



Fractionation and biodisponibility of phosphorus in the sediments of the river Mékrou

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Abstract

The watershed of the Mekrou River is a large cotton production area where there is an overuse of agricultural inputs. This exaggerated use of agricultural fertilizers is likely to lead to phosphorus pollution of this river. The objective of this research work is to study the fractionation of phosphorus in the sediments of the Mekrou River to assess its bioavailability. For this, samples were taken from eight sites along the Mekrou River in two campaigns. The physicochemical parameters as well as the total phosphorus content and its fractionation were determined. The results obtained reveal a high rate of total phosphorus in the sediments, which amounts to 3465.73 µg/g of sediment on average for the two campaigns, indicating phosphorus pollution. Similarly, the total phosphorus content increases from 3016.58µg/g in December 2021 to 3914.88µg/g in February 2022. The fractionation results are as follows: labile P (0.41% of total P), Fe-P (1.68% of Ptotal), Al-P (0.23% of Ptotal), Ca-P (0.20% of Ptotal) Porg (15.43% of Ptotal) and P-residual (82.04% of Ptotal). The directly assimilable labile fraction is low, but the relatively high proportion of the organic fraction constitutes a danger for the watercourse because under certain optimal conditions, it can end up in the water column through the phenomenon of salting out and contribute to the eutrophication. To effectively assess the pollution rate of this river, it is desirable to study the effect of pH on the release of phosphorus and also to conduct the same study on the other pollutants in this river. The same studies could be carried out on other rivers in Benin whose watersheds are agricultural production areas.

Keywords: Mekrou River, bioavailability, fractionation, phosphorus pollution, salting out, eutrophication.

Introduction

Phosphorus was recognized like nutriment the most critical limiting the primary productivity of the lakes on long scales of time^{1,2}. It was shown that the sediments of the lakes can act like an internal source of phosphorus for overlying water even after the complete control of the specific external sources and not ponctuelles³⁻⁶. The stability and the chemical shape of particulate phosphorus in the sediments, in partnership with the environmental conditions, were indicated as the principal factors of control which affect the release of phosphorus of sediments^{5,7,8}. The long-term behavior of phosphorus related to the sediments in the promotion of the eutrophication of fresh water can be evaluated more effectively on the basis of fraction various of phosphorus, instead of the total phosphorus content (TP). According to former studies', phosphorus in the sediments is generally divided into inorganic phosphorus (Pi) and organic phosphorus (Po) by procedures of extraction séquentielle^{2,9-11}.

Thus, it is necessary to make related studies which include/understand the distribution of the various fractions of phosphorus in the sediments, and to clarify the mechanism of rejection of the phosphorated fractions of the various polluted sediments⁸.

The phenomenon of massive proliferation of algae has developed for several years, parallel to the extension of the use of artificial fertilizers, of the intensive breeding in agriculture, like with the increase in the industrial and urban wastes. This phenomenon is also related to many physicochemical factors such as: the temperature, pH, dissolved oxygen content, the solar radiation. It is however shown that these massive proliferations of the phytoplankton (algae and cyanobacteria) are mainly ascribable with the presence in high concentrations of nutriments (nitrogenizes and phosphorus in particular)¹².

Agriculture knew a strong growth and intensification in order to be able to satisfy a high industrial request. In the majority of the countries of West Africa (Mali, Niger, Benin, Côte.d'ivoire, Nigeria, etc), the chemicals are used in the form of manure and of pesticides in order to increase the productivity. Studies indicate that husbandries led to the contamination of not very deep subsoil waters and of surface water by heavy nitrates, phosphates, hydrocarbons, metals and fluorites¹³⁻¹⁵.

The communes of Kérou, Pèhounco and Kouandé are the great zones of cotton production or the use of the agricultural intrants is high producing in considerable quantity of the phosphorus

drained towards the Mékrou river which is likely to be polluted by phosphorus. It is what justified our study on this river.

This research task aims at evaluating the biodisponibility of phosphorus in the sediments of the Mékrou river in the North of the Benin one. Specifically it will be about to identify the phosphorus proportion in the various samples, to make the speciation of phosphorus in the taken samples and to evaluate the biodisponibility of phosphorus on the studied sites.

Thus, our work aims at the study of the fractionation and the biodisponibility of phosphorus in the sediments of the Mékrou river.

Materials and Methods

Sampling campaigns: In accordance with the established calendar, the investigations into the ground and the first countryside were carried out in December 2021 which corresponds at the end of the rain season and to the period of harvests. The second countryside was carried out in February 2022. This countryside enabled us to know the quality of water and sediments before the cultures and during the dry season.

Test sample selection of water and sediments: Eight (08) intake points of the sediments in the Mékrou river were selected by taking account of the position of the fields of culture compared to this river, of the various anthropic activities and the uses of the water of the river. It is the same for the samples for water.

On each taken sample, is marked following information: i. identity of the sampler; ii. date and hour of taking away; iii. locality of taking away; iv. number of the sample.

Then these samples are conveyed in a refrigerator at the laboratory in order to carry out the various analyses.

Methods: Preparation of the samples of sediment for analysis: The samples were dried with the ambient air at the laboratory, without inducing significant modification their characteristics¹⁶. The Drying of the sediments at high temperature (100 C) armature of the modifications of the sample and is not consequently adapted for the study.

Within the framework of this study, the sediments are filtered to 2 mm, as recommends it standard AFNOR of the grounds X31-101¹⁷.

For more the share of the chemical physico analyses, standards AFNOR on the Quality of the grounds were used. This choice was justified by the similarities of physicochemical composition and characterization between the grounds and the sediments.

Methods of analyses: Characterization of the sediments: Measure pH_{water} and pH_{KCl} : The pH of the sediment is an

essential data because the existence of a mineral phase, its speciation and its toxicity are as many parameters related to the pH of the medium.

The measurement of the pH is generally done in an aqueous suspension. The report/ratio of mass of sediment to the volume of water varies according to the methods or the texture of the medium. The ratio generally employed is 1/2.5¹⁸.

The values of pH obtained by this method of measurement are regarded as closest to the medium considered. They express real acidity and take into account the ions H_3O^+ free in the liquid phase.

This measurement is determined by standard NF X31-103. The principle of the method is the setting in ionic balance of certain masses of solids with a given volume of demineralized water. The ratio of the mass of sediment to the volume of water being fixed at 1/2.5.

Procedure: The samples (10g) are prepared for analysis in a bécher, one adds to its 25ml distilled water, one agitates then with a magnetic stirrer during 60 min in a part whose ambient temperature is of 20 ± 2 C. That makes it possible to put in suspension the totality of the sample and to thus obtain a balance between the solid phase and that aqueous. The suspension is then left at rest 2 hours safe from the air then one measures the pH of the suspension.

To measure the pH_{KCl} , the same protocol is respected with the difference that one replaces here the 25ml of water distilled by the same volume of potassium a molar chloride solution (KCl).

Determination of total phosphorus and its fractionation: The content phosphorus is determined by mineralisation with the potassium persulphate of acid medium (H_2SO_4) at $120^\circ C$ during 2 hours¹⁹. Phosphorus is proportioned according to the same method as in water (by spectrophotometry). The evaluation of total phosphorus stock constitutes a very good approach to study the degree and the extent of the contamination of the sediments. However, in the majority of the cases, this type of analysis gives only little information on the mobility of this element in the sediments like on its biodisponibility.

With this intention, the sequential extraction of phosphorus is carried out according to the protocol of Rydin and Welch²⁰, modified by Hietltjes and Lijklema²¹ and Psenner R. et al²². This protocol was selected because it made it possible to evaluate the quantity of phosphorus related to the aluminium hydroxides the difference of the other protocols listed in the literature.

Procedure: After drying, crushing and sifting, 1g of each sample of ground are introduced into a Eppendorf tube of 15 ml.

Extraction of the various phosphorus shapes. This mode of extraction makes it possible to separate: The exchangeable

phase or unstable phosphorus (P unstable):1M NH₄Cl with pH 7 during 2x2 hours S (double extraction); With each sample (1g) of ground contained in the Eppendorf tube one adds 10mL ammonium chloride solution. One agitates during 2h and passes to centrifugation to collect the supernatant. Experiment to make continuation twice. Volume of extraction 20mL. The unstable one is proportioned according to standard AFNOR IN 1189. The phase related to the manganese and iron hydrides (Fe-P):0.11M. Na₂S₂O₄ / 0.11M NaHCO₃ during 1 hour;

To the residue of the first extraction one adds 10mL solution, 1h of agitation, centrifugation, collection of the supernatant then proportioning of Fe-P to the spectrophotometer. The phase related on the aluminium hydroxides and the organic matter is obtained while placing the sample in medium NaOH (0.1M) during 16 hours. The digestion of this extract in the presence of persulphate in acid medium, is carried out according to the protocol of Gachter R. et. al¹⁹. It makes it possible to determine the phosphorus content related to the aluminium hydroxides and that related to the organic matter pelogene or biogene. By making the difference between the value determined before and after digestion, one obtains the quantity of phosphorus related to the organic matter (Org/Bact-P).

The phase related to calcium (Ca - P) is obtained while placing the sample in HCl (0.5M) during 16 hours. The residual phase is determined by difference between the sum of the various preceding fractions and the total phosphorus value is determined by the protocol of Gachter R. et. al¹⁹. Proportioning of phosphorus after extraction (According to method AFNOR Nt90-023).

Determination of the physicochemical parameters of water:
Parameters of ground: On each site of taking away, the water sample underwent in situ the measurement of the hydrogen potential (pH) by a pH-meter. The multi-parameter analyzer enabled us to determine in situ the temperature, the solids total dissouts (TDS), electric conductivity and the title hydrotimetric (TH).

Analyze water at the laboratory: Each water sample with fact the object of determination of the contents in nitrites, nitrates, ammonium, total phosphorus according to AFNOR (T90)²³. The physicochemical parameters of water enable us to evaluate the total quality of

water²⁴ according to the grid multi-use of the criteria of overall assessment of the quality of water. The dissolved oxygen contents and the pH enabled us to evaluate some major implications²⁴ according to respectively the grid of implications of the contents of dissolved O₂ and that of the pH²⁵.

Results and Discussion

Diagrams of the results and their interpretations: Physicochemical characteristics of the water samples: pH:

The pH is a parameter measured *in situ* on the ground. The pH gives an indication of the acidity of a substance. It is calculated starting from the quantity of hydrogen ions free (H⁺) contained in the substance. Acidity is one of the most significant parameters of the properties of water. Water is a solvent for almost all the ions and the pH makes it possible to compare the most water soluble ions. The values of the pH of water at the time of the December 2021 campaign vary from 5.84 to 6.54 (Figure-1). The greatest value is obtained on the level of site 2 and the smallest value is obtained on the level of site 4. These values indicate an acidity of the medium, favorable to the solubility and the biodisponibility of the pollutants, therefore of their toxicity. At the time of the February 2022 campaign (Figure-2) the values of the pH vary from 6.81 to 7.9. The greatest value is obtained on the level of site 6 and the smallest value is obtained on the level of site 8. One observes on Figure-3 that by December 2021 to February 2022, on the same site, the pH of water increased significantly.

Content nitrate: The concentration in ions nitrates of the water samples of the December 2021 campaign varies from 1mg/L with 3.4mg/L. the smallest value is observed on the level of site 3 and the greatest value is obtained on site 4. With regard to the February 2022 campaign, the values vary from 0.036 mg/L on site 4 to 4.76mg/L on site 8. Figure-4 shows us that by December 2021 to February 2022 the nitrate concentration of the water samples increased on sites 2. 7 and 8 whereas it decreased on sites 1, 3, 4, 5 and 6.

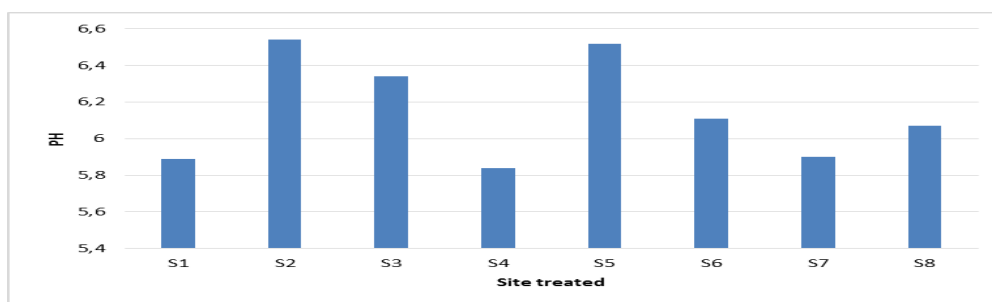


Figure-1: Variation of the pH of the water of the sites of sampling at the time of the November 2021 campaign.

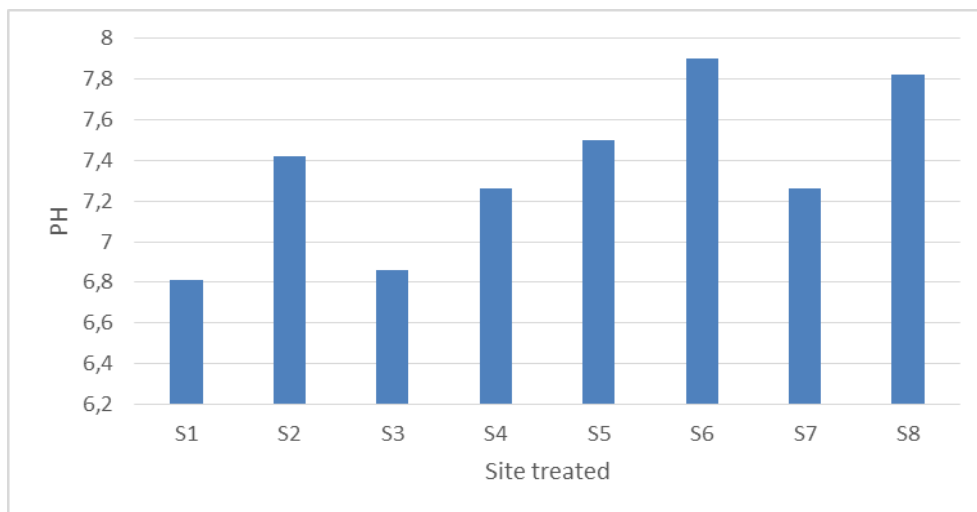


Figure-2: Variation of the pH of the water of the sites of sampling at the time of the February 2022 campaign.

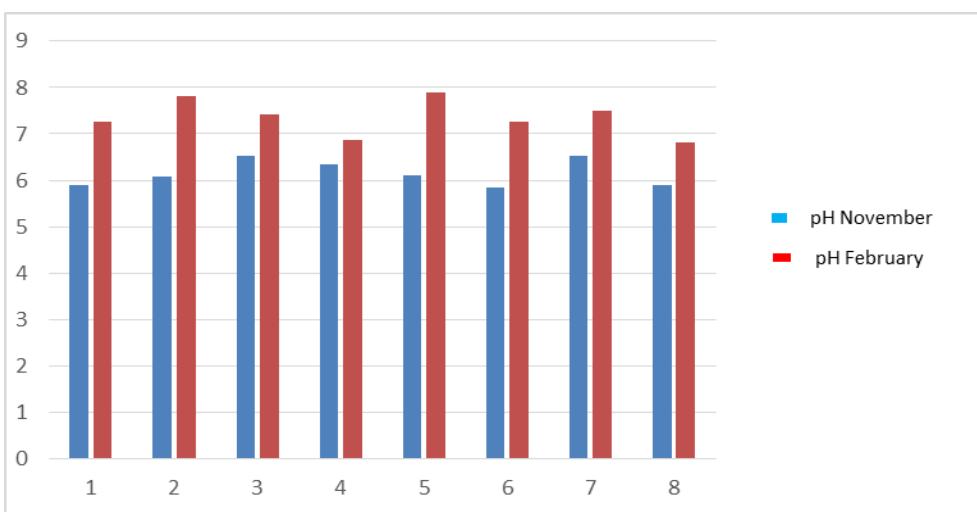


Figure-3: Variation of the pH of the water of the sites of sampling from November 2021 to February 2022.

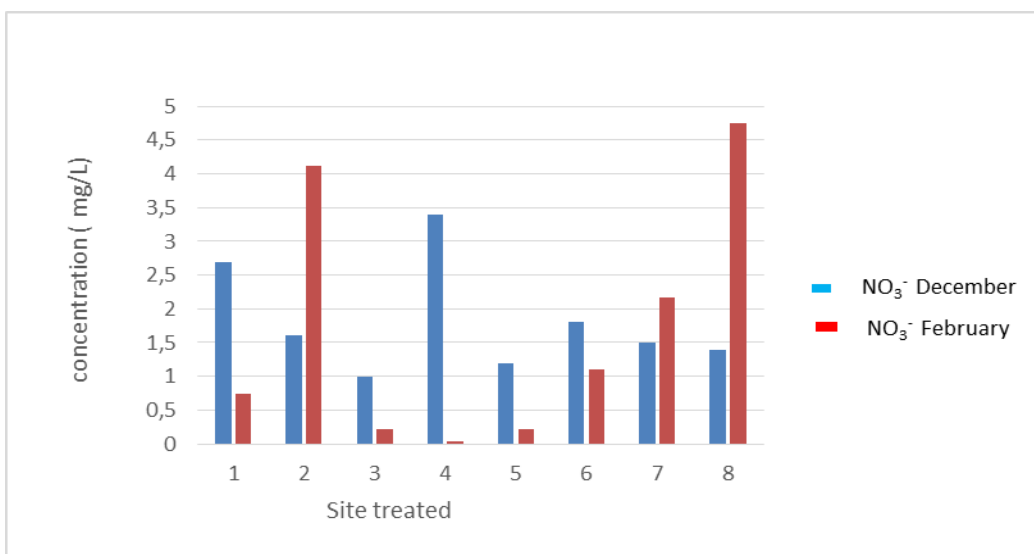


Figure-4: Variation of the concentration in ion nitrate of the water samples from December 2021 to February 2022.

Content nitrite: The concentration in ions nitrites of the water samples taken at the time of the December 2021 campaign varies from 0.024 mg/L with 0.071 mg/L. The smallest value is obtained on site 7 and the greatest value is obtained on site 6. With regard to the February 2022 campaign, the values vary from 0.05 mg/L on site 2 to 1.254 mg/L on site 8. According to Figure-16, the concentration in ion nitrite of the water samples increased on all the sites from December 2021 to February 2022.

Content ammonium: The concentration in ions ammoniums of the water samples of the December 2021 campaign varies from 0.11 mg/L with 0.35 mg/L. The smallest value is obtained on the level of site 8 and the greatest value is obtained on site 6. At the time of the February 2022 campaign, the values of the

concentration in ions ammoniums vary from 0.028 mg/L (site 2) to 1.068 mg/L (site 8). Figure-17 shows us that by December 2021 to February 2022, the concentration in ion ammonium decreased on sites 1, 2, 3 and 5 whereas it increased on sites 4, 6, 7 and 8.

Total solids dissouts: The TDS of the water samples of the December 2021 campaign varies from 23 ppm with 66 ppm. The smallest value is observed on site 2 and the greatest value is observed on site 3. With regard to the February 2022 campaign, the values vary 36ppm (site 8) to 103 ppm (sites 3 and 4). Figure-18 enables us to note that from December 2021 to February 2022; the TDS of the water samples increased on all the eight sites of study.

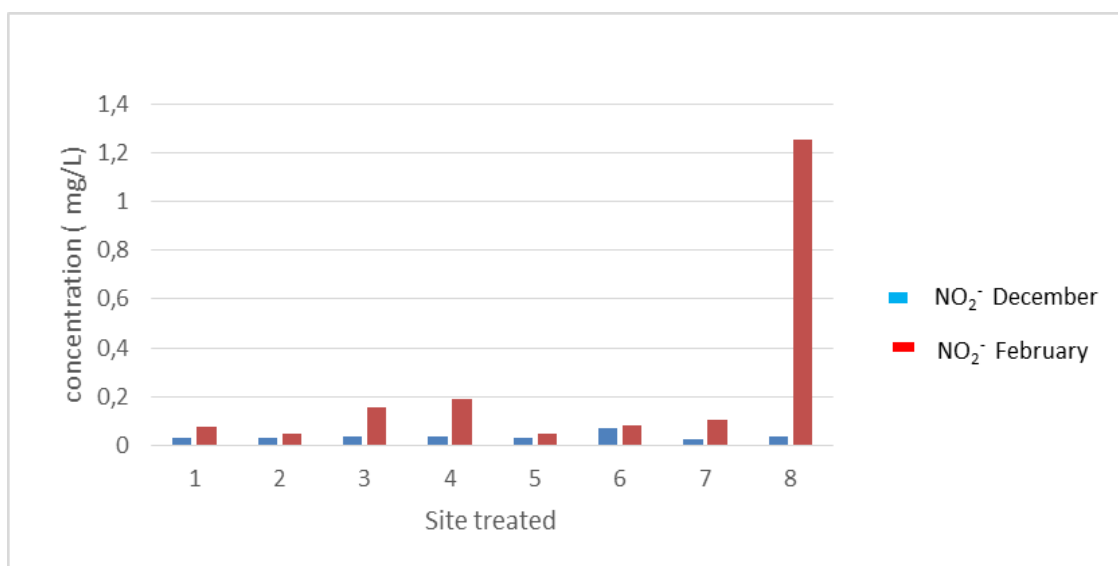


Figure-5: Variation of the concentration in ions nitrites of the water samples from December 2021 to February 2022.

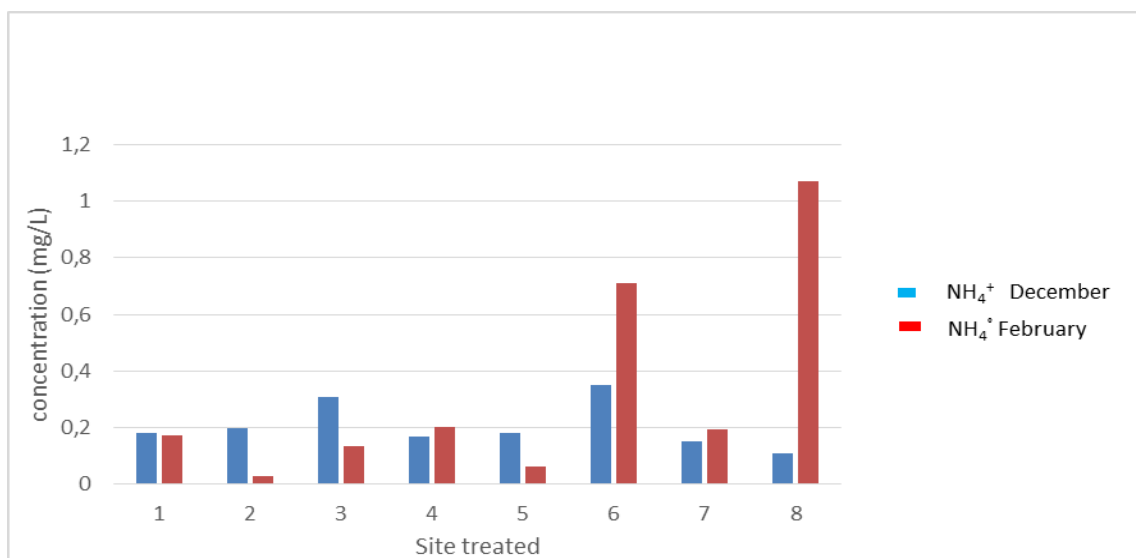


Figure-6: Variation of the concentration in ions ammoniums of the water samples from December 2021 to February 2022.

Electric conductivity: The electric conductivity of the water samples taken at the time of the December 2021 campaign varies from 46 $\mu\text{s}/\text{cm}$ with 142 $\mu\text{s}/\text{cm}$. The smallest value is obtained on site 2 and the greatest value is obtained on site 3. During the February the 2022 campaign values of electric conductivity varies from 72 $\mu\text{s}/\text{cm}$ (site 8) to 220 $\mu\text{s}/\text{cm}$ (site 4). By December 2021 to February 2022 electric conductivity increased on all the eight (8) sites (Figure-8).

Title hydrotimetric (TH): The title hydrotimetric of a water represents the hardness of the latter. At the time of the December 2021 campaign, the values of the hardness of the water samples vary 67.2F with 75.2F. The smallest value is obtained on site 5 and the greatest value is obtained on site 4.

With regard to the February 2022 campaign, the values vary 60.4F (site 3) to 87.4 (site 1). On Figure-9 one notes that the title hydrotimetric increased December 2021 at February 2022 on sites 1, 5 and 7. It decreased on sites 3, 4, and 8 whereas it kept an almost constant value on sites 2 and 6.

Temperature: The temperature of water at the time of the December 2021 campaign presents a maximum of 24.3°C on the sites 3 and 6 and one minimum of 19.3°C on site 5. At the time of the February 2022 campaign, the temperature varies from 16.3°C (site 3) at 24.5°C (site 7). By December 2021 to February 2022, the temperature increased on sites 1, 5 and 7 whereas it decreased on sites 2, 3, 4 and 8 (Figure-10).

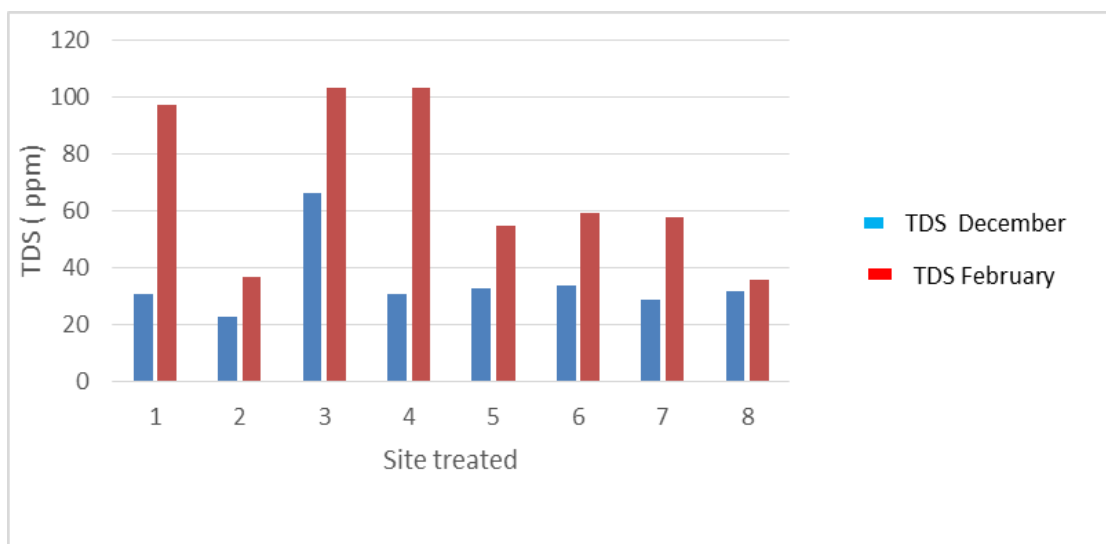


Figure 7: Variation of the TDS of the water samples from December 2021 to February 2022.

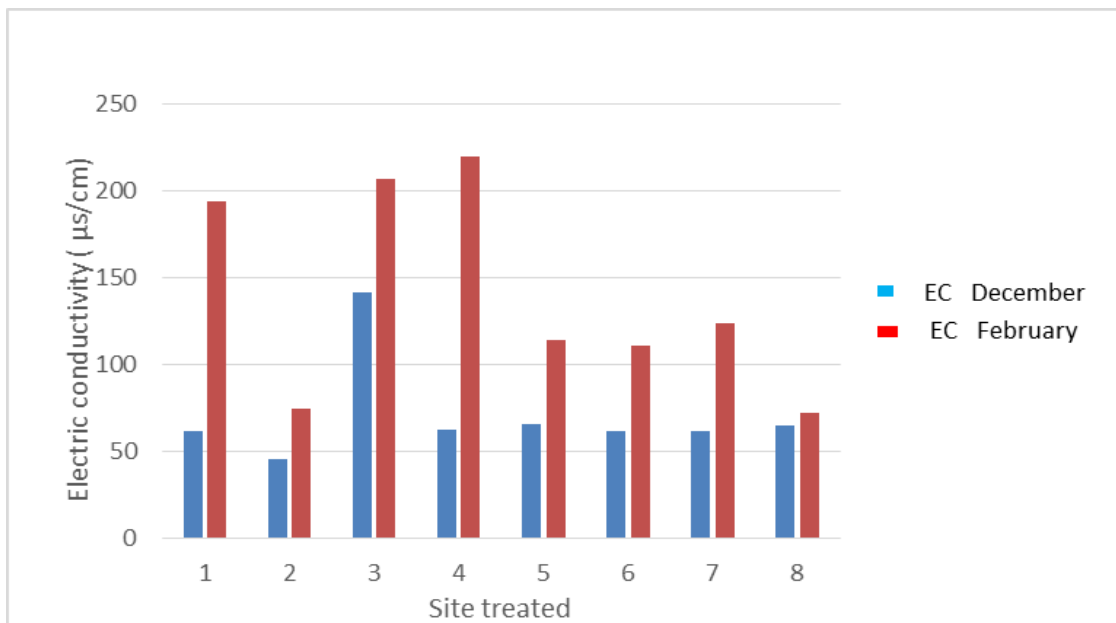


Figure-8: Variation of the electric conductivity of the water samples from December 2021 to February 2022.

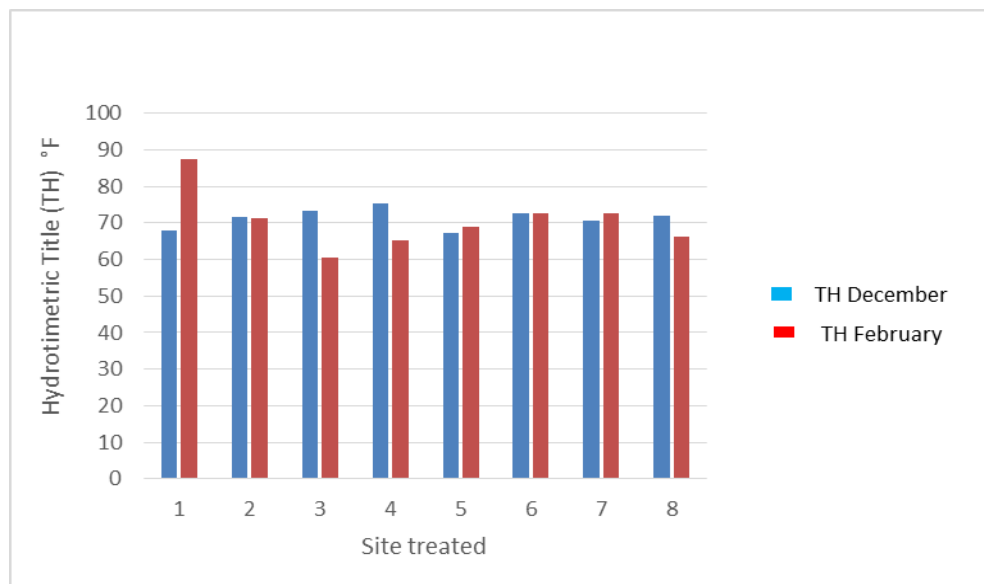


Figure-9: Hydrotimetric variation of the title (TH) of the water samples from December 2021 to February 2022.

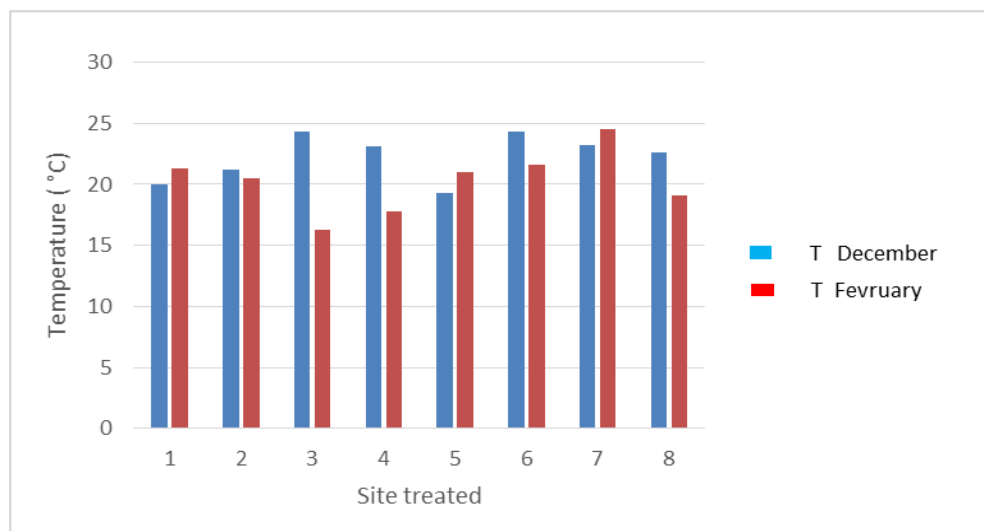


Figure 10: Variation in the temperature of the water from December 2021 to February 2022.

Physicochemical characteristics of the sediments: pH_{water} and pH_{KCl} : The value of the pH_{water} of the sediments taken at the time of the December 2021 campaign varies from 6.86 to 9.82. The smallest value is obtained on site 6 and the greatest value is obtained on site 7. At the time of the February 2022 campaign, the pH_{water} of the sediments varies from 6.66 (site 8) to 9.86 (site 7).

The value of the pH_{KCl} of the sediments taken at the time of the December 2021 campaign varies from 5.66 to 6.36. The smallest value is obtained on site 2 and the greatest value is obtained on site 7. At the time of the February 2022 campaign, the pH_{KCl} of the sediments varies from 5.71 (site 1) to 6.11 (site 2).

Figure-23 shows that by December to February the pH_{water} of the sediments increased on sites 1, 6 and 7 whereas it decreased on sites 2, 3, 4, 5 and 8.

Figure-13 shows that by December to February the pH_{KCl} of the sediments increased only on site 2 and decreased on sites 1, 3, 4, 5, 6 and 7 whereas there remained constant on site 8.

Figures-14 and 15 present to us the comparison of the pH_{water} to the pH_{KCl} of the two campaigns. It is noticed that for all the two sampling campaigns the value of the pH_{water} is higher than that of the pH_{KCl} . This is due to the fact that real acidity takes into account only the ions H_3O^+ released in the solution by the ground, whereas potential acidity (K^+) also takes into account the ions H_3O^+ exchangeable and adsorbed by the organic matter contained in the ground.

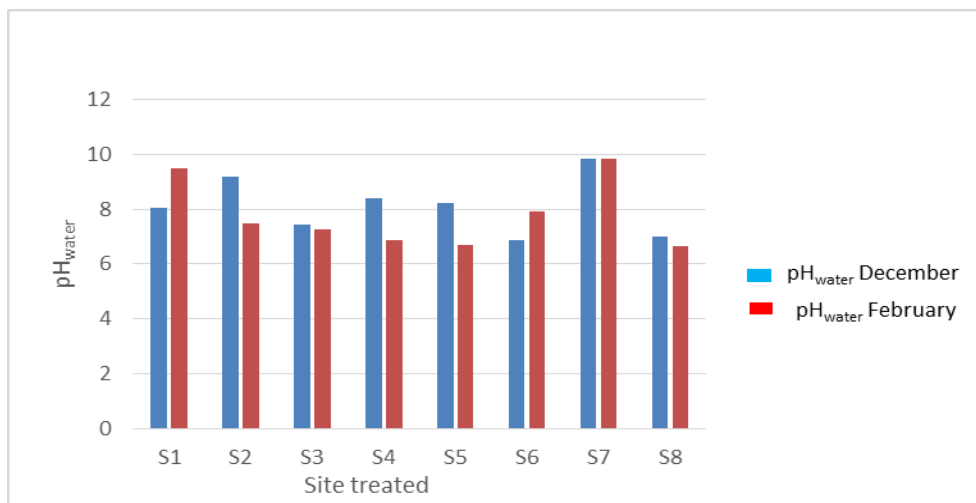


Figure-11: Evolution of the pH_{water} of the sediments from December to February.

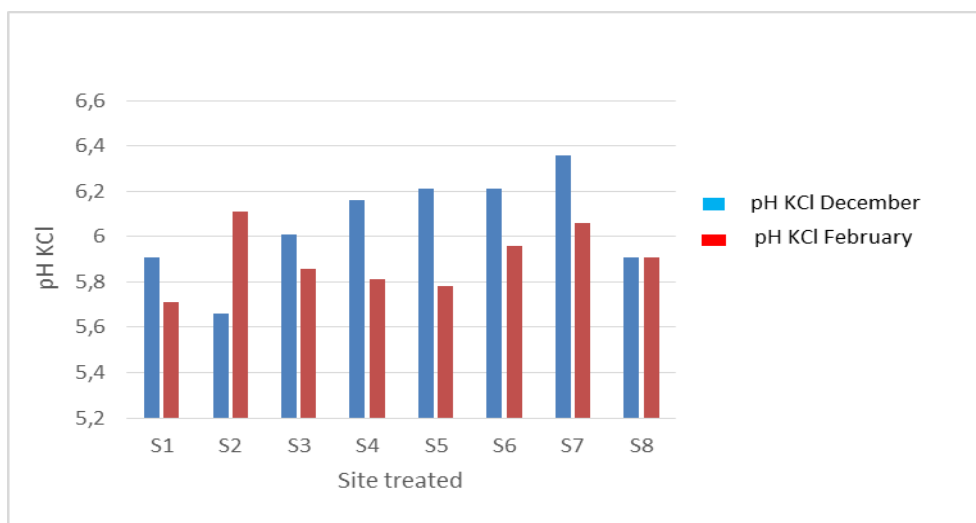


Figure-12: Evolution of the pH_{KCl} of the sediments from December to February.

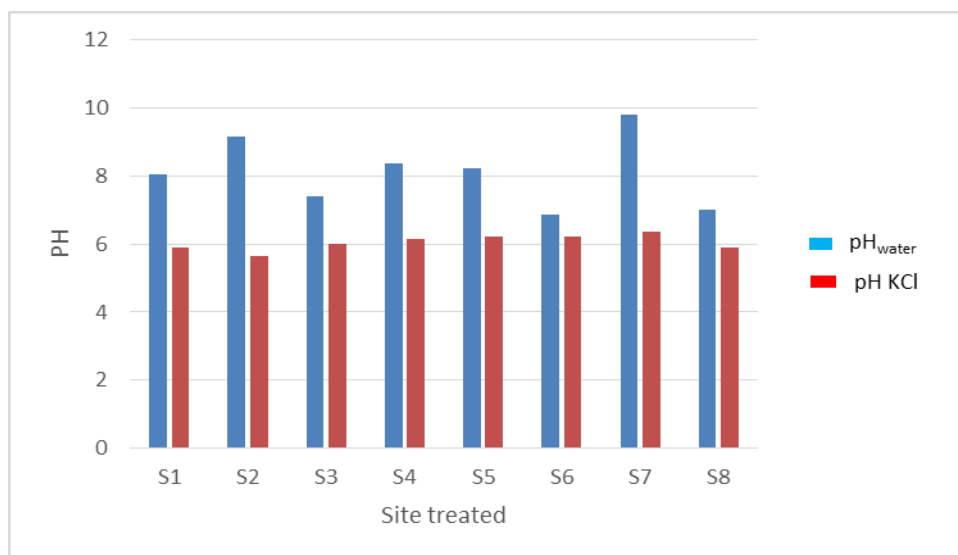


Figure-13: Comparison of the pH_{water} and the pH_{KCl} of the sediments of the December 2021 campaign.

Total phosphorus: The total phosphorus content of the sediments of December 2021 varies 1359.83µg/g with site 3 with 4027.84µg/g with site 5 with an average of 3016.57 ± 1µg/g whereas in February the total phosphorus content of the sediments varies 2995.06µg/g with site 2 with 6480.69µg/g on site 7 with an average of 3914.87 ± 1µg/g. We note that by December to February the total phosphorus content of the sediments increased on sites 1, 2, 3, 4 and 7 whereas it decreased on sites 4 and 5 then guard a constant value on site 8 (Figure-16).

Fractionation of phosphorus: The fractionation of the eight (08) samples of sediments revealed the presence of phosphorus in form assimilable (P-unstable), particulate (Fe-P, Al-P, Cape), residual and organic in each sample.

Fractionation of the phosphorus of the sediments of December 2021: The fractionation of phosphorus in the eight samples of sediments taken in December 2021 presents the six fractions of phosphorus as Figure-28 indicates it. The most significant fraction is the residual fraction varying between 865.60 µg/g with site 3 to 3539.44 µg/g on site 5 with an average of 2349.58 µg/g. The second most significant fraction is the organic fraction presenting a minimum of 392.46 µg/g on site 7 and one maximum of 926.06 µg/g on site 8 with an average of 577.49 µg/g. The assimilable fraction i.e. the unstable fraction is present in very small proportion varying between 12.59µg/g on site 7 and 15.14 µg/g on site 1 with an average of 14.05 µg/g. The particulate fraction made up of

phosphorus related to iron (Fe-P), of phosphorus related to aluminium (Al-P) and of phosphorus related to calcium (Cape) is present also in small quantity. The fraction related to iron (Fe-P) is the most significant fraction of particulate phosphorus with a content going of 46.97 µg/g (site 3) to 69.70 µg/g (site 1) with an average of 60.97 µg/g. It is noticed that these sediments reveal the presence of a mineral fraction more significant than the organic fraction. On each site the directly biodisponible fraction is found by calculating the average between the unstable fraction and that organic whereas the biodisponible total fraction is found by calculating the average of all the six fractions.

Fractionation of the phosphorus of the sediments of February 2022: The fractionation of the phosphorus of the sediments of February 2022 also reveals all the six fractions of phosphorus as Figure-17 indicates it. The residual fraction is most significant varying from 2201.99 µg/g (site 1) with 5939.47µg/g (site 7) with an average of 3336.98 µg/g. The second fraction is the organic fraction with a minimum of 246.15 µg/g (site 2) and a maximum of 796.96 µg/g (site1). Particulate phosphorus is also present at small quantity in its three forms with the fraction related to iron (Fe-P), its most significant fraction. The fraction Fe-P varies from 32.11 µg/g (site 5) to 66.07 µg/g (site 8) with an average of 55.7 5µg/g. On each site the directly biodisponible fraction is found by calculating the average between the unstable fraction and that organic whereas the biodisponible total fraction is found by calculating the average of all the six fractions.

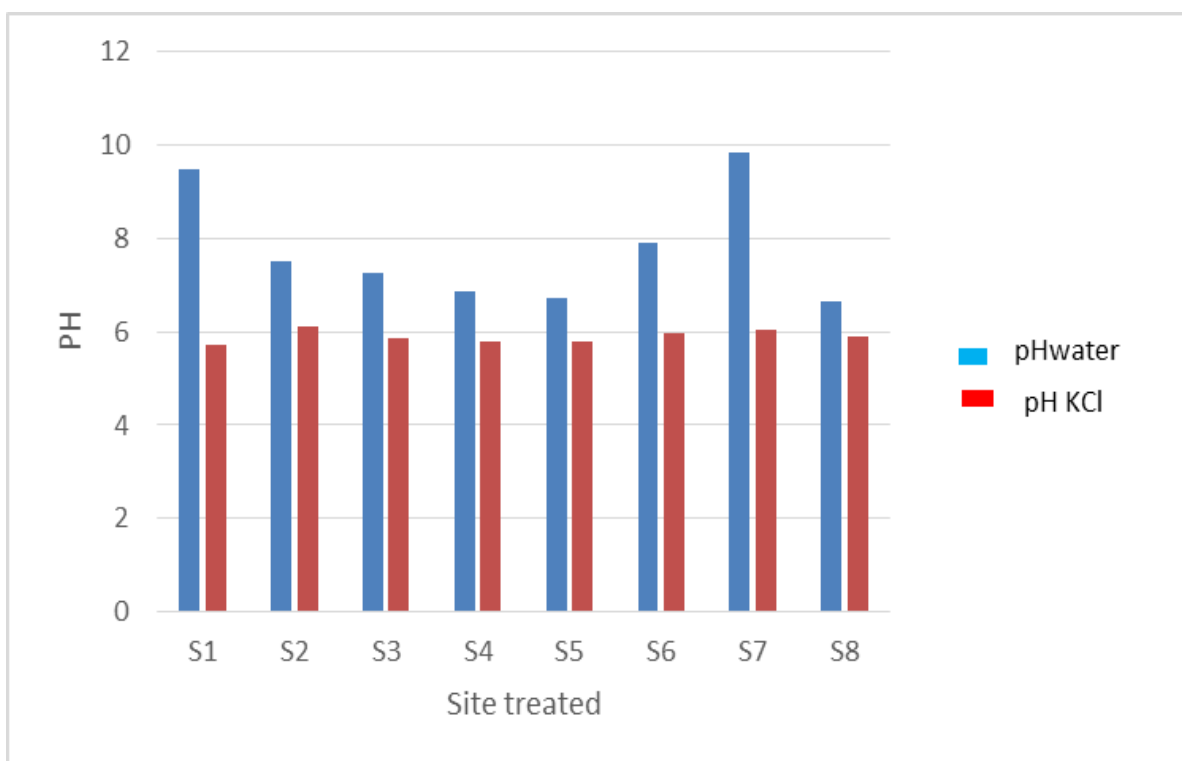


Figure-14: Evolutions of the pH_{water} and the pH_{KCl} of the sediments of the February 2022 campaign.

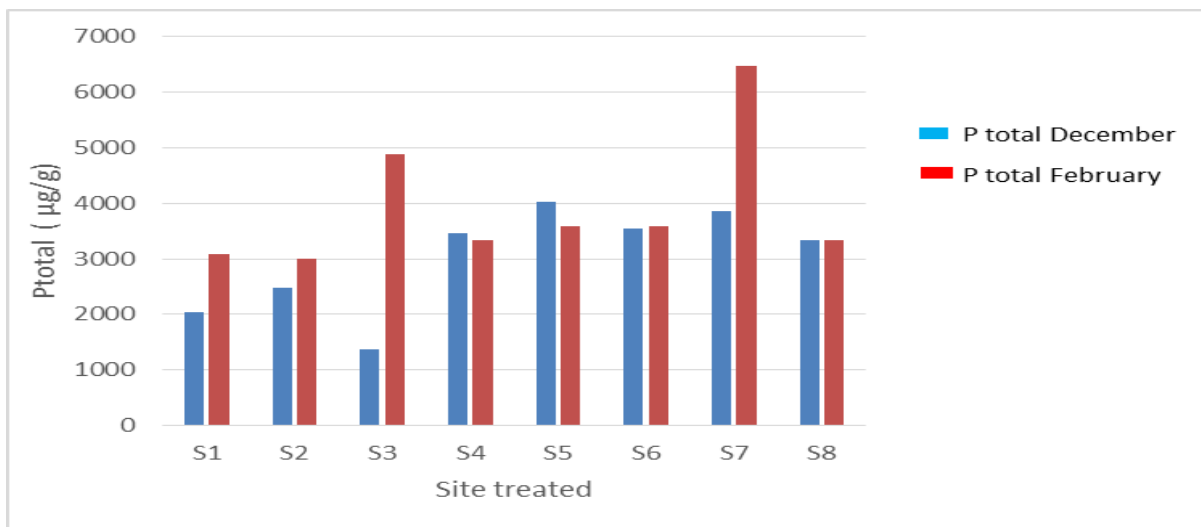


Figure-15: Variation of the total phosphorus of the sediments from December 2021 to February 2022.

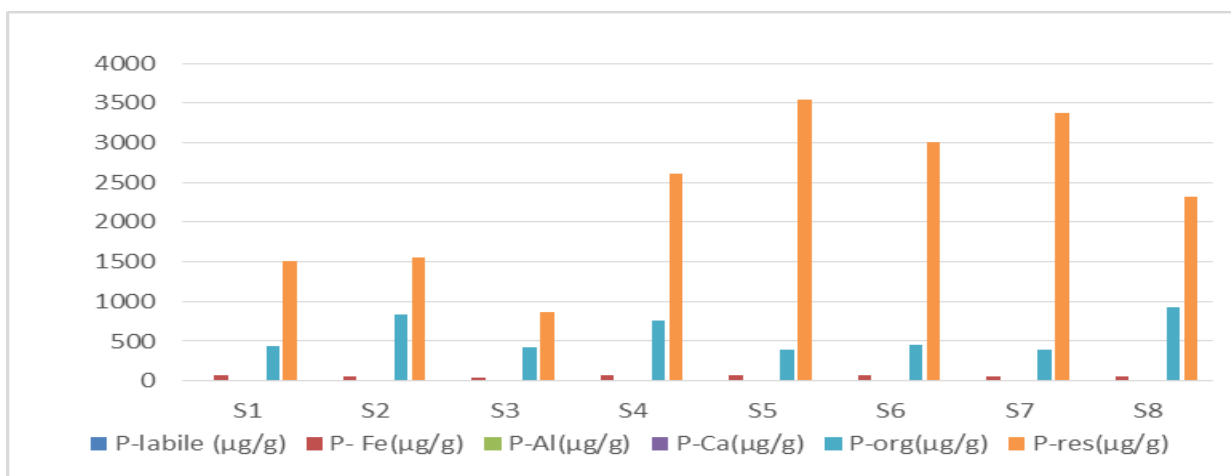


Figure-16: Diagram of the various fractions of the phosphorus of the sediments of December 2021.

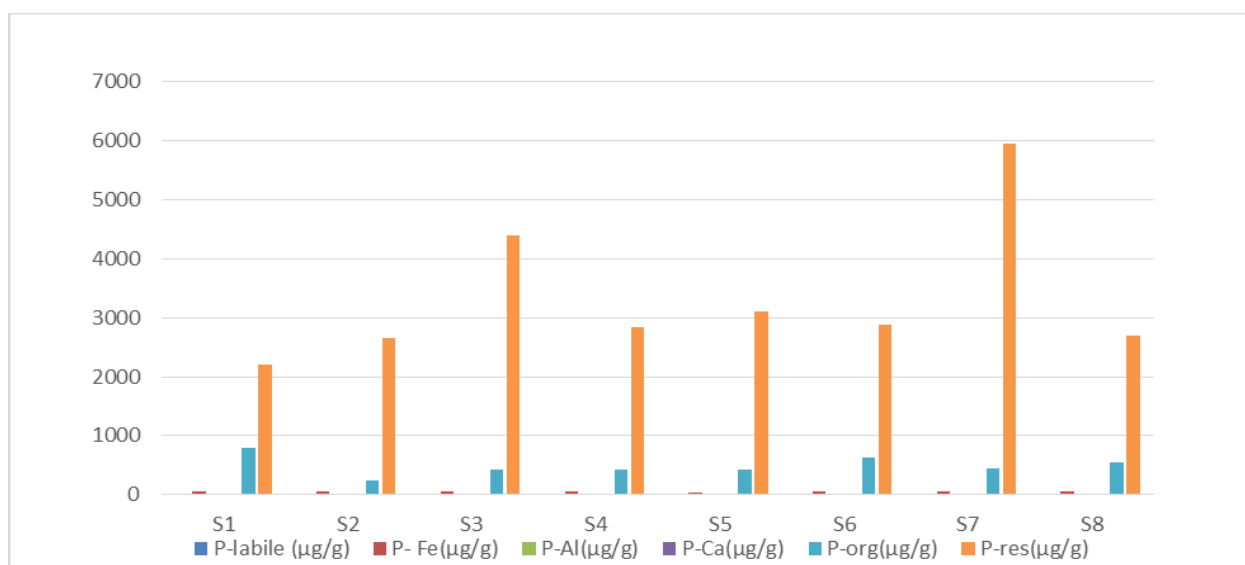


Figure-17: Diagram of the various fractions of the phosphorus of the sediments of February 2022.

The fractionation of phosphorus enabled us to obtain for each of the eight samples of sediments of each countryside the six fractions of phosphorus: P-unstable, Fe-P, Al-P, Cape, P-org and Close which the average values are presented in Table-1.

Table-1: Average values of the various fractions of phosphorus

Fractions	Sediments of December 2021	Sediments of February 2022
P-labile (µg/g)	14.05 0.01	14.310.01
P-Fe(µg/g)	60.97 0.02	55.750.01
P-Al(µg/g)	7.52 0.01	8.660.02
P-Ca(µg/g)	6.950.02	6.640.01
P-org(µg/g)	577.490.01	492.500.01
P-res(µg/g)	2349.580.02	3336.980.01

On all the sites of sampling, the residual fraction highest is followed organic fraction. The third most significant fraction is the fraction related to the hydroxides of iron and magnesium (Fe-P) followed assimilable fraction (P-unstable). The fractions related on the aluminium hydroxides (Al-P) and to the carbonates (Cape) come respectively in fifth and sixth position.

On the basis of the Ptotal diagram = Porganic + Pinorganic and Pinorganic = Plabile + Pparticulate + Presidual, one concludes that the mineral fraction is most significant. The relatively high organic fraction can be justified in the case of our study by the presence of the ox dungs and other remains (the zone of study having a livestock rich in particular in cattle and caprine) then the decomposition of the vegetable organic matter. The significant inorganic fraction can be justified through two

sources: contributions in mineral manure (the zone of study being an agricultural zone of production) drained towards the river and the degradation of the bed rock. The particulate fraction and the unstable fraction represent each one a small proportion of the inorganic fraction. Thus the high rate of inorganic phosphorus is due to the residual fraction, a fraction difficult to mobilize. For particulate phosphorus (Fe-P + Al-P + Cape), the fraction related to the iron hydroxides (Fe-P) accounts for 80.82%. This can be explained by the fact why the grounds of the 2KP are ferralitic and ferruginous.

The various samples of analyzed sediments present very weak assimilable phosphorus concentrations directly by the watery plants and organizations such as the algae, the crustacean ones, the fish. On average 0.46% of total phosphorus are in the form of exchangeable phosphorus unstable between the solid phase and the liquid phase in contact with the sediments, which can be easily introduced into the organizations living in the water column. Let us note that this proportion of phosphorus is that directly mobilizable of the sediment towards the other compartments of the environment. When the optimal conditions are met part of the fractions related on iron and calcium as well as part of organic phosphorus will be also biodisponibles (Table-2, Table-3).

Discussion: The content nitrite of the water samples of the two sampling campaigns varies from 0.024 ± 0.002 (site 7, December 2021) to 1.254 ± 0.001 (site 8, February 2022). Only on the level of site 8 in February that one observes a content higher than 0.5mg/L, therefore according to standard NF IN 806 only the water sample taken on site 8 in December 2021 is polluted. In the same way the content nitrate of all the water samples gives a value lower than 50 mg/L. Thus this water is not polluted out of nitrates.

Table-2: Biodisponibility of the samples of sediments of December 2021.

Samples	S1	S2	S3	S4	S5	S6	S7	S8
Plabile(µg/g)	15.14	14.87	14.47	12.99	14.2	14.07	12.59	14.07
Ptotal(µg/g)	2048.34	2478.67	1359.83	3468.41	4027.84	3554.48	3855.71	3339.32
Biodisponibility (%)	0.74	0.60	1.06	0.37	0.35	0.40	0.33	0.42

Table-3: Biodisponibility of the samples of sediments of February 2022.

Samples	S1	S2	S3	S4	S5	S6	S7	S8
Plabile(µg/g)	12.86	19.71	14.07	14.33	13.66	11.78	14.2	13.93
Ptotal(µg/g)	3081.12	2995.06	4888.49	3339.32	3597.51	3597.51	6480.69	3339.32
Biodisponibility (%)	0.42	0.66	0.29	0.43	0.38	0.33	0.22	0.42

With regard to the pH, one notes that at the level of the samples of December 2021 only sites 3 and 7 have a pH ranging between 6.5 and 8.5; optimal with the life and the reproduction of fish. All the water samples taken at the time of the February 2022 campaign have an optimal pH at the life and the reproduction of fish taking account of the grid of implication of the pH.

The measurement of total phosphorus in the sediments gives values ranging between 1359.83 $\mu\text{g/g}$ and 6480.69 $\mu\text{g/g}$ of sediment. What is largely higher than the threshold of environmental risk and indicates the exposure of the river to eutrophication.

The fractionation of phosphorus enabled us to find all the six fractions of phosphorus in the sediments taken on the eight sites of sampling of the Mékrou river. For all the two sampling campaigns the residual fraction is most significant with an average of 2349.58 \pm 0.3 $\mu\text{g/g}$ in December 2021 and one average of 3336.98 \pm 0.3 $\mu\text{g/g}$ in February 2022. The second most representative fraction is that organic with an average of 577.49 \pm 0.2 $\mu\text{g/g}$ in December 2021 and one average of 492.50 \pm 0.3 $\mu\text{g/g}$ in February 2022. The assimilable fraction i.e. the unstable fraction is present in very small proportion with an average of 14.05 \pm 0.01 $\mu\text{g/g}$ in December 2021 and one average of 14.32 \pm 0.01 $\mu\text{g/g}$.

The fraction related to iron (Fe-P) is the most significant fraction of particulate phosphorus with an average of 60.97 \pm 0.01 $\mu\text{g/g}$ in December 2021 and one average of 55.75 \pm 0.01 $\mu\text{g/g}$ in February 2022. It is noticed that the mineral fraction of phosphorus is largest. This can be explained by the abusive use of mineral manure on the catchment area of the Mékrou river. The three towns traversed by the river are large producing towns of cotton to the Benin. These results are contrary with those on the sediments of the Porto-Novo lagoon where it is the organic fraction which is dominant. This difference is explained by the fact why the lagoon of Porto-Novo is subjected to an organic pollution characterized by the discharge of the industrial organic pollutants in the river and the use of organic manure for agriculture on the catchment area of the lagoon.

Let us note that the organic fraction is also in considerable proportion, it is the second most representative fraction. The Mékrou river is thus likely to be exposed to the phenomenon of eutrophication.

Conclusion

Our study enabled us to note that the sediments of the Mékrou river are generally basic with an average pH equal to 7.95.

All the samples of sediment are rich in phosphorus with an average phosphorus concentration equalizes with 3465.73 \pm 1 $\mu\text{g/g}$. The sediments of the Mékrou river thus constitute a large tank and well of phosphorus which can under certain optimal conditions pass in the water column by the phenomenon of

salting out, which can entrainer thereafter a risk of eutrophication. By December 2021 to February 2022 the total phosphorus content increased by an average of 3016.58 \pm 1 $\mu\text{g/g}$ to an average of 3914.88 \pm 1 $\mu\text{g/g}$. Consequently we can say that more the dry season evolves, the concentration of total phosphorus increases.

The speciation of phosphorus enabled us to note the six fractions of phosphorus in all the samples of sediment. The result of speciation arises as follows: P unstable (0.41% of Ptotal), Fe-P (1.68% of Ptotal), Al-P (0.23% of Ptotal), Ca-P (0.20% of Ptotal) Porg (15.43% of Ptotal) and P-residual (82.04% of Ptotal). The phosphorus of the analyzed sediments is thus mainly in inorganic form (85.56% of Ptotal). This can be related to the abusive use of mineral manure for the cotton culture on the catchment area of the Mékrou river.

The results of this research task can constitute a cry of alarm to the environmental risk of eutrophication which the Mékrou river is incurring. They can allow the policies local gouvernances to have an index on the rate of phosphorated pollution of the Mékrou river and to think of the depollution of this river. To effectively evaluate the rate of pollution of this river, it is desirable to study the effect of the pH on the salting out of phosphorus and also to undertake the same study on the other pollutants in this river. The same studies could be made on the other rivers of Benin having for basins slopes of the zones of agricultural production.

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