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RESEARCH ARTICLE

ASSESSMENT OF HEAVY METAL CONTAMINATION IN NTSINI RIVER SEDIMENTS FROM THE COASTAL PROTECTED AREA OF LIBREVILLE, NORTHWEST GABON

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Abstract

To assess the trace element contamination status of sediments from the Ntsini River and the ecological risk to aquatic biocenosis, we analyzed physicochemical properties of six trace metal contents (Cd, Cu, Cr, Ni, Pb, and Zn) in twelve (12) sediment samples from four sampling sites (Ngwamba, Moka, Pages and Nende) using Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES). The results show that the sediments generally contain significant amounts of organic matter, have an acidic pH and exhibit similar concentrations of Cd, Cr, Cu, Ni, Pb and Zn, except for sediments from the Nende site, which are characterized by neutral pH and higher Cd concentrations. The contamination factors (CF) for Cd (CF > 2), Pb and Zn (1 ≤ CF < 2) and Cr, Ni, and Cu (CF < 1) indicate sediment contamination at the following sites :Moka for Cr and Pb, Pages for Zn and Nende for Cd. Only Cd potentially presents a moderate to considerable ecological risk for the studied sediments. The ecological risk index (RI) values in the most Cd-contaminated sediments from the Ngwambaand Nende sites (95 ≤ RI < 190) indicate a moderate contamination risk to biocenosis in the Ntsini River.

Introduction:-

Gabon, a country located in Central Africa, is crossed by the equator and covers a territory of 267,670 km^2. Its western border is delimited by approximately 800 km of coastline, providing access to the Atlantic Ocean [1]. With a population of approximately 2.5 million inhabitants, 89% live in urban areas and this rate is projected to reach 95% by 2050 [2]. The political and administrative capital, Libreville, is the most populated city with 3,700 inhabitants/km² [3]. As part of its policy to preserve and enhance natural ecosystems, particularly in the coastal zone

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around Libreville, the Gabonese government has created three protected areas that constitute the Emeraude Arc. These three areas are located between the Komo estuary and Mondah Bay and include the Raponda Walker Arboretum (a coastal rainforest) and two national parks (NP): Pongara NP to the south and Akanda NP to the Northeast of Libreville [4].Akanda National Park consists mainly of mangrove forests and rivers that support traditional fisheries [5]. Among these rivers, the Ntsini is the primary one, connecting the capital of Libreville to Mondah Bay. However, the work of Leboulangeret al.[6] revealed significant contamination by fecal indicator bacteria (FIB: Escherichia coli and fecal streptococcus) in the coastal waters of Libreville, particularly in the Ntsini River, associated with intensified urbanization and increasing human activities in the coastal zone. Furthermore, deforestation of the mangrove in Akanda Park has been documented [7], along with contamination of marine organisms by persistent organic pollutants and heavy metals [8]. However, no study has reported the levels of trace metal contamination in the sediments of the Ntsini River.

However, Ntsini River is regularly exposed to heavy pollution due to heavy fishing boat traffic, agricultural inputs, and urban and industrial effluents. In the aquatic environment, the study of sediments is of interest because they are indicators of environmental contamination, due to their ability to bind both organic and inorganic pollutants [9]. Sediments thus contaminated with trace metal elements constitute a reservoir and a potential source of contamination for water. Indeed, the slightest modification of environmental parameters, such as reactions accompanying natural or anthropogenic changes in redox potential or pH [10]; for example, the decrease in pH below a threshold defined for each metal causes its release [11] as well as the formation of complexes with organic or inorganic matter, easily mobilizable[12, 13]. Knowing the state of contamination of sediments is an interesting decision-making tool because it allows for appropriate measures to be taken for sustainable management of an aquatic ecosystem [14].

Trace metal elements are considered dangerous pollutants because of their tendency to accumulate in biological organisms [15, 16]and to degrade the quality of ecosystems, thus threatening human health [17]. Due to its exposure to various sources of contamination, the Nstini River could have contaminated sediments acting as a reservoir and endogenous source of trace element pollution for water.Trace metals (TMs) are natural components of the Earth's crust that cannot be degraded or destroyed [18]. They enter aquatic ecosystems through various natural and anthropogenic sources, including atmospheric deposition, soil erosion and wastewater discharge [19]. Although some TMs such as Cu, Zn, and Ni are essential micronutrients for biological functions, others like Cd and Pb have no known biological role and are toxic even at low concentrations [20]. In aquatic ecosystems, TMs accumulate in sediments, which serve as both sinks and potential sources of contamination for the water column and aquatic organisms [21]. The assessment of TMs contamination in sediments is therefore crucial for understanding the environmental quality and ecological risks in aquatic systems.Thus, the study aims were to determine the physicochemical properties and trace metal concentrations in sediments of the Ntsini River, to assess the degree of sediment contamination using contamination indicesand to evaluate the potential ecological risks posed by trace metals to the aquatic ecosystem.

Material and Methods:-

Geographical location of the study Area:

The Ntsini River is located in the Northern part of Libreville, within the Akanda National Park (0°41'N, 9°25'E), which covers an area of approximately 540 km^2[22, 23]. The park is characterized by a humid equatorial climate with an average annual temperature of 26°C and annual precipitation ranging from 2,000 to 3,000 mm [24]. The river flows through mangrove forests before discharging into Mondah Bay. Four sampling sites (Figure 1) were selected along the river: Ngwamba (upstream), Moka and Pages (middle course) and Nende (downstream, near the river mouth).

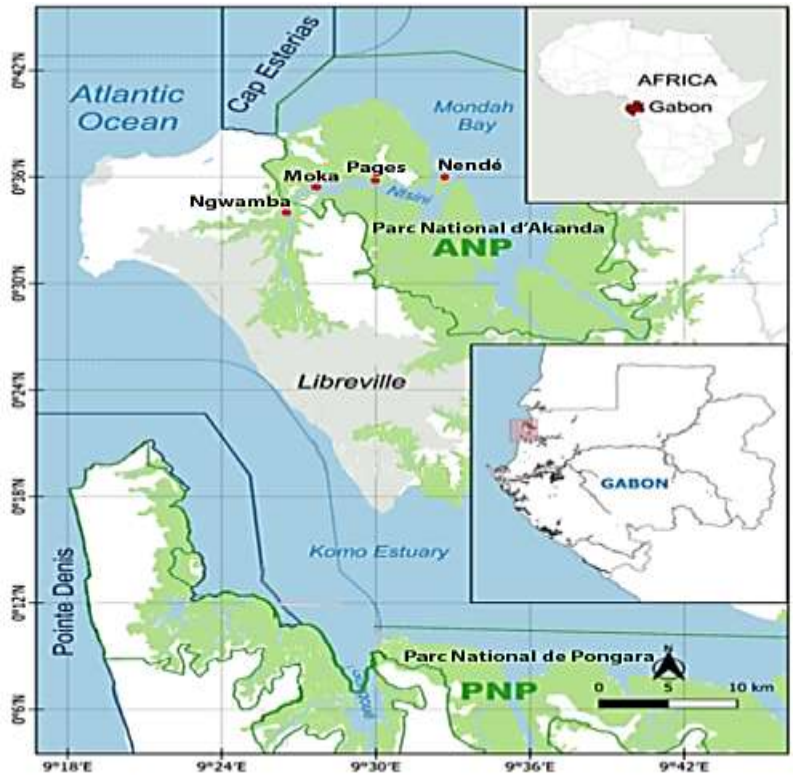


Figure 1: Location of sampling stations (in red points) in Akanda National Park (ANP) of the Emeraude Arc.

Sediment samples were collected during the ruinning season (october to january 2019) at four sites along the Ntsini River (Ngwamba, Moka, Pages and Nende). Sediment samples were taken at low tide at each site.Three replicate samples were collected on the 0-20 cm of the mudflats using a cylindrical corer, resulting in a total of 12 samples.The characteristics of these stations are given in Table 1.The samples were immediately stored in polyethylene bags, transported to the laboratory and kept at room temperature until analysis. In laboratory, for the various analyses, the samples were air-dried at 25°C for 48 hours and in an oven at 60°C for 48 hours. A portion of the dry samples was powdered and then stored for physicochemical analyses.

Table 1:Location and description of sampling sites

Stations	Samples	Reason for choosing the station	GPS coordinates
Ngwamba	Ngwamba 1	Further upstream, station subject to high anthropogenic discharges.	N 00°34'26.3'' E 009°27'16''
	Ngwamba 2		N 00°34'36.1'' E 009°27'39.8''
	Ngwamba 3		N 00°34'23.4'' E 009°27'15.3''
Moka	Moka 1	Intermediate station located on the bank of a tributary that flows into the Ntsini River.	N 00°35'34.4'' E 009°28'19.0''
	Moka 2		N 00°36'04.2'' E 009°28'13.8''
	Moka 3		N 00°36'18.2'' E 009°28'24.7''
Pages	Pages 1	Closer to the reference station (Nende), located at the point where a tributary meets the Ntsini River.	N 00°35'44.33'' E 009°29'34.6''
	Pages 2		N 00°35'36.1'' E 009°29'59.6''
	Pages 3		N 00°35'36.1''

			E 009°29'46.6''
Nende	Nende 1	Corresponding to the reference station, it is located far from the domestic anthropogenic inputs of the study area.	N 00°35'55.3'' E 009°32'45.9''
	Nende 2		N 00°35'38.9'' E 009°32'43.5''
	Nende 3		N 00°36'01.9'' E 009°32'35.5''

Determining the pH, electrical conductivity and organic matter of sediment samples :
Sediment samples were dried for 6h at 60°C, sieved through a 2 mm mesh diameter and homogenized for analyses. Sediment pH was measured in a 1:5 (w/v) sediment-to-water suspension using a multi-parameter (OAKTON instrumental). Organic matter (OM) content was determined by loss on ignition at 550°C for 4 hours[25].The results are expressed as percentages on a dry weight basis.

Extraction of Metal from sediments:
For trace metal analysis, 0.5 g of dried sediment was digested using a mixture of concentrated HNO_3, HCl, and HF acids in a microwave digestion system (CEM Mars 5)at temperature between 125 and 150 °C. After digestion, the samples were diluted to 50 mL with ultrapure water and filtered through 0.45-µm membrane filters. The concentrations of six trace metals (Cd, Cr, Cu, Ni, Pb, and Zn) were determined by Inductively Coupled Plasma-Atomic Emission Spectroscopy (ICP-AES, Thermo Scientific iCAP 6000 Series). All analyses were performed in triplicate and the results are expressed in $mg.kg^{-1}$ on a dry weight basis.

Calculation of pollution indices:
Several indicators such as the geo-accumulation index (I_{geo}), contamination factor (CF), contamination degree (CD), and potential ecological risk index (RI) were used for the first time in the Ntsini River to assess the status of river sediment pollution with potential toxic element. The selected indices are explained below.

Geo-accumulation Index (I_{geo}):-
The I_{geo} was proposed by Muller [26]to quantify pollution intensity in the environment using the following mathematical formula:

$$I_{geo} = \log_2\left(\frac{C_1}{1.5xC_b}\right)$$

Where $C_i$is the metal concentration in the sample, C_b is the UCC geochemical background concentration of metal [27], and 1.5 is the background matrix correction factor due the changes that may occur in lithology.The results are interpreted by Muller[26]as follows: $I_{geo} < 0$; unpolluted; $0 < I_{geo} \leq 1$: unpolluted to moderately polluted; $1 < I_{geo} \leq 2$: moderately polluted; $2 < I_{geo} \leq 3$: moderate to heavily polluted; $3 < I_{geo} \leq 4$: heavily polluted; $4 < I_{geo} \leq 5$: heavy to extremely polluted; and $I_{geo}>$: extremely polluted.

Contamination Factor (CF):-
The CF is an indicator often used to evaluate anthropogenic contributions and is obtained based on the following relationship:

$$CF = \frac{C_i \text{ (sediment sample)}}{C_r \text{ (Background)}}$$

Where C_i represents the concentration of an element in the sample and C_r the concentration in the sediment selected reference backgroud. Given that the predominant the bedrock in Akanda Park are limestone and sandstone, and since reference concentrations of heavy metals in aquatic sediments in the study area are currently unavailable, the average reference concentrations in sedimentary rocks determined by Rudnick and Gao[27]were used as geochemical background values. The CF values were interpreted according to Hakanson[28], where: $CF < 1$ indicates no enrichment; $1 < CF < 3$ is moderate enrichment; $3 < CF < 6$ is significant enrichment; and $CF > 6$ is very high enrichment.

Contamination degree (CD):-
The contamination degree (CD) proposed by Hakanson[28]can assess the overall contamination in a specific area, considering the sum of all the individual contamination factors (CFs). The CD index is calculated according to the following formula:

$$DC = \sum_{i}^{n} FC$$

Where n is the number of elements analyzed, FC is the concentration factor. The classification of CD values according to Hakanson et al. [28]is as follows: CD < 8: low contamination; 8 < CD < 16: moderate contamination; 16 ≤ CD < 32: considerable contamination; and CD > 32: very high contamination indicating serious anthropogenic pollution.

Potential Ecological Risk Index (RI):-

This index is a mechanism for assessing the impact of potentially harmful components on aquatic behavior. The RI is obtained using following formula according to Hakanson[28] and Yi et al. [29]:

$$RI = \sum_{i=1}^{i} E\,r^{i} \text{avec } E_r^{\,i} = Tr \times FC$$

Where Er is the ecological risk factor for metal; Tr is the toxic response factor for a metal, which is defined for Cd = 30, Cr = 2, Cu = Pb = 5, Ni = 6, and Zn = 1 [30]. FC is the contamination factor. The ecological risk values are interpreted according to Hakanson[28], as shown in Table 2 below:

Table 2: Scale used to describe the risk factors of Er and RI [28](1980).

Er	Potential ecological risk	RI	Ecological risk index
Er< 40	Low ecological risk	RI < 95	Low ecological risk
40 ≤ Er< 80	Moderateecologicalrisk	95≤ RI<190	Moderateecologicalrisk
80 ≤ Er < 160	Considerableecologicalrisk	190 ≤ RI < 380	Considerableecologicalrisk
160 ≤ Er < 320	High ecologicalrisk	380 ≤ RI	Very high ecologicalrisk
320 ≤ Er	Very high ecologicalrisk		

Statistical Analyses:

Analyses of variance (ANOVA) were performed at the four stations to test for significant differences in sediment parameters: organic matter, pH, electrical conductivity, and trace metal content. The spatial distribution and relationships between trace elements and sediment parameters at the different stations were examined using Principal Component Analysis (PCA). Relationships between the analyzed elements were tested using Pearson's coefficient with a threshold set at $p < 0.05$. Statistical analyses and graphs were performed using R software version 4.4.3.

Results:-

Physicochemical properties:

Table 3 presents the mean values of organic matter (OM), pHand electrical conductivity (EC) in the surface sediments of the Ntsini River. The average amount of OM recorded for all sites exceeds 30% for the first three stations located upstream, following the order Pages (33.31%) >Ngwamba (32.18%) >Moka (31.15%) (Table 3). The lowest mean of 24.45% is recorded for the Nende station located furthest downstream. There appears to be a very significant difference ($p < 0.005$) between the Ngwamba, Moka, Pages and Nende station which has the lowest OM mean.Mean pH values range from 5.53 to 7.13 (Table 3). Acidic pH values characterize stations more exposed to upstream anthropogenic pressures, such as Ngwamba (5.53), Moka (5.77), and Pages (5.47). Only the Nende station has a mean pH of 7.13, indicating the neutral nature of this station. The mean pH of the three stations upstream of the Ntsini River differs very significantly ($p < 0.005$) from that of the Ntsini.For the electrical conductivity (EC), the results show that it varies on average from 7.64x103 to 10.23x103 $\mu S.cm^{-1}$ for all sites studied (Table 3). The measurements recorded at the Ngwamba (9.38x103 $\mu S.cm^{-1}$), Moka (10.23x103 $\mu S.cm^{-1}$) and

Pages (9.98x103 µS.cm^{-1}) stations are significantly higher ($p < 0.05$) compared to those obtained at the Nende station (7.64x103 µS.cm^{-1}).

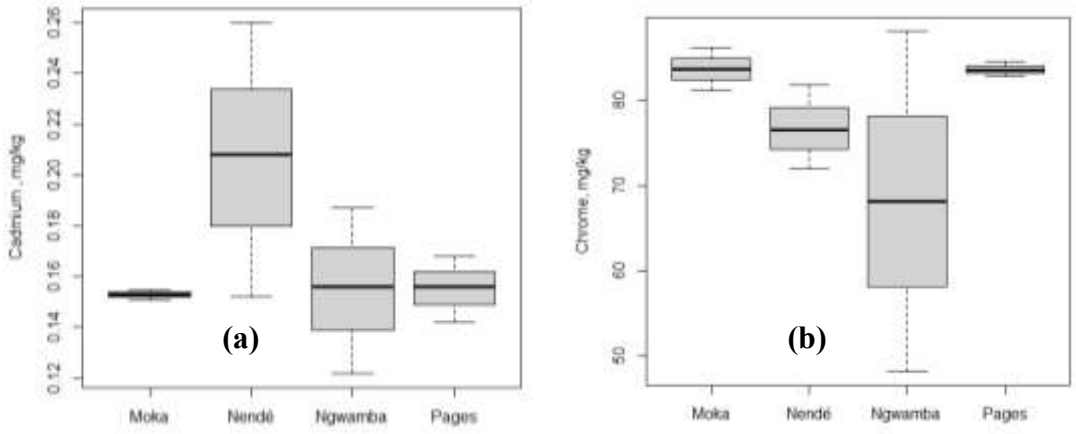
Table 3: Physicochemical parameters of sediments.

Sites		OM (%)	pH	EC (x10^3 µS.cm^{-1})
	minimum	29.91	5.45	9.36
Ngwamba	maximum	33.82	5.58	9.41
	mean	**32.18**	**5.53**	**9.38**
	s. deviation	2.029	0.07	0.02
	minimum	30.88	5.52	9.71
Moka	maximum	31.53	6.01	10.76
	mean	**31.15**	**5.77**	**10.23**
	s. deviation	0.34	0.24	0.52
	minimum	32.7	5.44	9.71
Pages	maximum	34.19	5.52	11.52
	mean	**33.31**	**5.47**	**9.98**
	s. deviation	0.77	0.04	1.53
	minimum	23.64	6.76	7.20
Nende	maximum	25.53	7.50	8.10
	mean	**24.45**	**7.13**	**7.64**
	s. deviation	0.34	0.37	0.45
ANOVA	F-value	32.87	35.98	5.79
	p-value	0.0000757***	0.0000542***	0.021*

OM : Organic Matter; EC : Electrical Conductivity ; p-value : probability value with *** p<0.001: Highly significant, **p<0.01: very significant, *p<0,05: significant.

Trace element contents in sediments:

Trace element contents and their distribution among the four stations along the Ntsini River are given in Figure 2. For all the sediments studied, cadmium (Cd) concentrations ranged from 0.155 ± 0.03 to 0.207 ± 0.054 mg/kg, chromium (Cr) from 68.13 ± 19.95 to 83.63 ± 2.55 mg/kg, copper (Cu) from 12.26 ± 2.99 to 14.95 ± 0.67 mg/kg, nickel (Ni) from 20.50 ± 6.30 to 25.67 ± 0.35 mg/kg, and lead (Pb) from 15.8 ± 4.3 to 19.15 ± 1.12 mg/kg, and zinc (Zn) from 53.33 ±16.60 to 88.63 ±21.75 mg/kg of dry sediment.



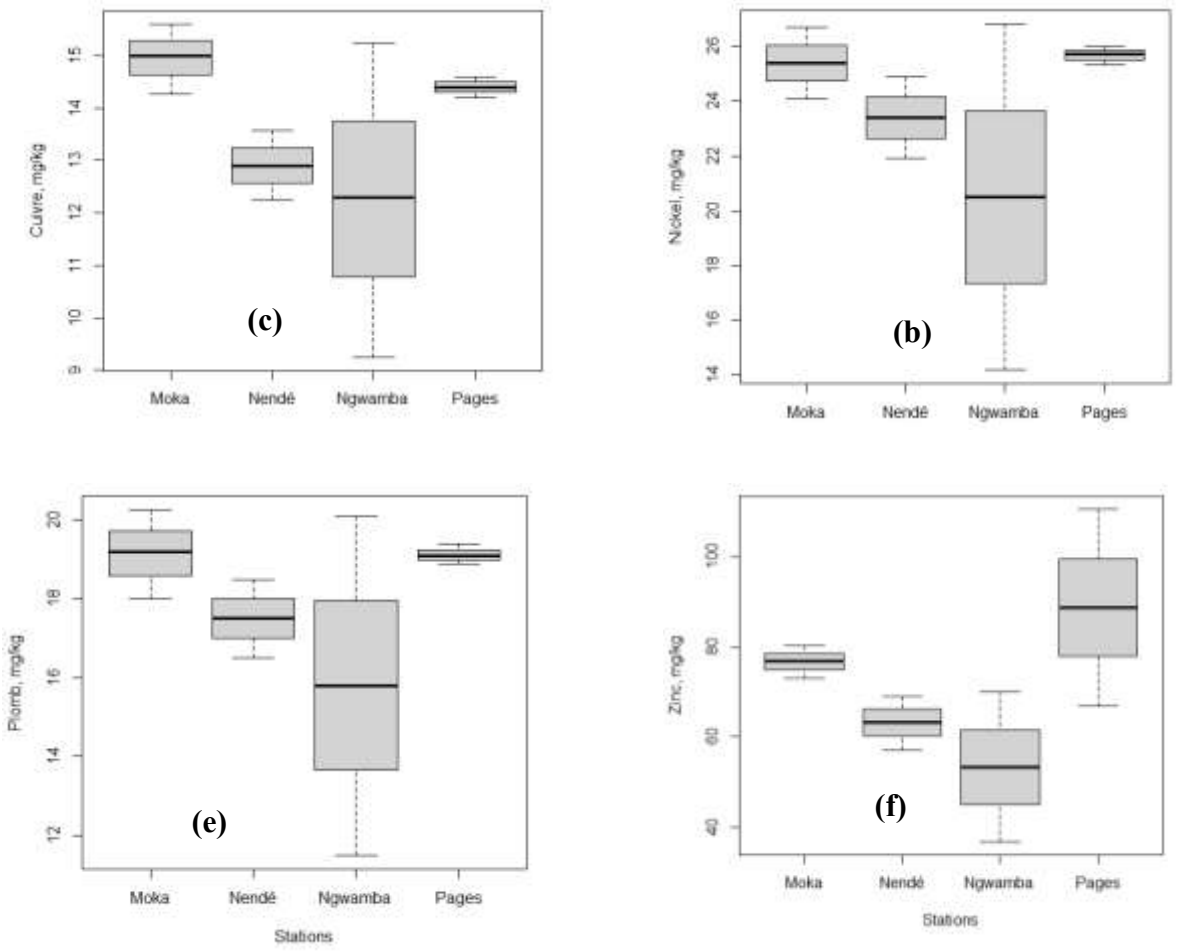


Figure 2: Heavy metal contents (en mg/kg) in the sediments of Ntsini River: Cd (a), Cr (b), Cu (c), Ni (d), Pb(e), and Zn (f).

Among all stations, the highest concentrations of Cr, Cu and Pb are obtained to Moka, Ni and Zn to Pages, and Cd to Nende. However, ANOVA results do not show significant differences between the different stations for Cd ($p = 0.196$), Cr ($p = 0.285$), Cu ($p = 0.205$), Ni ($p = 0.273$), Pb ($p = 0.294$) and Zn ($p = 0.066$). Results show that the higher average concentrations of Cr and Pb (Moka), Zn (Pages) and Cd (Nende) are higher compared to the geochemical background of the UCC continental crust, with Cr = 76 mg/kg, Pb = 15.12 mg/kg, Zn = 69.5 mg/kg and Cd = 0.061 mg/kg [27]. These results indicate a probable contamination of the sediments from three stations: Moka (Cr and Pb), Pages (Zn) and Nende (Cd).

Relationship between physicochemical parameters and trace metal elements:

The results of the Principal Component Analysis (PCA) (Figures 3a and 3b) highlight the relationships between physicochemical parameters and trace element concentrations in the sediments, on the one hand, and between the different sampling stations, on the other. Two principal axes, Dim 1 and Dim 2, account for 81.09% of the total variance in sediment parameters (Dim 1: 50.51%, Dim 2: 30.58%). Figure 3-a shows the projection of the sediment sampling sites at the four stations.It shows two types of sediments in the Ntsini River arranged in two groups: group G1 is formed by sediments from the three stations Ngwamba, Moka and Page located upstream of the Ntsini River, and group G2 exclusively groups the sediments from the Nende station located furthest downstream of the Ntsini River towards Mondah Bay. Group G1 is carried by the Dim 1 axis (50.51%), the main component responsible for the greatest variability, which is positively defined by Cr, Cu, Ni, Pb and Zn (Figure 3-b), includes on the one hand the sediments from the Moka, Pages and Ngwamba stations significantly richer in OM, with higher EC and acidic pH, and on the other hand the sediments from Moka and Pages more polluted by Cr, Zn, Ni, Pb and Cu from anthropogenic activities and certainly from the Earth's crust. While group G2 is carried by the Dim 2 axis composed

mainly of sediments from the Nende station, it is defined in its positive part by pH and Cd then in its negative part by OM and electrical conductivity (figure 3-b). Cd has a strong affinity for sediments in group 2 that are less rich in organic matter, have a neutral pH, and lower electrical conductivity. The correlation matrix highlighting the relationships between OM, pH, EC parameters and metal contents in the sediments is summarized in Table 4. According to Pearson's correlation coefficients, a highly significant positive correlation ($p < 0.001$) was observed between the metallic elements Cr, Cu, Ni, and Pb, reflecting a common source of these elements and their similar behavior in the sediments. Similarly, a significant positive correlation ($p < 0.05$) was observed between Zn and the trace elements Cr, Cu, Ni, and Pb. Among the physicochemical parameters, only EC showed a significant positive correlation ($p < 0.05$) with a single metallic element (Zn). Furthermore, EC is negatively and significantly correlated ($p < 0.05$) with sediment pH, while OM shows a very highly significant negative correlation ($p < 0.001$) with pH (Table 4).

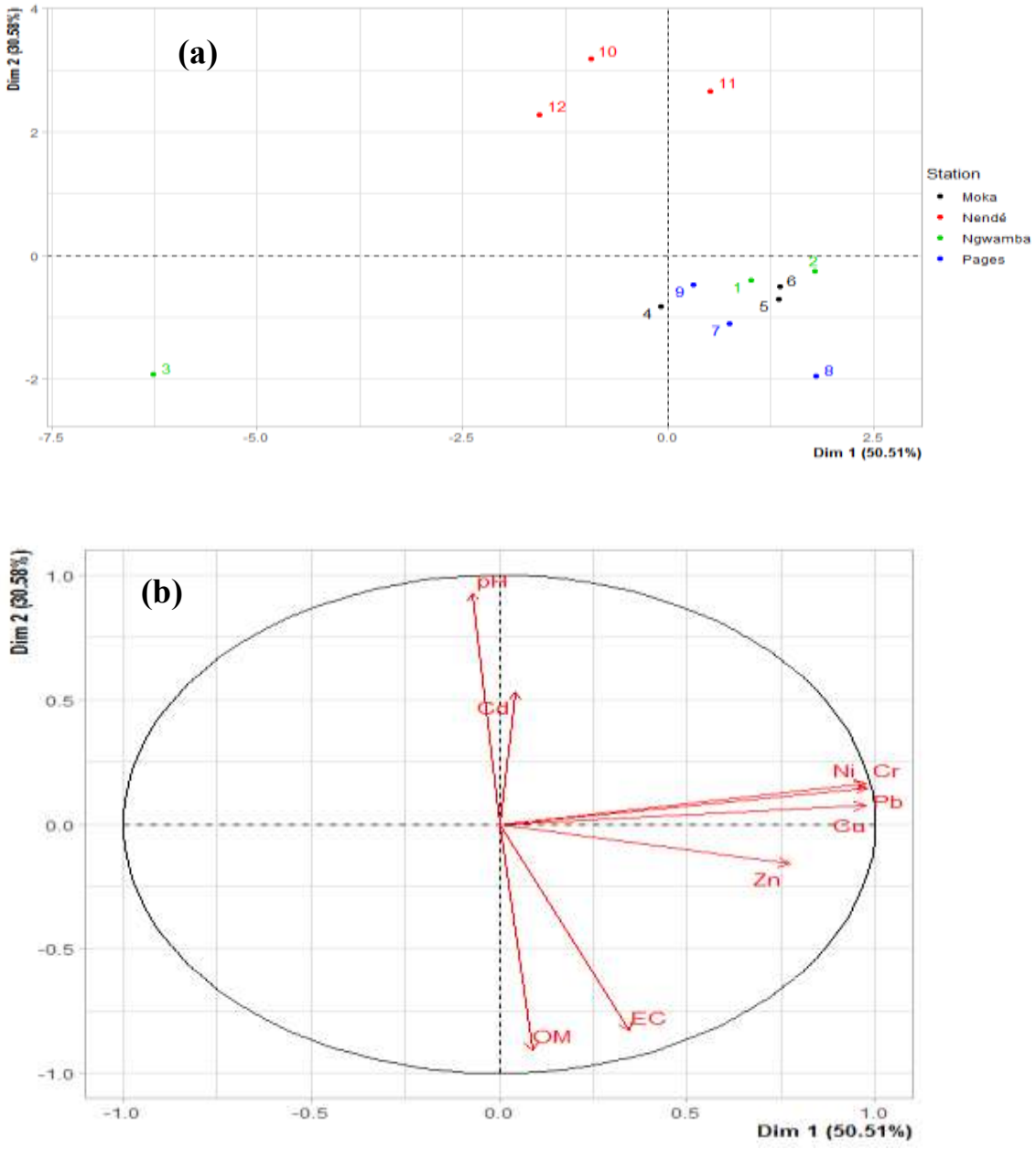


Figure 3: PCA characterization of the Ntsini River sediments based on: (a) the different sampling areas; (b) physicochemical parameters and trace metal element concentrations.

Table 4: Pearson correlation coefficients between parameters.

	Cd	CE	Cr	Cu	MO	Ni	Pb	pH
Cd								
CE	-0.40							
Cr	0.09	0.16						
Cu	0.08	0.21	0.98***					
MO	-0.22	0.69 *	-0.05	0.06				
Ni	0.07	0.16	0.99***	0.98***	-0.06			
Pb	0.09	0.17	0.99***	0.99***	-0.03	0.99***		
pH	0.38	-0.66*	0.05	-0.05	-0.93***	0.05	0.04	
Zn	0.03	0.58*	0.66*	0.62*	0.12	0.65*	0.66*	-0.06

****: Significant correlation at the 5% level ($p<0.05$);**
*****: Significant correlation at the 0,1% level ($p<0.001$)**

Assessment of the contamination degree of sediment:
The geo-accumulation index (I_{geo}) values for trace elements in sediments are given in Table 5. The Igeo values of all samples from the four stations for the elements Cr, Zn, Ni, Pb, and Cu are less than 0 ($I_{geo}< 0$), indicating that the sediments are not contaminated with these elements. As for Cd, its average values ($0 <I_{geo}< 1$) reveal slight Cd contamination in all Ntsini River sediments analyzed in this study [26].The contamination factors (CF) and the contamination degree (DC) values are summarized in Table 6. The CF values for the trace elements Cr, Cu, and Pb are less than 1, indicating that these sediments are uncontaminated or slightly contaminated in these three metal elements. However, for all samples, the CF values for Zn range from 0.22 to 2.07; those for Pb from 0.35 to 1.25 and the CF values for Cd from 1.91 to 5.41. The sediments from all stations show moderate contamination with Zn and Pb ($1 <Igeo< 3$) [28]. For Cd, there is moderate contamination ($1<CF<3$) in sediments from Moka and Pages stations and some sediments from Ngwamba and Nende stations, and significant contamination ($3<CF<6$) of at least one sampling site from Ngwamba (CF = 3.70) and Nende (CF = 5.41) stations.The contamination degree (CD) values confirm that the sediments at the Moka and Pages stations have a low degree of contamination in Cr, Zn, Ni, Pb and Cu ($CD < 8$), while for the Ngwamba and Nende stations, 1/3 of the sampling sites have an $8<CD<16$ indicating moderate contamination, particularly in Cd. This Cd contamination of the sediments appears to be more significant for the Nende station located furthest downstream of the Ntsini River, towards Mondah Bay.

Table 5: Geo-accumulation index (I_{geo}) of the metal elements in sediments.

Sites	**Geo-accumulation index (I_{geo})**					
	Cr	Zn	Ni	Pb	Cu	Cd
Ngwamba	- 0.30 ± 0.36	- 0.38 ± 0.39	- 0.48 ± 0.38	- 0.22 ± 0.31	- 0.55 ± 0.27	0.21 ± 0.16
Moka	- 0.14 ± 0.03	- 0.13 ± 0.04	- 0.30 ± 0.04	- 0.07 ± 0.05	- 0.42 ± 0.04	0.22 ± 0.01
Pages	- 0.14 ± 0.01	- 0.10 ± 0.20	- 0.29 ± 0.01	- 0.08 ± 0.01	- 0.43 ± 0.01	0.23 ± 0.05
Nende	- 0.18 ± 0.05	- 0.22 ± 0.08	- 0.34 ± 0.06	- 0.11 ± 0.05	- 0.48 ± 0.04	0.32 ± 0.21
***UCC**	76	69.5	33.5	15.12	26	0.061

***UCC: Reference values of the Earth's crust in mg/kg[27].**

Table6: Contamination factors (CF) and contamination degrees (CD) of sediments witgh metallic trace elements.

Sites	Contamination factor (CF)						CD = $\sum CF_i$
	Cr	Zn	Ni	Pb	Cu	Cd	
Ngwamba	0.74 ± 0.43	0.79 ± 0.49	0.44 ± 0.27	0.93 ± 0.50	0.44 ± 0.21	2.56 ± 0.99	5.90 ± 2.55
Moka	0.91 ± 0.06	1.15 ± 0.11	0.54 ± 0.05	1.13 ± 0.13	0.54 ± 0.05	2.50 ± 0.07	6.76 ± 0.39
Pages	0.91 ± 0.01	1.32 ± 0.65	0.55 ± 0.01	1.12 ± 0.02	0.51 ± 0.01	2.55 ± 0.31	6.97 ± 0.60
Nende	0.83 ± 0.10	0.94 ± 0.17	0.50 ± 0.07	1.03 ± 0.11	0.46 ± 0.04	3.41 ± 1.75	7.17 ± 1.68

The potential risk factor (Er) and ecological risk index (Ri) values are summarized in Table 7. The results show that the Er values are much lower than 40 (Er<40) for the elements Cr (from 0.4 to 2.1). Zn (from 0.7 to 2.1). Ni (from 0.8 to 3.7). Pb (from 1.8 to 6.3) and Cu (from 1.0 to 2.9), which indicates that the potential ecological risk for these elements is low according to Hakanson[28] (Table 2). In contrast, for the element Cd, the Er values in the sediments of the Ngwamba (from 57.3 to 111.0), Pages (from 72.9 to 77.4), Pages (from 69.2 to 87.3) and Nende (from 65.4 to 162.4) stations potentially imply moderate ecological risks for Cd (40 ≤ Er< 80) for the sediments of the Moka and Pages stations, and potentially considerable ecological risks for Cd (80 ≤ Er< 160) for some sediments of the Ngwamba and Nende stations. The Ri values indicate that there is an existing ecological risk for the element Cd that is moderate (95 ≤ Ri< 190) for the Ngwamba and Nendestations [28].

Table 7: Potential risk factor (Er) and ecological risk index (RI) of trace elements in sediments.

Sites	Potential risk factor (Er)						RI
	Cr	Zn	Ni	Pb	Cu	Cd	
Ngwamba	1.48 ± 0.87	0.79 ± 0.49	2.62 ± 1.61	4.65 ± 2.52	2.19 ± 1.06	76.91 ± 29.68	88.65 ± 33.40
Moka	1.82 ± 0.12	1.15 ± 0.11	3.25 ± 0.31	5.64 ± 0.64	2.68 ± 0.24	75.12 ± 2.2	89.65 ± 3.38
Pages	1.82 ± 0.03	1.32 ± 0.65	3.28 ± 0.08	5.61 ± 0.09	2.57± 0.06	76.63 ± 9.47	91.23 ± 9.10
Nende	1.66 ± 0.21	0.94 ± 0.17	2.98 ± 039	5.15 ± 0.55	2.30 ± 0.23	102.29 ± 52.50	115.34 51.85

Discussion:-

Physicochemical parameters show that the sediments of the first three stations Ngwamba, Moka and Pages have a very similar average pH (pH ~ 5.5 to 5.7), electrical conductivities (between 9400 and 10200 µS/cm), with same order of organic matter levels (31 to 33%). The sediments of these three stations are very significantly different from those sampled in the Nende station which are characterized by a neutral pH (pH ~ 7.1), a lower electrical conductivity (EC = 7610 µS.cm^{-1}) and a low quantity of organic matter (24.4%) compared to the three other sites located further upstream of the Ntsini River. An acidic pH would promote the trace elements solubilization in the sediments of the first three stations (Ngwamba, Moka and Pages), while a neutral pH would promote their adsorption on the sediments of the Nende station[19].For all studied sediments, the electrical conductivity values are significantly higher compared to the OMS standard value (2500 µS/cm) [31]. These sediments would contain a lot of free or exchangeable ions in solution and would be highly mineralized. The differences observed between the analyzed sediments could result from multiple sources of enrichment in ionic elements and organic matter from the first three stations (Ngwamba, Moka and Pages) located near human habitations and mangroves. Indeed, Kristensen et al. [32] reported that mangrove litter and suspended matter imported from various sources constitute the major sources of organic matter in mangrove sediments. Along the Ntsini River, the mangrove is composed of mangrove trees, which develop in tidal swing zones [33]. It is an ecosystem that plays a vital role for many species thanks to its

significant production of organic matter [34].These organic matter enrichment in the sediments of stations near the mangrove would be favored by the withdrawal of tidal waters; this is the case of the Ngwamba, Moka and Pages stations. Generally, the high mineralization of these organic matters makes it possible to appreciate the very high degree of mineralization of the sediments of the Ntsini River [35].

According to the levels of trace metal elements obtained, the concentrations of Cd in all the sediments studied, as well as those of Cr, Pb and Zn in the Moka and Pages stations are higher than those of the geochemical background of the continental crust [27], which indicates contamination of the sediments with these trace elements. The results of the Principal Component Analysis (PCA) highlight a correlation between the three stations upstream of the Ntsini River (Ngwamba. Moka. Pages) on the one hand, and a clear difference between these three stations and the one located downstream (Nende) on the other hand.The sediments from the first three stations have an acidic pH, are richer in organic matter, more mineralized and their ACP axis is positively defined by the trace elements Cr, Cu, Ni, Pb and Zn, which differs from those of the Nende station which are characterized by a neutral pH, less organic matter, and the axis which carries it is positively defined by Cd.

The highly significant positive Pearson correlations ($p < 0.001$) observed between the elements Cr, Cu, Ni and Pb would indicate a common source of anthropogenic contamination of these metals [36, 37], certainly linked to solid waste discharges, agricultural effluents, and/or the intense river traffic of fishing canoes along the Ntsini River from the Ambouwè landing stage to Mondah Bay. Given the high Cd concentrations in all samples, electrical appliances, plastic materials, fertilizer runoff and fuel leaks from some canoes would constitute multiple sources of trace element contamination of the Ntsini sediments. Concerning the contamination factors (CF) and the degree of contamination (DC), the trace elements that have most contaminated the sediments follow the following order: Cd>Zn>Pb>Cr>Ni>Cu, and the most contaminated sediments are classified in the stations according to the order Nende>Ngwamba>Pages>Moka. These trace elements discharged upstream would be redistributed along the river by the tidal current which is favored by a moderately high flow (74 m^3/s) of the MondahBay [38],which would explain a low degree of contamination of the sediments ($DC < 8$) in Cr, Cu, Ni, Pb, Zn and moderate ($8<DC<16$) in Cd along the Ntsini channel [28]. For all trace elements, only Cd potentially presents a moderate ecological risk ($40 \leq Er< 80$) in sediments for the Moka and Pages stations, and a considerable ecological risk for the Nende and Ngwamba stations. However, the highest ecological risk index (Ri) value for Cd obtained in sediments from the Nende station ($Ri = 174.9$) shows that these sediments present a greater ecological risk compared to sediments from other stations. According to this Ri index, the quality of the sediments from the stations is ranked following this order: Nende>Ngwamba>Moka> Pages.

After assessing the degree of contamination of the sediments by trace elements, Cd is the only element that presents a significant ecological risk. It is a bioaccumulative trace element with high toxicity in living organisms [39, 40]. Trace elements that are adsorbed on sediments can be released at the slightest modification of environmental parameters such as changes in redox potential, salinity or pH, thus causing their concentration in the water column[10, 11].In the coastal zone, Cd founded in dissolved form and associated with chloride ions [41], is bioavailable to fish species, which could have deleterious effects on aquatic life and the health of consumer peoples of fish and shellfish caught in the Ntsini River. Since the main source of Cd contamination of sediments is not clearly identified, special monitoring should be carried out, in particular on the reservoirs of fishing canoes, and the types of urban waste, agricultural and industrial effluents that are discharged along the Ntsini River and in this part of the Akanda National Park.

Conclusion:-

In this work, the contamination status of the surface sediment samples along Ntsini River were analyzed with heavy metal contamination and ecotoxicological indexes, in Akanda National Park in Libreville, Northwestern Gabon. In this protected estuarine area, there are two types of sediments from four different stations: sediments from the Ngwamba, Moka, and Pages mangrove mudflat stations characterized by an acidic pH, a high amount of organic matter, and similar Cr, Cu, Ni, Pb, and Zn contents, and sediments further downstream from the Nende station, characterized by a neutral pH, a lower amount of organic matter, and especially higher Cd contents. The results showed Cd contamination in all sediments, and Cr, Pb, and Zn in the sediments from the Moka and Pages stations, their concentrations being higher than those of the geochemical background of the continental crust.

The highly significant positive Pearson correlations ($p < 0.001$) between the elements Cr, Cu, Ni, Pb and Zn indicate a common anthropogenic source of these metal elements. In this study, the contamination factors (CF) and the degree of contamination (DC) respectively reveal the contamination status of sediments by the elements following the order Cd>Zn>Pb>Cr>Ni>Cu, and the ranking of stations according to their overall contamination state: Nende>Ngwamba> Pages >Moka. However, the element Cd was determined as the only one to have significantly contaminated the sediments of the Ntsini ($0 < I_{geo} < 1$) and to have caused a moderate ecological risk ($40 \leq Er < 80$) for the Moka and Pages stations, and considerable ($40 \leq Er < 80$) for the sediments of the Nende and Ngwamba stations. The values of the ecological risk index (Ri) confirm an ecological risk for the element Cd which is moderate for the sediments of the Ngwamba and Nende stations ($95 \leq Ri < 190$).

Conflits of interest

The authors do not have any possible conflicts of interest.

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