



# Phosphorus and nitrogen speciation in waters and sediments highly contaminated by an illicit urban landfill: The Akouedo landfill, Côte d'Ivoire



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## ARTICLE INFO

### Article history:

Received 1 August 2018

Received in revised form 7 June 2019

Accepted 21 August 2019

Available online 23 August 2019

### Keywords:

Phosphorus

Nitrogen

Speciation

Coastal sediments

Coastal waters

Groundwater

Landfill

## ABSTRACT

Phosphorus and nitrogen pollution in groundwater, surface and marine waters results in tremendous economic, environmental and human health issues. This study examined phosphorus and nitrogen fate in sediments and the landfill leachate around the Akouedo landfill, the only landfill of the megacity Abidjan (Cote d'Ivoire, West Africa). The reactive phosphorus ( $255 \pm 22.3$  mg/L as  $\text{PO}_4^{3-}\text{-P}$ ) and ammonium ( $49 \pm 4.2$  mg/L as  $\text{NH}_4^+\text{-N}$ ) concentrations in the leachate were significantly high and relatively low compared with the literature, respectively. The reactive phosphorus made up 60% of total phosphorus in the leachate, while inorganic nitrogen (nitrate + nitrite + ammonium) concentrations represented 80% of total nitrogen. All phosphorus and nitrogen forms showed a decreasing gradient along the leachate, a decreasing trend with sediment depth, and a sharp peak at the 0–20 cm depth. The leachate pollution and water quality indexes revealed that the Akouedo landfill has a substantial impact on groundwater quality.  $\text{NO}_3^-$  contributed to 97% of inorganic nitrogen in the sediments. Very high iron-bound (82%) and very low calcium-bound (5%) phosphorus were found in the sediments. The results from this study suggest that highly contaminated sediments adjacent to the Akouedo landfill are significant sources of bioavailable phosphorus to groundwater and surface waters.

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## 1. Introduction

Tropical coastal areas are facing rapid population growth and intense anthropogenic pressures including urban land expansion (Tiquio et al., 2017; Marchant et al., 2018; Lu et al., 2018), agriculture (Kroon et al., 2014), industry (Allen, 2011) and mining (Kinimo et al., 2018). Consequently, water quality has become a major issue for policy makers (David and Tobin, 2017; Francés et al., 2017; Adams, 2018). Moreover, the situation has been worsened by rapid global warming. In the context of resilience and adaptive management for coastal water systems, it is critical to understand the fate and transport of phosphorus and nitrogen from contaminated sediments/soils to coastal groundwater, surface waters and ponds which are highly vulnerable to eutrophication.

Coastal groundwater, surface waters and lagoons are highly vulnerable to eutrophication (Sena and de Melo, 2012; Zouiten

et al., 2013; Hernández-Terrones et al., 2015). Because phosphorus (P) and nitrogen (N) are the predominant limiting factors of eutrophication in most tropical coastal waters, recent studies have documented the sources and fluxes of P and N toward estuaries and coastal marine waters (Cao et al., 2015; Wu et al., 2017). Diffusive sources from fertilizers, soils/sediments and atmospheric deposition account for a significant portion of P and N loads into surface waters in agricultural areas, while the point sources such as domestic and industrial effluents, and livestock manure are the highest sources in urban areas (Braga et al., 2000). Sediment plays a key role in controlling the biogeochemical cycle of P and N. It acts as both a sink and source of P and N to groundwater and surface waters (Rodellas et al., 2018). The P mobilization from sediment to groundwater and surface water depends on the distribution of P in sediment fractions and biological and physical environmental factors such as microbial activity, salinity and redox conditions in the sediment (Bai et al., 2007; Liu et al., 2012). Sedimentary phosphorus can be operationally divided into iron bound P (Fe-P), calcium bound P (Ca-P), exchangeable (Ex-P) and organic P (OP) (Williams et al., 1976; Wang et al., 2013). Previous research suggests that Fe-P can be

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readily released from sediment as opposed to Ca-P (Wang et al., 2013; Márquez-Pacheco and Hansen, 2017). However, few studies have examined P and N fate and transport in tropical coastal sediments, especially in West Africa, and this was the motivation of the present study.

Developing countries are confronted with increasing urban waste management issues, creating enormous risks to public health and the environment (Ağdağ and Sponza, 2005; Manaf et al., 2009; Zainol et al., 2012). Bulk urban solid wastes are dumped into uncontrolled landfills. Leachates from such landfills are highly loaded with suspended solids and soluble components from waste and by-products from waste degradation (Hakkou et al., 2001; Renou et al., 2008a). Moreover, the landfill leachates are discharged into the environment without any treatment. Consequently, the quality of the surrounding groundwater and surface water is of concern. Therefore, sediments in the vicinity of uncontrolled leachates constitute an ideal matrix for the study of the geochemical processes of P and N in highly contaminated environments.

The purpose of this study was to examine the fate of phosphorus and nitrogen in sediments and the landfill leachate around the Akouedo landfill, the only landfill of the megacity Abidjan (Cote d'Ivoire, West Africa). The general characteristics of the leachate were determined seasonally through analysis of physicochemical parameters such as temperature, electrical conductivity, salinity, pH, dissolved oxygen, redox potential, turbidity, total dissolved solids, suspended particles, biological oxygen demand in five days (BOD<sub>5</sub>), chemical oxygen demand, reactive phosphorus, total phosphorus, nitrate, nitrite, ammonium, total nitrogen and sulfates. The leaching capacity of the landfill and its impact on surface and groundwater was evaluated through examination of the leachate pollution index (LPI) and the water quality index (WQI). Horizontal and vertical distributions of sedimentary nutrient profiles were examined along the leachate from the landfill to the Ebrie Lagoon. Finally, phosphorus speciation in sediment cores was examined along the leachate in term of P fractionation. In the context of global warming, this study may help the understanding of the fate of N and P in coastal sediments subject to increasing nutrient loads in the near future.

## 2. Material and methods

### 2.1. Study site and samplings

The Akouedo Landfill (5°21'8.1"N, -3°56'42"W) is the only dump of Abidjan (Côte d'Ivoire). The Abidjan District has 4,653,592 inhabitants (INS, 2014). The Akouedo landfill consists of a natural ravine that extends to 153 ha and has an average depth of 25 m. It is unlined; therefore, bulk urban waste is deposited on the ground. The leachate discharges into M'Badon Bay (Ebrie Lagoon) through a ravine that is 20 to 40 m deep, 2000 m long from north to south and 200 to 500 m wide. The Akouedo landfill is surrounded by residential houses. The Akouedo area is part of the Côte d'Ivoire coastal sedimentary basin. From top to bottom, the lithology consists of clay sands, medium sands, and coarse sands resting on a granite and schist basement at an average depth of 120 m (Kouamé et al., 2006). The climate is comprised of four seasons including a long dry season (December–March), a long rainy season (April–July), a short dry season (August–September), and a short rainy season (October–November).

Before the sampling, all laboratory wares were rinsed 3 times with tap water, washed with laboratory soap, rinsed 5 times with distilled water, then soaked in 10% HCl for 5 days, and rinsed 5 times with Milli-Q (Millipore) water. The samplings were carried out in July 2016, November 2016, and March 2017. During each sampling campaign, leachate and surface sediments were

sampled at five stations (L1–L5) located 200, 400, 750, 1100, and 1450 m away the landfill, respectively, followed by collection of two wells P1 and P2 located 300 and 2000 m away the leachate (Fig. 1). Replicates samples were collected at station L5 and P2. Finally, two sediment cores of 50 cm each were sampled with minimal disturbance using a circular polycarbonate tube (7 cm in inner diameter; 90 cm long) (McCarthy et al., 2007) at stations L2 and L3. The sediment cores were sectioned at 0–10, 10–20, 20–30, 30–40, and 40–50 cm depths and sealed in 100 mL high-density polyethylene bottles. A total of 18 leachate, 42 sediment and 9 well water samples were collected. Water samples for ammonium (NH<sub>4</sub><sup>+</sup>), nitrite (NO<sub>2</sub><sup>-</sup>), nitrate (NO<sub>3</sub><sup>-</sup>) and phosphate (PO<sub>4</sub><sup>3-</sup> and TP) analyses were collected in 1 L polythene bottles, filtered through cellulose acetate membranes (Millipore, 0.45 μm pore size) and kept in 0.5 L polyethylene bottles. As for BOD<sub>5</sub> and COD (chemical oxygen demand), water samples were collected in 1 L polyethylene bottles. Surface sediment samples were collected using a Van Veen stainless steel grab of 0.02 m<sup>2</sup> area and put in 0.5 L polyethylene bottles. All the samples were immediately stored at 4 °C on ice in a cooler, transported to the laboratory, and water samples were processed within 24 h of collection.

Water temperature, pH, dissolved oxygen, electrical conductivity, redox potential, total dissolved solids and salinity were measured in situ using a Hanna HI-9828 multiparameter meter with GPS (Hanna Instruments, USA).

### 2.2. Leachate chemical analyses

Phosphorus was determined at 700 nm using the molybdenum blue spectrophotometric method (Murphy and Riley, 1962), ammonium at 630 nm using the indophenol blue spectrophotometric method described by Aminot and Chaussepied (1983), and nitrate at 430 nm using the sodium salicylate spectrophotometric method (Rodier et al., 1996). NO<sub>2</sub><sup>-</sup> was determined using the colorimetric method. At pH 1.9, in the presence of orthophosphoric acid, NO<sub>2</sub><sup>-</sup> ions form a diazonium cation with 4-aminobenzene sulfonamide, which is subsequently coupled with N-(1-naphthyl)-ethylenediaminedihydrochloride to form a stable pink dye (Aminot and Chaussepied, 1983). Kjeldahl N was measured using modified micro-Kjeldahl method (APHA, 1999; Hanief et al., 2015). TN was derived as the sum TKN + NO<sub>3</sub><sup>-</sup> + NO<sub>2</sub><sup>-</sup>. Total phosphorus (TP) was determined using American Public Health Association procedure (APHA, 2005) based on hot mineralization in the presence of concentrated sulfuric acid and sodium persulfate. The spectrometer was calibrated daily. Samples were analyzed in triplicate, and a standard dilution was analyzed every 10 samples. Chemical oxygen demand (COD) and biological oxygen demand (BOD<sub>5</sub>) were determined following Standard Methods (APHA, 2005). The other parameters such as chloride (Cl<sup>-</sup>), and sulphates (SO<sub>4</sub><sup>2-</sup>) were measured as per APHA (1999). The detection limits of nutrients were 0.005, 0.002 and 0.004 mg/L for nitrate, ammonium and phosphate, respectively.

### 2.3. Total phosphorus, total nitrogen, ammonium, and nitrates extraction in sediments

Sediment samples were freeze-dried, gently homogenized with a mortar and pestle and sieved with a nylon sieve (100 meshes) after removing solid waste and stones, and then stored in sealed polyethylene bottles until analysis. NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> were extracted in sediments as described in Hou et al. (2013). Briefly, 0.5 g of dried sediments was put into 100 mL acid-washed screw-cap polyethylene centrifuge tubes with 2 mol/L of KCl; then, the tube was shaken mechanically at 25 °C for 2 h. The mixture was immediately centrifuged at 5000 rpm for 15 min and filtered through 0.45 μm GF/F filter membrane. The TP extraction method

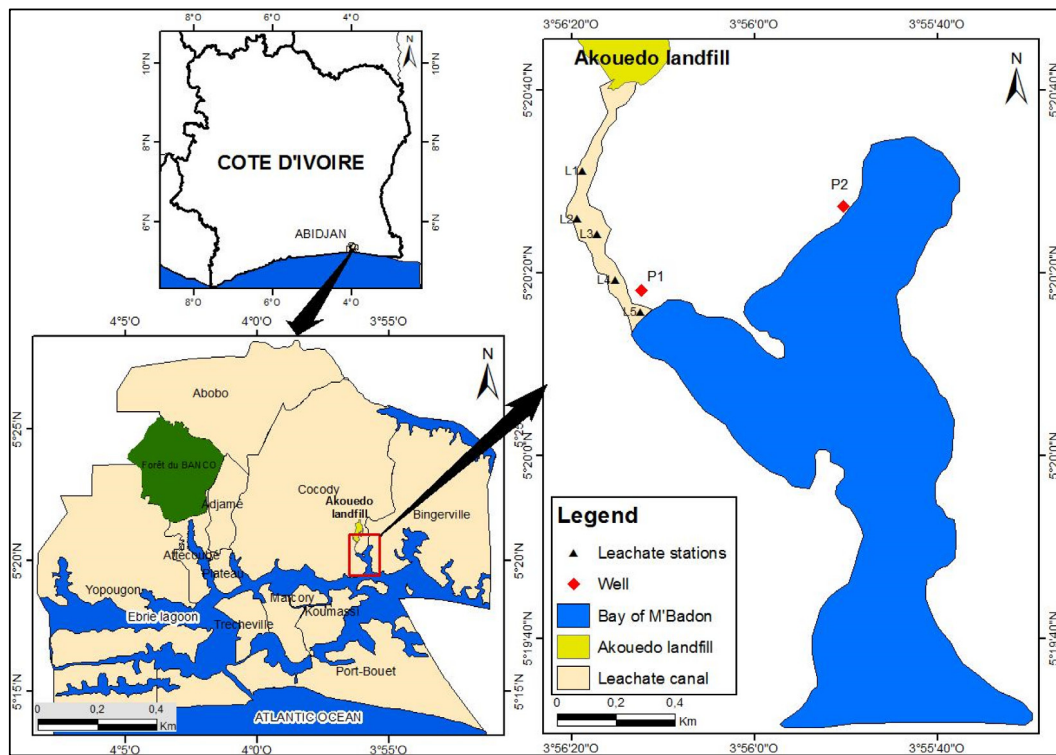


Fig. 1. Study area and sampling stations.

was based on the procedure described by Wuenschel et al. (2015). Briefly, sediment samples (200 mg) were placed in a porcelain crucible and calcined in a furnace at 450 °C for 3 h. TP was then extracted at room temperature from ashes using 3.5 mol/L HCl (20 mL; 16 h). The supernatant was removed from the residue after centrifugation for 15 min at 2500 rpm (Ruban et al., 2002). Sediment TN was determined by the Kjeldahl nitrogen method (Bremner et al., 1996). H<sub>2</sub>SO<sub>4</sub> was used for digestion, KMnO<sub>4</sub> to oxidize organic matter, and Na<sub>2</sub>SO<sub>4</sub> to raise the temperature of the digestion. Total organic carbon (TOC) was determined by loss on ignition (in percentage) of 1.0 g of dried sediments in an oven at 550 °C for 4 h (Nelson and Sommers, 1982; Carbonell-Barrachina et al., 2000). Sediment pH was measured after shaking with 1 mol/L KCl (1:2.5, mass:volume) for 15 min and settling for 30 min (Santos et al., 2013).

#### 2.4. Phosphorus fractionation in sediments

Sedimentary phosphorus was separated into iron bound P (Fe-P), calcium bound P (Ca-P), exchangeable (Ex-P) and organic P (OP) following the sequential extraction procedure developed by Williams et al. (1976) and recommended by Ruban et al. (2002). The Fe-P and Ca-P fractions were sequentially extracted in 0.2 g of dry sediment, and the Ex-P and OP fractions were sequentially extracted in a subsample of 0.2 g dry sediment. All extractions included a shaking for 16 h (overnight) at room temperature, using a mechanical shaker. The extract was separated from the solid residue by centrifugation for 15 min at 2000 rpm, and the supernatant liquid was transferred into a polyethylene volumetric flask. The residue was washed two times by adding 12 mL of 1 mol/L NaCl, mechanically shaken for 5 min on an end-over-end shaker (model Rotospin, Tarsons), and centrifuged for 15 min at 2000 rpm. The liquid aliquots were analyzed using the Murphy and Riley colorimetric method. The extraction procedures in this study can be broadly summarized as follows.

Step 1 (Fe-oxides associated phosphorus). About 20 mL of 1 mol/L NaOH was added to 0.2 g of dry sediment in a centrifuge tube and mechanically stirred overnight for 16 h. After centrifugation, 4 mL of 3.5 mol/L HCl was added to 10 mL of the supernatant in a test tube, stirred for 20 s, and left to stand overnight (16 h). At that level, a brown precipitate settles. The extract was then separated by centrifugation and the filtrate was separated by decantation for phosphate analysis.

Step 2 (Calcium carbonate associated phosphorus). The residue from step 1 was put into a test tube, followed by addition of 20 mL of 1 mol/L HCl and a mechanical shaking for 16 h overnight. The extract was separated as previously described, after centrifugation; then, phosphate concentration was determined.

Step 3 (Exchangeable or loosely phosphorus bound). About 20 mL of 1 mol/L HCl was added to 0.2 g of dry sediment in a centrifuge tube and mechanically stirred overnight for 16 h, followed by centrifugation. Then, the filtrate was separated by decantation for phosphate analysis.

Step 4 (Organic phosphorus bound). The residue from step 3 was oven-dried at 80 °C in the test tube, put in an ultrasonic bath for 10 s and oven-calcined in a porcelain crucible at 450 °C for 3 h. The ash was cooled and transferred into a test tube, followed by the addition of 20 mL of 1 mol/L HCl and a mechanical shaking for 16 h (overnight). The extract was then separated by centrifugation and the filtrate was separated by decantation for phosphate analysis as previously described.

#### 2.5. LPI calculation

The landfill pollution index (LPI), an index formulated using the Rand Corporation Delphi Technique, has been widely used to evaluate the leachate pollution potential of groundwater and surface waters surrounding landfills (Kumar and Alappat, 2003, 2005a,b, 2009; Umar et al., 2010; Bhalla et al., 2014a; De et al., 2016; Naveen et al., 2017). In general, 18 parameters are used to calculate the LPI. However, when the data of some pollutants is

**Table 1**

General characteristics of the Akouedo leachate (minimum, maximum, average  $\pm$  SD values of all combined stations for n = 45 samples).

Parameters	Minimum	Maximum	Average	Loss rate (%) <sup>a</sup>	Effluent standards in CIV <sup>b</sup>
T (°C)	29.08	33.2	30.9 $\pm$ 1.62		40
EC (mS/cm)	9.03	23.2	15.6 $\pm$ 6.10		
TDS (g/L)	4.64	13.2	8.70 $\pm$ 3.27		0.5
Salinity (psu)	6.15	12.9	9.23 $\pm$ 2.80		
pH	8.26	8.61	8.45 $\pm$ 0.14		6.5–8.5
DO (%)	41.9	49.8	45.5 $\pm$ 3.06		
ORP (mV)	–147	–129	–139 $\pm$ 6.97		
Turbidity (NTU)	307	880	639 $\pm$ 216		
SS (mg/L) <sup>c</sup>	737.3	1066	919 $\pm$ 128		100
COD (mg/L)	1560	7485	4272 $\pm$ 113.3		300
BOD <sub>5</sub> (mg/L)	800	2994	1563 $\pm$ 129.8		100
COD/BOD <sub>5</sub>			2.75 $\pm$ 0.17		1.5
BOD <sub>5</sub> /COD	0.31	0.44	0.38 $\pm$ 0.03		
PO <sub>4</sub> <sup>3-</sup> (mg/L)	17.4 $\pm$ 0.78	1497 $\pm$ 123.4	255 $\pm$ 22.3		2
NO <sub>3</sub> <sup>-</sup> (mg/L)	44.8 $\pm$ 7.57	359 $\pm$ 35.1	169.5 $\pm$ 15.43	91.91 $\pm$ 38.03	
NH <sub>4</sub> <sup>+</sup> (mg/L)	25.9 $\pm$ 1.98	76.9 $\pm$ 6.00	49.1 $\pm$ 4.20	90.69 $\pm$ 15.27	10
NO <sub>2</sub> <sup>-</sup> (mg/L)	0.70 $\pm$ 0.06	2.06 $\pm$ 0.46	1.31 $\pm$ 0.15	68.10 $\pm$ 26.88	
SO <sub>4</sub> <sup>2-</sup> (mg/L)	237 $\pm$ 8.02	1177 $\pm$ 230.2	710 $\pm$ 109	58.88 $\pm$ 66.14	250
TP (mg/L)	37.6 $\pm$ 3.68	1922 $\pm$ 123.7	422 $\pm$ 47.3	90.68 $\pm$ 21.67	
TN (mg/L)	82.3 $\pm$ 9.55	528.5 $\pm$ 41.07	261 $\pm$ 19.6	36.67 $\pm$ 42.50	15

<sup>a</sup>The loss rate was calculated as the percentage of nutrient loss between station L1 and L5.

<sup>b</sup>CIAPOL (Centre ivoirien antipollution).

<sup>c</sup>SS : Suspended solids.

not available as in the present study, the LPI is calculated using the Equation described in Kumar and Alappat (2003, 2005a,b).

$$LPI = \frac{\sum_{i=1}^m w_i p_i}{\sum_{i=1}^m w_i}, m < 18 \text{ and } \sum_{i=1}^m w_i < 1 \quad (1)$$

where LPI is the leachate pollution index,  $w_i$  the weight factor of the  $i$ th pollutant variable,  $p_i$  the sub-index score of the  $i$ th leachate pollutant variable, and  $m$  the number of leachate pollutant parameters available for calculating LPI. The significance, pollutant weight ( $w_i$ ) and sub-index value ( $p_i$ ) were adapted from Kumar and Alappat (2005a,b). According to Kumar and Alappat (2005a,b), the LPI can be categorized in three sub-indexes (LPI<sub>or</sub>, LPI<sub>in</sub>, and LPI<sub>tm</sub>) by grouping the leachate pollutants into organic, inorganic and heavy metals. In the present study, the total LPI was calculated through three steps as fully described in Kumar and Alappat (2005a,b): calculation of sub-index scores based on the concentration or value of each parameter, aggregation of the sub-index scores for organic, inorganic, and trace metals sub-LPIs, and aggregation of the sub-LPIs. LPI<sub>tm</sub> was calculated using data from Sangare (2017). The LPI value ranges between 5 and 100. A value of 5 indicates a good leachate quality while a value of 100 indicates a bad leachate quality. In India, Municipal solid waste MSW (Management and Handling) Rules, 2000 has set a LPI value of 7.378 for leachate disposal into surface waters.

## 2.6. WQI calculation

The Water Quality Index (WQI) is an effective tool for assessing the overall water quality. The WQI calculation method is based on the model used by Brown et al. (1970), Kumar and Alappat (2009), Tyagi et al. (2013) and Wu et al. (2018) approved by the National Sanitation Foundation (NSF). Multiple environmental parameters are combined into a single value that reflects the status of the water quality.

In the present study, temperature, pH, turbidity, dissolved oxygen, biochemical oxygen demand, total phosphates, nitrates and total solids were used to calculate the WQI following methods proposed by Misaghi et al. (2017).

$$WQI = \frac{\sum_{i=1}^n W_i * Q_i}{\sum_{i=1}^n W_i} \quad (2)$$

$Q_i$  is the sub-index for the  $i$ th water quality parameter,  $W_i$  the weight associated with  $i$ th water quality parameter, and  $n$  the number of water quality parameters.

The WQI value ranges from 0 and 100 with high values representing good water quality conditions. WQI is categorized into 5 water quality groups: excellent (91–100), good (71–90), moderate (51–70), low (26–50), and bad (0–25) (Wu et al., 2018).

## 2.7. Statistical analysis

The one way analysis of variance (one-way ANOVA) was performed to examine differences among the seasons. The Tukey test and Kruskal–Wallis One Way Analysis of Variance on Ranks were performed to investigate statistically significant differences at  $p < 0.05$ . Statistical analyses were performed with SigmaPlot 13.0 Software. Normality was tested using the Shapiro–Wilk test using Statistica 7.1 Software. The distribution was judged normal for  $p > 0.05$ . The parameters studied followed a normal distribution.

## 3. Results and discussion

### 3.1. General characteristics of the leachate

The ranges and average values for the measured parameters of the Akouedo Landfill leachate (all stations combined) are shown in Table 1. The leachate was hot with an average temperature of 30.9 °C, alkaline with an average pH value of 8.45  $\pm$  0.14, and relatively anoxic with percentages of dissolved oxygen less than 50%. It had high amounts of dissolved salts (e.g., sodium and chlorides) indicated by high salinities varying between 6–13 psu, and extremely high suspended particle concentrations (up to 1067 mg/L). The BOD<sub>5</sub> and COD concentrations ranged between 800–2994 mg/L (1563 mg/L on average) and 1560–7485 mg/L (4272 mg/L on average), respectively. The BOD<sub>5</sub>/COD ratio is usually used to describe the biodegradability of a leachate. BOD<sub>5</sub>/COD ratio values between 0.5–1 indicate a high biodegradability of organic compounds in the leachate, values ranging between 0.1 and 0.5 indicate a medium biodegradability, while BOD<sub>5</sub>/COD values less than 0.1 indicate high concentrations of non-biodegradable organic compounds or low biodegradability

**Table 2**  
Spatial distributions of nutrients in the Akouedo landfill leachate.

Parameters (mg/L)	L				
	L1	L2	L3	L4	L5
PO <sub>4</sub> <sup>3-</sup>	567 ± 43.6	487 ± 42.7	89.1 ± 7.19	85.5 ± 10.6	45.9 ± 7.40
NO <sub>3</sub> <sup>-</sup>	264 ± 19.0	152 ± 16.9	182 ± 21.5	141 ± 13.3	109 ± 6.43
NH <sub>4</sub> <sup>+</sup>	47.2 ± 3.20	43.4 ± 5.86	55.3 ± 3.96	50.4 ± 1.72	48.9 ± 6.23
NO <sub>2</sub> <sup>-</sup>	1.48 ± 0.11	1.62 ± 0.13	1.36 ± 0.16	1.13 ± 0.14	0.94 ± 0.23
SO <sub>4</sub> <sup>2-</sup>	616 ± 458	427 ± 343	580 ± 222	432 ± 168	450 ± 146
TP	901 ± 107	705 ± 59.8	231 ± 36.0	187 ± 22.7	83.9 ± 11.1
TN	375 ± 22.2	250 ± 22.8	286 ± 25.5	236 ± 14.9	197 ± 12.7

(Ntampou et al., 2006; Naveen et al., 2017). The BOD<sub>5</sub>/COD ratio values in the present study ranged from 0.31 to 0.44 with an average value of 0.38, suggesting a relatively high biodegradability of organic compounds in the leachate. Thus, the leachate from the Akouedo landfill can be classified as intermediate, and it is in a relatively active degradation phase.

### 3.2. Orthophosphates and total phosphorus

The average PO<sub>4</sub><sup>3-</sup> and TP concentrations in the Akouedo landfill leachate for all the combined stations are presented in Table 1, their spatial gradient along the leachate in Table 2, and seasonal variations are shown in Fig. 2.

As shown in Table 1, the average values of PO<sub>4</sub><sup>3-</sup> and TP in the Akouedo landfill leachate were 255 ± 22.3 and 422 ± 47.3 mg/L, respectively. These values are significantly higher than those found in the literature (Robinson and Luo, 1991; Alver and Altaş, 2017). The reactive P represented 60.5% of the TP. A decreasing gradient of P was observed from the nearest station to the landfill (L1) to the farthest station (L5). During the leachate flow toward the bay, about 91% of P loss was recorded between the L1 and L5 through sedimentation and infiltration which may represent a significant threat to the groundwater (Table 1). Over the study period, there was a significant difference between the three seasons for PO<sub>4</sub><sup>3-</sup> ( $p < 0.05$ ). The rainy season caused a strong accumulation of P in the leachate (Fig. 2) as a result of increased waste decomposition. Nevertheless, diffusive sources such as land erosion, wastes from nearby livestock and agricultural inputs may have also contributed to the increased P concentrations in the leachate. Reactive phosphorus was strongly correlated with temperature, electrical conductivity, total dissolved solids and suspended solids ( $r = 0.9$ ,  $p = 0.04$ ). This means that P increases with temperature, dissolved inorganic and organic matter in the leachate.

### 3.3. Nitrate, ammonium, nitrite and total nitrogen concentrations in the leachate

The average values of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and TN concentrations in the Akouedo landfill leachate for all the combined stations are presented in Table 1, their spatial gradient along the leachate in Table 2, and seasonal variations are shown in Fig. 2. The average NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and TN concentrations were 169 ± 15.4, 49.0 ± 4.20, 1.31 ± 0.15 and 261 ± 19.6 mg/L, respectively (Table 1). NO<sub>3</sub><sup>-</sup> concentrations were far higher than NH<sub>4</sub><sup>+</sup> concentrations at all stations during the study period, suggesting a rapid conversion of NH<sub>4</sub><sup>+</sup> to NO<sub>3</sub><sup>-</sup>. Inorganic nitrogen (nitrate + nitrite + ammonium) concentrations represented 80% of TN. Similarly to phosphorus, NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and TN concentrations decreased along the leachate toward the bay (Table 2).

As shown in Fig. 2, NO<sub>3</sub><sup>-</sup> and TN reached their maximum concentrations during the flood season, while NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup>

reached their peaks during the dry season. NO<sub>3</sub><sup>-</sup> varied significantly between the seasons ( $p = 0.03$ ) while NH<sub>4</sub><sup>+</sup>, NO<sub>2</sub><sup>-</sup> and TN did not. Various complex transformations among the different compounds of nitrogen occur in the leachate. When ammonium and nitrite concentrations were low, nitrate and total nitrogen concentrations showed very high concentrations. This may be a result of nitrification (Öman and Junestedt, 2008). Indeed, NH<sub>4</sub><sup>+</sup> uses oxygen in the leachate to nitrify into NO<sub>2</sub><sup>-</sup>, this being unstable is oxidized into NO<sub>3</sub><sup>-</sup>. The nitrification reaction might be more important during the flood season with a significant increase in NO<sub>3</sub><sup>-</sup> content, in opposition to lower NO<sub>2</sub><sup>-</sup> and NH<sub>4</sub><sup>+</sup> values. Additionally, the relatively low NH<sub>4</sub><sup>+</sup> values could be explained to a lesser extent by the anaerobic ammonium oxidation (anammox), a reaction mediated by bacteria in which NH<sub>4</sub><sup>+</sup> and NO<sub>2</sub><sup>-</sup> combine to form nitrogen gas (N<sub>2</sub>). Kuypers et al. (2005) have suggested that anammox is the major process responsible for nitrogen loss in oxygen-minimized zones. From the landfill to the bay, the rate of N loss through infiltration into sediment and evaporation was 92% for NO<sub>3</sub><sup>-</sup>, 91% for NH<sub>4</sub><sup>+</sup>, 68% for NO<sub>2</sub><sup>-</sup> and 37% for TN. The high N load in the leachate may pose eutrophication of the Ebrie Lagoon waters and the gaseous ammonia form may harm aquatic animals and produce odor problems in the nearby area.

### 3.4. Leachate pollution index (LPI) and water quality index (WQI)

The leaching capacity of the landfill and its impact on surface and groundwater was evaluated through examination of the leachate pollution index (LPI) and the water quality index (WQI). As shown in Table 3, the Akouedo landfill leachate showed a high LPI<sub>or</sub> value (50.1), a moderate LPI<sub>in</sub> value (12.0), and a low LPI<sub>tm</sub> value (7.36). These results indicate that the Akouedo landfill leachate has a high concentration of organics, a moderate concentration of inorganics, and a relatively low concentration of trace metals. However, LPI does not include phosphate concentration in the calculation. Because P is the limiting factor of water eutrophication in most surface waters, the high P concentration in the Akouedo landfill leachate should be of great concern. The results of the sub-LPIs are comparable to the ones found by Kumar and Alappat (2005a,b) in North Yorkshire, UK. The overall LPI was found to be 18.5. This value was much higher than the references values (5–7.4), indicating the relatively bad quality of the Akouedo landfill leachate. As a result, leachate from the Akouedo landfill is a potential threat to surface waters and groundwater. Moreover, the LPI value from the Akouedo landfill leachate was in the range of the ones from Mexico and India (Arunbabu et al., 2017; Guerrero-Rodríguez et al., 2014) (Table S1 in supplementary information). Therefore, the leachate should be treated before being discharged into the surrounding waters.

The WQI scores of well waters P1 and P2 collected at 30 and 2000 m from the leachate, respectively, are shown in Table 4. The waters of well P1 had a low quality indicated by a WQI score of 46.3. The waters of well P2 had a moderate quality (WQI = 69.7). These results underline the fact that the Akouedo landfill has a substantial impact on groundwater quality.

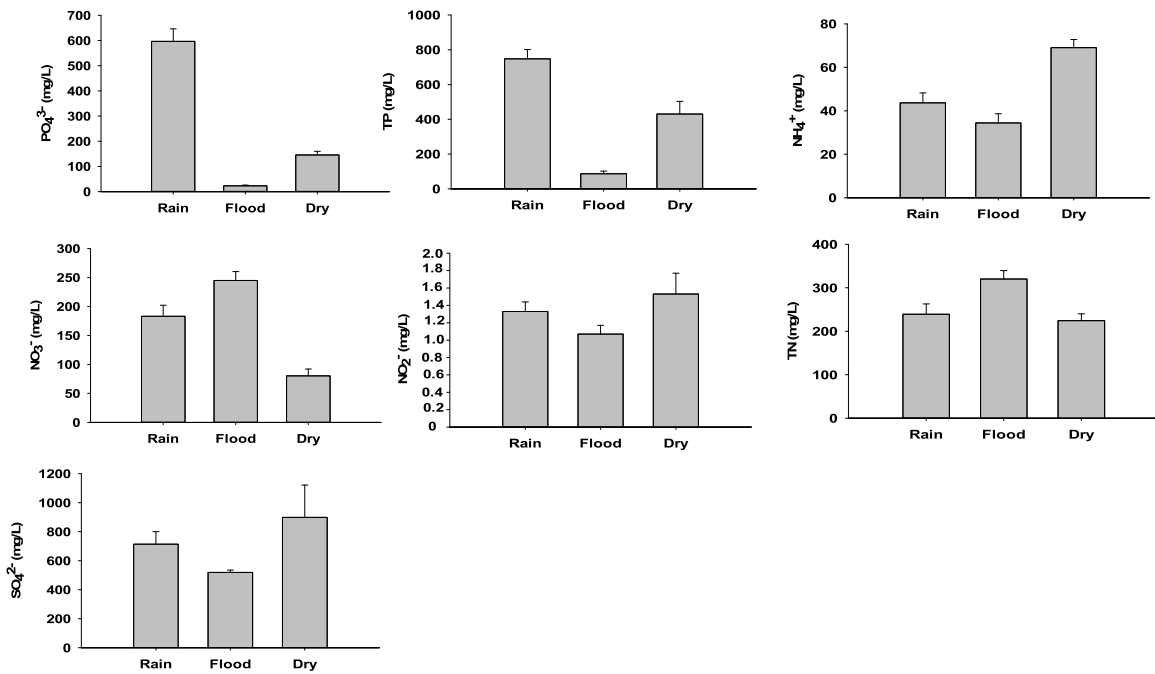


Fig. 2. Seasonal distributions of nutrients in the Akouedo landfill leachate.

**Table 3**  
Three sub-LPIs and the overall LPI of the Akouedo landfill leachate.

Index	Parameters	Significance	Weight factor $w_i$	Pollutant conc. <sup>a</sup>	Sub-index value $p_i$	$w_i \cdot p_i$
LPI organic LPI <sub>or</sub>	COD	3.963	0.267	4272	65	17.36
	BDO <sub>5</sub>	3.902	0.263	1563	35	9.210
	Phenolic	3.627	0.246	-	-	-
	TCB	3.289	0.224	-	-	-
	Summation		0.530			26.56
	<b>LPI<sub>or</sub></b>					<b>50.11</b>
LPI inorganic LPI <sub>in</sub>	pH	3.509	0.214	8.450	5.0	1.070
	TKN	3.367	0.206	212.2	14	2.884
	NH <sub>4</sub> <sup>+</sup>	3.250	0.198	49.05	6.8	1.346
	TDS	3.196	0.195	8698	20	3.900
	Chlorides	3.078	0.187	1678	15	2.805
	Summation		1.000			
	<b>LPI<sub>in</sub></b>					<b>12.00</b>
LPI heavy metals <sup>b</sup> LPI <sub>hm</sub>	Chromium	4.057	0.125	-	-	-
	Lead	4.019	0.123	0.550	15	1.845
	Mercury	3.923	0.121	-	-	-
	Arsenic	3.885	0.119	-	-	-
	Cyanide	3.694	0.114	-	-	-
	Zinc	3.585	0.110	0.515	5.0	0.550
	Nickel	3.321	0.102	0.315	5.0	0.510
	Copper	3.170	0.098	0.400	5.0	0.490
	Iron	2.830	0.088	6.450	5.0	0.440
Summation		0.521				3.860
	<b>LPI<sub>hm</sub></b>					<b>7.360</b>
Overall LPI			0.232 LPI <sub>or</sub> + 0.257 LPI <sub>in</sub> + 0.511 LPI <sub>hm</sub>			<b>18.46</b>

<sup>a</sup>All values are in mg/L except pH.

<sup>b</sup>Heavy metal concentration were obtained from Sangare (2017).

### 3.5. Spatial distributions of surface sedimentary nutrients

The horizontal distribution patterns of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, TN, and TP in the top 10 cm depth of the sediments during the rainy, flood and dry seasons are shown in Fig. 2. The average NH<sub>4</sub><sup>+</sup> concentrations in the sediments at all the stations over the study period ranged from 5.27 to 13.1 μg/g. These values were significant but did not reflect as much the high amount of NH<sub>4</sub><sup>+</sup> (49.0 mg/L) measured in the leachate. The NH<sub>4</sub><sup>+</sup> concentration values in sediments from this study were similar to the ones reported by Kuwano et al. (2017) in soils amended with leachate from the

Londrina municipal landfill, Brazil. The maximum concentration, 16.7 μg/g, was observed during the rainy season, while the minimum, 2.20 μg/g, was recorded during the flood season. NH<sub>4</sub><sup>+</sup> underwent a more accentuated decrease from L1 to L5 during the rainy season than in the dry and the flood seasons. In addition, NH<sub>4</sub><sup>+</sup> showed a significant difference between the seasons ( $p < 0.05$ ) and a strong positive correlation with TOC ( $r = 0.88$ ;  $p < 0.05$ ).

Unlike NH<sub>4</sub><sup>+</sup>, the NO<sub>3</sub><sup>-</sup> values were relatively high and varied from 169 to 381 μg/g with an average value of  $270 \pm 101$  μg/g in the sediments. NO<sub>3</sub><sup>-</sup> recorded its highest (757 μg/g) and lowest

**Table 4**  
Water quality index of open wells around the Akouedo landfill.

Parameters	Weighting factor (Wi)	Well P1			Well P2		
		Parameter value	Qi	Wi * Qi	Parameter value	Qi	Wi * Qi
T (°C)	0.10	28.5	12	1.20	27.6	15	1.50
BOD <sub>5</sub> (mg/L)	0.11	4.31	58	6.38	0.68	98	10.8
TDS (mg/L)	0.07	88.5	80	5.60	77.5	90	6.30
pH	0.11	6.6	70	7.70	7.15	91	10.0
DO (%)	0.17	38.8	26	4.42	36.4	25	4.25
Turb. (NTU)	0.08	87.2	24	1.92	4.84	90	7.20
NO <sub>3</sub> <sup>-</sup> (mg/L)	0.10	1.31	96	9.60	2.88	88	8.80
PO <sub>4</sub> <sup>3-</sup> (mg/L)	0.10	3.02	21	2.10	0.12	97	9.70
$\sum Wi = 0.84$		WQI (P1) = 46.3			WQI (P2) = 69.7		

(120 µg/g) values during the rainy and dry seasons, respectively. Precipitations may have accelerated the decomposition process of wastes, resulting in high loads of NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> in sediments. The NH<sub>4</sub><sup>+</sup> and NO<sub>3</sub><sup>-</sup> contributed to about 3.20% and 96.8% of inorganic nitrogen in the sediments, respectively. This means that NO<sub>3</sub><sup>-</sup> was the predominant form of inorganic nitrogen in the sediments.

Nutrient contents in sediments can be controlled by numerous factors, such as the rate of sedimentation, sediment type, amount and type of organic matter, intensity of mineralization of organic matter in the sediment and overlying water, and redox conditions in the sediment (Xiang and Zhou, 2011). The relatively low NH<sub>4</sub><sup>+</sup> concentrations observed in sediments in contact with the leachate may result from rapid NH<sub>4</sub><sup>+</sup> nitrification, loss of ammonia (NH<sub>3</sub>) through volatilization (Santos et al., 2013), infiltration in deep sediments or NH<sub>4</sub><sup>+</sup> released from the sediments into the leachate in alkaline conditions (Hou et al., 2013). Fast nitrification was also observed in soils that had received treated sewage effluent (Gloaguen et al., 2007), tannery sludge (Martinês et al., 2010), and landfill leachate (Santos et al., 2013; Panchoni et al., 2016). The organic matter undergoes ammonification to generate NH<sub>4</sub><sup>+</sup>, a significant part of which is transformed into NO<sub>3</sub><sup>-</sup>. Over the study period, the pH of surface sediments ranged between 7.4 and 9 with an average of 8.33 (Fig. 3), which may reflect the influence of the alkaline leachate on sediment charges. This may promote the accumulation of NO<sub>3</sub><sup>-</sup> in the sediments, indicated by a strong positive correlation between NO<sub>3</sub><sup>-</sup> concentration and pH ( $r = 0.95$ ). Moreover, the average NO<sub>3</sub><sup>-</sup> concentration showed a significant positive correlation with TOC ( $r = 0.96$ ), which may confirm NH<sub>4</sub><sup>+</sup> nitrification.

The contents of TN in surface sediments ranged between 325 and 1451 µg/g with an average value of  $655 \pm 278$  µg/g. A high accumulation of TN was observed in the rainy season. Most of this increase was attributable to an increase in NO<sub>3</sub><sup>-</sup> (positive correlation  $r = 0.99$ ). TN concentration decreased sharply from the rainy season to the dry season for stations L1, L2, and L3 close to the landfill. This likely reflects mineralization of organic N in the sediment, and subsequent nitrification. Contrary to what was found in the leachate, organic nitrogen made up a significant portion of TN (50%–60%) in the sediments. Moreover, a strong correlation was found between total organic carbon (TOC) and TN in the sediments of the leachate ( $r = 0.92$ ;  $p < 0.05$ ). These results suggest that the TN concentration in the sediments might be regulated by organic carbon (Hou et al., 2013). Because of the strong correlation between TOC and TN in the sediments, it could be inferred that any change in total organic matter will be associated with a similar change in organic nitrogen.

The horizontal distribution pattern of TP contents in the top 10 cm of the soils was illustrated in Fig. 3. There was a statistically significant difference between the TP values among the seasons ( $p = 0.008$ ) and a large spatial variability over the study period. Like ammonium, TP recorded its maximum value of  $1166.7 \pm 218$  µg/g in the rainy season and its minimum value of  $500 \pm 104$

µg/g in the flood season with a mean of  $865 \pm 143$  µg/g over the study period.

The high amount of TP concentration in the sediments may be attributable to their large specific surface area. According to Zhu et al. (2017), ignited sediments have a huge adsorption capacity for P. Thus, the high TP content in the sediment during the dry season could be explained by an increase in sediment temperature. Spatially, TP decreased in general from station L1 close to the landfill to the stations near the bay, indicating that sediments closer to the landfill are more impacted and constitute a large reserve of P.

### 3.6. Distributions of vertical sedimentary nutrient profiles

The nutrient profiles in the 0–10, 10–20, 20–30, 30–40 and 40–50 cm depths of the sediments are shown in Figs. 4 and 5. The Leachate sediments were heavily contaminated with N and P. The profiles decreased sharply with increasing depth in NH<sub>4</sub><sup>+</sup>, TN, and TP concentrations from the first 0–20 cm to deep sediments during all of the seasons. The NO<sub>3</sub><sup>-</sup> concentration profile followed the same trend during the flood and dry seasons. On the contrary, the NO<sub>3</sub><sup>-</sup> concentrations increased gradually from 0–20 cm depth toward the deeper sediment layers. The decrease in nutrients with increasing sediment depth may result from leaching, while the slight increase in NO<sub>3</sub><sup>-</sup> concentration in deeper sediments during the rainy season may be explained by high NO<sub>3</sub><sup>-</sup> loss in the 0–20 cm sediment layer. In addition, the high amount of Cl<sup>-</sup> (1678 mg/L) in Table 3 in the leachate may compete with NO<sub>3</sub><sup>-</sup> for adsorption sites, making more free NO<sub>3</sub><sup>-</sup> in the sediment solution (Ji and Kong, 1992) and subject to loss to the deeper sediment layers.

During the rainy season, the highest NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, TN, and TP concentrations were recorded in the top 0–10 cm layers, while during the flood and dry seasons the highest concentrations were observed in the 10–20 cm layers. This result indicates that the leachate is a source of nutrients for the sediment, and the sediment acts as a sink for NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, TN, and TP. Rainfall may leach nutrients more readily from surface sediments (Gudimov et al., 2011) and carry them to deep sediment. The accumulated N and P may continue to leach toward deeper depths after the input declines from wet to dry seasons. The leaching process may accelerate with desorption that may happen when N or P contents exceed the sediment sorption capacity (Heredia and Cirelli, 2007).

Moreover, the results showed that the NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, TN, and TP concentrations bottomed out in the 10–20 cm layers during the rainy season, especially at station L2, and decreased dramatically at the 0–10 cm depth. These results suggest a significant reduction of nitrates and nitrites, and oxidation of ammonium, and escape of nitrogen and nitrous oxide into the air at the top 0–20 cm sediment depth. The high nutrient supply by the leachate during the rainy season hid the N loss in the top 0–10 cm depth of the sediment. In contrast, the low N concentrations in the 0–10 cm depth during the dry and flood season may result from a

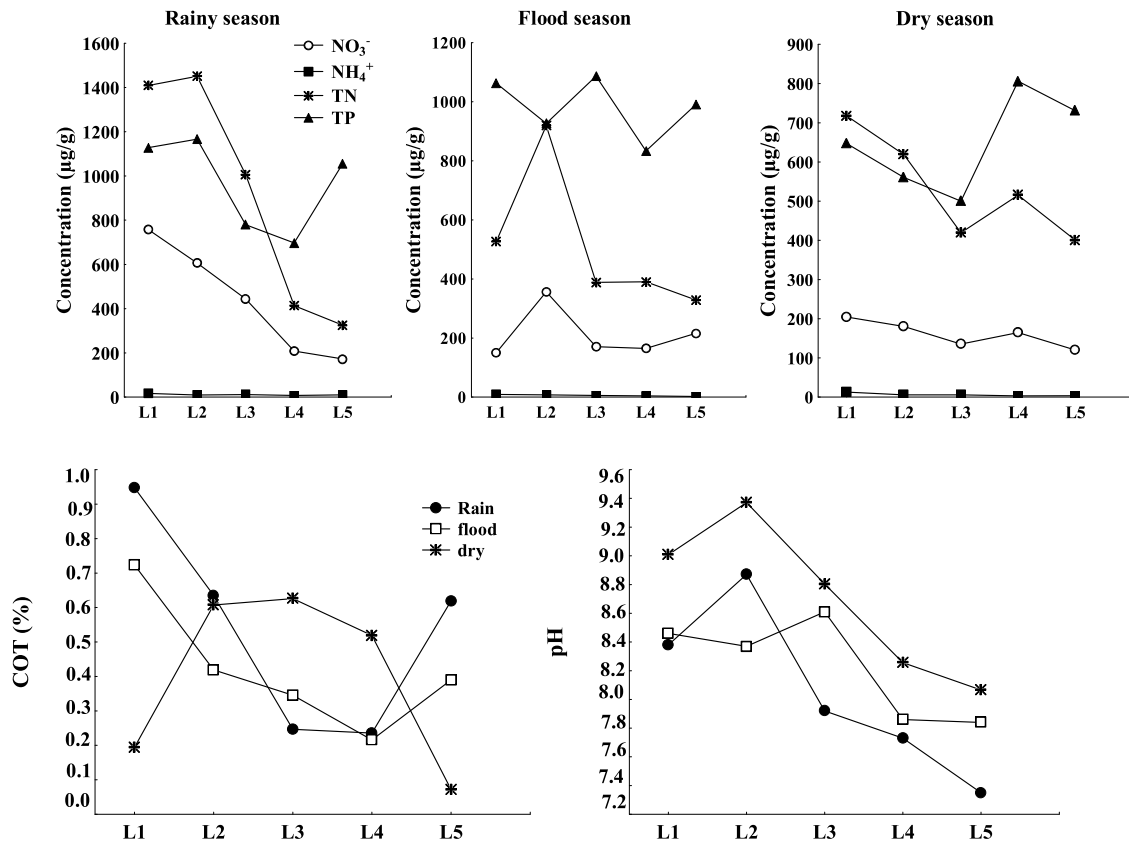


Fig. 3. Spatio-temporal distributions of the horizontal sediment profiles of TOC, pH, and nutrient concentrations (NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, TN, and TP).

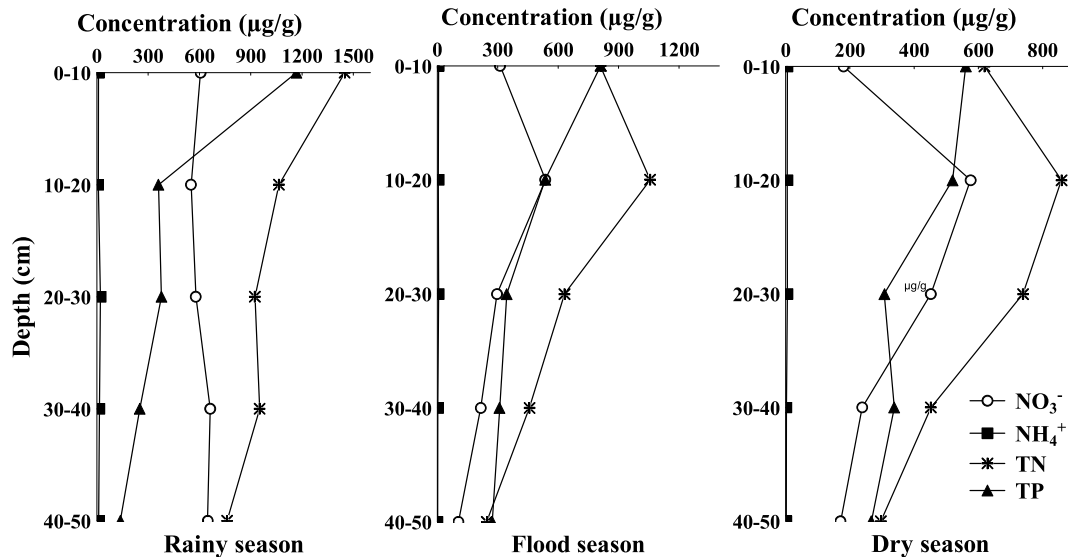


Fig. 4. Profile distributions of NO<sub>3</sub><sup>-</sup>, NH<sub>4</sub><sup>+</sup>, TN, and TP in 50 cm depth during the rainy, flood and dry seasons at station L2.

decline or absence in N supply. Further investigation is needed to explain the sudden drop or rise in TP concentrations at the 10–20 cm depth in this study.

The TN and TP concentrations remained high below 50 cm from soil surface with an average of  $684 \pm 130 \mu\text{g/g}$  and  $40.2 \pm 15 \mu\text{g/g}$ , respectively. It should be noted that TN and TP concentrations were significantly higher in deep layer sediments at station L3 than at station L2, due to additional nitrogen and phosphorus supplies from the underground sewerage pipeline of the Akouedo district. Sediments acted as a sink of N but also as source of N loss.

### 3.7. Phosphorus speciation in sediments

In the absence of certified reference material, the pseudo-TP (sum-TP), i.e., the sum of the four fractions was compared with TP concentrations to validate the performance of the extraction method (Adhikari et al., 2015). The sum-TP concentration values showed good agreement with TP, indicated by recoveries ranging from 81.28%–116% (Table S2 in supplementary material). The spatiotemporal partitioning of TP to the Fe-P, Ca-P, Ex-P and OP

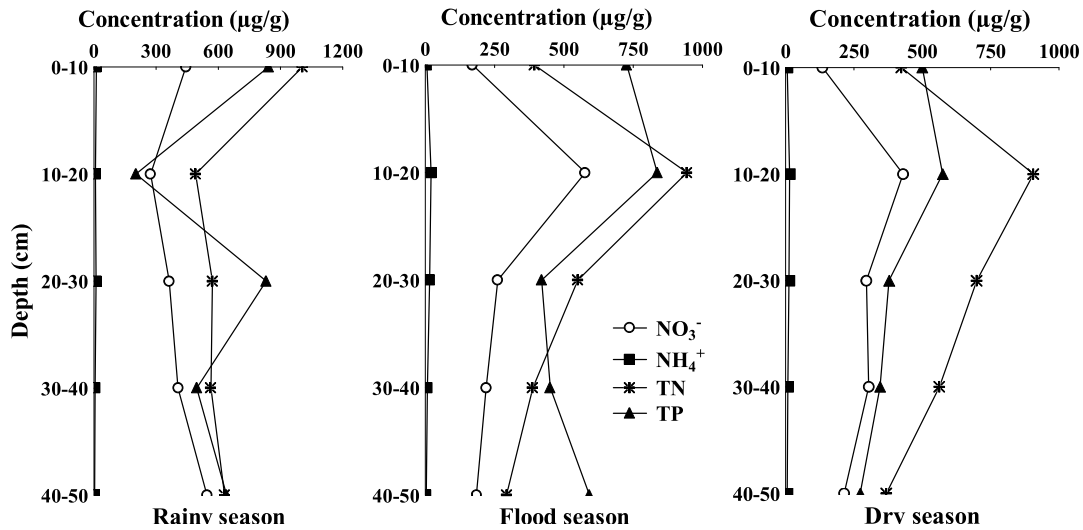


Fig. 5. Profile distributions of  $\text{NO}_3^-$ ,  $\text{NH}_4^+$ , TN, and TP in 50 cm depth during the rainy, flood, and dry seasons at station L3.

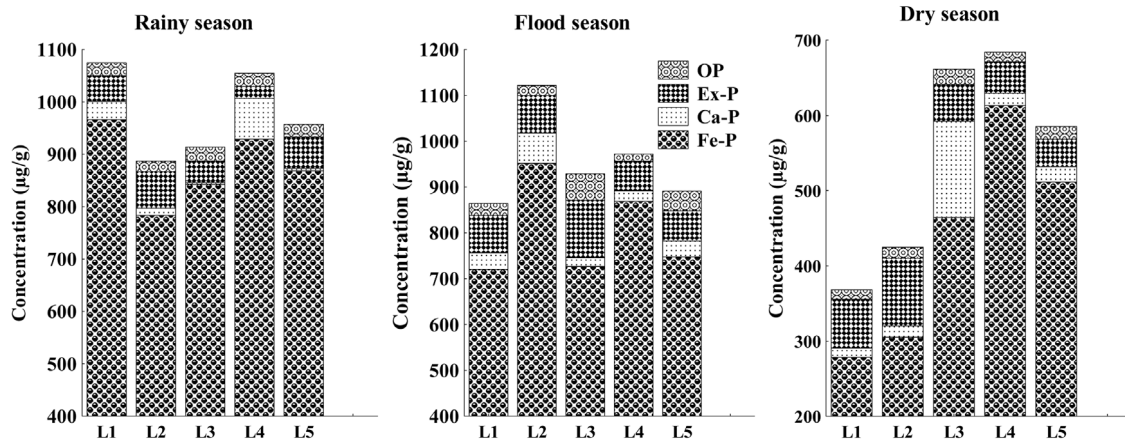


Fig. 6. Distribution of phosphorus fractions in the Akouedo landfill leachate.

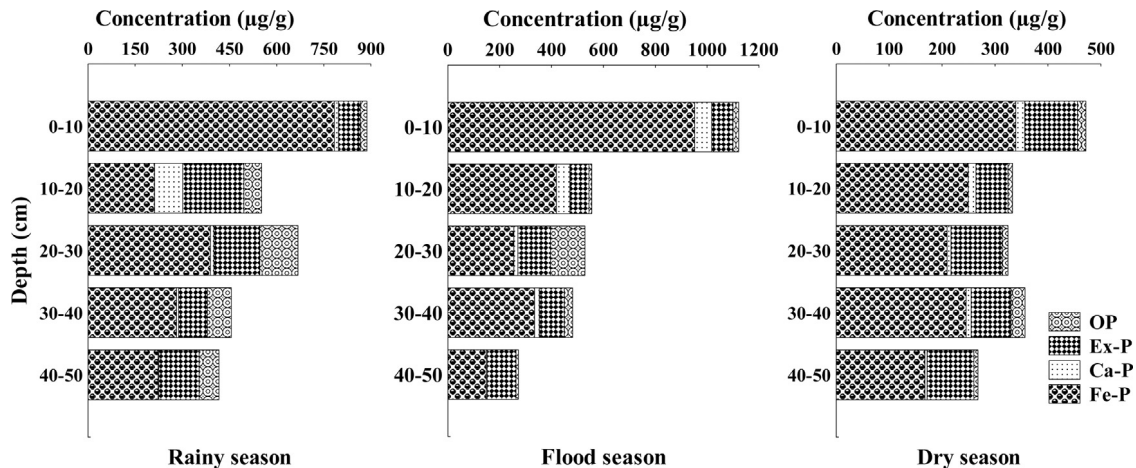


Fig. 7. Vertical profiles for phosphorus fractions at station L2.

fractions of surface sediments along the leachate are shown in Fig. 6; the depth profiles are shown in Figs. 7 and 8.

The Fe-P concentrations dominated the TP fractions over the study period. The highest surface sediment concentrations occurred during the rainy season (966 µg/g; station L1), while the lowest concentration was observed during the dry season

(278 µg/g; station L1). The concentration level followed the order: rainy season > flood season > dry season. The seasonal average Fe-P concentrations were  $878 \pm 71.9$  µg/g in the rainy season,  $803 \pm 103$  µg/g in the flood season, and  $435 \pm 141$  µg/g in the dry season. In term of percentages, these correspond to 95%, 83%, and 67% of TP bound to surface sediments in the

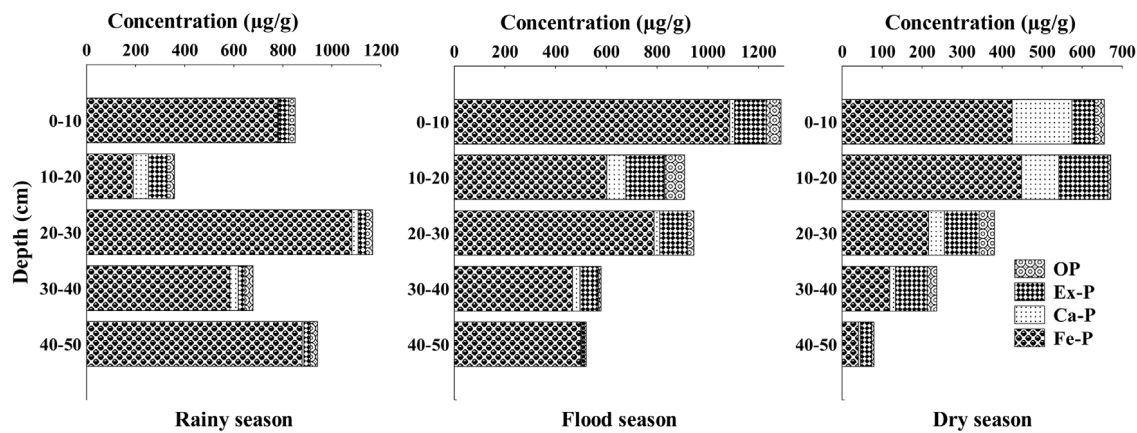


Fig. 8. Vertical profiles for phosphorus fractions at station L3.

three seasons, respectively. Compared to similar studies in the world (Table S3 in supporting information), these percentages are much more higher than data from the literature (Şahin et al., 2012; Młynarczyk et al., 2013; Liang et al., 2015; Adhikari et al., 2015; Cavalcante et al., 2018; Coumar et al., 2018). Furthermore, Fe-P concentrations increased significantly downstream of the leachate during the dry season, although no concentration gradient was found along the leachate during the rainy and flood seasons. Previous studies have shown that Fe-P can be released from sediments in anoxic conditions (Malecki et al., 2004; Zhang et al., 2012). It has been reported that Fe oxides/hydroxides exist in both amorphous and crystalline forms, and that amorphous Fe-P dissolves more rapidly than crystalline Fe-P (Lindstrom and White, 2011). No data exist with regard to which Fe-P form (amorphous or crystalline) predominates in sediments collected in this study. However, our results suggest that sediments under the leachate of the Akouedo landfill constitute a significant Fe-P reservoir for M'Badon Bay.

As shown in Table S4 in the electronic supporting information, a significant negative correlation (performed after the normality test of Shapiro–Wilk) was observed between the Fe-P and TOC ( $r = -0.69$ ,  $p < 0.05$ ), Fe-P and pH ( $r = -0.64$ ,  $p < 0.05$ ), implying that TOC and pH were the potential main factors for concentration and distribution of Fe-P in sediments. The depth profiles of the two stations L2 and L3 showed generally a strong dominance of the Fe-P fraction irrespective of the depth (Figs. 7 and 8). Moreover, the Fe-P fraction decreased significantly with depth at all stations and seasons, except for the wet season at station L3. These results indicated that the top 0–10 cm sediment was the preferred storage area for the Fe-P fraction, which is consistent with findings by Márquez-Pacheco and Hansen (2017) in Mexican reservoir sediments.

Conversely, the Ca-P, Ex-P, OP contributed very little to the TP of the sediments as shown in Figs. 6–8. The Ca-P proportions of TP during the rainy, flood and dry seasons were 3%, 4% and 7%, respectively. The Ex-P fraction represented 4.9%, 8.5% and 9.2% of TP in sediments during the rainy, flood and dry seasons, respectively. Finally, the OP percentages were 2.64%, 3.28%, and 2.49% during the rainy, the flood and dry season respectively. No significant concentration gradient was found along the leachate. In general, the TP fractions in the sediments decreased with depth, and their concentrations followed the order Fe-P > Ex-P > OP > Ca-P. Compared with data from the literature, the Ca-P (the most stable fraction in sediments) values of the present study fell in the lowest range of other studies (Table S3 in supporting information). The Ex-P, Fe-P and OP fractions are readily released through physical, chemical, and/or biological reactions (Coelho et al., 2004; Meng et al., 2015), and are considered to

be potentially bioavailable and represent the upper limit of P that can be released into overlying waters (Andrieux and Aminot, 1997; Hou et al., 2009; Prasad and Ramanathan, 2010; Meng et al., 2014). Therefore, the results from this study suggest that highly contaminated sediments in P adjacent to the Akouedo landfill are a significant source of bioavailable TP to groundwater and Ebrie Lagoon waters.

## Conclusion

Phosphorus and nitrogen distribution in sediment phases and landfill leachate were investigated in this study. Leachate characterization showed that the Akouedo landfill is in an active degradation phase and represents a potential threat to surface waters and groundwater. The inorganic nitrogen and bioavailable phosphorus are the predominant forms of nitrogen and phosphorus in the leachate, respectively. The results also revealed that  $\text{NO}_3^-$  concentrations in leachate varied across the seasons, while  $\text{NH}_4^+$ ,  $\text{NO}_2^-$  and TN did not.  $\text{NO}_3^-$  was the predominant form of inorganic nitrogen (97%) in the sediments. TN and TP were significantly higher in the rainy season than in the flood and dry seasons and decreased along the leachate, indicating that sediments closer to the landfill are more impacted and constitute a large reserve of P. Phosphorus speciation in sediments revealed that the Fe-P concentrations dominated the TP as high as 82%. Thus, the highly contaminated sediments in P adjacent to the Akouedo landfill are a significant source of bioavailable TP to groundwater and Ebrie Lagoon waters. The results from this study suggest that iron bound phosphorus could be the highest fraction of sedimentary phosphorus in most coastal sediments along the Gulf of Guinea.

## Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

## Acknowledgments

Authors are thankful to the Director of Centre de Recherches Oceanologiques (CRO) for his encouragement and support. They also thank Mary Zawoysky at Woods Hole Oceanographic Institution (WHOI) for improving the edits. A special thank you goes to the reviewers for their critical contribution.

## Appendix A. Supplementary data

Supplementary material related to this article can be found online at <https://doi.org/10.1016/j.rsma.2019.100805>.

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