

Phosphorus fractionation in sediment and agricultural soils surrounding ~~the~~ Lake Toho (~~southern Benin~~) in the rainy season

ABSTRACT

In recent years, land use related to anthropogenic activities has contributed to high surface water contamination ~~of surface waters~~. During the last decade, Lake Toho, in the ~~republic~~ Republic of Benin, has suffered ~~enormous~~ anthropogenic pollution ~~caused~~ by the use of fertilizers from farmers around the lake. ~~To assess the impact of these activities, w~~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 ~~the~~ different horizons. The content of organic matter is ranged from 40.30% to 49.70%. ~~In the majority of sites, the surface layer contains a high rate of organic matter~~. 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 ~~in the majority of the sites~~. The high contents of total phosphorus recorded at the superficial horizon ~~is 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 ~~with the exception of~~ sites located outside crop fields. The strong correlation ~~recorded~~ between the TP, the Pr, the P-L, and the P-OM ~~shows showed~~ that the high phosphorus contents ~~of phosphorus~~ at the upper horizon of the soil ~~is 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 ~~the phenomenon of~~ eutrophication which can cause the death of fish ~~and as well as the appearance of harmful toxins development harmful to aquatic species~~.

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

INTRODUCTION

Phosphorus is one of the essential elements for ~~the life of living beings~~. ~~Indeed, i~~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 ~~in humans~~.

Phosphorus is involved in plant growth ~~processes~~ [2, 3, 4, and 5]. Before agricultural industrialization, in the terrestrial biogeochemical cycle of phosphorus, plants assimilated phosphate ~~ions~~ present in the soil ~~solution~~, while the heterotrophic processes of organic matter decomposition ~~of organic matter~~ 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 the surface water toxicity ~~of surface waters~~⁶. Eutrophication can lead to surface water anoxia due to ~~the plant~~ respiration ~~of plant biomass~~ 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 ~~uptaked~~ 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. The ~~main cause mentioned is y attributed the condition to~~ the use of organic fertilizers ~~in agriculture~~ 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 This phenomenon led the fish into a state of~~ deoxygenation and ~~cost them their lives~~ deaths. In 2018 and 2021, the same drama happened again on the same lake with a ~~change in color~~ 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. ~~In addition, s~~ Studies have shown that Lake Toho is subjected to nitrogen, phosphorus, organic, and metallic pollution [14 and 15]. They ~~contributed the case to probable causes mentioned by these authors are related 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 ~~the toxin formation of toxins; or the other consequence is~~ 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 ~~in order~~ 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 is very high and varies from 65% in January to 80.6% in June¹⁵.

2.2 Sampling

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

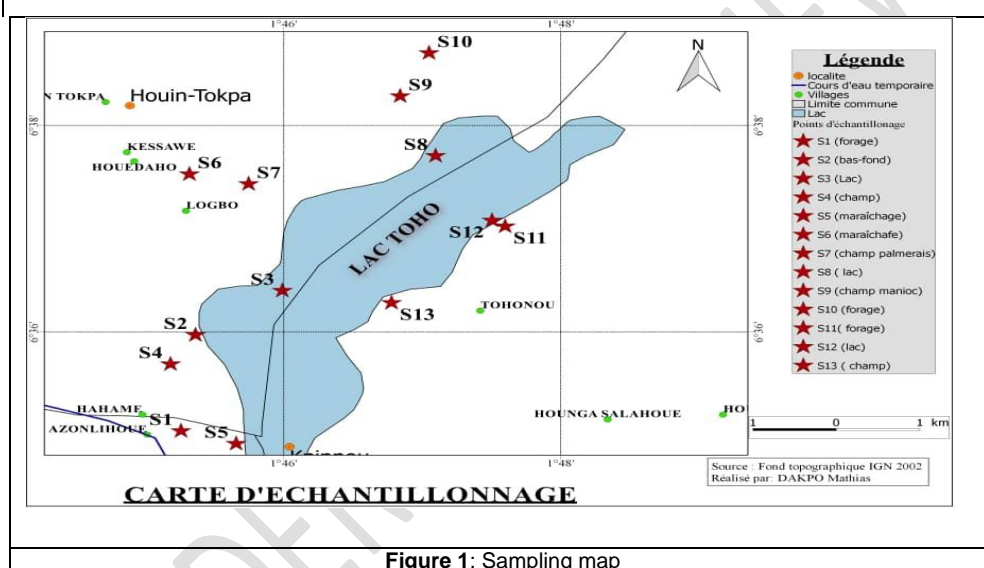


Figure 1: Sampling map

2.3 Analytical methods

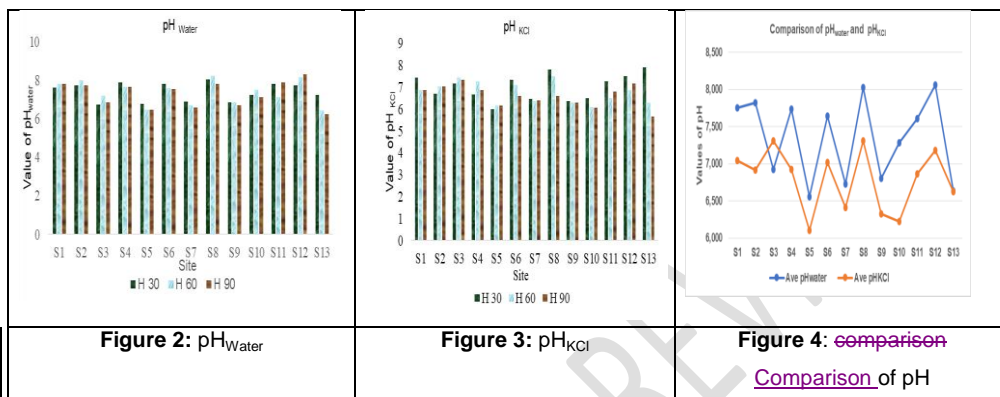
Physicochemical parameters were analyzed. The pH of the sediments was measured according to standard NF X 31-103 1992 while the humidity was determined according to standard AFNOR X31-102, AFNOR 1994. As regards organic matter, the Walkley method-Black [18] was used. The phosphorus content is was determined by mineralization with potassium persulfate in an acid medium (H₂SO₄) at 120°C for 2 hours. The fractionation of phosphorus was carried out following Rydin and Welch¹⁹ scheme.

RESULTS AND DISCUSSION

3.1 Physicochemical parameters

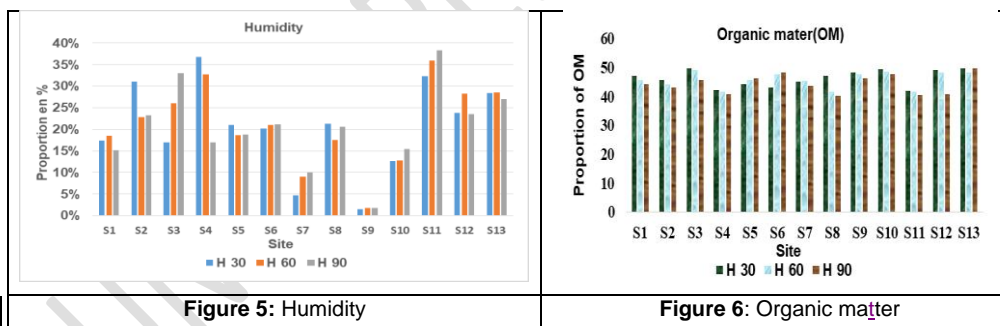
pH and pH_{KCl} :

The water pH of the soils around Lake Toho ranges from 6.25 to 8.3 (Figure 2). The highest pH value ~~is was~~ recorded at the site 12 to 90 cm deep and the lowest ~~value~~ at the site 13 to 90 cm deep. At the same site, the pH varies very slightly passing from one horizon to another ~~with the exception of except~~ ~~for sites~~ 12 and ~~site~~-13 which ~~are sites were~~ located near Lake Tohonou. The pH_{KCl} ranges from 5.66 to 7.91 (Figure 3); the highest and lowest values ~~are were~~ recorded at site 13. On 9/13 of the sites, the pH_{KCl} ~~is 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.



~~The~~ Figure 6 presented~~s~~ the variation of organic matter in soils. The highest levels of soil organic matter are recorded at sites 3 (~~lake~~) and 13 (~~field not far from the lake~~). For the majority of sites, the organic matter content is higher in the upper horizon and decreases towards the bottom. This ~~is was~~ explained by the fact that ~~it is~~ this part of the ground ~~that~~ 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 $\mu\text{g.g}^{-1}$ to 1049.74 $\mu\text{g.g}^{-1}$. The highest value ~~is was~~ observed at site 2 and the lowest at site 11. For the majority, phosphorus ~~is 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.

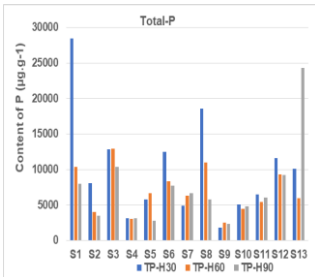


Figure 7: Total phosphorus

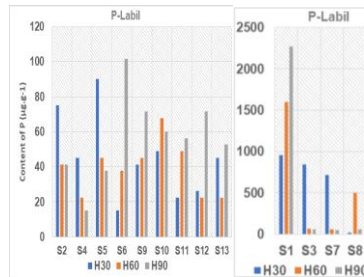


Figure 8: ~~mobile~~ Mobile phosphorus

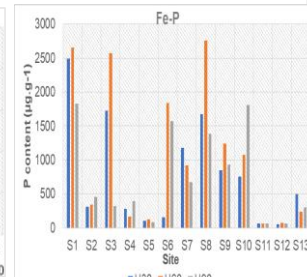


Figure 9: Phosphorus bound to iron

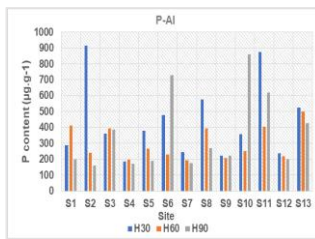


Figure 10: Phosphorus bound to aluminum hydroxides

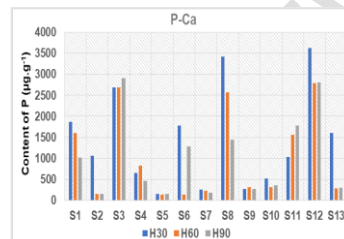


Figure 11: Phosphorus bound to calcium

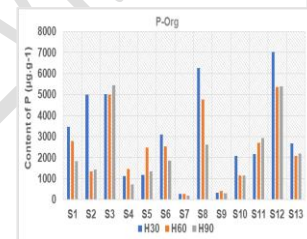


Figure 12: Phosphorus bound to Organic

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 the depth. At sites S3, S4, S5, and S7, labile phosphorus exists more in the H30 horizon than in the other horizons, while at sites S8 and S10 ~~were labile phosphorus is more present in higher levels in the H60 horizon than in the other horizons~~. 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 S13, phosphorus is strongly bound to iron in the upper horizon H30 while at sites S2, S4, and S10, phosphorus ~~is was~~ strongly bound to iron in the lower horizon, H90.

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

According to Figure 11, the fraction of phosphorus bound to calcium ~~is 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 ~~at~~ 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.

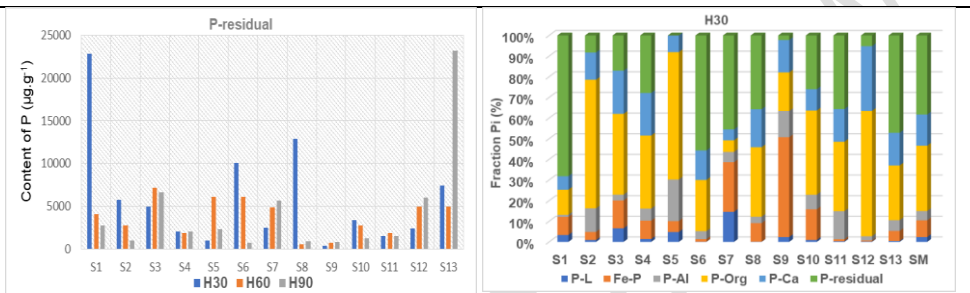


Figure 13: Residual phosphorus

Figure 14: ~~cumulative~~ Cumulative proportions of the phosphorus fractions at H 30

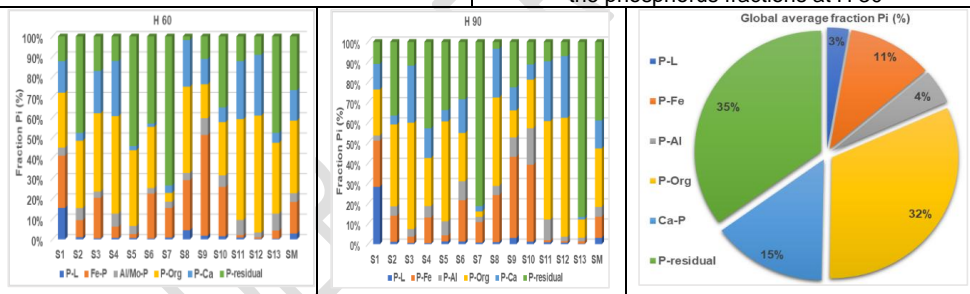


Figure 15: ~~cumulative~~ Cumulative proportions of the phosphorus fractions at H 60

Figure 16: ~~cumulative~~ Cumulative proportions of the phosphorus fractions at H 90

Figure 17: Global average fractions proportion

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

According to ~~figure~~ 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.

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

Statistical analysis

The results of the principal component analyzes (PCA) 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 Figure 18 shows 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 on the one hand 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 shows 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.

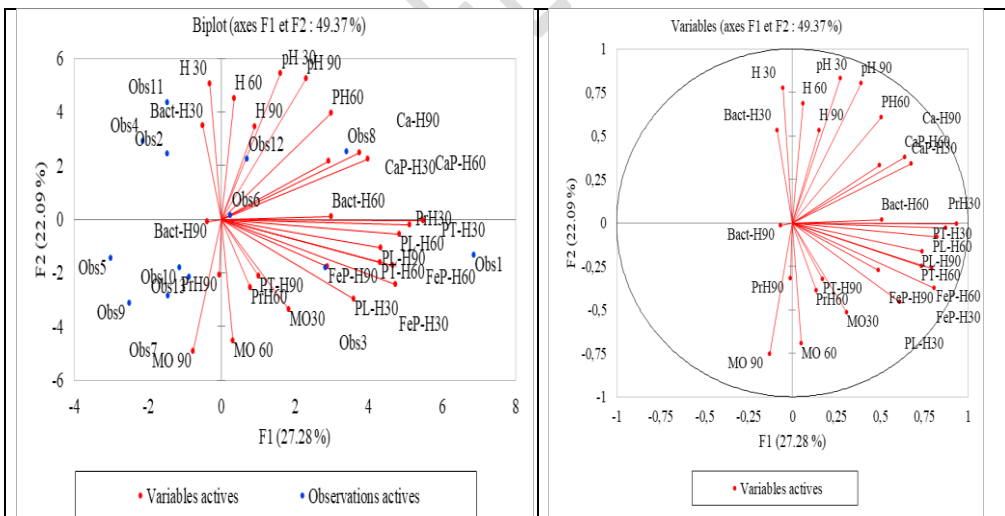


Figure 18: Correlation circle showing the different forms of phosphorus and the different soil parameters

Figure 19: Distribution of sampling sites on the factorial graph

Discussion

The results ~~obtained in the present study~~ showed that the cultivated soils around ~~the~~ 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 ~~was-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 ~~the~~ Lake Toho are therefore now weakly acidic to weakly basic.

~~According to the work of~~ Schwartz 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 ~~the~~ different horizons. Sites S1 and S10 are located next to boreholes, therefore the ~~decreased-in~~ humidity ~~recorded~~ from the surface to the depth at sites S1 and S10 ~~is-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 ~~explains-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. ~~Indeed,~~ pH and humidity influence the dynamics ~~that that~~-exist between the organic and inorganic fractions of the soil through ~~the process of~~ immobilization [22, 23].

Organic matter has sorption sites allowing it to fix phosphorus²⁴. The ~~organic matter contents of organic matter~~ recorded in the present study ~~is-were~~ between 40.30 to 49.70%. In the majority of sites, the surface layer ~~contains-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 ~~explains-explained~~ the high ~~organic matter contents of organic matter~~ recorded on the surface layer of the soil ~~compared to the lower layer~~. Those values remain higher than they ~~founded~~ 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 presents 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 ~~determined-determination~~.

The analysis carried out showed that the total phosphorus ~~is-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 an~~-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 of total phosphorus~~ recorded at the level of the superficial horizontal in cultivated fields ~~is-were~~ due to the use of fertilizers to amend the soil. This fact can lead to ~~the surface water~~ contamination of ~~surface water~~ by runoff or groundwater by filtration. ~~In addition, the enrichment of the upper layer of the soil in phosphorus gives the runoff a high phosphorus content and an enrichment of the subsoil by filtration [5]. By comparison, the~~ total phosphorus content recorded in the cultivated soils around Lake Toho is much higher than ~~those~~

~~content~~ recorded by Renneson [10] in the agricultural soils of Wallonia (508-717 mg.kg⁻¹), in the ferruginous tropical soils ~~in-of~~ southern and central Benin (118.40 mg.kg⁻¹) [20], Le Noe [1] in agricultural soils ~~in-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 ~~explains explained~~ the high total phosphorus contents recorded at the level of the surface horizon of the lake shore (S3, S8_i and S12). ~~This-therefore~~Therefore constitutes a medium-term risk for the aquatic environment.

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

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_i 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 ~~predominates-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 ~~predominates-predominated~~ in the upper layer (H30) in most sites. The dominance of these fractions on the upper soil layer ~~explains-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_s found in cultivated soil ~~is-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_i and P-MO ~~shows-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, ~~shows-showed~~ that the phosphorus enrichment of cultivated soils around the lake is due to anthropogenic activities.

Conclusion

~~The-poor-agricultural-activities-practice-characterized-among-others-by-the-use-of-chemical-fertilizers-causes-enormous-environmental-concerns-particularly-to-water-resources.~~The results show that the soils cultivated around ~~the~~Lake Toho are weakly acidic or even weakly basic with high organic matter contents_s in the surface layer of the soil. There ~~is-was~~ a high phosphorus content in cultivated soils with

a predominance in the organic fraction on the upper layer of the soil ~~with the exception of~~ ~~except for~~ sites located outside crop fields. The high total phosphorus ~~contents of total phosphorus~~ recorded at the level of the superficial horizontal ~~is were~~ due to the use of fertilizers ~~to amend the soil~~. The domination of mobile phosphorus fractions leads to ~~the phenomenon of~~ eutrophication that can cause the death of fish in Lake Toho. But phosphorus is not the only element of chemical fertilizers ~~used in agriculture~~, the determination of nitrogen and its different forms in the soils cultivated around ~~the~~ 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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Comment [es3]: MUST BE UPDATED as 28.5% (8 out of 28) of the listed references were published in the past five years. The percentage has to increase to 30-40%. The old reference indicates less interest in the study field.

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