Study Of Water And Sediment Contamination In The Mekrou River

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Abstract:

Background Life on earth is possible thanks to certain vital resources, including water, which is essential for the sustainable socio-economic development of a country. Faced with anthropogenic pressures on this blue gold, it is necessary to have better monitoring of water resources. It is in this context that this work studied the level of contamination of the waters and sediments of the Mékrou River related to agricultural activities. The aim was to characterize the samples, assess the level of eutrophication of the waters and propose mitigation measures.

Materials and Methods: Water and sediment samples were taken from 8 sites along the river for physico-chemical analyses.

Results: The results of the analysis of these samples showed high contamination in conductivity, COD, BOD5, SO4 2- and suspended solids mainly in the village of Gorgoba and in the village of Sakabo. The conductivity varies between and 1662 μ S/cm with a maximum value recorded at the level of the Tokoro village. The pH is relatively neutral, on the other hand, the nitrite and ammonium contents are negligible.

Conclusion: This study inferred that the quality of the water and sediments of the river has been altered by anthropogenic activities and natural phenomena.

Healthy agricultural actions are on the horizon.

Key Word: Mekrou, sediment, water, contamination

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I. Introduction

Life on earth is possible thanks to the existence of certain vital resources, including water, a commodity of great importance for living beings¹. It is an indispensable element for life and for the real and sustainable socioeconomic development of a country, so it is necessary to have a better knowledge of existing water resources, especially information concerning: the vulnerability of these resources to a possible factor, the measures needed to develop, manage and protect them². The problems associated with water pollution and anthropogenic pressure on highly vulnerable aquatic ecosystems require continuous monitoring of their physico-chemical, hydrodynamic and biological properties. Household and industrial waste sometimes contains trace metals and organic matter that can harm human health. These different chemical elements spread all over the soil end up in bodies of water in general and in rivers in particular. However, the latter are environments of high biological productivity and high opportunities for fish production, which makes them of great economic importance. the determination and disposal of metals in river sediments is an important concern for the protection of ecosystems ³. It is therefore important to determine the level of pollution of the sediments of the Mékrou River of the Niger River and to assess the health risk to aquatic species, the environment, as well as the populations of this area. As the Mékrou River is under threat from anthropogenic activities, the present work aims to study "the influence of agricultural activities on the waters and sediments of the Mékrou River.

II. Material And Methods

To study the impact of agricultural activities on the quality of water and sediments in the Mékrou River basin, water and sediment samples were taken in September 2021 on eight (08) sites in the communes of Péhunco and Kouandé (Yakabissi, Gorgoba, Somboko, Tokoro, Makrou, Kpékpakara, Sakabou and Gnémasson).

Sample Preparation

Water samples were collected in 1.5 L polyethylene bottles that had been previously cleaned. For each site, a sediment core 10 cm long and 2 cm in diameter was collected using a tube. The different water samples were taken in the Mekrou River basin at 3 different distances across the width in order to have a representative sample of the site. All samples were quickly transported to the laboratory for storage at 4°C and in the dark prior to analysis.

In the laboratory, water samples were numbered from S1 to S8. As far as sediments are concerned, the cores were cut into 2 cm thick slices. The first 2 cm were analysed. For trace metal analysis, sediments labelled Se1 to Se8 were dried in a laminar flow hood for 24 hours and then screened. The method used for sediment mineralization is that of the NF X31-147 standard. The sediment dried at room temperature for a few days is sieved and dried in an oven at 40°C for 1 hour. The part smaller than 2 mm is then ground to obtain a powder with a particle size of less than 250 μ m. Mineralization is performed on approximately exactly 0.5 g of this powder with 6 mL of hydrochloric acid and 2 mL of nitric acid (aqua regia). This step is done at 95°C for 75 minutes on a heating block. The mineralize is then adjusted to 50 mL in a flask with demineralized water. The solution that is centrifuged or filtered before the different assays is called the distillate50.

Scan settings

Temperature, conductivity and pH were measured in situ using a WTW 340i digital multiparameter pH meter.

Principle of sulphate determination

Sulphates are measured by nephelometry according to the AFNOR method (T90-040)4. Sulphate ions react in the presence of barium chloride in hydrochloric acid to form a barium sulfate precipitate, which is stabilized with a stabilizing agent that absorbs at a wavelength of 650 nm.

Principle of nitrite dosing

Nitrite was measured according to the AFNOR method (T90-013)⁵. Sulphanilic acid in hydrochloric media, in the presence of ammonium ion and phenol (ZAMBELLI reagent), forms with nitrite ions a yellow colour complex whose intensity is proportional to the nitrite concentration and which absorbs at a wavelength of 435 nm.

Principle of nitrate dosing

The AFNOR method (T90-012)⁶ was used to measure nitrates. In the presence of sodium salicylate, nitrates react to yellowish sodium paranitrosalicylate. The absorbance of the solution obtained is measured by colorimetry at a wavelength of 415 nm.

Principle of chloride dosing

The chlorides were analysed according to the AFNOR method (T90-014)⁷. Mohr's method is a neutral precipitation assay. It is based on the titration of chlorides in neutral media by a solution of silver nitrate (0.1 N) in the presence of a coloured indicator which is potassium chromate.

Chemical Oxygen Demand (COD) Measurement

This parameter was analysed according to the standard AFNOR8 T90-101 method. This method is based on reflux boiling of a test sample in an acidic medium, in the presence of a known amount of potassium dichromate, silver sulphate acting as a catalyst and mercury (II) sulphate to complex the ions.

Measurement of 5-day biochemical oxygen demand (BOD5)

The method with OxiTop® is based on a pressure measurement in a closed system. The microorganisms in the sample consume oxygen by forming CO₂. This is absorbed by NaOH and a depression ensues, the measurement of which can be directly translated into mg of O₂/L⁹.

Determination of dissolved organic carbon (DOC)

Measurements of dissolved organic carbon in the sampled water and sediment extracts were made using a Shimadzu TOC-V CSN type instrument, using the NPOC method which removes inorganic carbon by acid addition (HCl 2M) prior to analysis. The principle is based on oxidative combustion at 720°C in the presence of a platinum-platinized alumina bead catalyst, in order to estimate the amount of carbon by CO_2 absorption in infrared. The detection limit for DOC is 0.1 mg/L.

Determination of Total Organic Carbon

Total organic carbon in sediments was determined by titration. To do this, a solution of potassium dichromate is added to a sample in the presence of sulphuric acid. After the reaction, the concentration of total organic carbon is determined by measuring the amount of dichromate that has not reacted with the sample.

Determination of total nitrogen

Using the Kjeldahl method, ammonia nitrogen and organic nitrogen are measured simultaneously. The determination of total Kjeldahl nitrogen is carried out in two steps. The first step is digestion in an acidic medium that converts all nitrogenous organic compounds into ammoniacal nitrogen. In the second step, the ammonium ions are measured by an automated system. Ammonium ions react with salicylate, nitroferricyanide and sodium hypochlorite to form an alkaline ammoniacal salicylate complex, the absorbance of which at 660 nm is proportional to the concentration of ammoniacal nitrogen.¹⁰

Determination of Cation Exchange Capacity (CEC)

This determination follows a three-phase process:

- Displacement of exchangeable cations and their substitution with a monovalent cation (NH4⁺): At this stage, the exchangeable cations and hydrogen of the adsorbent complex (clay-humic soil complex) are displaced by a monovalent cation (ammonium from a buffered ammonium acetate solution, pH = 7); At the end of this phase, the complex is saturated with the ammonium acetate solution and the collected filtrate
- is used to determine the exchangeable cations (Ca, Mg, K and Na).
 Washing the material with ethyl alcohol 95°: Outside the complex, an excess of the monovalent saturation cation moistens the material: these excesses must therefore be removed by washing with alcohol.
- Displacement of the saturating cation by another monovalent cation (K⁺): The NH4⁺ cation is recovered using a solution of KCl, 10%. It is then measured by distillation and makes it possible to determine the number of sites available on the adsorbent complex and consequently the cation exchange capacity of the latter¹¹.

Determination of phosphates and ammonium

The determination of phosphate and ammonium is a two-step process. The first step is acidic digestion that converts all phosphorus into orthophosphate and all nitrogenous organic compounds into ammonia nitrogen. In the second step, orthophosphate and ammonium ions are measured by an automated system.

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The orthophosphate ion reacts with the molybdate ion and the antimony ion to form a phosphomolybdate complex. The latter is reduced with ascorbic acid in an acidic medium to cause the appearance of molybdenum blue, whose absorbance at 660 nm is proportional to the concentration of the orthophosphate ion. Ammonium ions react with salicylate, nitroferricyanide and sodium hypochlorite to form an alkaline ammoniacal salicylate complex, whose absorbance at 660 nm is proportional to the concentration of ammoniacal nitrogen.¹²

III. Result

The results of the physico-chemical analyses (pH, conductivity and temperature) of the water samples collected at the sites are reported in Table I below.

Tuble 1. Variation in p11, conductivity and temperature by sampling site								
Parameters	Site 1	Site 2	Site 3	Site 4	Site 5	Site 6	Site 7	Site 8
рН	7,50	7,18	7,50	6,81	7,10	7,26	7,02	7,18
Conductivity (µS/cm)	251	336	257	1662	544	363	464	351
Temperature (°C)	28	30,2	26,3	28	28,6	29,2	30,5	29,2

Table 1: Variation in pH, conductivity and temperature by sampling	; site
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Based on the results in the table, the pH values measured at the sites range from 6.81 to 7.50. The elevated pH is recorded in the villages of Yakabissi and Soboko at sites 1 and 3 respectively. The lowest value is observed in the village of Tokoro which is site 4 and with a value of 6.81. These values do not exceed the Beninese standards for surface water (6.5-8.5) and it can be concluded that these pH values are favourable to the development of aquatic species13.

Conductivity is a parameter that allows the evaluation of the degree of ionization of water. This parameter depends mainly on the presence of the different ions $(Ca^{2+}, Mg^{2+}, K^+, Na^+, HCO3^-, SO4^{2-}, Cl^-)$ and also on their concentrations14. From the results obtained (Table I), it can be seen that the conductivity values are well above the standard. The increase in conductivity at the localized sites is probably related to the precipitation measured during the sampling campaign. This led to soil leaching and re-solubilization of magnesium and calcium.

The temperature is high in the villages of Gorgoba and Sakabo at sites 2 and 7 respectively with an average value of 30°C and low in the villages of Soboko with a value of 26.3 at site 3.



Figure 1: Ammonium, nitrate and nitrite content by water sampling site

Figure 1 shows the variations in ammonium content of water samples analysed with a high concentration in the village of Gorgoba (site 2) (0.55mg/L) and a low concentration in the village of Sakabo (site 7) (0.23mg/L).

According to the figure, nitrate (NO_3^-) and nitrite (NO_2^-) concentrations are higher in Gorgoba village (site 2) with levels of 1.4 mg/L and 0.025 mg/L respectively; their low values are obtained in Makrou villages (site 5) and Sakabo villages (site 7) with respective levels of 0.6 mg/L and 0.001 mg/L.

Nitrite (NO_2^{-}) concentrations are below the Beninese standard of 3.2 mg. L⁻¹ for drinking water. Nitrate (NO_3^{-}) concentrations range from 0.60 mg. L⁻¹ (Site 5) and 1.4 mg. L⁻¹ (Site 2). All nitrate concentrations are well below the standard of 45 mg. L⁻¹ in force in Benin in relation to drinking water. Nitrite and nitrate concentrations are low despite the fairly intensive agricultural activities in the region. This assumes that the dissolved nitrogen could be in organic and/or ammoniacal form.



Figure 2: Content of suspended solids (SS), sulphates in water

There are no standards to limit the presence of suspended solids in surface water intended for drinking water in Benin and to assess the quality of this water. TSS often carries various contaminants into the water column that are adsorbed to particulate matter. TSS values range from 201 to 460 mg. L^{-1} . The main sources of suspended solids in rural areas are anthropogenic activities (agriculture) or natural leaching of soils, especially during the wet period. The low flow of water and the evaporation of water during the dry period resulting in a concentration of the solid phase, which induces an increase in suspended solids.

The sulphate concentrations obtained are higher in the village of Gorgoba (site 2) with a value of 614.5 mg/L, while in the villages of Sakabo (site 7) and Saramarou (site 8) values of 505.2 mg/L were recorded.

Sulphate concentrations are well above the Beninese standard of 500 mg. L^{-1} at all stations during both seasons. Sulphates can be of natural origin (dissolution of rocks and oxidation of sulphide minerals) and/or

anthropogenic origin (atmospheric deposition and wastewater). In this region, sulphates could be used as fertilizers (agricultural activities).



Figure 3: COD and BOD5 content in water

The high concentrations of COD and BOD5 are highest in Sakabo village (site 7) with levels of 25.18 mg/LO2 and 11 mg/LO2 respectively; their low values are obtained in the village of Yakabissi (site 1) with levels of 2.7 mg/LO2 and less than 1 mg/LO2 respectively.

For COD, the measured values range from 1.13 to 25.18 mg O2. L-1. Organic loads that are difficult to degrade are significant at site 7. This could be explained by the leaching of organic compounds accumulated in soils after precipitation.

BOD5 is elevated at site 7 and low at site 1. The high BOD5 value recorded at site 7 (11 mg O2. L-1) could be explained by the rejection of the highly developed agricultural and livestock activities in this part of the river.

In order to estimate the biodegradation of the organic matter present in the different water samples, we calculated the COD/BOD5 ratio, which is often used in the literature to characterize water15. Then:

COD/BOD5<2: readily biodegradable effluent;

2< COD/BOD5<3: biodegradable effluent;

COD/BOD5>3: non-biodegradable effluent.

The results of COD/BOD5 ratio calculations are summarized in the following table:

Samples	COD/BOD5 ratio	Biodegradability			
S1	1,14	Easily biodegradable			
S2	2,31	Biodegradable			
S3	2,60	Biodegradable			
S4	2,49	Biodegradable			
S5	2,30	Biodegradable			
S6	2,30	Biodegradable			
S7	2,28	Biodegradable			
S8	3,04	Non-biodegradable			

Table 2: COD/BOD5 ratio values for water

The results of calculations show a ratio of 2< COD/BOD5<3 on the majority of the samples, which indicates that the pollutant load contained in these waters is biodegradable.



Figure 4: Phosphate, total phosphorus and NKT content in water

For phosphates, concentrations range from 0.27 to 0.49 mg/L. The high phosphate levels are obtained in Yakabissi with an average value of 0.49 mg/L and the low value obtained in the villages of Kpekpakara and Sakabo with an average value of 0.27 mg/L.

High concentrations of NKT were obtained in the village of Yakabissi (site 1) with a mean value of 6 mg/L and low in the village of Tokoro with a mean value of 0.04 mg/L.

From the results obtained, we can see that the waters of the Mékrou River basin are characterized by high values of SO4²⁻, BOD5 and suspended solids.

Physico-chemical parameters of sediments

Sediment is considered to be an effective interpretive and reading tool in terms of environmental management. Indeed, they constitute an integrating compartment of contamination that complements the results obtained in the waters, which are representative of a given moment. In general, sediment acts both as a storage compartment and/or as a source of metal contamination depending on the conditions of the aquatic environment through the two phenomena of trapping and solution of particles contaminated by metallic elements. The study of sediment quality in aquatic environments has been the subject of several studies at the international^{16,17} and local scales¹⁸.



Figure 5: Nitrate, nitrite and phosphate content in sediments

Figure 5 shows the variations in nitrate, phosphate and nitrite values between the different sites analyzed. The analysis of Figure 5 reveals that the maximum nitrate content is recorded at site 1 and the minimum

The analysis of Figure 5 reveals that the maximum nitrate content is recorded at site 1 and the minimum value is recorded at site 3. Their nitrite content ranges from 165mg/Kg to 2570mg/Kg.

According to the same figure, the maximum value of total phosphorus content is recorded at Site 4 and the minimum value is recorded at Site 8.



Figure 6: pH, MOT, CEC in sediment

Analyzing the results in Figure 6, we can see that the pH is less than 7. The maximum value is recorded at the level of Tokoto village with a value of 6.63 and the minimum value is recorded in Saramarou village with a value of 4.93.

From the results of this same figure, we can deduce that the percentage of organic matter in all our samples is low with values between 0.38% (site 3) and 3.14% (site 8).

Regarding CEC, the maximum value is noted in the village of Saramarou (site 8) with a value of 19,200 meq/100g and the minimum value is noted in the village of Gorgoba (site 2) with a value of 1,280 meq/100g.

IV. Discussion

Temperature is a parameter that influences the various biological and chemical activities in water and plays a main role in the distribution and development of fauna and flora. This is because high water temperatures are harmful to aquatic life as they contribute to the reduction of oxygen content in the water. As a result, it helps to increase the rapid growth of algae and microorganisms. Our measurements show that the temperature of the analyzed water samples is between 28° C and 30.5° C. These differences simply depend on the day and time the temperature was measured. In addition, the temperature in southern Benin is generally higher for this time of year. Therefore, for a better comparison, a measurement of the temperature of the different sites should be carried out in the same day. Nevertheless, temperatures seem to be within the limit for this time of year.

pH indicates how acidic or alkalinistic the water is. pH values at various sites range from 6.81 to 7.50. It therefore varies between neutral and slightly alkaline pH, a sign of the presence of carbonates. However, the pH of all sites is within the acceptable limit by the World Health Organization (pH between: 6.5-8.5). Therefore, aquatic life in these different sites is not threatened.

Conductivity is the measure of the ability of water to conduct electric current and it depends on the concentration of ions. For this reason, it can also be an indirect measure of total dissolved solids. Conductivity values for selected sites range from 251 to 1662μ S/cm. However, the only value above the WHO limit (1500μ S/cm) is that of Site 4. These values likely indicate the presence of high amounts of ions or contaminants in the water, compared to other sites. This could be due to significant human activities in this area, especially sewage discharges. It was observed that the concentration of nitrite in the water samples did not exceed the limit determined by the WHO (0.1mg/L) at the 8 sites. However, we found the opposite at the sediment level with levels that are much higher than that of the limit, this is a sign of major pollution.

It should be noted that a high concentration of nitrite in water is often due to the biological decomposition of nitrogenous organic matter present in wastewater and animal and plant waste. Therefore, we can conclude that the sediments in site 1 may constitute a danger risk for the inhabitants of this village (nitrite can cause the development of cancer and methaemoglobin disease.

Nitrate concentrations at the various sites ranged from 0.6 to 1.4 mg/L. The highest concentration is observed in Gorgoba (1.4 mg/L), but it is still below the WHO limit (which is equal to 50 mg/L). In sediment samples, concentrations range from 18000mg/Kg to 72000mg/Kg. These high values may be due to excessive use of fertilizers in agriculture, plant and animal waste, and domestic effluents.

All water samples have sulphate concentrations well below the maximum acceptable WHO limit for sulphate (250mg/L).

Negligible amounts of phosphate were observed in most water samples. But we see a high concentration in the sediments, especially those at site 4. This high phosphate concentration could be due to the use of phosphate fertilizers and manure from farms at very high rates near this village.

The consultation of sulphate water is higher than the limit value required according to the Beninese standard for drinking water (1200mg/kg). This allows us to say that the presence of sulphates in these waters would explain their slight acidity and this could have a risk on the environment.

CEC is an important indication of sediment fertility. The higher the CEC, the more cations it can retain in the sediment, the less these cations can be used to improve sediment structure (e.g., Ca^{2+}) or to feed plants (e.g., NH4⁺). The CEC depends on the quantities and types of clays and the organic matter present, the more there are, the higher the CEC. It should be noted that the CEC values of our samples are not high, they vary between 1.280meq/100g and 19.200meq/100g and this is directly attributable to the low levels of organic matter in all the water samples.

V. Conclusion

The present work is part of the assessment of the environmental quality of the waters and sediments of the Mékrou River, whose waters are used in particular for drinking water and irrigation. The choice of our study area was the communes of Kouandé and Pehunco, crossed by the Mékrou River.

In recent decades, the Mékrou River has been under strong anthropogenic pressure due to significant population growth and intense agricultural activities. These activities produce large volumes of waste of all kinds that are discharged directly into the natural environment, which can threaten humans and their environment.

This study is the first comprehensive study of aquatic environments by integrating physico-chemical parameters in the water and sediment compartments.

This work allowed us to assess the impact of these agricultural activities on the water and sediment quality of the eight selected villages. The waters of the Mekrou River revealed water and sediment pollution mainly at site 2 in the village of Gorgoba. Elevated concentrations of COD, TSS and SO42- were recorded. Water samples from Sakabo village (site 7) are characterized by high concentrations of COD and BOD5.

The contamination of the waters of these rivers is strongly linked to discharges from agricultural activities, but also from artisanal activities such as tanneries located near sampling sites. It is also linked to diffuse pollution along the Mékrou River, which often complicates the identification of sources of pollution.

The present study showed that agricultural discharges cause the degradation of water and sediment quality in the Mékrou River. This makes the water in the rivers unsuitable for irrigation and the production of drinking water.

In the context of the recent and rapid demographic change in this geographical area, improving water quality represents a real challenge for the Mékrou River, the main source of irrigation water and drinking water in northwestern Benin.

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