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Fractionation, bioavailability and mobility of phosphorus in agricultural soils of the Mékrou River watershed

Désiré PANEWAI AYOLA[1,2], Waris Kéwouyèmi CHOUTI[2], Comlan Achille DEDJIHO[*2,3], Paulin AMLAN[2], Lyde TOMETIN[1] and Nafiou E. CHITOU[2]
[1]Laboratoire Kaba de Recherche en Chimie et Applications (LaKReCA), ENS- Natitingou, Bénin
[2]Laboratoire de Chimie Inorganique et de l'Environnement (LaCIE), Faculté des Sciences et Techniques (FAST), Université d'Abomey-Calavi, 01 BP 526 Cotonou, Bénin
[3]Laboratoire d'Hydrologie Appliquée (LHA), Institut National de l'Eau, Université d'Abomey-Calavi, 01 BP 526 Cotonou, Bénin
dedjiho1@yahoo.fr

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Abstract

The object of this study is to assess the phosphorus content, its different forms, its mobility and its bioavailability in the soils of the Mékrou River watershed. The measurement of pH, the determination of total phosphorus and its different fractions are the main axis of our work. As a result, the soils of the Mékrou basin are generally acidic with an average water pH of 6.46. These soils are rich in phosphorus with a general average concentration of 4155.58µg/g (i.e., 1813.55µg/g in P_2O_5): these soils are polluted (1813.55µg/g>500µg/g) (Dyer, 1894). Total phosphorus concentrations increase (from 4027.83µg/g in December 2021 to 4283.34µg/g in February 2022) as the dry season progresses and when approaching the Mékrou River (from 3957.90µg/g, 10m soils, at 4353.26µg/g, 5m soils). Fractionation presents soil phosphorus in six forms: Labil-P (0.35% Total-P), Fe-P (1.64% Total-P), Al-P (0.21% Ptotal), Ca-P (0.19% of Total-P), Org-P (38.94% of Total-P) and residual-P (58.64%). The assimilable phosphorus (Labil-P) is very low and varies slightly depending on the pH of the soil; it is weakly mobile and very poorly bioavailable.

Keywords: Mékrou River, polluted soils, mobility, bioavailability, fractionation.

Introduction

Nutrition is one of the basic human needs. To satisfy this need, he uses agricultural products from fertilized cultivation soils. In Atacora in northern Benin, the 2KP zone (grouping the municipalities of Kérou, Kouandé and Péhunco) and crossed by the Mékrou River represents the agropastoral production pole[1]. The use of agricultural inputs, in particular NPK fertilizers (36% phosphorus) and/or organic fertilizers to fertilize the soil and then the decomposition of plants, could increase the concentrations of some elements including Phosphorus (P) in the soil. This can cause pollution of the soils of the watershed and that of the waters of the Mekrou River by diffuse process. Phosphorus stimulates root growth and the smooth running of flowering and fruiting processes, but in excess, it can cause an environmental problem, such as eutrophication. Eutrophication reduces water quality and influences the life of aquatic fauna. This phenomenon is also linked to many physico-chemical factors such as temperature, pH, dissolved oxygen content, and solar radiation[2]. Phosphorus exists in different forms in the soil but only the orthophosphates present in small quantities in the soil are available and therefore assimilable by plants. The strong affinity of phosphorus with soil particles has long led the scientific community to consider this element as completely immobile in the soil[3]. But in reality, phosphorus can be mobile and its movements take place by runoff, erosion, leaching or leaching[4]. To determine the different forms of soil phosphorus, fractionation is used, which is a speciation method. The speciation of phosphorus in a soil corresponds to its distribution between the different chemical forms present in this soil[5]. Doing phosphorus fractionation therefore involves measuring phosphorus in different operationally defined pools, depending on the method used[6]. There are therefore several splitting methods. By comparative study, it appears that the method[7], for example, makes it possible to extract the organic fraction more efficiently compared to the[8,9].

Several studies[10-12] have focused on determining the amounts of the different phosphorus fractions in the waters and sediments of the basins of Benin to develop an explanation for the eutrophication phenomenon. But the dosage of phosphorus in Beninese soils is limited to the determination of total phosphorus and/or assimilable phosphorus[13-15].

It is therefore necessary to carry out the fractionation of phosphorus to determine its different forms in the agricultural soils of the watershed of the Mekrou River.

This is what justifies the importance of this work, which aims to assess the environmental risk associated with phosphorus and then determine its different fractions, its bioavailability and its mobility in this region.

Materials and methods

Presentation of the study environment: The 2KP area comprising the municipalities of Kérou, Kouandé and Péhunco is located in the eastern part of the Atacora department in northern Benin. It is crossed by the Mékrou River (480km) and occupies nearly half of its watershed (5034km² out of 10500km²). The soils of this area are ferralitic and ferruginous.

Taking samples: Figure-1 represents the sampling map in the study area.

As part of this study, two sampling campaigns were conducted in the dry season. The first in December 2021 and the second in February 2022. During each campaign, we took water samples from eight different sites (S1 to S8). At each water sampling point we took a soil sample 5m from the river and another 10m. Thus, for each campaign, we took 8 water samples and 16 soil samples, for a total of 48 samples for the two campaigns. This makes it possible to evaluate the relationship between the pollution of the soils of the basin and that of the waters in the vicinity, then the variability of the contents of total phosphorus and its different fractions in time and space. The soil samples taken are placed in polyethylene bags. All samples are kept at a temperature below 10°C in coolers and transported to the laboratory.

Analysis of samples: In the field, each water sample was subject to in situ measurement of field parameters such as pH and temperature by a multi-parameter analyzer and then the dissolved oxygen content by an oximeter.

As for the soil samples, they were analyzed in the laboratory by measuring water pH and pHKCl by a pH-meter then by dosing total phosphorus and its various fractions (at 708nm) using a UV-1700 spectrophotometer after agitation and centrifugation. AFNOR standards are respected[16].

Data analysis: The data from the laboratory analysis and those measured in the field were subjected to a describable statistical analysis. The Microsoft Office Excel tool was used for the construction of the histograms. The curves were obtained using MATLAB programming.

Results and discussion

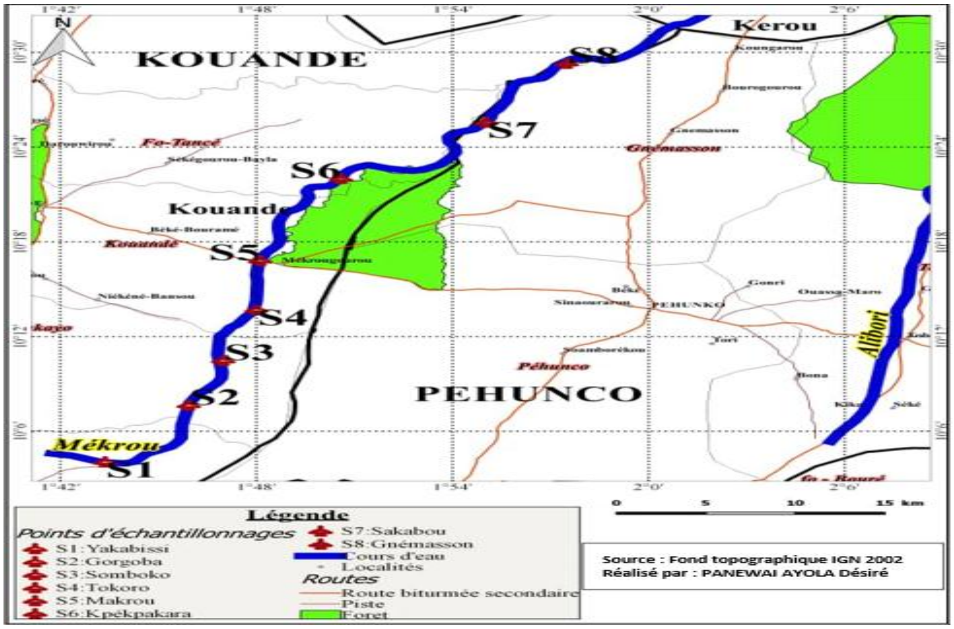
Variability of physico-chemical parameters of water samples: The water pH at each site in December remained at or below that of February. In December the pH varies from 5.84 (at point S4) to 6.54 (at point S2) while in February it varies from 5.9 (at point S7) to 7.5 (at point S5).

The water temperature varies in December from 19.3°C (at point S6) to 24.3°C (at point S4) while in February it varies from 16.3 (at point S2) to 24.5° C (at point S5).

As for dissolved oxygen levels, they vary from 0.42mg/L (at point S6) to 2.79mg/L (at point S8) in February.

Variability of physico-chemical parameters of soils: For both campaigns, each sample presented a KCl pH lower than its water pH. This confirms that the water pH does not make it possible to evaluate the acidity reserve of a soil.

Determination of total phosphorus and its different fractions: Variability of total phosphorus: Figure-4 and Table-1 present the variability of the phosphorus contents and the average phosphorus values respectively.



Source : Fond topographique IGN 2002
Réalisé par : PANEWAI AYOLA Désiré

Figure-1: Sampling Map.

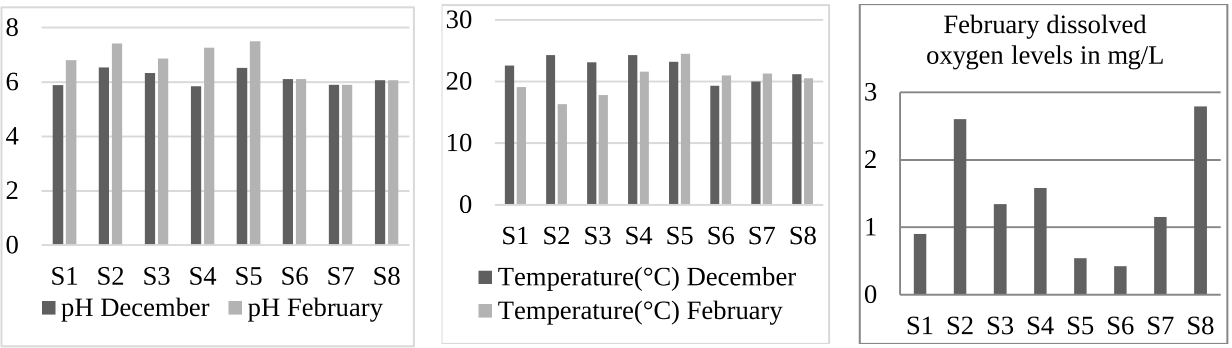


Figure-2: Variability of physico-chemical water parameters.

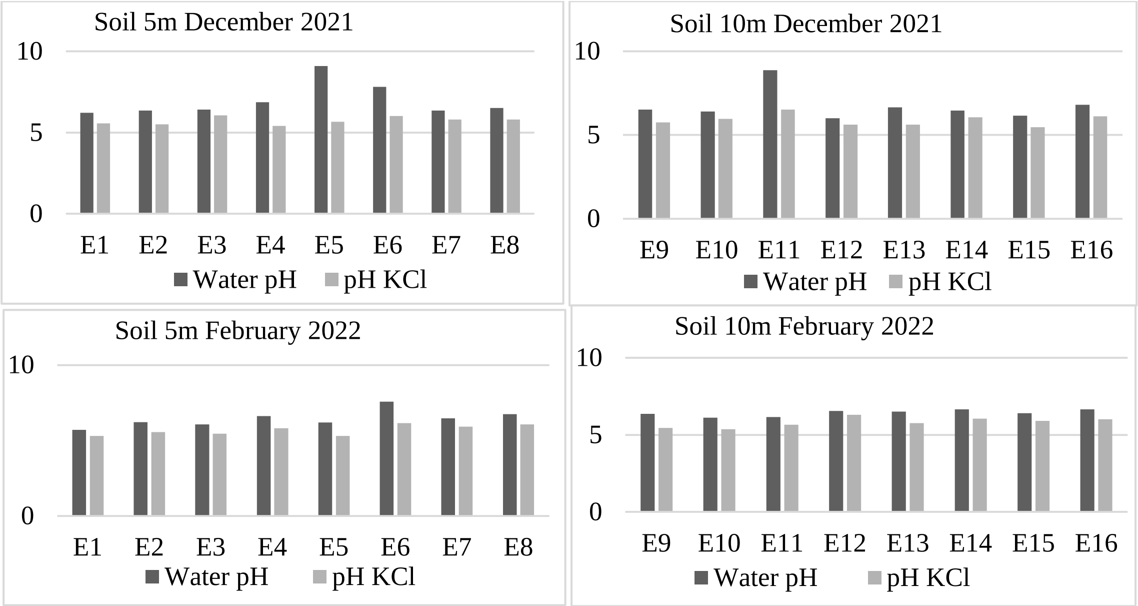


Figure-3: Variability of physico-chemical parameters of soils.

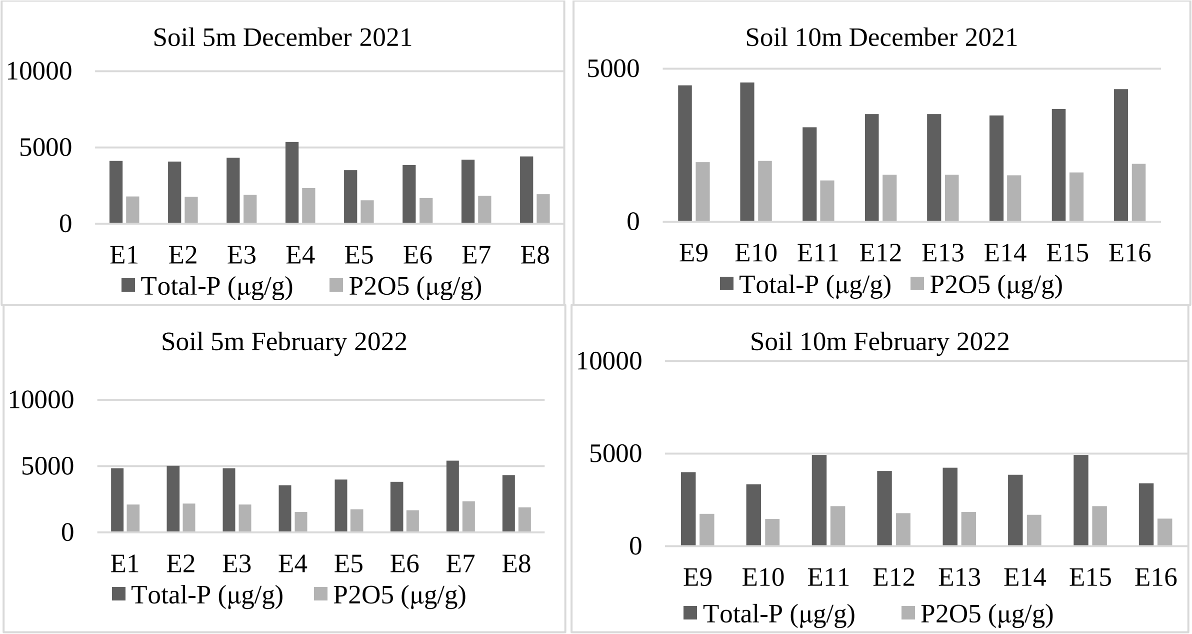


Figure-4: Variability of total phosphorus and P_2O_5 content of soils.

Total phosphorus concentrations increase as the dry season progresses. An average value of 4027.83µg/g is recorded in December 2021 and an average value of 4283.34µg/g in February 2022. This increase is explained by the fact that in the rainy season the concentrations of compounds in the soil are diluted by precipitation. It is also noted that the phosphorus concentrations in the soil generally increase when approaching the river. An average value of 3957.908µg/g is recorded for 10m soils and an average value of 4353.269µg/g for 5m soils. This is explained by the phenomenon of drainage which transports the elements of the soil to the water courses.

The fractionation made it possible to obtain for each of the 32 soil samples analyzed six phosphorus fractions (Labil-P, Fe-P, Al-P, Ca-P, Org-P, Residual-P) whose average values are presented in Figure-9.

Table 1: Average Soil Phosphorus Values.

Average	Soil 5m December 2021	Soil 10m December 2022	Soil December 2021	Soil 5m February 2022	Soil 10m February 2022	Soil February 2022
Total P (µg/g)	4232.24	3823.43	4027.83	4474.29	4092.38	4283.34
P_2O_5 (µg/g)	1847.00	1668.59	1757.79	1952.63	1785.96	1869.30

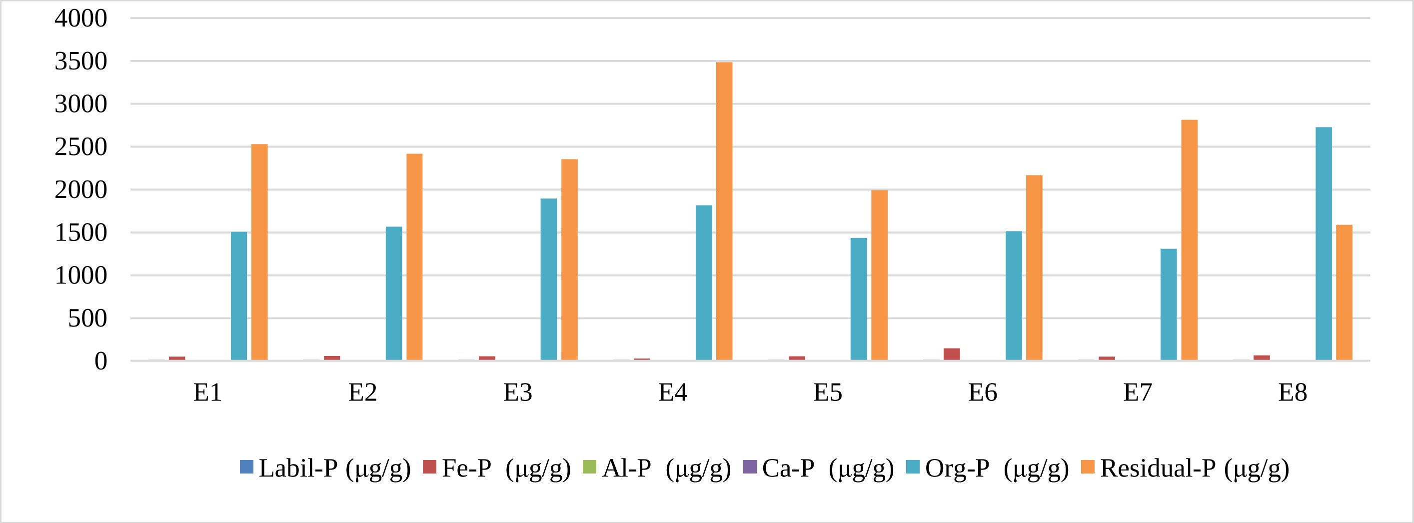


Figure-5: Contents of different phosphorus fractions in soils 5m from December.

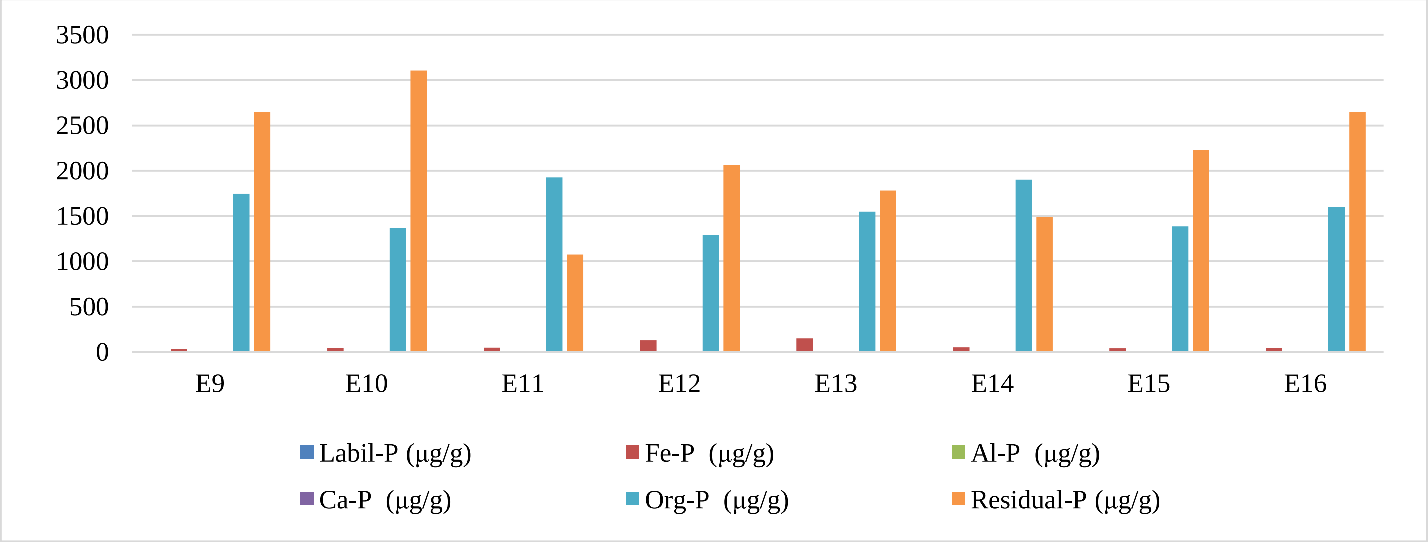


Figure-6: Contents of different phosphorus fractions in soils 10m from December.

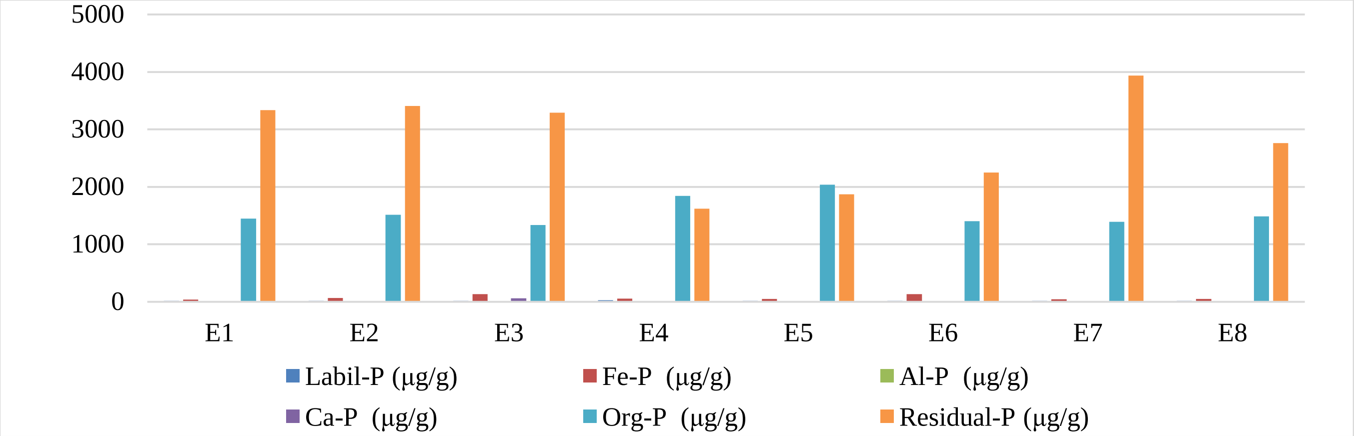


Figure-7: Contents of different fractions of phosphorus in soils 5m from February.

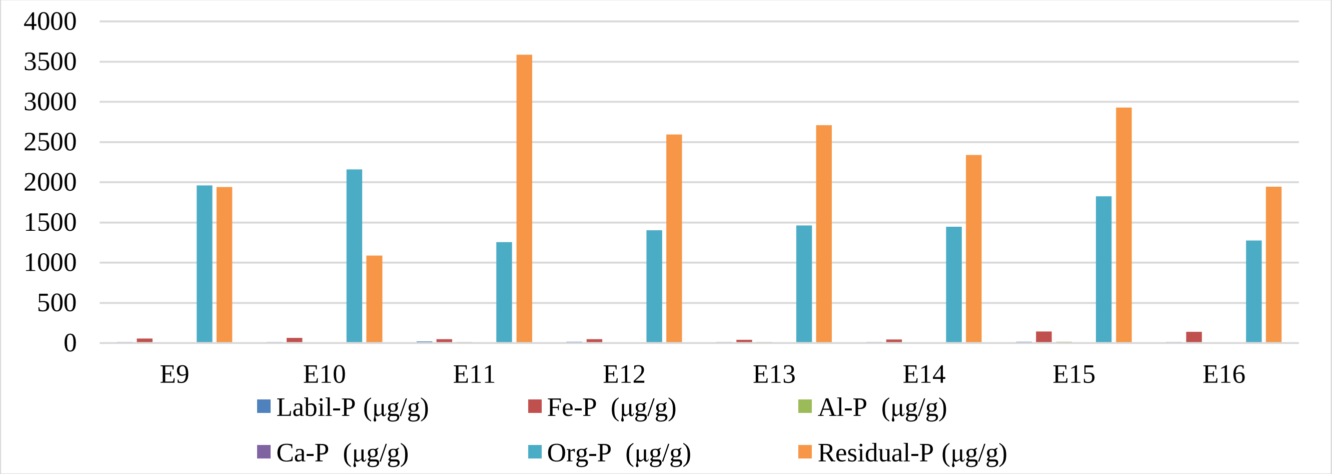


Figure-8: Contents of different fractions of phosphorus in soils 10m from February.

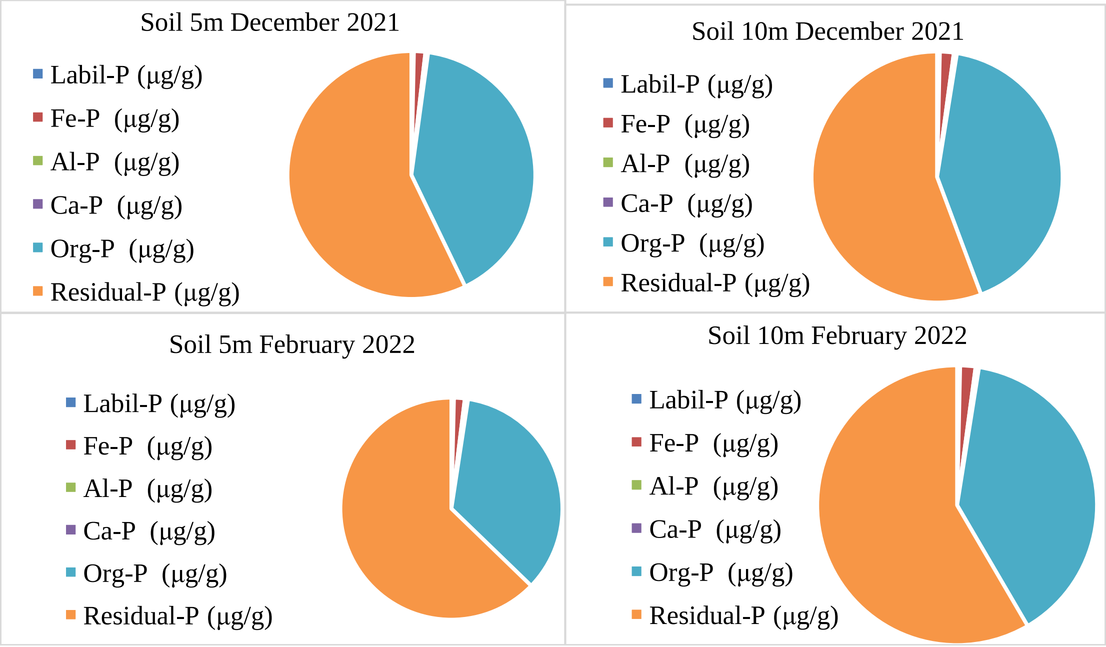


Figure-9: Average values of different fractions of phosphorus in soils.

In general, the different fractions obtained are presented from the largest to the smallest according to: (residual-P)>(Org-P)>(Fe-P)>(Labil-P)> (Al- P)>(Ca-P).

Starting from the diagram Total-P = Organic-P + Inorganic-P and Inorganic-P = Labil-P + particulate P + residual-P, we conclude that the mineral fraction is the most important. The relatively high organic fraction can be justified by the presence of cattle dung and other debris (the study area having a rich livestock especially in cattle and goats), the decomposition of organic plant matter. The significant inorganic fraction can be justified through two sources: mineral fertilizer inputs (the study area being an agricultural production area) and the degradation of the source rock. The particulate fraction and the labile fraction each represent a small proportion of the inorganic fraction. So, the high rate of inorganic phosphorus is due to the residual fraction, a fraction difficult to mobilize. For particulate phosphorus (Fe-P + Al-P + Ca-P), the fraction bound to iron hydroxides (Fe-P) represents 80.17%. This can be explained by the fact that the soils of the 2KP are ferralitic and ferruginous[1].

Evaluation of bioavailability: To evaluate the bioavailability, we expressed the ratio of the concentration of assimilable phosphorus to the concentration of total phosphorus as a percentage. This availability is on average 0.34% in December and 0.36% in February.

Table-2: Bioavailability of P from 5m soils from December 2021.

Sample	E1	E2	E3	E4	E5	E6	E7	E8
Labil-P (µg/g)	13.39	13.93	14.46	12.58	12.72	14.06	14.33	14.60
Total P concentration in µg/g	4113.90	4070.86	4329.06	5361.84	3511.44	3855.70	4199.96	4415.12
Bioavailability in %	0.32	0.34	0.33	0.23	0.36	0.36	0.34	0.33

Table-3: Bioavailability of P from soils 10m from December 2021.

Sample	E9	E10	E11	E12	E13	E14	E15	E16
Labil-P (µg/g)	14.46	12.85	13.52	13.79	14.60	13.79	12.04	14.46
Total P concentration in µg/g	4458.16	4544.22	3081.12	3511.44	3511.44	3468.41	3683.57	4329.06
Bioavailability in %	0.32	0.28	0.43	0.39	0.41	0.39	0.32	0.33

Table-4: Bioavailability of P from 5m soils from February 2022.

Sample	E1	E2	E3	E4	E5	E6	E7	E8
Labil-P (µg/g)	14.33	14.33	18.10	27.24	16.35	13.79	14.60	14.06
Total P concentration in µg/g	4845.45	5017.58	4845.45	3554.47	3984.80	3812.67	5404.87	4329.06
Bioavailability in %	0.29	0.28	0.37	0.76	0.41	0.36	0.27	0.32

Table-5: Bioavailability of P from soils 10m from February 2022.

Sample	E9	E10	E11	E12	E13	E14	E15	E16
Labil-P (µg/g)	13.12	12.99	20.11	14.06	12.72	13.79	14.06	13.39
Total P concentration in µg/g	3984.80	3339.31	4931.51	4070.86	4242.99	3855.70	4931.51	3382.34
Bioavailability in %	0.32	0.38	0.40	0.34	0.29	0.35	0.28	0.39

Evaluation of phosphorus mobility: Figures-10 and 11 show variations in P-labile as a function of the pH of the soils analyzed. It is observed that the P-labile varies according to the pH of the soil. For alkaline soils (pH≥7.4) the Labil-P concentration generally decreases as the pH increases. But for acid soils (pH≤6.5) we have curves with a generally increasing trend with sudden decreases in places. The highest P-labile concentrations are observed in the neutral soil range (6.6≤pH≥7.3). The variation of assailable phosphorus as a function of pH looks like a bell[5]. Also, Table-9 presents average concentrations of P-labile which increase when approaching the river. This is explained by the fact that when approaching the river, the hydrology of the plot may change. Because the plots have slopes in the vicinity of the water courses, which promotes the transport of chemical compounds to the water course. The mobility of phosphorus therefore also depends on the hydrology of the plot.

Discussion: The different results obtained reveal a variability in the values of the measurements carried out in time and space. In December, only the waters of sites S2 and S6 presented an optimal pH (6.5-8.5) for the life and reproduction of fish[17]. During the month of December, the life and reproduction of fish are threatened in the Mekrou River. But in February all the waters had pH values between 6.5 and 8.5. So, in February the Mékrou River is an optimal zone for the life and reproduction of fish in terms of pH. The measurement of soil pH allowed us to obtain an average global water pH of 6.63 and an average global pHKCl of 5.68. The pHKCl always remained lower than the water pH for each sample. This is due to the fact that the actual acidity takes into account only the hydronium ions released into solution by the soil, while the potential acidity (K^+) also takes into account the exchangeable hydronium ions adsorbed by the organic matter contained in the soil[18]. These soils are generally acidic. An acidity favored by the ferralitic and ferruginous nature of these soils. Because ferralitic and ferruginous soils are more acidic than eutrophic brown soils[19]. Also, the use of NPK fertilizers (28% N) for the fertilization of these soils contributes to this acidity. Ammoniacal fertilizers lead to acidification of plots[20]. The pH KCl measurement therefore allowed us to determine the acidity reserve of these soils. This reserve of acidity leads to a drop in the pH of the waters in December. They become acidic and therefore unsuitable for the balance of the aquatic ecosystem. These two values are close to those found (water pH = 6.30; pHKCl=5.72) as mean values of pH eau and pHKCl of soils in northern Benin[19].

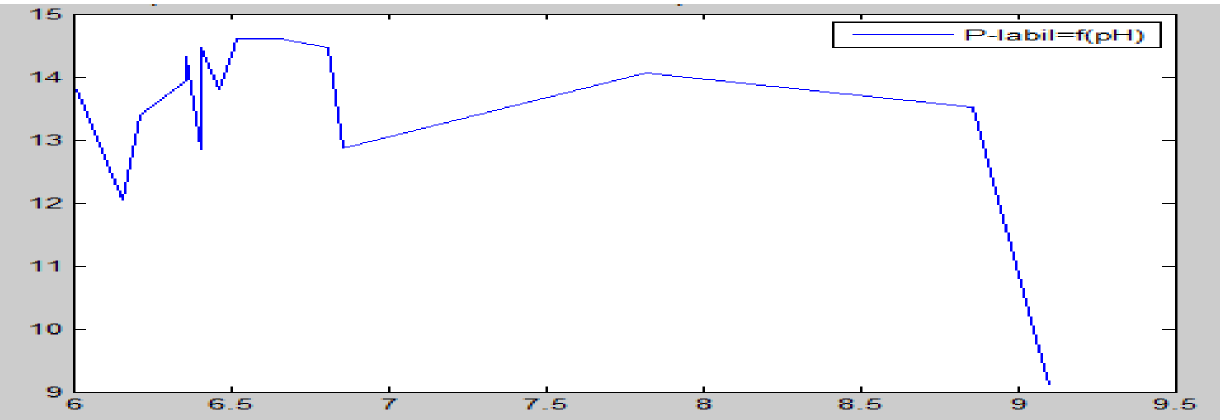


Figure-10: Representation of variations in P-labile as a function of soil pH in December 2021.

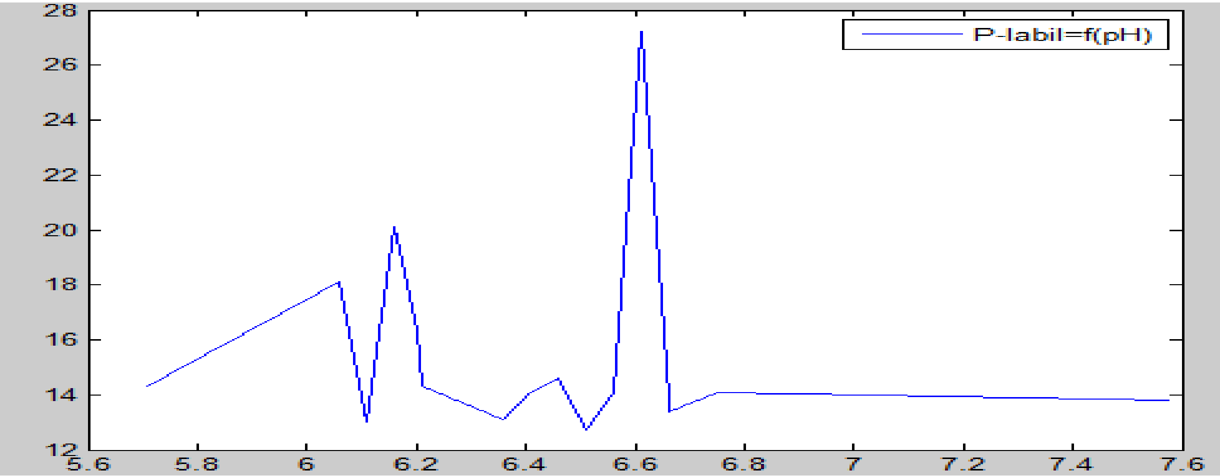


Figure-11: Representation of variations in P-labile as a function of soil pH in February 2022.

The determination of the total phosphorus of our samples revealed concentrations which vary between 3339.31µg/g (E10) and 5404.87µg/g (E7) with an average value of 4155.58µg/g. These concentrations are all above the low environmental risk threshold for phosphorus (500mg/kg of P_2O_5) established by Dyer, B.[21]. This means that the soils in this area are subject to phosphorus pollution favored by the use of NPK fertilizers (36%P). These values are higher than those found by Anato, I.F.[15] (concentrations which vary between 1005.98mg/kg and 3496.00mg/kg with an average of 2286.34mg/kg) who worked on soils in the same area. This difference can be explained by the phenomenon of dilution because[15] work was carried out in the month of September, a month of high rainfall (in this area intense precipitation is observed between July and September). The soil phosphorus concentrations are low in this period in the study area. This confirms the difference between our results obtained in December 2021 and those of February 2022. We observed an increase in the concentration of phosphorus when the dry season evolves (average value of 4027.83µg/g in December 2021 and an average value of 4283,34µg/g in February 2022). Also, we see that the total phosphorus concentrations in the soil generally increase when approaching the river. An average value of 3957.90µg/g is recorded for 10m soils and an average value of 4353.26µg/g for 5m soils. This can be explained by the phenomenon of drainage. In the vicinity of the Mekrou River, the soils have slopes. This facilitates the transport of compounds which causes phosphorus concentrations to increase as one approaches the river. Also, the presence of vegetation cover along the river can increase the amount of organic phosphorus in the soil and consequently an increase in the concentration of total phosphorus in the soil.

The fractionation of phosphorus in the soil samples, by sequential extractions according to literature[7,22] allowed us to know the different forms of phosphorus present in the soils of the study area. We note as from literature[10,12] that effective presence of the six fractions: i. The labil-P assimilable fraction with an average concentration of 14.58µg/g, i.e., 0.35% of the average value of total phosphorus; ii. The fraction bound to iron hydroxides (Fe-P) with an average content of 68.77µg/g or 1.64% of the average value of total phosphorus; iii. The fraction linked to aluminum hydrides and hydroxides (Al-P) with an average concentration of 8.77µg/g, i.e., 0.21% of the average value of phosphorus; iv. The fraction bound to carbonates (Ca-P) with an average value of 8.15µg/g, i.e., a percentage of 0.19%. v. The fraction linked to organic matter (P-org) with a concentration of 1618.55µg/g, i.e., 38.94% of total phosphorus; vi. And the residual fraction (Res-P), the most important with an average concentration of 2437.10 or 58.64% of the average value of total phosphorus.

It results that the inorganic form of phosphorus is the majority one (dominated by the residual P 58.64%). Also, we find[23] that the particulate inorganic phosphorus is dominated by the fraction (Fe-P) bound to iron and magnesium hydroxides (80.25% of the PIP). The quantity of labil-P is close to that (12.8µg/g) of the soils of Sinendé (Northern Benin)[14]. Although inorganic phosphorus is the dominant form of phosphorus in our samples, we find that the particulate inorganic fraction (PIP) is low (28.44µg/g or 0.68% of total phosphorus). This is explained by the presence of Apatitic Inorganic Phosphorus and Non-Apatitic Inorganic Phosphorus. In other words, they result from the phosphorus attached to the surface of the particles or that combined with crystalline compounds. Note that the different fractions may vary if another protocol is used because the relative shares of the different fractions vary according to the protocol used[24].

Conclusion

From the various analyses, it follows that the waters of the Mekrou River have pH values that are not favorable to fish in December. The soils of the Mekrou watershed are acidic and polluted with phosphorus. The phosphorus of these soils has six forms including assimilable phosphorus which represents 0.35% of Ptotal. Soil phosphorus is weakly mobile and not readily available.

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