Impacts of pollutants (phosphorus, nitrogen and potassium) from agricultural activities on the soils and waters of Toho Lake (Benin)

ABSTRACT

We evaluated the impacts of agricultural activities on the cultivated soils around Lake Toho as well as the waters from the streams through phosphorus, nitrogen and potassium pollution of the soils and waters from the streams heading towards Lake. In the soil, pHwater and pH_{KCl} organic matter, moisture total phosphorus and its fractionation were determined. The various supernatants obtained are analyzed using a 1600PC UV spectrophotometer as well as the waters for the determination of ammonium, nitrite, nitrates and phosphate. In soils, the determination of ammonium, nitrite, nitrate, phosphate and potassium was carried out by DR 5000MP-AES spectrometry method.Soils around this lake are weakly acidic with an average water pH of 6.91. The humidity increases from surface to depth (8% to 28%), while organic matter (11% on average) and organic carbon decrease from surface to depth. These soils are rich in phosphorus with an overall average concentration of 10.10 mg/g. The fractionation made it possibe to extract the following forms of phosphorus in soil in the order: P-residual >P-org&Al> P-Ca> P-Fe > P-Labile. The physicochemical analysis of the waters show that these waters are moderately loaded and present an increased risk of eutrophication with multifaceted consequences. In soils, nitrate is the dominant form of nitrogen. Cultivated soils provide an abundant source of nitrogen and phosphorus nutrients to Lake Toho via its recharge sources.

Keywords: Lake Toho, phosphorus, nitrogen, potassium, stream waters, fractionation.

1. INTRODUCTION

Since his existence and for his survival, man has always used the environment for his various needs. And since that time man has used the resources of that environment for his sustenance and development. With the population explosion, these needs have increased exponentially, leading man to over-exploit the environment; especially for agriculture, construction, energy and transport through the industrial revolution. All these sectors have caused imbalance in the environment through destruction of plant cover, emissions into the atmosphere and use of chemicals leading to pollution of soils and water resources. in 2008, [1] showed that the use of phosphorus was necessary to increase crop yields. This has led to the automation of agriculture through the production of chemical fertilisers. The nitrogen and phosphorus contained in these chemical fertilisers is the cause of environmental problems such as eutrophication and toxicity of surface and ground water [2]. Modern agriculture today requires the use of chemical fertilisers to increase production yields. This leads to uncontrolled use of these agents, which are now the main cause of soil and water

resource pollution. This phenomenon is intensifying with the non-compliance of the technical routes of agricultural production and the uncontrolled production of chemical fertilisers.
The mobility of phosphorus, nitrogen and potassium in soils and their transfer to surface waters depends on the different forms available. The presence of phosphorus in surface waters leads to eutrophication of water bodies and nitrite adversely affects the quality and functions of water [3]. This pollution leads to a loss of aquatic species. For example, Lake Toho in southern Benin experienced several fish kills in 2012, 2018 and 2021. In 2012, according to PNE-Benin, the fish kill occurred after a stormy rain that changed the turbidity of the water. This phenomenon is a cause of deoxygenation of the aqueous medium and cost these fish their lives. In 2018 and 2021, the same drama occurred in the same lake. This time when the main cause of this phenomenon in 2018 and 2021 is associated with the leakage of pollutants from unknown sources with colour change PNE Benin. Studies have shown that the lake is exposed to anthropogenic pollution [4,5]. Since agriculture is the main activity developing around the lake, it is therefore essential to study the mobility and bioavailability of phosphorus, nitrogen and potassium, which are the essential elements of chemical fertilisers used in the region.

2. MATERIAL AND METHODS

2.1 Study area

The study was carried out around Lake Toho which is located between 6°35 to 6°40 north latitude and 1°45 to 1°50. It covers an area of 9.6 km^2 in the dry season and 15 km^2in the rainy season [6]. Lake Toho is surrounded by several cultivable soils where samples have been taken.

2.2Sampling

A total of thirty (36) samples were taken, including 9 water samples on three sites and 27 soil samples on nine sites along the three horizons] 0, 30];] 30, 60];] 60, 90] cm

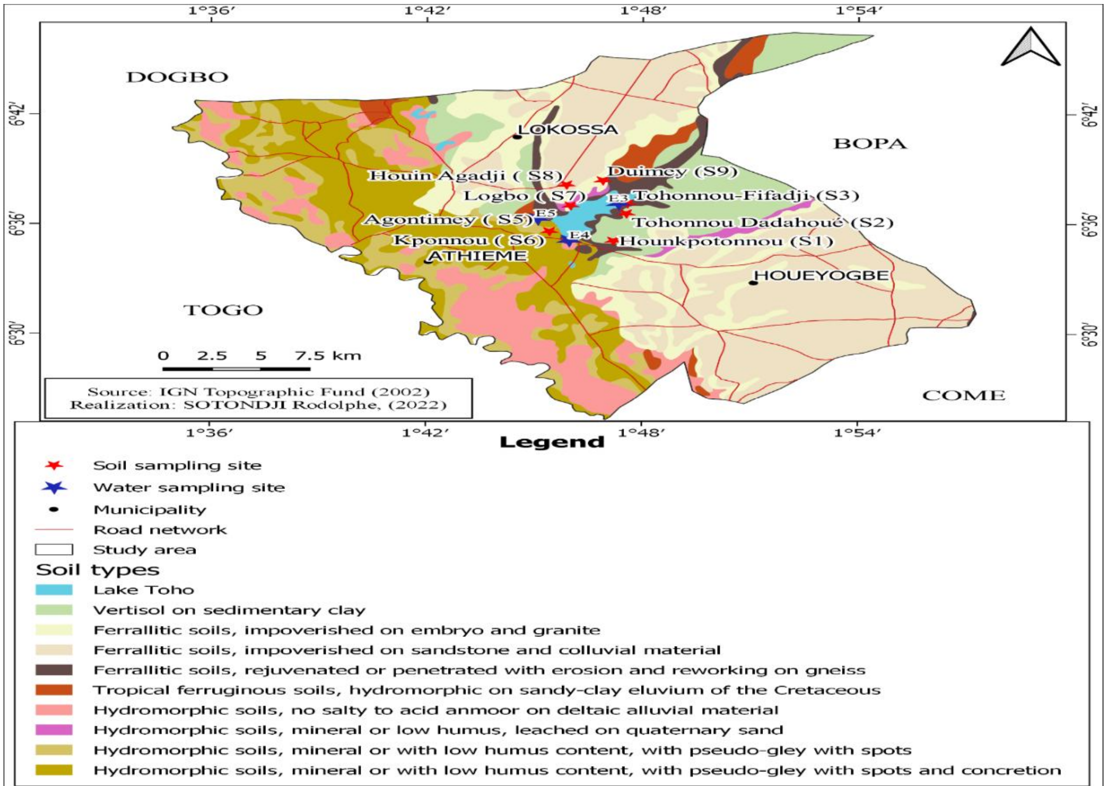

Figure 1: Sampling map

Table 1: Characteristics of sampling stations

SITES	Geographical coordinates	Characteristic	Samples
S1 (HOUNKPOTONNOU)	6°35'53.35"N 1°47'11.84"E	-Next to a usable borehole -Surrounded by cornfields - Presence of public toilets nearby - Presence of an old abandoned borehole	Soil
S2 (TOHONOU DADAHOUE)	6°36'34.66"N 1°47'33.33"E	-Fields of corn, okra, teak and banana trees. -Use of herbicides on site soil	Soil
S3 (TOHONOU FIFADJI)	6°37'7.40"N 1°47'22.10"E	-Proximity to houses not far from the lake -activities carried out fishing, agriculture, - Laundry	Water Soil Sediments
S4 (KPINNOU)	6°35'5.12"N 1°45'59.17"E	-Houses not far from the lake - fields of crincrin not far from the lake - fishing on the lake	Water Soil Sediments
S5 (AGONTIME)	6°36'16.35"N 1°45'6.06"E	-Large fields of horsehair - use of herbicides -Presence of stream	Water Soil Sediments
S6 (KPONNOU)	6°36'36.49"N 1°45'25.13"E	-Immediate proximity to the lake -laundry and fishing on the lake	Soil

S7 (LOGBO)	6°37'0.65"N 1°46'0.42"E	-Cornfield -corn fields by the lake -Laundry by the lake -sin - discharge of fish waste into the lake	Soil
S8 (HOUIN AGADJI)	6°38'9.14"N 1°45'53.54"E	- large corn fields -palmerais	Soil
S9 (DUIME)	6°38'23.33"N 1°46'54.10"E	- corn fields not far from the lake Presence of fish farm	Soil

2.3 Analysis methods

The soil samples were oven-dried at 40°C for 24 hours without any significant change in their properties. The pH of the water and the $pH_{KC}l$ were measured with the multiparameter conductivity metre of the brand HANNA according to the standard NF X 31-103. Humidity was determined according to AFNOR X31-102 standard, [7]. Organic matter was determined according to the Walkley-Black method [8]. Total phosphorus was determined by mineralisation with potassium persulphate in an acidic medium (H_2SO_4) at 120° C for 2 hours [9]. Fractionation was performed according to the protocol of Rydin and Welch [10]. The extractions were analysed using a UV-1600 PC spectrophotometer. The phosphate and potassium content of the soil was determined using the spectrometry method DR 5000 MP-AES. The determinations of nitrite, nitrate, ammonium, orthophosphates and potassium were carried out with the colorimetric method using a UV-1600 PC spectrophotometer. The Ifremer diagnostic grid for eutrophication risks [11] was used to assess the eutrophication risk of the investigated soils and waters.

3 RESULTS

- **Physicochemical characterization of soils**

The results of the physicochemical parameters of the soils showed that the pH of the water varies from one site to another and from one horizon to another, ranging from 5.23 to 7.89 with an average of 6.91. These soils are moderately acidic (Figure 2).

The recorded pH_{KCl} varies between 4.2 and 7.09 with an average of 5.73 (Figure 3). At the sites (S1, S2, S4, S7, S8 and S9), the value decreases from the surface to the depth while it increases at the other sites.

The water content (moisture) of the soil around Lake Toho decreases from the surface to the depth at sites (S2, S4, S5, S7 and S9), increases at sites (S3, S6 and S8) and remains constant at site (S1) Figure 4.

Soil organic matter content varies between 3% and 11%, with the highest content recorded at site S2 at the surface (horizon 30). The lowest content is observed at horizon 90 at sites

(S2, S3, S5 and S7). In the upper layer, the organic matter content is higher at sites (S2, S3, S5 and S7) than at the other sites (Figure 5).

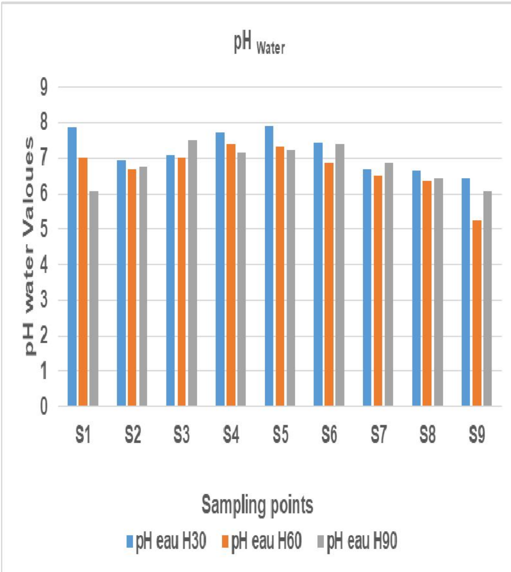

Figure 2: Variations in soil of pH_{water}

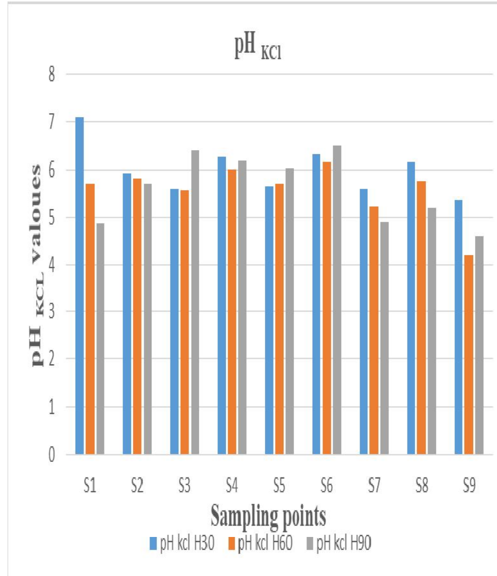

Figure 3: Variations in soil of pH_{KCl}

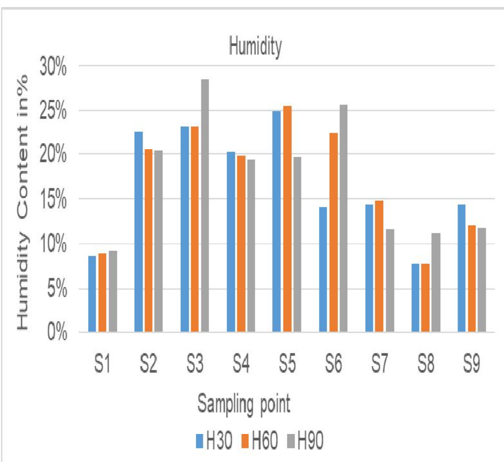

Figure 4: Soil humidity content

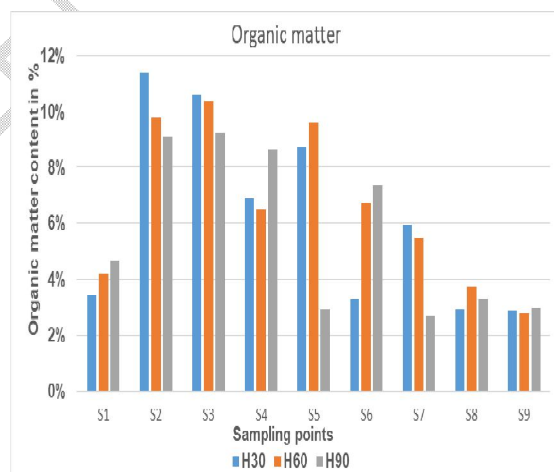

Figure 5: Soil organic matter content

- **Phosphorus and its derivatives in soils**

As shown in Figure 6, the proportion of total phosphorus in horizon H30 predominates at all sites, the concentration of total phosphorus increases from the surface towards depth at site S3, it decreases from the surface towards depth at sites (S1, S4, S6, S7 and S8), except for sites (S2, S5 and S9) where the opposite is observed. The phosphorus present in the different soil layers is bound to different particles or elements of the soil in different forms.

- **The variation of each form of phosphorus according to soil profiles**

According to Figure 7, the proportion of labile phosphorus in horizon H30 predominates at all sites, and the phosphorus concentration decreases from the surface to the depth at the levels (S1, S6, S7 and S8), except for the sites (S2, S3, S4, S5 and S9) where the opposite is observed.

According to Figure 8, the proportion of phosphorus bound to iron (P-Fe) in the H30 horizon predominates at all sites. The concentration of iron-bound phosphorus decreases from the surface towards depth at sites (S1 and S8), except for sites (S2, S3, S4, S5, S6, S7 and S9) where the opposite is observed.

According to Figure 9, the proportion of phosphorus bound to organic material in the H90 horizon predominates at all sites. The concentration of phosphorus bound to organic material increases from the surface towards depth at sites (S2 and S5), while it decreases from the surface towards depth at site S9, except for sites (S1, S3, S4, S6, S7 and S8) where the opposite is observed.

According to Figure 10, the proportion of phosphorus bound to calcium in the H30 horizon predominates at all sites, and the concentration of phosphorus bound to calcium decreases from the surface to depth at the site level (S1 and S7) and increases from the surface to depth at the site level S9, except for the sites (S2, S3, S4, S5, S6 and S8) where the opposite is observed.

According to Figure 11, the proportion of residual phosphorus in the H30 horizon predominates at all sites. The concentration of residual phosphorus increases from the surface to the depth at sites (S5 and S7) and decreases from the surface to the depth at site S8, except for sites (S1, S2, S3, S4, S6 and S9) where the opposite is observed.

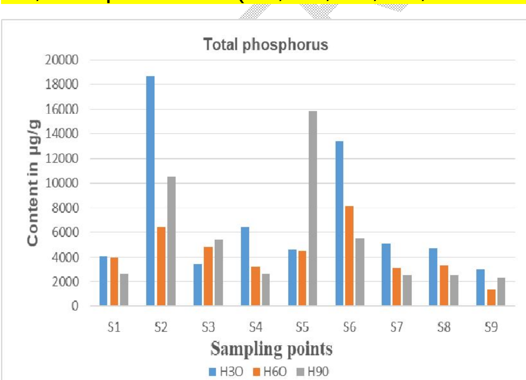

Figure 6: Content of the total fraction

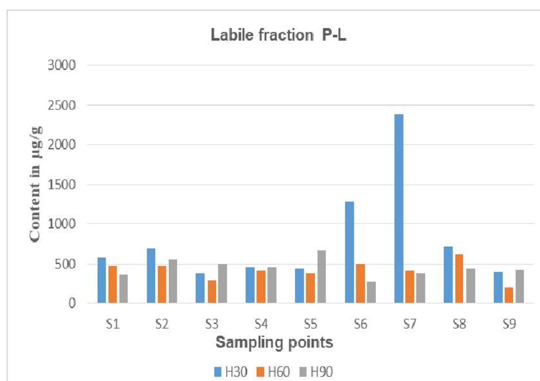

Figure 7: Content of the labile fraction

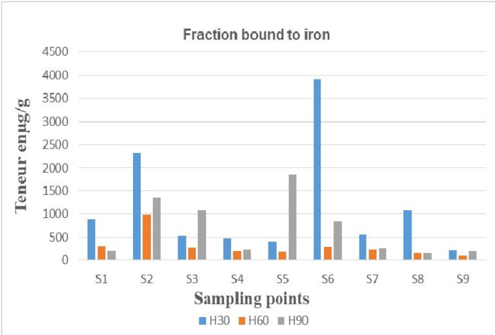

Figure 8: Content of iron-bound fraction

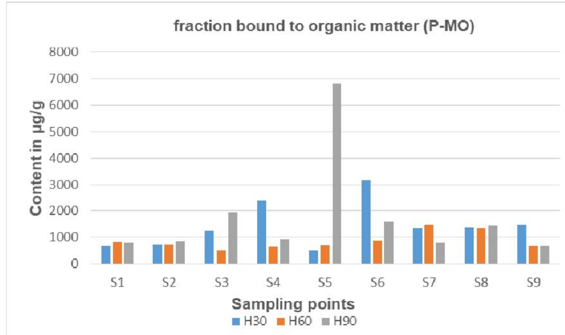

Figure 9: Content of the fraction bound to organic matter

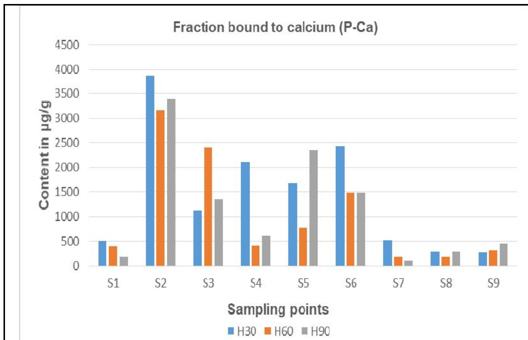

Figure 10: Content of the fraction bound to calcium

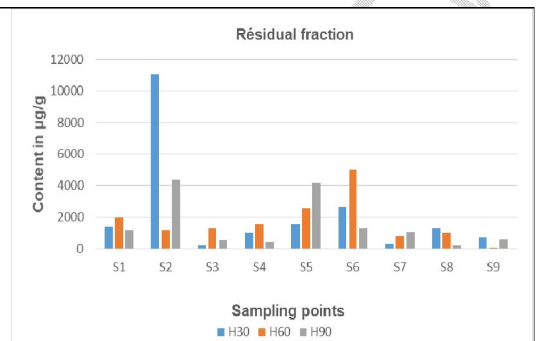

Figure 11: Content of the residual fraction

- The predominance of different forms according to Horizon

According to Figure 12 at horizon [0 - 30]. The labile fraction is low at all sites except site S7. The residual fraction (P-residual) predominates in the H30 horizon at the site levels (S1 and S2) compared to the others. On the other hand, the organic fraction (P-Org) predominates over the other fractions at the site level (S3, S4, S8 and S9), the fraction bound to iron predominates at the site level (S6) and the fraction bound to calcium predominates at the site level (S5). Of all fractions, the organic fraction predominates at horizon H30.

According to Figure 13, the labile fraction (P-L) at horizon [30-60] is low at all sites. The residual fraction (P-r) predominates at the sites (S1, S4, S5 and S6). At sites (S7, S8 and S9) the organic fraction predominates, while at sites (S2 and S3) the fraction associated with calcium predominates. At horizon H60, the organic fraction occupies the second position after the residual fraction.

Figure 14 shows that labile phosphorus (P-L) is low in horizons [60-90] at all sites. At the site level (S1, S2 and S7), residual phosphorus (P-r) predominates. At the site level (S3, S4, S5, S6, S8 and S9), the organic fraction (P-org) predominates.

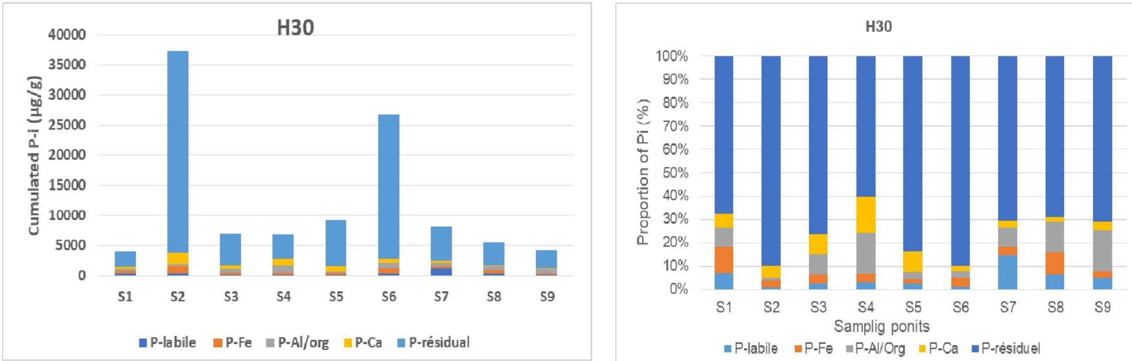

Figure 12: the cumulative value (a) and proportions (b) of the phosphorus fractions at H 30 cm

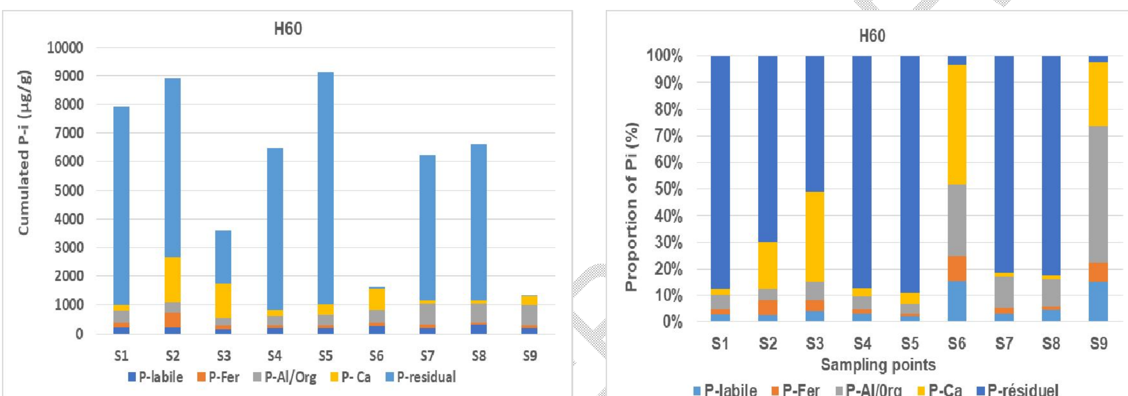

Figure 13: Cumulative value (a) and proportions (b) of phosphorus fractions at H 60 cm

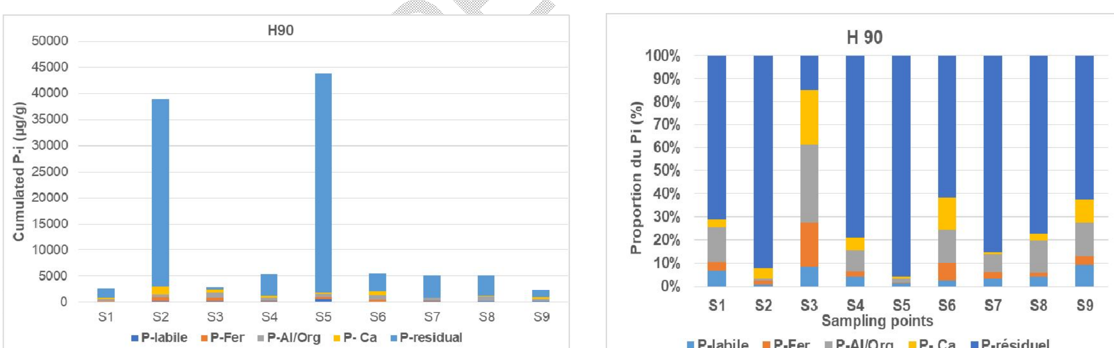

Figure 14: the cumulative value (a) and proportions (b) of the phosphorus fractions at H 90 cm

- The different forms of nitrogen in the soil

The analysis of Figure 15 shows that ammonium content in soil at 30 cm varies from 2.747 mg/kg at site (S5) to 7.771 mg/kg at site (S1), while at 60 cm it varies from 2.014 mg/kg at site (S1) to 6.255 mg/kg at site (S4), while the same content at 90 cm varies from 3.649 mg/kg at site (S7) to 6.823 mg/kg at site (S1). Ammonium is more concentrated in the surface horizon, with the exception of sites S2 and S5, where the ammonium content is slightly elevated at horizon 90

According to Figure 16, nitrite content in soil at 30 cm ranges from 5.878 mg/kg at site (S5) to 21.058mg/kg at site (S1), while at 60 cm it ranges from 5.457mg/kg at site (S1) to 15.748mg/kg at site (S5) and at horizon 90 cm it ranges from 6.937 mg/kg at site (S4) to 18.489mg/kg at site (S1). Nitrite is more concentrated in the surface horizon, with the exception of sites S2 and S5 where nitrite is slightly elevated at horizon 90.

According to Figure 17, soil nitrate content at 30 cm varies from 17.763mg/kg at site level (S8) to 35.155mg/kg at site level (S1), while at 60 cm it ranges from 9.110mg/kg at site level (S1) to 28.297mg/kg at site level (S4), while at 90 cm it ranges from 16.509mg/kg at site level (S7) to 30.867mg/kg at site level (S1). Nitrate levels decrease with depth, except for sites (S2, S5 and S9) where nitrite levels are slightly elevated at horizon 90.

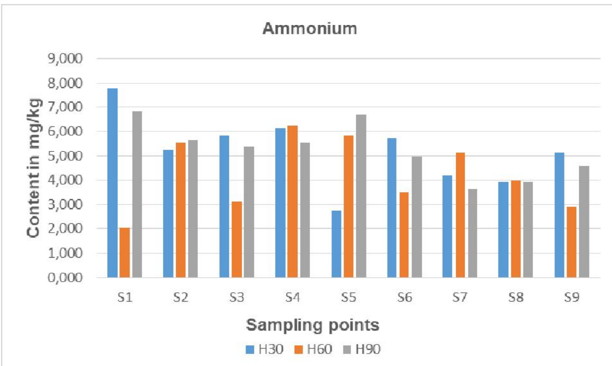

Figure 15: Ammonium content in soils

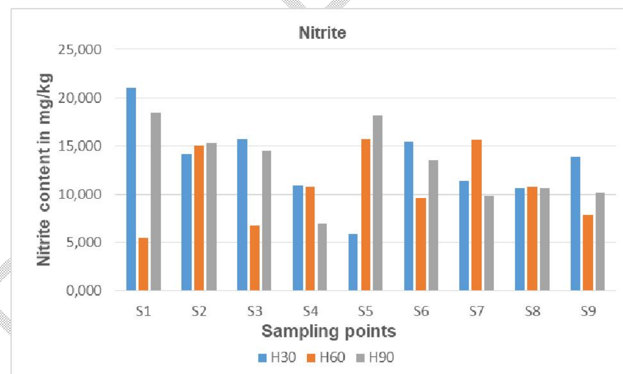

Figure 16: Nitrite content in the soil

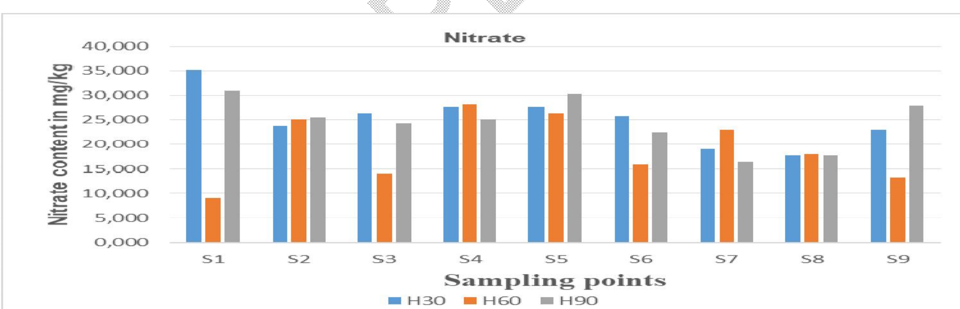

Figure 17: Nitrate content in the soil

Table 2: Rapport N/P

	Sites	S1	S2	S3	S4	S5	S6	S7	S8	S9
Depth	H30	0.016	0.001	0.007	0.007	0.004	0.002	0.004	0.006	0.010
	H60	0.002	0.005	0.007	0.007	0.005	0.018	0.007	0.005	0.018
	H90	0.021	0.001	0.015	0.007	0.001	0.007	0.006	0.006	0.018

The N/P ratio between the soil nitrogen content and the calculated soil phosphorus content (N/P) is much less than 1 at all sites, showing that the phosphorus content in the soils around Lake Toho outweighs the nitrogen content (Table 2).

- **Assessment of the risk of mobility of soil elementsto water resources**

According to the eutrophication risk assessment grid, the cultivated soils around Lake Toho are classified in the very poor group in terms of eutrophication risk (Table 3).

Table 3: Positioning of sediment samples (S1 to S9) in the grid of Ifremer's eutrophication risk diagnostic framework (2000).

Parameters	Very good (no risk of eutrophication)	Good (low risk)	Medium (50% risk)	Bad (high risk)	Very bad (very high risk of eutrophication)
MO(%)	3.5	5	7.5	10	S1 to S9
NT (g/kg DW)	1	2	3	4	S1 to S9
PT (mg/kg DW)	400	500	600	700	S1 to S9

Water results

Figures 18 and 19 show that nitrite and nitrate are present in the waters of the stream and vary in the same way. The highest value is measured at site 5 (35.5 mg/L for nitrate and 0.57 mg/L for nitrite) and the lowest value at site 3 (0.55 mg/L for nitrate and 0.112 mg.L-1 mg/L for nitrite).

In Figure 20, we also see the presence of ammonium in the waters of the stream. Compared to nitrite and nitrate, the highest ammonium value is observed at site S3 (0.825 mg/L) and the lowest value at site S4 (0.407 mg/L).

According to Figure 21, the phosphate concentration at these sites varies between 0.063 mg/L at site 3 (S3) and 0.393 mg/L at site 4 (S4).

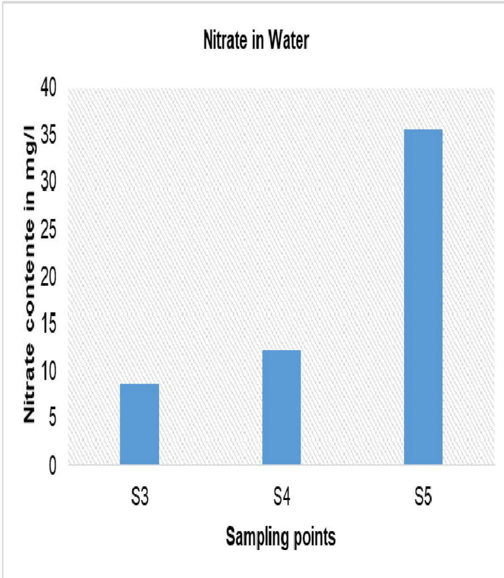

Figure 18: Nitrate concentration in water

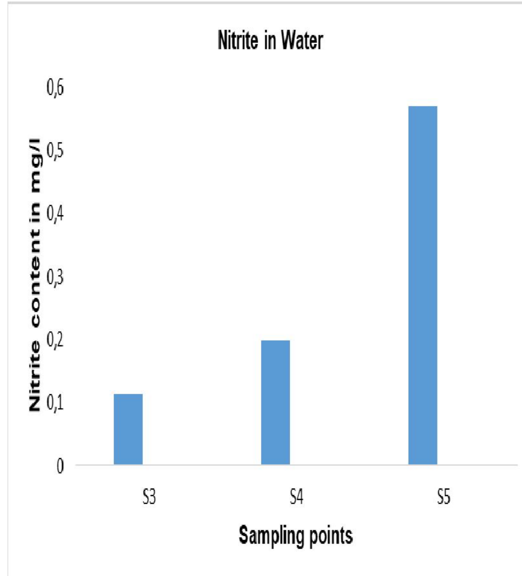

Figure 19: Nitrite concentration in water

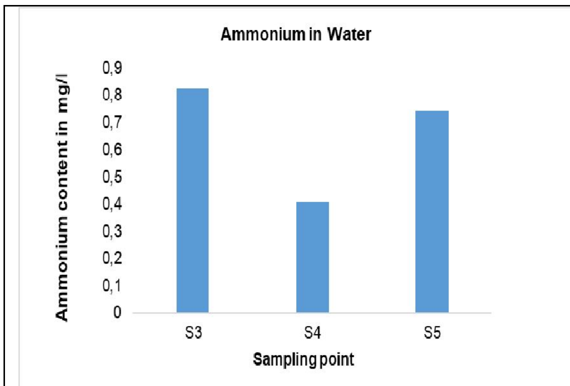

Figure 20: ammonium concentration in water

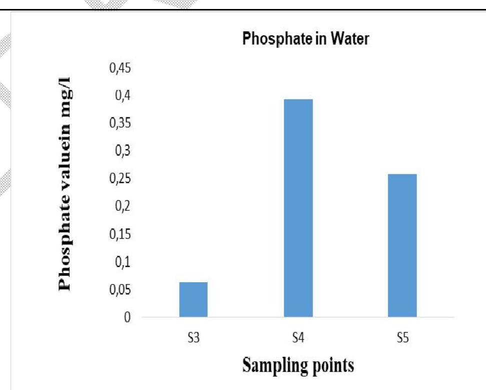

Figure 21: phosphate concentration in water

Assessment of the trophic status of the waters of the stream in contact with Lake Toho

According to Table 4, the nitrate ions found in the waters of the stream are classified in the wrong class. Similarly, phosphorus classifies 2/3 of the waters of the stream in the poor class and nitrite ions in the medium class.

Table 4: Diagnostic grid of the trophic state of stream water in contact with Lake Toho

Variables(mg.L-1)	Very good	Good	Average	Poor	Bad
Nitrate	0 0.43	0.62	1.24	1.86	S3, S4, S5

Nitrite	0	0.023	0.046	S3, S4	0.23		0.46	S5
Total Phosphorous	0	0.023	0.079		0.119	S5	0.316	S3, S4

Discussion

The condition of a soil depends on these physicochemical and chemical properties. The behaviour of the chemical substances present in the soil depends on various factors such as pH, organic matter and inorganic matter.

Analysis of the soils around Lake Toho during the dry season (May 2022) shows that the pH of the soils is 6.91 on average. When the pH is below 7 in an acidic medium, this promotes the mobility of inorganic phosphorus. On the other hand, when the pH is above 7, desorption decreases; in an alkaline medium, an increase in pH decreases the mobility of inorganic phosphorus according to Gérard [12]. The pH of the soils around Lake Toho is close to 7 and is thus slightly acidic or even neutral. This pH is within the range of different values measured in 2022 [13] in the same environment (6.25-8.3) during the rainy season, and slightly higher than the value (6.25) in 2022 [14] around the Mekrou River. The overall average pH_{KCl} value is 5.72, which is close to the values obtained by [15, 14].

The moisture content of cultivated soils around Lake Toho varies between 8% and 28%, while the maximum value in the rainy season is 38% [13]. This shows that the soils are wetter in the rainy season than in the dry season. As [16] states, there is a constant exchange of phosphates between the particles and the solution in which they are bathed. Sites S2, S4, S5 and S9 are far from the shore of the lake, which explains the decrease in moisture with increasing depth, while sites S3, S6 and S8 are more or less close to the lake, which explains the increase in moisture.

The carbon content of the soils around Lake Toho is at most 20% and the mineral content at most 35%, confirming that these soils are mineralised. Organic matter is one of the essential elements of the soil capable of forming compounds with phosphorus. Its percentage in the cultivated soils around the lake is on average 11% lower than the value determined by [17] in Lake Nokoué, which varies between 13.8 and 23.9%, with maximum values that can reach 38.22% of the dry weight of the sediment. The authors find an average value of around 24.62% in the sediments of the Okpara reservoir [18]. Others find 16 to 28% organic matter in the sediments of Porto-Novo lagoon [19]. So we can remember that the soils are then less rich in organic matter than the reserves in which the water that passes through them is stored. The percentage of organic matter in the soil samples is higher than the value [20], which states that the percentage of organic matter is normal when it is 2 to 4%. According to the same author, soil that exceeds a proportion of 4% is considered humus. The collected samples are therefore considered humus.

The total phosphorus content determined in our samples varies from 1335.5764 µg/g at site (S9) at 60 cm to 18644.95 µg/g at site (S2) at 30 Cm. These concentrations are all above the low environmental risk threshold for phosphorus (500 mg/kg P_2O_5) established [21]. This means that the soils around Lake Toho in southern Benin are polluted with phosphorus. These measured values are lower than the values measured [13] at the end of the rainy season in the centre. This difference is due to the period and mobility of phosphorus, which can pass from the solid phase of the soil to the liquid phase of the soil and infiltrate or run off into watercourses and water bodies. However, they are higher than the levels found in the soils of the Mekrou River in northern Benin [14; 22]. We note that the total phosphorus concentration in the soil generally increases the closer one gets to Lake Toho. The highest value is measured at site S2 at a depth of 30 cm in a field near the lake. This can be explained by the use of chemical fertilisers, because [23] the surface application of fertilisers that are not buried leads to accumulation in the upper soil layer.

Fractionation of phosphorus in soil samples showed that all five phosphorus fractions are actually present in the soil around Lake Toho. The residual fraction occupies the first position in the soil in all horizons. This result is consistent with that of 2022 in the same environment [13] and in cultivated soils around the Mekrou River [14]. After the residual fraction, the phosphorus fraction bound to organic material predominates. This predominance is due to the high organic matter content in the surface horizon of the soil. The assimilable P-labile fraction represents the lowest fraction in all layers (813.65-448.21-451.23 µg/g). In the H30 horizon, the labile fraction predominates compared to the other layers of the soil, which is due to the high phosphorus content and moisture responsible for the dissolution of phosphorus into orthophosphates.

The assessment of soil quality according to the Ifremer grid shows that these soils pose a risk of eutrophication. The phosphate ions (HPO42-) found in the surface waters originate mainly from wastewater discharges and agricultural application [24]. Physico-chemical analyses of agricultural effluents discharged into Lake Toho show that the water is moderately polluted by nitrogenous elements such as nitrite and ammonium, ranging respectively from 0.112 mg/L at site 3 (S3) and 0.57 mg/L at site 5 (S5) and 0.407mg/L at site 4 (S4) and 0.825mg/L at site 3 (S3), all of which exceed the WFD recommended limit of 0.1 mg/L. For nitrate, the values vary between 8.56 mg/L at site (S1) and 35.513mg/L at site (S3) and for phosphate between 0.063 mg/L at site (S1) and 0.393 mg/L at site (S2). The results of the trophic status diagnosis place these water bodies in the wrong class. This leads to a change in water quality and reduces their potential forcertain uses. However, it has been shown that the presence of a high concentration of nutrients (nitrogen and phosphorus in particular) is mainly responsible for the massive proliferation of phytoplankton (algae and cyanobacteria) [3]. In addition, cyanophyceae secrete toxic substances that affect both zooplankton and higher organisms. Recreational and fish-farming waters are also severely depleted. The very low values of the N/P ratio confirm the table of Thomann and Mueller[25]. According to the authors for small lakes, when the N/P ratio <<10, nitrogen proves to be a limiting factor in the proliferation of aquatic plants with a call for the intensification of the activities of cyanobacteria. Because these authors summarize the usual values of the N/P ratio of several aquatic environments and show that phosphorus is the most often limiting element, especially in natural areas. When nitrogen becomes the limiting element, certain algae (cyanobacteria) compensate for this deficiency by fixing the nitrogen contained in the atmosphere. The proliferation of aquatic plants, especially macrophytes, is at the origin of the formation of a screen at the interface which constitutes an obstacle to the oxygenation of the environment. Moreover, their decomposition leads to an increase in the quantity of organic matter in the medium, the degradation of which consumes oxygen and makes the medium reduce. The production of sulfide and nitrite (toxic), through the reduction of sulfates and nitrates, inhibits the development of other primary producers and highly sensitive fish. This can cause an imbalance in the trophic chain (production/consumption) of a body of water and lead to significant adverse ecological consequences. The ecological impact of toxin-producing cyanobacteria is little known. Hepatotoxins, which have the particularity of inhibiting certain protein phosphatases, are potentially capable of affecting a range of organisms in nature. Sometimes cyanobacteria are considered responsible for fish and bird kills. However, in many cases, the direct relationship between mortality and the presence of toxins is difficult to demonstrate. Fish death is more often associated with anoxia caused by bacteria that use compounds from the proliferation of aquatic plants. Fish can be affected by clogging of bronchitis by phytoplankton; which then reduces the efficiency of water filtration at the level of the gills.

This observation is in agreement with the results of the assessment of the risks of soil contamination which classifies these soils in the class of soils at risk of eutrophication. Despite some losses associated with water runoff, the observation is that cultivated soils are enriched in phosphorus, which leads to increased risks of transfers to aquatic ecosystems.

4. CONCLUSION

The soils cultivated around Lake Toho are subject to strong anthropogenic pressure due to the use of fertilizers in agriculture. The results show that the soils cultivated around Lake Toho are weakly acidic or even neutral with an acidic pH_{KCl} subjecting the mobility of the bioavailable forms of phosphorus. This mobility could be increased with the proliferation of cyanobacteria because the N/P ratio is much lower than 10, which draw abundant atmospheric nitrogen by consuming phosphorus. There are high levels of organic matter in the surface layer of the soil, a high content of phosphorus, nitrogen and potassium in cultivated soils. The fractionation of phosphorus in the soils taken around the lake shows that the labile fraction is the lowest. It is important to point out that the residual fraction takes precedence over the other fractions in some sites. A predominance in the organic fraction on the upper soil layer is also noted with the exception of sites located outside crop fields.

Indeed, the high content of phosphorus at the surface horizon of the soil leads to the conclusion that the contamination of the soil by phosphorus, nitrogen and potassium around Lake Toho is an anthropogenic pollution due to the use of chemical fertilizers and pesticides in the 'agriculture. These elements have appeared in the waters of streams flowing into the lake. The phosphorus accumulated in the soils during the period of over-fertilization makes these soils potential sources of continuous pollution.

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