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ORIGINAL ARTICLE

Distribution, Speciation and Bioavailability of Nutrients in M'Badon Bay of Ebrie Lagoon, West Africa (Côte d'Ivoire)

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Abstract

Rapid economic development and rampant urbanization are accelerating the eutrophication of coastal environments. This is the case of the bay of M'Badon in Côte d'Ivoire, located in an area not far from an open dump, which is under strong anthropogenic pressure. However, no data is available on nitrogen and phosphorus distribution in the water column and sediments of the M'Badon bay. This study not only targets the distribution of phosphorus and nitrogen, but also the speciation of phosphorus in sediments in order to assess its bioavailability. In order to do this, the waters of the bay of M'Badon were analyzed with a spectrophotometer and the speciation of phosphorus in the sediments was made according to the method of Williams. The results showed that PO_4^{3-}, TP, NO_3^-, NO_2^- and TN concentrations in the water column varied significantly among the seasons. While, that of NH_4^+ did not vary between the seasons. In the water column, inorganic phosphorus (0.94 ± 0.12 mg L^{-1}) is high and represents 65.3% of the TP. In addition, inorganic nitrogen concentration (0.33 ± 0.14 mg L^{-1}) was low and organic nitrogen constituted 85% of TN in the water column. The results also indicated that Fe–P concentration (522.8 ± 233.4 µg g^{-1}) represented the highest fraction of phosphorus in sediments with a percentage of 59.5%. Potential bioavailable P accounted for an average of 95.4% of TP in sediments. So, M'badon bay is an important reservoir of bioavailable phosphorus which might accentuate the eutrophication during several decades in the bay.

Keywords Phosphorus · Nitrogen · Speciation · Bioavailability · Bay · Sediment

1 Introduction

Coastal systems such as bays, lagoons and coastal beaches are important contributors to the productivity and survival of life worldwide [1, 2]. Urbanization disrupts the hydrology of coastal systems [3]. Intense human activities generate significant quantities of nutrients whose transport in coastal waters modify the biogeochemical processes that occur. Urban and industrial waste, river inputs as well as submarine groundwater inputs are among the main sources of nitrogen (N) and phosphorus (P) in lagoon [4]. Lagoons are generally shallow, but have deep light penetration. Lagoons play an important role in the primary productivity and respiration of aquatic fauna and flora. They are a reservoir for regular storage and recycling of nutrients and carbon [5–7], which makes them vulnerable to eutrophication [8, 9]. Eutrophication is a major problem that deteriorates aquatic ecosystems around the world, resulting in economic losses, biodiversity [10], harmful algal and cyanobacteria blooms. These blooms of cyanobacteria can have a significant impact on people's health [11, 12]; they can trigger intense turbidity, anoxic conditions and massive fish kills, alter the food chain by producing foul odors and carry dangerous toxins [13, 14]. Several authors show that phosphorus (P) is a key nutrient that contributes significantly to reducing marine phytoplankton blooms and primary productivity of lagoon and marine ecosystems [15–18]. In addition,

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the sediments constitute an important reservoir of phosphorus and nitrogen which results from the interactions of complex biogeochemical process [19, 20]. In reality, nutrient cycles are not isolated from each other. A joint reduction of the inputs of N and P is therefore essential to slow down eutrophication along the land-sea continuum [21]. Sediments are also a significant source of phosphorus for the maintenance and productivity of marine ecosystem and estuarine production, but this depends on the sedimentary speciation of phosphorus. This is why knowledge of the main forms of phosphorus in sediments is essential for understanding its cycle and assess its bioavailability in estuaries.

In developing countries, such as Côte d'Ivoire, the management of household and industrial waste, rampant urbanization and urban wastewater has compromised the health of aquatic environments [22]. These aquatic environments are therefore very regularly loaded with nutrients (phosphorus and nitrogen) from diffuse (e.g. agricultural activities) and occasional (e.g. domestic and industrial wastewater) sources [23]. The release of P and N into sediments is a significant factor in the dynamics of P and N cycling in aquatic systems. This is particularly the case of the Ebrié lagoon in the megacity Abidjan, which has experienced significant population growth in recent decades. It is severely tested by human activities such as the untreated leachate from the Akouédo landfill and urban wastewater. Its banks proliferate algae permanently disturbing the activities of fishermen, who revealed during our investigation that they found fish sometimes dead on it. However, the urban wastewater connected to it is not treated, specifically the leachate from the landfill in M’Badon Bay. Indeed, pollution by phosphorus and nitrogen in groundwater, surface and marine waters causes serious consequences on the economy, the environment and deteriorates the quality of human health [24–26]. Bay sediments not far from the uncontrolled landfills were sampled to study the geochemical processes of phosphorus and nitrogen in highly contaminated environments. Understanding these processes can provide useful information for managing coastal waters. In this study, the purpose was to examine the speciation of phosphorus in the sediments of M’Badon Bay in order to assess its bioavailable fraction. More specifically, this work determined the spatial and seasonal variations of phosphorus and nitrogen in the waters of the bay as well as the factors influencing them. The different fractions of P present in the sediments to quantify the potentially mobile P and the origin of phosphorus in the bay estimated.

2 Materials and Methods

2.1 Study Area

M'Badon Bay is located between latitude 3° 89′ E and latitude 3° 90′ E, at latitude 5° 34′ N and at an altitude of 73 m above sea level. It is one of several bays in the Ebrie Lagoon (Fig. 1). This bay covers an area of 3.91 km^2 and has a perimeter of 8 km. Its depth is generally less than 3 m, with an average length and width of 2.3 km and 1.70 km respectively. The volume of water in this bay is estimated at 9.8×10^6 m^3. Its watershed is estimated at 78,000 km^2. This bay is unique because of its geographical location. It is sequestered by leachate from the Akouédo landfill near it, which receives almost all of the medical, household and industrial waste from the city of Abidjan. Macrophytes are permanently installed on its banks, but they increase during flood periods over the whole bay with the inflow of river water from the Comoe and ocean water. This bay undergoes changes throughout the year. The particle size of the sediments is composed of silt, clay and sand with a strong sandy.

2.2 Samples Collection

All laboratory equipment used for sampling was washed with soap, rinsed 3 times with tap water. This sampling material was then rinsed 5 times with distilled water, before being left for 5 days in 10% HCl. Finally, the material was rinsed 5 times with Milli-Q water (Millipore) to avoid contamination. Field sampling was carried out during July 2016, November 2016 and March 2017. During each sampling trip, surface and bottom water samples were collected using a Niskin bottle. A stainless steel Van Veen bucket with a surface area of 0.02 m^2 was used for surface sediment sampling at stations numbered M1 to M12. Finally, a circular polycarbonate tube (7 cm internal diameter; 90 cm long) [27] was used to make a 50 cm sediment profile at station M2 in March 2017 with minimal disturbance. Samples from depths of 0–10, 10–20, 20–30, 30–40 and 40–50 cm were collected and placed in 100 mL high density polyethylene bottles. The different campaigns resulted in the collection of 72 water samples and 41 sediment samples. The samples were placed in 1 L polyethylene bottles of water, filtered through cellulose acetate membranes (Millipore, 0.45 µm pore size) before being collected in 0.5 L polyethylene bottles for analysis of ammonium (NH_4^+), nitrite (NO_2^-), nitrate (NO_3^-) and phosphate (PO_4^{3-} and TP) in the laboratory. The collected surface sediment samples were placed in 0.5 L polyethylene bottles. All samples were immediately placed in a cooler to be stored at 4 °C. In the laboratory, the water samples were analysed within 24 h of collection.

The parameters such as temperature, pH, dissolved oxygen (DO), salinity, EC, total dissolved solids (TDS), Turbidity, total suspended solids (SS), and depth were measured in situ using a multiparameter HACH (YSI). Before measurement, the storage (calibration) cup was removed, and the Data Sonde of the multiparameter HACH was placed in the water. After the completion of measurements, the probes

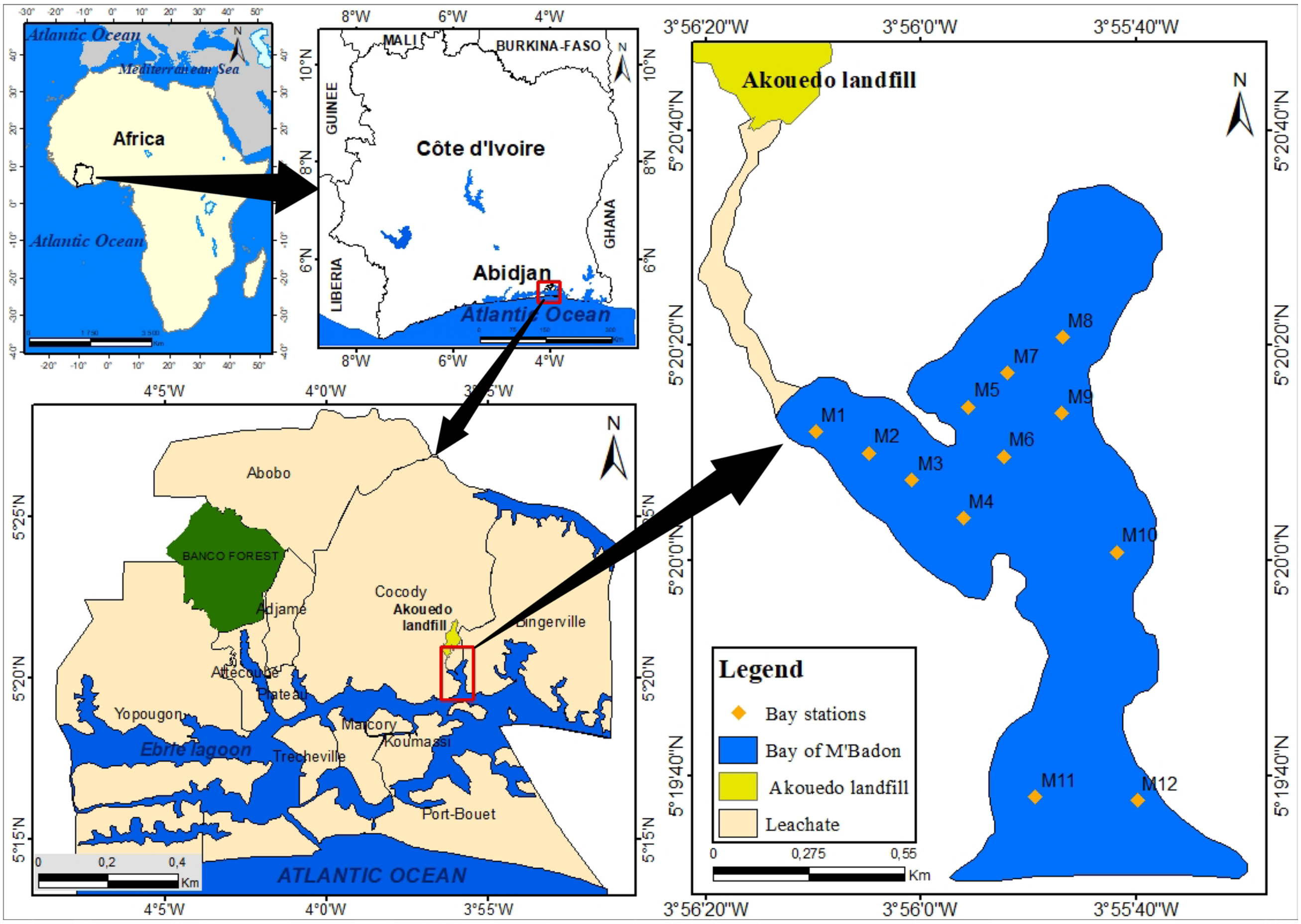

Fig. 1 Study area and sampling stations

were rinsed with distilled water followed by the replacement of a storage cup, with tap water [28].

The water transparency was determined using a Secchi disk depth. To do this, the disk is lowered into the water while observing the depth at which it disappears. It is lowered some more and then raised while observing the depth at which it reappears.

2.3 Water Sample Analysis Methods

The water samples were analysed using a spectrophotometer HACH. The Murphy and Riley method [29] was used for the determination of phosphorus at 700 nm. The indophenol-based method of Aminot and Chaussepied [30] was used for the determination of ammonium at 630 nm. Nitrate was determined by the sodium salicylate and sulphuric acid method after treatment with alkali [31] at 430 nm, nitrite by diazotization with formation of a stable pink dye [30]. The modified micro-Kjeldahl method [32] was used to determine Kjeldahl nitrogen. The total nitrogen was determined by calculating the sum of TKN + NO_3^- + NO_2^-. APHA [33] which consists of hot mineralisation using concentrated sulphuric acid and sodium persulphate was used to measure total phosphorus (TP). At the beginning of the analysis, the spectrophotometer was calibrated. Each sample was analysed three times. After ten samples, a standard dilution was analysed. The detection limits for the nutrients were calculated as three times the deviation standard of the blank concentrations [34]. They were 0.005 mg L^{-1}, 0.002 mg L^{-1} and 0.004 mg L^{-1} for nitrate, ammonium, and phosphate, respectively.

To test the accuracy and precision of the data, triplicates measurement tests were performed. The error obtained were within 5% (Table S1, supplementary material).

2.4 TOC and pH in Sediments

After freeze-drying the sediment samples, they were ground in an agate mortar and a nylon sieve (100 mesh) was used to screen them. After removal of solid waste and stones, the sediments were placed in protected polyethylene bottles for analysis. The determination of total carbon (TOC) was done by loss on ignition (%). This method involves the destruction of organic elements by high heat. 1 g of dry sediment was placed in a porcelain crucible then in an oven heated to 550 °C. for 4 h. The sample is removed from the oven and cooled in a desiccator and then weighed [35]. The pH analysis was performed as described by Kuwano et al. [36]. The dry sediment sample is mixed in distilled water in a mass to volume ratio of 1:2.5. The mixture obtained was stirred for 15 min and decanted for 30 min. The pH was measured on the supernatant using a pH-meter.

2.5 Total Phosphorus (TP) in Sediments

The extraction of PT from sediments is carried out according to the Williams method [37]. The procedure consists of collecting 0.2 g of dry sediment in porcelain crucibles. After calcining the sediment at 450 °C for 3 h, 20 mL of HCl (3.5 mol L^{-1}) is added to the tubes after cooling. It is important to add the HCl directly to the porcelain crucibles to facilitate the transfer of the calcined sediment into the tubes. The tubes are shaken overnight (16 h) and then centrifuged at 2000 rpm for 15 min. The supernatant is collected and then assayed using the colorimetric method of Murphy and Riley used for water and leachate samples.

2.6 Phosphorus Speciation in Sediments

Using the sequential extraction method developed by Williams et al. [37], four different sediment phosphorus fractions were determined, namely iron-bound P (Fe–P), calcium-bound P (Ca–P), exchangeable P (Ex-P) and organic P (OP). All prepared dry sediment samples were shaken vigorously with a mechanical shaker overnight (16 h). These samples were then centrifuged at 2000 rpm for 15 min and the extract was placed in a volumetric polyethylene flask for analysis. The residue was washed twice with 1 M NaCl solution and shaken on a rocker shaker (Rotospin model, Tarsons) for 5 min, then centrifuged at 2000 rpm for 15 min. The supernatants collected in cases were analysed by the colorimetric method of Murphy and Riley. The Fe–P and Ca–P fractions on the one hand and the Ex-P and OP fractions on the other hand were described using 0.2 g of dry sediment by the following procedures [9, 38].

Step 1 (Fe–P): 0.2 g of dry sediment placed in centrifuge tubes with 20 mL of 1 M NaOH was shaken overnight (16 h), centrifuged. In test tubes containing 10 mL of the supernatants, 4 mL of 3.5 M HCl was added, shaken vigorously for 20 s and left to stand for 16 h (overnight) which favoured brown deposit formation. The extract was centrifuged again and analysed.

Step 2 (Ca–P): 20 mL of 1 M HCl was added to the rinsed residue from the first step in test tubes. After shaking for 16 h and centrifugation, the extract was analysed.

Step 3 (Ex-P): 0.2 g of dry sediment placed in centrifuge tubes with 20 mL of 1 M HCl was shaken overnight (16 h), centrifuged. The extract was centrifuged again and analysed.

Step 4 (OP): Using an oven at 80 °C the rinsed residues from the third step were dried, placed in an ultrasonic bath for 10 s and transferred to porcelain crucibles for calcination in an oven at 450 °C for 3 h. The calcined sediments were again transferred to centrifuge tubes by adding 20 mL of 1 M HCl and shaken overnight (16 h). After centrifugation, the extract was analysed.

Each sample was analysed three times for quality assurance. The reliability of the sequential extraction protocol was checked by comparing the sum of the four fractions (Fe–P + Ca–P + Ex-P + OP) with the total phosphorus concentration measured [39]. The recoveries of samples ranged 87–113% (Table 2).

3 Results and Discussion

3.1 Physico-Chemical Parameters of M'Badon Bay

The minimum, maximum and average values for the determined physic-chemical parameters of M'Badon Bay are presented in Table 1. The average depth of the sampling stations was 3.02 ± 1.41 m, with values between 1.1 m (M1) and 6.63 m (M2) (Table 1). Temperature ranged from 25.39 to 31.82 °C, with an average of 29.57 ± 1.85 °C. During our investigation, the stations (M1, M2, and M3) in the bay near the leachate were the hottest. Insolation and leachate influence this parameter in the bay [40]. The pH varied from 6.19 at the M12 station to 8.47 at the M10 station, with an average of 7.2 ± 0.64. So, bay waters were basic at the stations near the landfill and acidic in its channel (Table 3). Dissolved oxygen (DO) values ranged from 1.50 (M1) to 4.21 mg L^{-1} (M6), with an average of 2.89 ± 1.09 mg L^{-1}. There is no significant difference (ANOVA, $p < 0.05$) between stations for dissolved oxygen. The waters of the lagoon bay are hypoxic. Salinity ranged between 2.07 and 5.97 psu (3.28 psu in average). These low values could be explained by the fact that M'Badon Bay is the bay of Ebrie Lagoon furthest from ocean waters. The high electrical conductivity (5.73 ± 2.18 mS cm^{-1}) and the high TDS values (2–7.21 g L^{-1}) reflect a strong mineral and organic charge in the bay, with high suspended solid (24.71 ± 4.74 mg L^{-1}). The inflows from the Comoe River further degrade these parameters with its procession of suspended solids. Secchi depth noted a low transparency (< 1 m) of the bay, reflecting a weak penetration of light and a decrease in photosynthetic activities.

Table 1 General characteristics of M'Badon Bay (minimum, maximum, average and SD values of all combined stations for $n = 36$ samples)

Parameters	Minimum	Maximum	Average	SD values
T (°)	25.39	31.82	29.57	1.85
pH	6.19	8.47	7.20	0.64
DO (mg L^{-1})	1.50	4.21	2.89	1.09
Salinity (‰)	2.07	5.97	3.28	1.02
EC (mS cm^{-1})	3.29	11.07	5.73	2.18
TDS (g L^{-1})	2.00	7.21	3.31	1.24
Turbidity (NTU)	4.00	45.50	21.16	11.20
SS (mg L^{-1})	14.00	38.50	24.71	4.74
Secchi depth (m)	0.28	0.68	0.44	0.09
Depth (m)	1.10	6.63	3.02	1.41
PO_4^{3-} (mg L^{-1})	0.44	1.49	0.94	0.35
NO_3^- (mg L^{-1})	0.27	15.49	2.88	3.59
NH_4^+ (mg L^{-1})	0.07	1.20	0.36	0.21
NO_2^- (mg L^{-1})	0.00	1.28	0.33	0.39
TP (mg L^{-1})	0.71	2.08	1.44	0.39
TN (mg L^{-1})	9.56	55.87	25.54	14.32

3.2 Nutrients Concentration and Distribution in Water

In study, the average concentrations at each station result from the average concentrations of surface and bottom water because no significant difference was observed in Table 1. Spatial and seasonal variations over the study period are shown in Figs. 2 and 3.

The mean concentrations in the bay are 0.94 ± 0.12 mg L^{-1} and 1.44 ± 0.23 mg L^{-1}, respectively for PO_4^{3-} and for TP (Table 1). During the study period, TP concentrations at all stations were greater than 0.1 mg L^{-1}. Inorganic phosphorus in bay water accounts 65.3% of TP. The seasonal evolution of PO_4^{3-} and TP indicates a predominance of these parameters in the dry season with respective mean concentrations 1.40 ± 0.05 mg L^{-1} and 1.72 ± 0.12 mg L^{-1}. We note the minima in the flood season for PO_4^{3-} (0.65 ± 0.18 mg L^{-1}) and in the rainy season for TP (1.02 ± 0.24 mg L^{-1}) (Fig. 3). We observe a statistically significant difference between seasons over the study period for phosphorus (PO_4^{3-} and TP) (ANOVA, $p < 0.001$). Phosphorus is potentially high in the bay, with a high bioavailability of phosphorus. These high values of PO_4^{3-} and TP reflect a significant exogenous input of P in the bay from the leachate. The results show that the lagoon bay of M'Badon is a hypereutropic environment marked by the permanent presence of aquatic vegetation (macrophytes) along its shore. This state reflects the vulnerability of the lagoon bay, and the structural and functional degradation of the bay's health. Furthermore, the available phosphorus and the TP remained homogeneous during the study period in bay water. This could be explained by the shallow depth of the bay. Therefore, we note a mobility of phosphorus from the water bay to sediments, where it is buried and stored to the sediment, where it is buried and stored. In the literature, several authors have shown that in the estuarine environment, soils and sediments mainly retain phosphorus [41]. In anoxic conditions or during the movement of sediments, P can be remobilized in the water column according to biological demand. Nitrate has the highest form of inorganic nitrogen with a mean value of (2.88 ± 2.49) mg L^{-1} (Table 1), with a large fluctuation at the stations. In contrast, nitrite is the lowest inorganic form (0.33 ± 0.14) mg L^{-1}. Total nitrogen (TN) reveals an average concentration of (25.4 ± 7.22) mg L^{-1} of which organic nitrogen represents 85%. Seasonal variations show significant differences ($p < 0.001$) for NO_3^-, NO_2^- and TN. Nitrate records the lowest value in the dry season with (0.45 ± 0.18) mg L^{-1}. NO_2^- and TN evolve in similar ways with peaks in the flood season respectively (0.81 ± 0.32) and (42.16 ± 9.71) mg L^{-1} (Fig. 3). Ammonium shows no particular evolution. The concentration of NH_4^+ in M'Badon bay was higher than that of Banco bay and similar to that of Cocody and Biétry bays. On the other hand, the concentration of NO_2^- in the bay of M'Badon was higher than these bays [42]. Total nitrogen accumulates in the bay during the flood with decreasing ammonium, unlike the rainy and dry seasons. The concentration of nitrate in M'Badon Bay is similar to that found in Johnstone Lagoon in Australia (2.66 mg L^{-1}) [43], but lower than in Marano and Grado lagoons in Italy (3.66 mg L^{-1}) [44] and Cachoeira in Brazil (6.01 mg L^{-1}) [45]. The concentration of nitrite in our study is also similar to that evaluated in the Porto-Novo lagoon (0.37 mg L^{-1}) [46] but lower than the average value obtained in Cachoeira in Brazil (1.92 mg L^{-1}). As for ammonium, the lagoons of Itajai-Açú [47], Cachoeira and Porto-Novo showed higher mean values. According to SEQ-EAU [48], aquatic life can be seriously affected for concentrations of 2 mg L^{-1} for NH_4^+, 0.5 mg L^{-1} for NO_2^- and 13 mg L^{-1} for NO_3^- [49]. The average concentrations of NH_4^+, NO_2^- and NO_3^- show that these parameters present no risk in the bay. However, in the literature, authors have shown that nitrogen is of anthropogenic origin for nitrate values greater than 2.7 mg L^{-1} [50, 51]. In addition, organic nitrogen is the most important form of TN. So, like the P, the nitrogen in the bay is beieved to be anthropogenic. The flood season seems to indicate that organic nitrogen transformed into NH_4^+ is oxidized by the action of nitrifying bacteria to NO_2^- and then to NO_3^-. The oxidation of NO_2^- to NO_3^- is more marked during the rainy season favored by good oxygenation [52]. The low nitrate content could be explained by its strong assimilation by biomass on the one hand and by denitrification due to the low oxygenation of the bay on the other [1, 53]. Nitrate, which is the most available form of total nitrogen,

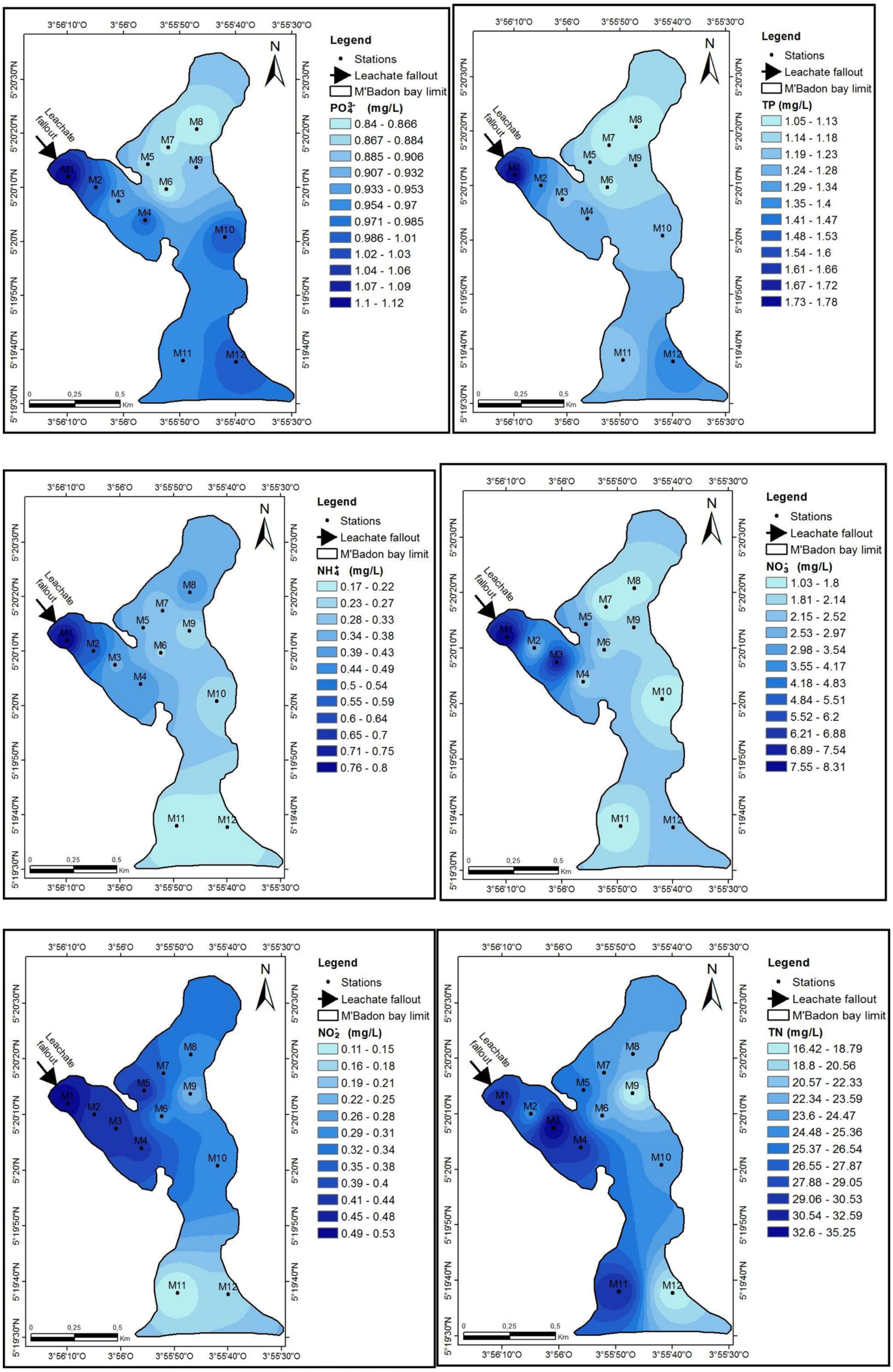

Fig. 2 Spatial variations of phosphorus ((PO$_4^{3-}$, TP) and nitrogen (NH$_4^+$, NO$_3^-$, NO$_2^-$, TN) in M'Badon Bay

can pose a risk of eutrophication to rivers or lakes from 1 mg L^{-1}. The increase in ammonium during dry and rainy periods would be due to ammonification of organic nitrogen, essentially provided by heterotrophic bacteria which use the oxidation of organic carbon to CO$_2$ as an energy source to release nitrogen in NH$_4^+$ form which undergoes nitrification. The shallow depth of the bay and heavy precipitation would expose the TN to a dilution phenomenon. The spatial distribution of nutrients over the study period is shown in Fig. 2. The results show that stations M1, M2 and M3 were generally more impacted for all these nutrients. However, we do see significant concentrations of PO$_4^{3-}$ at station M10 and total nitrogen at station M11. In fact, the leachate is directly linked to the bay, first touching these stations. This

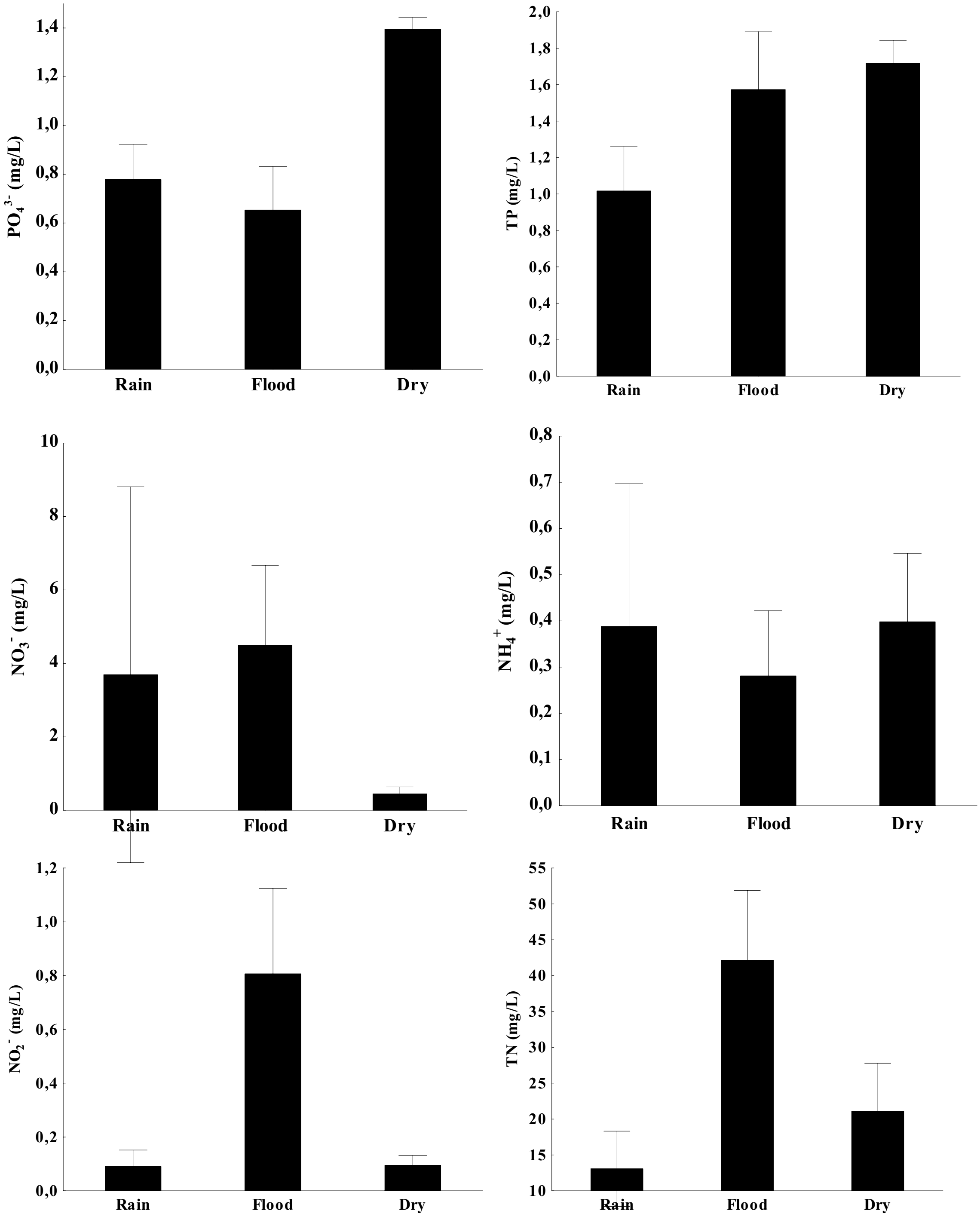

Fig. 3 Temporal variations of phosphorus (PO_4^{3-}, TP) and nitrogen (NH_4^+, NO_3^-, NO_2^-, TN) in the M'Badon Bay

finding proves that the anthropogenic source of nutrients emanates preferentially from the Akouédo landfill. During our study, the dredging operation to the eastern side of the site promoted the release of PO_4^{3-} from the sediments into bay water. Wastewater discharges via underground pipes and freshwater from the Comoe River would be additional sources of nitrogen entering the bay (Table 2).

3.3 Statistical Relationship

The principal component analysis (PCA) of the variables in the factorial plane F1 × F2, presented in the form of a circle of correlations in Fig. 4 highlights the factorial axis F1 which is defined on the one hand, in negative by the dissolved oxygen (− 0.59), salinity (− 0.71), EC (0.74),

Table 2 Values of calculated TP and measured TP at the different stations

Stations	ΣTP	TP	Recovery (%)
M1	1196.2	1327.5	90.11
M2	1540.8	1367.4	112.67
M3	1488.0	1343.2	110.77
M4	661.6	721.5	91.70
M5	598.7	683.4	87.61
M6	429.3	454.7	94.48
M7	889.2	795.8	111.74
M8	964.5	851.1	113.2
M9	788.3	798.8	98.68
M10	1059.6	1024.6	103.41
M11	922.3	1015.6	90.81
M12	1031.0	948.5	108.70

ΣTP = Fe–P + Ca–P + Ex-P + OP

TDS (− 0.67) and transparency (− 0.52) and on the other hand in positive by TP (0.83), NO_3^- (0.89), NH_4^+ (0.88), NO_2^- (0.67), TN (0.61), temperature (0.58) and SS (0.82). Thus, the main component F1 reflects the control of nitrogen and phosphorus enrichment by physical parameters such as temperature, SS, EC, TDS, salinity and dissolved oxygen. The component F2 is defined in negative by PO_4^{3-} (− 0.83) and in positive by NO_2^- (0.55) and temperature (0.72). The representation of individuals (sampling stations) in the factorial plane F1 × F2 juxtaposed with that of the variables (Fig. 4) shows that stations M1 and M2 are more marked by mineral and organic pollution (TP, NO_3^-, TN and PO_4^{3-}) and the M3 station more marked in organic nitrogen. The strong correlation between the physicochemical parameters highlights, through the PCA, the anthropogenic origin of the chemical and organic pollution of the bay of M'Badon. However, the transport, stability, bioavailability of P and N, their toxicity to aquatic life depend on the one hand on their concentration in the aquatic environment, on the various associations with the mineral phase and/or organic in the various aquatic compartments and on the other hand, variations of certain parameters, in particular pH, redox potential, dissolved oxygen, electrical conductivity [54].

3.4 Different Fractions of Phosphorus in Sediments

The spatio-temporal concentrations of the different fractions of phosphorus (Fe–P, Ca–P, Ex-P, OP) in the surface and deep sediments are shown in Table 3 and in Figs. 5 and 6. The concentrations Fe–P, Ca–P, Ex-P and OP fractions oscillate, respectively from 101.7 to 1046.6 µg g^{-1} (522.8 ± 233.4 µg g^{-1}), 2.9–216 µg g^{-1} (46.4 ± 46.8 µg g^{-1}), 22.9–471.5 µg g^{-1} (205.1 ± 125.5 µg g^{-1}) and 9.6 to 258 µg g^{-1} (110.3 ± 70.0 µg g^{-1}). The proportions of the Fe–P, Ca–P, Ex-P and OP fractions of P vary, respectively from 38.5 to 95.5%, 0.4–13.0%, 2.9–43.3% and 1.2–30.1%. The order of the average percentages of the different P fractions in the sediments was as follows: Fe–P (59.5%) > Ex-P (23.1%) > OP (12.8%) > Ca–P (4, 6%). Fe–P is the dominant fraction of P at all stations and during the study period. Fe–P does not show any significant difference between seasons.

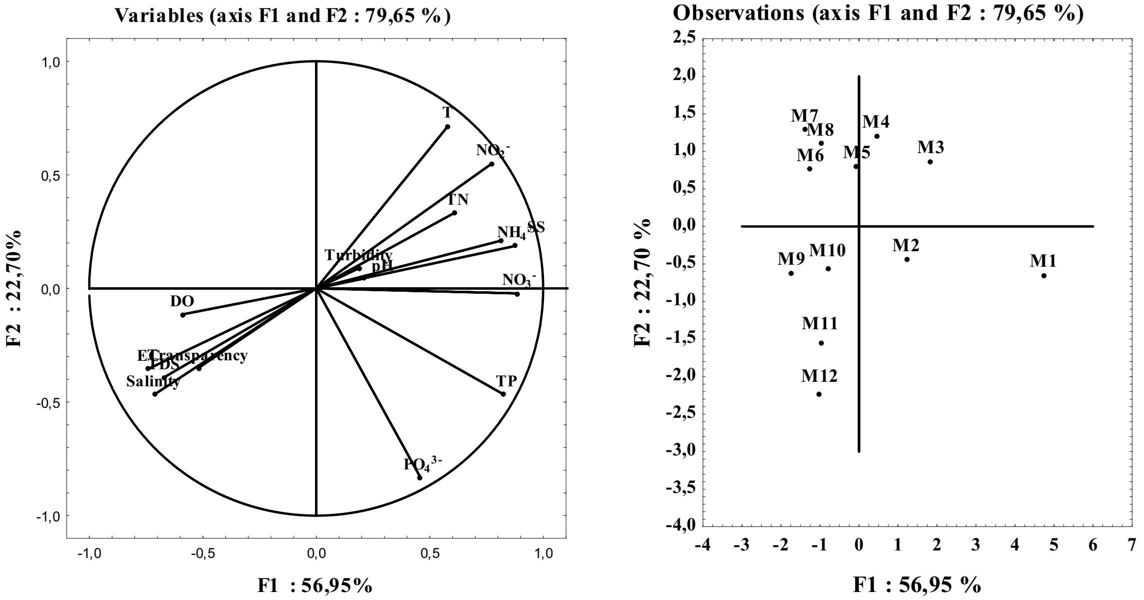

Fig. 4 PCA ordination diagram of the variables and observations. The first two principal components (F1 and F2) accounted together for 79.65% of the total variance

Table 3 Concentrations of different P species, including Fe-bound P (Fe–P), authigenic P (Ca–P), exchangeable or loosely adsorbed P (Ex-P), organic P (OP), as well as pH and the molar ratios of TOC over OP in surface sediments of the M'Badon Bay

Sampling site	pH	TOC (%)	Fe–P (μg g^{-1})	Ca–P (μg g^{-1})	Ex-P (μg g^{-1})	OP (μg g^{-1})	BAP (μg g^{-1})	TOC/OP
M1	8.35	4.188	588.6	106.5	347.6	153.5	1089.7	547.30
M2	7.53	2.899	769.1	119.3	444.2	208.1	1421.4	225.05
M3	7.80	3.927	765.7	96.8	431.3	194.2	1391.2	379.88
M4	6.64	5.750	377.8	41.4	209.6	32.8	620.2	908.74
M5	6.48	0.158	300.3	26.3	163.3	108.9	572.4	694.45
M6	6.10	4.918	244.0	15.5	129.7	40.0	413.7	613.73
M7	7.02	4.013	492.2	15.5	253.9	127.7	873.7	502.68
M8	6.87	10.638	483.3	64.0	273.7	143.5	900.4	754.23
M9	6.88	1.148	407.2	20.6	213.9	146.6	767.7	347.84
M10	5.74	5.607	680.2	12.4	346.3	20.6	1047.2	2135.58
M11	6.39	8.696	536.3	21.7	279.0	85.4	900.6	1238.20
M12	7.38	4.918	628.9	17.0	323.0	62.2	1014.1	702.01

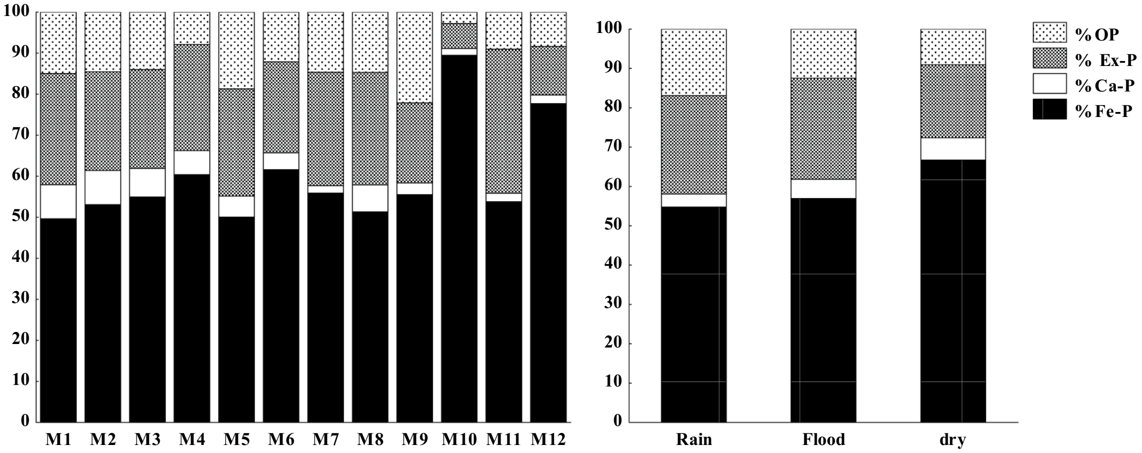

Fig. 5 Spatial and temporal distributions (%) of phosphorus species concentrations of surface sediments in M'Badon Bay

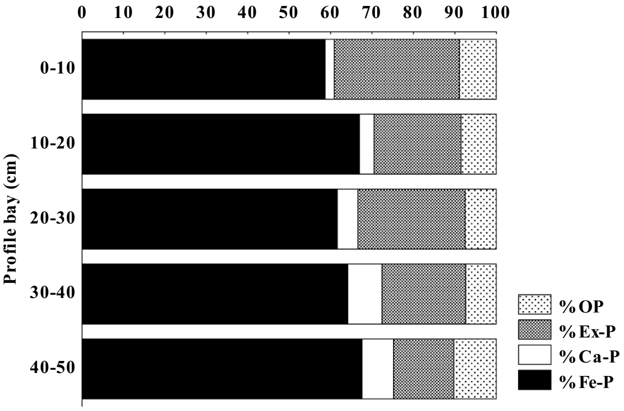

Fig. 6 Vertical profiles for different phosphorus fractions in M'Badon Bay

On the other hand, there is a statistically significant difference ($p=0.0038$) in the spatial distribution between station M10 and the other stations in the bay. The concentration of Fe–P is highest in the dry season (Fig. 5). Fe–P is inversely correlated with Ex-P ($r=-0.89$) and with OP ($r=-0.74$) (Table 4). The fraction of P bound to calcium (Ca–P) was the lowest. Figure 5 shows that the stations close to the landfill leachate have a higher proportion of Ca–P which decreases progressively overall, marked by a statistically significant difference ($p=0.0016$) between the stations (M1, M2) on the one hand and the stations (M7, M10) on the other. Like Fe–P, the dry season has the highest concentration of Ca–P ($5.68\pm3.05\%$). Ca–P is correlated with pH ($r=0.55$). The Ex-P is homogeneous over the study period, except for stations M11 and M10 which showed a significant difference (p = 0.021). The minimum and maximum concentrations are reached, respectively in the dry season (18.56%) and during the flood (25.70%). There is a strongly negative correlation (r = − 0.89) between Ex-P and Fe–P. With regard to OP, the maximum concentration is reached in the rainy season with an average proportion of 16.91% which gradually decreases. A significant difference (p = 0.00024) is found between stations close to the leachate (M2, M3) and stations in the bay channel (M5, M6, M8, M10). The OP fraction is negatively correlated with the Fe–P fraction (r = − 0.74) (Table 3). Like Fe–P, the Ca–P, Ex-P and OP fractions of P show no significant difference between seasons.

The distribution of the fractions of Fe–P, Ca–P, Ex-P and OP in the depth of the sediments of the bay at station M2 is given by Table 5 as well as the pH and TOC. The pH in the sedimentary layers gradually decreased with depth, but remained weakly basic. We observe a positive correlation between pH and fractions such as Fe–P (r = 0.93), Ca–P (r = 0.93) and OP (r = 0.98) (Table 6). No gradient was observed for TOC, which recorded its highest concentration (3.521%) at 30–40 cm depth. TOC is negatively correlated with Ex-P (r = − 0.87). The Fe–P, Ca–P, Ex-P and OP fractions of P show a loss of their concentration with depth. The Fe–P fraction is the most preponderant with an average proportion of 63.8%, while Ca–P is the lowest (5.3%). The concentrations of the Fe–P, Ca–P and Ex-P fractions are higher in the 10–20 cm layer. Statistical analysis of the data shows positive correlations between the fractions Fe–P and Ca–P (r = 0.97), Fe–P and OP (0.94), and Ca–P and OP (r = 0, 90) (Table 4).

Our results show that the Fe–P fraction in the sediments of M’Badon Bay has a dominant distribution with 59%. In addition, Naminata et al. [40] reported a high concentration of Fe (220–1120 µg L^{-1}) in the bay of M'Badon, which could explain this important affinity between P and Fe. To our knowledge, no data is available on the sequential extraction of P in the sediments of the Ebrie Lagoon. Therefore, no data from this area can be compared directly to our results. However, our results agree with those of Sutula et al. [55] where the significant fraction of P was Al/Fe–P (47%) in the sediments of the Mississippi. In contrast, Ca–P fraction observed in this study is much lower than that of the sediments of the Gulf of Mexico dominated by 79% Ca–P [56] and sediments from Florida Bay [57]. Fe–P fraction controlled by organic matter plays a major role in the release of P from sediments. Indeed, the anaerobic degradation of organic matter or the solubilization of the Fe-coated OP releases Fe–P in the sediments of

Table 4 Pearson correlation matrix for different P species, pH and TOC in surface sediments of the M’Badon Bay

	pH	TOC	%Fe–P	%Ca–P	% Ex-P	%OP
pH	1.00					
TOC	0.08	1.00				
%Fe–P	− 0.23	− 0.44	1.00			
%Ca–P	0.53	0.02	− 0.32	1.00		
% Ex-P	0.09	0.42	− 0.89	0.14	1.00	
%OP	0.14	0.33	− 0.74	0.05	0.41	1.00

Table 5 Concentrations of different P species, including Fe-bound P (Fe–P), authigenic P (Ca–P), exchangeable or loosely adsorbed P (Ex-P), organic P (OP), and pH in depth sediments of the M’Badon Bay

Depth (cm)	Fe–P (µg g^{-1})	Ca–P (µg g^{-1})	Ex-P (µg g^{-1})	OP (µg g^{-1})	pH	TOC (%)
0–10	951.5	106.8	204.8	144.2	7.53	2.899
10–20	1003.0	129.4	315.0	115.9	7.42	0.943
20–30	634.5	51.2	266.7	77.3	7.26	1.031
30–40	576.5	30.4	180.4	73.5	7.16	3.521
40–50	285.4	10.7	146.8	43.3	7.11	2.717

Table 6 Pearson correlation matrix for different P species, pH and TOC in depth sediments of the M’Badon Bay

	P-Fe	P–Ca	P-Ex	PO	pH	% COT
P-Fe	1.00					
P-Ca	0.97	1.00				
P-Ex	0.72	0.74	1.00			
PO	0.94	0.90	0.48	1.00		
pH	0.93	0.93	0.54	0.98	1.00	
% COT	− 0.37	− 0.46	− 0.87	− 0.14	− 0.28	1.00

the bay [58, 59]. Authors such as Malecki et al. [60] and Zhang et al. [59] generally reported that at the onset of anaerobic conditions, the P released was relatively large. In aquatic environments, iron is mainly found in colloidal and particulate forms due to its low solubility. Among the different types of natural particles, iron hydroxide and iron oxides have the highest phosphate adsorption capacity [61–63]. Accordingly, the concentration of iron hydroxide in the bottoms and suspended solids can play a major role in managing phosphorus storage in sediments. The arrival of fresh water from the Comoe River identified in the rainy season after heavy rains giving an earthy color to the lagoon could be an important route for the transport of land iron, mainly in the form of particles of colloidal form, in M'Badon Bay. However, amorphous P bound to Fe solubilizes more quickly than crystalline P bound to Fe [64]. The importance of Fe–P in the sediments seems to indicate that the forms of Fe in this environment may be more crystalline. The particle size and the pH influence the Ca–P in the sediments of the bay. The low proportion of Ca–P can be explained by the abundance of sand (Fig. 5) in bay sediments. However, Ca–P fraction increases according to the proportion of clayey silt in the sediments observed at the stations (M1, M2), but also with the pH. On the other hand, Christophoridis and Fytianos [65] reported that the Ca–P fraction increases slightly with pH, mainly due to the partial absorption of P on the limestone part of the sediment. Ex-P is easily exchangeable and readily available to phytoplankton, resulting from the adsorption of phosphate directly to the sediment mineral surface [66]. The higher Ex-P concentrations in rainy and flood seasons and at stations (M1, M2) suggest an anthropogenic impact (leachate, wastewater) and/ or the release by recycling of sediments. The proportion of OP in the sediments of M'Badon Bay is close to that observed obtained in Jiaozhou bay (17.56%) [67] and in the Changjiang estuary and the nearby eastern coast of China (16.1%) [19]. Our results showed that TOC is a potential factor that contributes to the increase and distribution of Ex-P and OP in sediments bay. As in leachate sediments, Ex-P and Fe–P fractions as well as OP and Fe showed opposite trends, confirming the impact of the leachate from the landfill on the distribution and cycling of P in bay sediments of M'Badon.

Our results showed that the Fe–P, Ca–P and Ex-P fractions are preferentially stored in 10–20 cm zone of the sediment profile, unlike the OP whose greatest reserve is found at the surface of the sediments (0–10 cm). The high concentration of Fe–P in depth of sediments cold show that phosphorus can be permanently fixed in an iron-bound form. The pH controls Fe–P, Ca–P and OP fractions in deep layers of sediments. The correlation between Ex-P and TOC highlights that this fraction of P can be mobilized and can indicate mechanisms determining interactions at water–sediment interface [68]. The close link between the different P fractions reflects the dynamism, mobility and complexity of P control in sediments.

3.5 Organic Matter to Phosphorus Ratio in Sediments

The results of TOC/OP ratio are shown in Table 3. In this study, the TOC/OP ratio in surface sediments during the study period and at all stations is greater than the ratio of 106 [69]. Molar ratios of organic matter and organic phosphorus (TOC/OP) in estuarine sediments can be used to interpret the dynamics and source of phosphorus in sediments [18, 19, 70–74], and to characterize the source and/ or the decomposition of organic matter [75, 76]. Higher TOC/OP ratios indicate the preferential loss of PO during organic matter degradation and early diagenesis. In addition, Ingall and Van Cappellen [70] found that TOC/OP ratios are indicative of the rate of sediment accumulation. Moreover, authors such as Ingall and Van Cappellen [70] have shown that the TOC/OP ratios are an indicator of the rate of accumulation of organic phosphorus in the bottoms. These ratios are comparable to those of Redfield in low sedimentation media, due to the high levels of P-bound organic residues or organic matter synthesized in the sediments by microorganisms [70]. Therefore, when in a coastal environment, the TOC/OP ratio higher than that of Redfield (106) is generally attributable to the predominance of terrestrial sources [71]. In addition, the high TOC/OP ratio could also imply preferential regeneration of P over carbon during decomposition of organic matter [76]. Our results suggest a predominance of terrestrial sources, with preferential release of P over C from organic matter, which occurs early in diagenesis [77]. Furthermore, Xu [78] reported that the content of terrestrial organic matter was higher compared to that coming from the sea in estuaries and coastal sediments of Hainan Island, which would likely explain the high TOC/OP ratio in M'Badon Bay.

3.6 Bioavailability of Phosphorus

The bioavailable phosphorus (BAP) representing P can be directed into the water-compounds composed of Ex-P, Fe–P and OP fractions in sediments [19, 66]. Mean concentrations of bioavailable phosphorus (BAP) ranging from 413.7 (station M6) to 1421.4 µg g^{-1} (station M2) and representing 95.4 ± 3.1% of TP in the sediment of the bath of M'Badon (Table 3). In this study, Fe–P was the most important fraction of BAP. The evaluation of bioavailable P is decisive in the management of eutrophication in coastal and marine environments [18, 66, 74]. When bioavailable P is released to higher waters, primary productivity will increase accordingly [64]. In the case of our investigation, sediments constitute a reservoir for storing and regulating phosphorus in the bay. The high bioavailability of P in the sediments constitutes a considerable reserve of P which can contribute to the eutrophication of the bay for a long time. Under certain physicochemical and biological conditions, bioavailable P in sediments can be released into water column accelerating the eutrophication phenomenon of the bay, which could explain the permanent presence of algae in certain places of the bay, especially at the entrance of the leachate from the landfill.

3.7 Implication of the Study

The study has wider implications, as the nutrient geochemistry of tropical estuaries impacted by dumpsites is poorly understood. This study can also provide useful inputs to the nutrient dynamics of tropical estuaries in developed countries, which experience large seasonal variations due to the profound influence of climate change. The knowledge acquired in this study is of crucial importance for management solutions, as efforts to reduce eutrophication in aquatic systems should consider the internal sources, despite a reduction of external loading. In these eutrophic systems, phosphorus availability may persist as a result of sediment supply, even after reducing the external point sources. For example, in the watershed of the Ebrie Lagoon, agricultural activities have grown a lot in the last few decades. In addition, vegetable crops are also practiced around the study area [79]. These agricultural practices use pesticides and phosphate fertilizers which are significant sources of phosphorus and nitrogen in the aquatic environment. Moreover, in Côte d'Ivoire, M'badon bay provides almost 80% of the fish products consumed by the southern Côte d'Ivoire population. Thus it is an important source of economic activity for the local population. Furthermore, M'badon bay's waters are often used for bathing by the surrounding population, which could have negative consequences for their health.

4 Conclusion

This study investigated phosphorus and nitrogen distributions, speciation and bioavailability of phosphorus in a tropical bay in West Africa. The characterization of the berry showed hypoxia, low transparency and a high mineral and organic load. Bioavailable phosphorus and organic nitrogen account for 65.3% of the TP and 85% of the TN, respectively. Stations near the bay leachate discharge area have the highest concentrations of phosphorus and nitrogen. Temperature, electrical conductivity, dissolved oxygen, total dissolved solids, suspended matter and salinity control the phosphorus and nitrogen in M'Badon Bay. The speciation of phosphorus in bay sediments follows the order Fe–P (59.5%) > Ex-P (23.1%) > OP (12.8%) > Ca–P (4.6%). These fractions decrease with depth. Fractions such as Fe–P, Ca–P and OP are controlled by pH and Ex-P by TOC. The sources of phosphorus in bay are terrestrial with preferential regeneration of phosphorus over carbon in organic matter. Phosphorus bioavailable in sediments represents 95.4% and is an important reservoir which can accentuate the phenomenon of eutrophication. This study established the first data on nitrogen and phosphorus concentrations in the water column and sediments from M'Badon Bay which is highly impacted by the bigger municipal dumpsite of Côte d'Ivoire.

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Data Availability The dataset used during this study is available from the corresponding author on reasonable request.

Declarations

Conflict to Interest No conflict of interest exists between the authors.

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