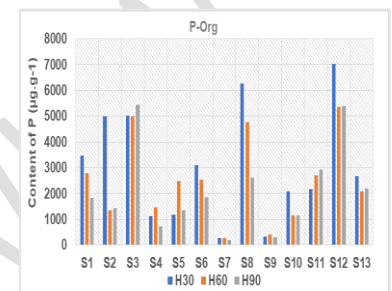


Figure 12: Phosphorus bound to Organic

The different phosphorus fractions obtained are as follows:

As reported in Figure 8, the labile form of phosphorus is found concentrated in the lower horizon H90 in more than 50% of the sites. This can be explained by the fact that this fraction of phosphorus can migrate to depth. At sites S3, S4, S5, and S7, labile phosphorus exists more in the H30 horizon, while at sites S8 and S10 were present in higher levels in the H60 horizon. At the seven (7) other sites, labile phosphorus exists more in the H90 horizon than in the other horizons.

According to Figure 9, phosphorus is strongly bound to iron in the majority of sites (8/13) at the level of the H60 intermediate layer. At site 13, phosphorus is strongly bound to iron in the upper horizon H30 while at sites S2, S4, and 10, phosphorus was strongly bound to iron in the lower horizon, H90.

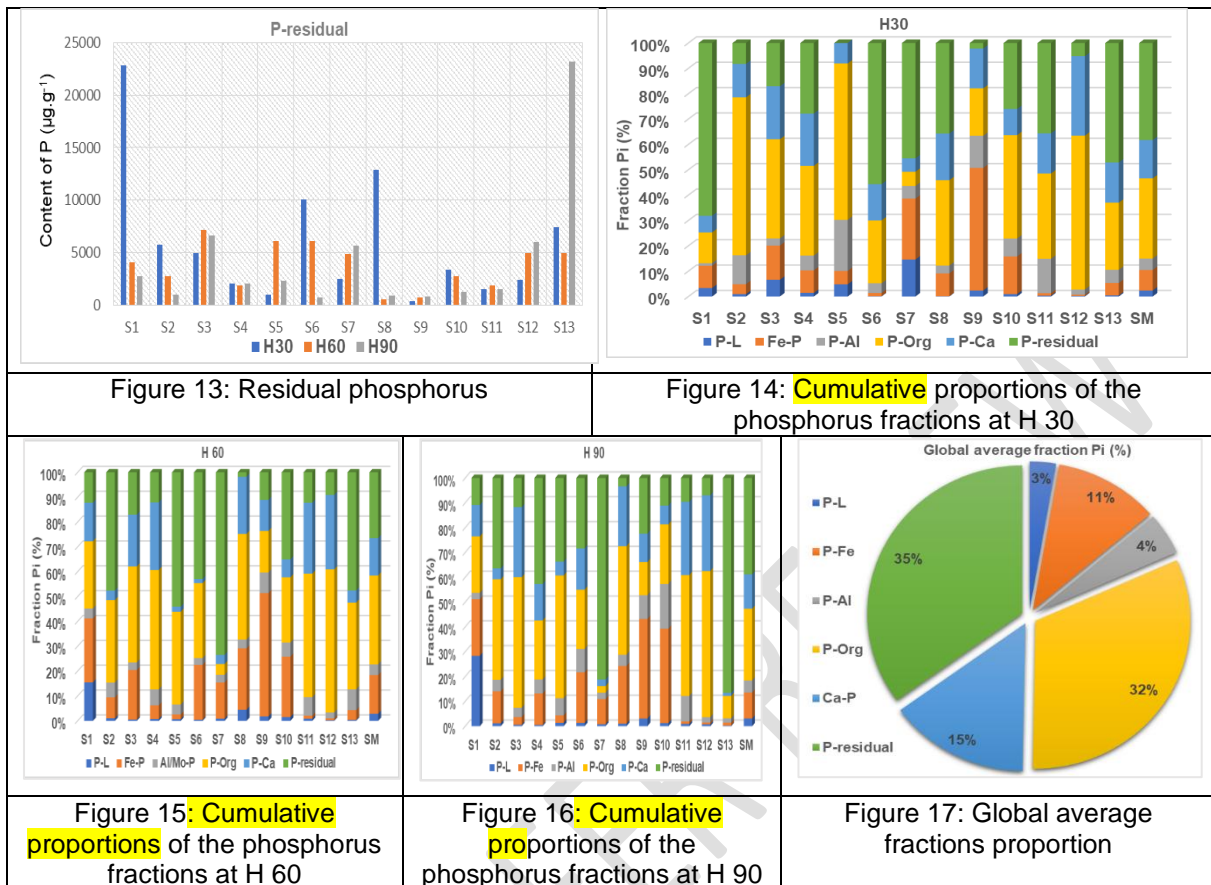
From Figure 10, phosphorus was bound to aluminum hydroxides and organic matter in the upper soil layer (H30) at most sites (8/13). Except for sites 6 and 10, the phase of phosphorus bound to aluminum hydroxides and organic matter decreased as it progresses from the surface to the depth.

According to Figure 11, the fraction of phosphorus bound to calcium was found preferentially in the upper layer of the soil (H30). In the majority of sites, this fraction of phosphorus decreases from the surface to the depth.

According to Figure 12, the organic phosphorus is more concentrated at the top layer of the soils. This fraction is more present than any others.

The residual fraction of phosphorus is found either at the surface (H30) or depth in the majority of sites (Figure 13). At sites 1, 2, 4, 6, 8, and 10 the residual fraction predominates in horizon 30; at sites 5

and 11, the residual fraction predominates in the 60 horizons, but at the other sites, the residual fraction predominates in the 90 horizons.



Spatial distribution of the different forms of phosphorus in the different horizons

According to Figures 14 and 16 on the H30 superficial horizon, the residual fraction predominates in the majority of sites except at sites 2, 3, 5, 9, and 12. Apart from the residual fraction which predominates, phosphorus is preferentially bound to organic matter, calcium iron oxide and. At the S1 site, the labile fraction of phosphorus predominates.

On figure 15, at horizon 60, the organic fraction predominates on the majority of sites except at sites 7, 8, and 9. In the other fraction, the residual fraction predominates, phosphorus is preferentially bound to iron oxide and calcium.

Figure 17 showed a global tendency of the fractionation. The residual and organic fraction predominates at (35%) followed by calcium (15%), and iron (11%). The two last fractions are aluminum (4%) and labile-P (3%)

Statistical analysis

The results indicated that the first two axes explain 49.37% of the initial information, which is sufficient to guarantee precision in the interpretations. The circle in Figure 18 showed the correlations between

the physicochemical parameters of the soil, the total phosphorus per layer, and the different forms available in the soil. The component axes indicated a strong correlation between the TP, the P-r, and the F1 axis. On the other hand, it indicates a strong correlation between the F2 axis and organic matter that opposes humidity. There is a strong correlation between the pH and the fractions linked to calcium according to the horizon.

Figure 19 showed that sites rich in organic matter contrast with sites dominated by moisture. The lower the humidity, the higher the organic matter. The S1 and S3 sites are dominated by Fe-P at the 60 horizons, the S9, S10, and S7 sites are dominated by residual P but low in organic matter at the 90 horizons, the S4 and S2 sites have a high rate of humidity at horizon 30 and sites S8 and S12 exhibit high pH and are dominated by Ca-P.

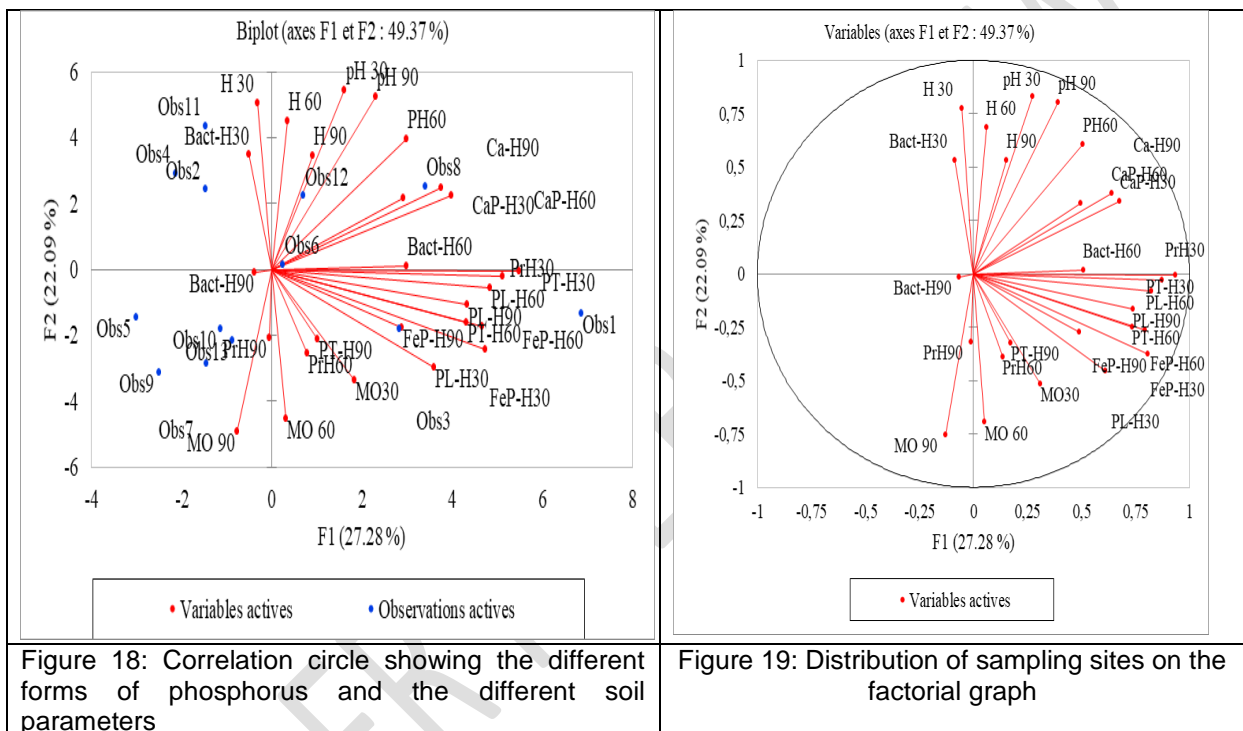


Figure 18: Correlation circle showing the different forms of phosphorus and the different soil parameters

Figure 19: Distribution of sampling sites on the factorial graph

Discussion

The results showed that the cultivated soils around Lake Toho have pH_{water} between 6.25 and 8.3 and pH_{KCl} between 5.66 and 7.91. The water pH values recorded are in agreement with the results of Igué et al. [20] which stipulate that the pH values of the soils of Benin are between 6.6 and 7.2 in the cultivation areas and were classified in the category of neutral to weakly acidic. We observe a weak evolution of the pH from neutral to weakly basic. The soils cultivated around Lake Toho are therefore now weakly acidic to weakly basic.

Schvartz et al. [21] revealed that soil moisture is one of the parameters that condition the phenomena of mineralization of organic matter and mobility of phosphorus. The humidity of the cultivated soils around Lake Toho varies from 1 to 38% on different horizons. Sites S1 and S10 are located next to boreholes, therefore the decreased humidity from the surface to the depth at sites S1 and S10 are due to the spillage, by the populations, of water on the surface and which migrates up to horizon 60. Site S11 is not only next to a borehole but also not far from the lake, which explained the increase in

humidity recorded on this site starting from the surface towards the depth. In addition, the same remarks were observed at the majority of the sites located not far from the lake (S3, S12, and S13). On the other hand, in the lowlands, the surface layers are more humid and therefore contain more water; this is due to the clayey nature of this part of the soil. pH and humidity influence the dynamics that exist between the organic and inorganic fractions of the soil through immobilization [22, 23].

Organic matter has sorption sites allowing it to fix phosphorus²⁴. The organic matter contents recorded in the present study were between 40.30 to 49.70%. In the majority of sites, the surface layer contained a high rate of organic matter. Organic matter includes all the organic constituents, dead or alive, of plant, animal, or microbial origin, transformed or not, present on the surface of the soil. This explained the high organic matter contents recorded on the surface layer of the soil. Those values remain higher than they found at the end of the dry season (May 2022) [25]. Also, those values could be highly estimated by the height of humidity which transferred carbon to the lower layer, and the possible oxidations of other metals highly present in the soils. This was revealed in the fractionation according to high values of phosphorus bound to iron, calcium, and aluminum. In the Walkley-Black method, the excess of non-reactive dichromate solution oxidizes a Fe (II) solution to determine the real dichromate solution uses for organic determination.

The analysis carried out showed that the total phosphorus was between 1049.74 $\mu\text{g.g}^{-1}$ and 28436.52 $\mu\text{g.g}^{-1}$ with a high rate of enrichment at horizon 30 on the majority of the sites. According to Beaudin [5], the surface application of non-submerged fertilizers causes the enrichment of the upper layer of the soil in phosphorus leading to the accumulation of inherited phosphorus stocks, which can represent, in certain regions, up to 80% of the stock of phosphorus present today in the first 30 cm of arable land [1]. The high total phosphorus contents recorded at the level of the superficial horizontal in cultivated fields were due to the use of fertilizers to amend the soil. This fact can lead to surface water contamination by runoff or groundwater by filtration. The total phosphorus content recorded in the cultivated soils around Lake Toho is much higher than those recorded by Renneson [10] in the agricultural soils of Wallonia (508-717 mg.kg^{-1}), in the ferruginous tropical soils of southern and central Benin (118.40 mg.kg^{-1}) [20], Le Noe [1] in agricultural soils of France over horizon 30 (750 mg.kg^{-1} - 900 mg.kg^{-1}). This difference can be explained by an accumulation of phosphorus in the soils in a non-mobile form. Shoreline materials can contain as much phosphorus as the surface horizon of agricultural land [26], which also explained the high total phosphorus content recorded at the level of the surface horizon of the lake shore (S3, S8, and S12). Therefore constitutes a medium-term risk for the aquatic environment.

Phosphorus is mainly found in the P-L, P-Fe, P-Ca, and P-Mo fractions. The organic fraction predominates in the upper soil layer except for sites located outside crop fields (S1; S10). This affinity of phosphorus with organic matter on this layer was due to the high organic matter content recorded.

The fraction bound to iron predominates in the lower layer from 60 cm. This observation is due to the ferritic nature of the soil. The first layer is made up of debris, dead leaves, and others; below this layer is the iron-rich soil for the majority of sites. This explains the high proportion of the iron-bound fraction at horizon 60.

The labile fraction predominated at the 30 and 60 horizons for the majority of sites. Also, this fraction is part of the mobile forms. This form of phosphorus is the dissolved form that can be taken up by plants in the soil solution but can also end up in a runoff.

As for the fraction of phosphorus bound to calcium, it predominated in the upper layer (H30) in most sites. The dominance of these fractions on the upper soil layer explained the high phosphorus content at this soil horizon.

The enrichment of soils with phosphorus is at the origin of the spatial variability of phosphorus concentrations in surface waters [27]. The high phosphorus contents found in cultivated soil were the cause of the high phosphorus concentration recorded in the waters of Lake Toho [15]. The strong correlation recorded between the TP, P-r, P-L, and P-MO showed that the high content of phosphorus at the upper horizon of the soil is due not only to the anthropogenic contribution but also to the source rock. The opposition of organic matter and observed humidity confirms the analysis made. This shows that humidity is inversely proportional to organic matter content.

Soil phosphorus is adsorbed by soil particles while that of chemical fertilizers and other soil fertilizers is soluble [28]. The predominance of different phosphorus fractions in the upper soil layer, with the exception of the residual fraction, showed that the phosphorus enrichment of cultivated soils around the lake is due to anthropogenic activities.

Phosphorus is a critical element for plant growth and soil fertility, and its distribution and fractionation in soils play a crucial role in soil fertility [29, 30] and agricultural productivity [31, 32]. In this paper, the authors investigate the phosphorus fractionation in sediment and agricultural soils surrounding Lake Toho in southern Benin during the rainy season.

The study found that total phosphorus (TP) concentrations in the sediment and agricultural soils were low, with an average of 11.1 mg kg^{-1} and 20.6 mg kg^{-1} , respectively. The sediment samples had a higher concentration of organic phosphorus (OP), while the agricultural soils had higher inorganic phosphorus (IP) concentrations. The IP fraction in the agricultural soils was dominated by the labile fraction, which is readily available for plant uptake [33].

The authors also found that the distribution of P fractions was influenced by the soil type, with the alluvial soils having a higher concentration of IP compared to the vertisols. The study also revealed that the presence of iron (Fe) and aluminum (Al) oxide minerals in the soils influenced the distribution of P fractions [34, 35, 36, 37]. The authors suggest that the observed differences in P fractionation between the sediment and agricultural soils could be due to the differences in soil properties, land use practices, and the inputs of P from human and natural sources.

Rainfall is a key factor that affects the availability of phosphorus in soil. Heavy rainfall can cause the leaching of phosphorus from the soil, making it unavailable to plants [38, 39]. This is because heavy rainfall can cause the water to move through the soil, taking the dissolved phosphorus with it and washing it out of the root zone of plants [40, 41].

In addition, high rainfall can also increase the acidity of the soil, which can further reduce the availability of phosphorus. This is because acidic soils can increase the chemical fixation of phosphorus, making it less available to plants [42, 43]. On the other hand, moderate rainfall can improve the availability of phosphorus in soil. This is because moderate rainfall can increase the infiltration of water into the soil, which can help to dissolve the phosphorus in the soil and make it available to plants [44, 45]. Rainfall has a significant impact on the availability of phosphorus in soil. Heavy rainfall can cause the leaching of phosphorus and reduce its availability, while moderate rainfall can improve it [46, 47]. This highlights the importance of understanding the effects of rainfall on soil phosphorus availability for the effective management of agricultural and natural ecosystems [48, 49].

In conclusion, the results of this study highlight the importance of considering the distribution and fractionation of P in agricultural soils, particularly in the rainy season, to better understand soil fertility and agricultural productivity in the Lake Toho region of southern Benin. Further research is needed to better understand the dynamics of P in these soils and how they can be managed to improve soil fertility and agricultural productivity.

Conclusion

The soils cultivated around Lake Toho are weakly acidic or even weakly basic with high organic matter contents in the surface layer of the soil. There was a high phosphorus content in cultivated soils with a predominance in the organic fraction on the upper layer of the soil except for sites located outside crop fields. The high total phosphorus contents recorded at the level of the superficial horizontal were due to the use of fertilizers. The domination of mobile phosphorus fractions leads to eutrophication that can cause the death of fish in Lake Toho. But phosphorus is not the only element of chemical fertilizers, the determination of nitrogen and its different forms in the soils cultivated around Lake Toho also remains essential to the study of the impact of agricultural activities on water resources mainly on Lake Toho.

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