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Evaluation of contamination risks in Metallic Trace Elements (MTE) in the sediments of Ouémé delta in Benin

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ABSTRACT: The Metallic Trace Elements (MTE) pollution of aquatic ecosystems and their intrusion and inclusion into the food chain exposes public health to enormous risks. This study assesses the risks associated with the pollution of surface sediments from Ouémé delta with Pb. Cu and Cd. In these sediments stratifications, the physicochemical characteristics of the sediments were evaluated. Total metal contents are determined by the inductively coupled plasma mass spectrometer. Risk indices are evaluated, followed by statistical processing in software R 3.3.2. On average, the pH is 5.50; the CEC is 84.24 meq / 100g and the organic carbon (OC) is 0.84 % of mass sediment. Means of Al_2O_3, Fe_2O_3 and CaO are respectively 8.14 %; 3.9 % and 6.08 %. The means of copper, lead and cadmium are respectively 32.92 ppm; 23.63 ppm and 1.43 ppm. Overall the degrees of risk related to contamination and ecological risks are low to high. Sites with a high degree of contamination and high ecological risk reflect the importance of the contribution of solid waste from Dantokpa market and the domestic discharges into the metal pollution of Ouémé delta.

KEYWORDS: Ouémé delta, Sediments, Metallic Trace Elements, Risk of contamination, Ecological risk.

1 INTRODUCTION

Contamination in Metallic Trace Elements (MTE) is one of the major environmental problems affecting human health and aquatic ecosystems. Anthropogenic activities such as agriculture, residential, urban and industrial waste generation are the potential sources of their release into rivers [1], [2]. Among these metals, Cd, Pb, Hg and Ni are classified as priority substances in Directive 2008/105 / EC (Water Framework) and are of major environmental concern due to their toxicity, non-biodegradable property, mobility and bioavailability [3] . In living organisms, these MTEs can lead to morphological abnormalities, neurophysiological disorders, affect enzymatic and hormonal activities [4] [5]. In order to attract the attention of governments and researchers, Dutch Hann called these metals "chemical time bomb" [6].

In Benin, about 25,000,000 hectares of arable lands are cultivated each year, including 320,000 hectares of irrigable lands in the valleys, including that of Ouémé [7]. Cotton is the main cash crop that consumes about 90% of the insecticide market [8] and 96 % of chemical fertilizers. These inputs cause post-harvest emissions and are the source of water pollution by runoff and infiltration. Better, in the context of the demographic boom in recent years, there is strong anthropogenic pressure on the Ouémé delta. Approximately 75,000 inhabitants live on and around Lake Nokoué [9]. Around the Sô river, over 20 years, the agglomerations have increased by 202 ha [10]. To the various strategies designed to master such a context, unfortunately grafted an indelicacy of some local population. Solid and liquid waste is dumped daily into the gutters and water collectors that open into Lake Nokoué, near the lake and its channels. To these wastes are added the discharges from the industrial units and the international market of Dantokpa in Cotonou (Fig.1). Moreover, in recent decades, the smuggling of hydrocarbons from

Nigeria has also been developed through Nokoué Lake and the Porto Novo Lagoon. The loading docks of Abomey-Calavi, Akassato and Sô-Ava represent a real distribution point where large spills occur. Given the importance of Oueme in its ability to supply more than 75% of national fish production [11], several studies have focused on the assessment of impacts related to these human activities.

All the research carried out to date has proved the vulnerability of Ouémé delta regarding MTEs. Reference [12] revealed levels of 13.94 and 22.07 mg / kg respectively for Pb and Cd in Nokoué Lake; while [13] revealed mean levels of 54.04 and 0.74 mg / kg in the city of Ganvié. Reference [14] had recorded very high Pb contents of 895.33 mg / kg at Calavi; 233.25 mg / kg in the middle of Nokoué Lake and 535.79 mg / kg in Dantokpa area. Total contents generally allow assessment of the potential risk of pollution [15]. Besides the disparity of the total contents in the sediments of Ouémé delta, the sectors studied are not categorized by reference to the various indices of risk level assessment. The study assesses the potential risk levels of Pb, Cu and Cd pollution in Ouémé superficial sediments and considers the physicochemical conditions that may influence their mobility.

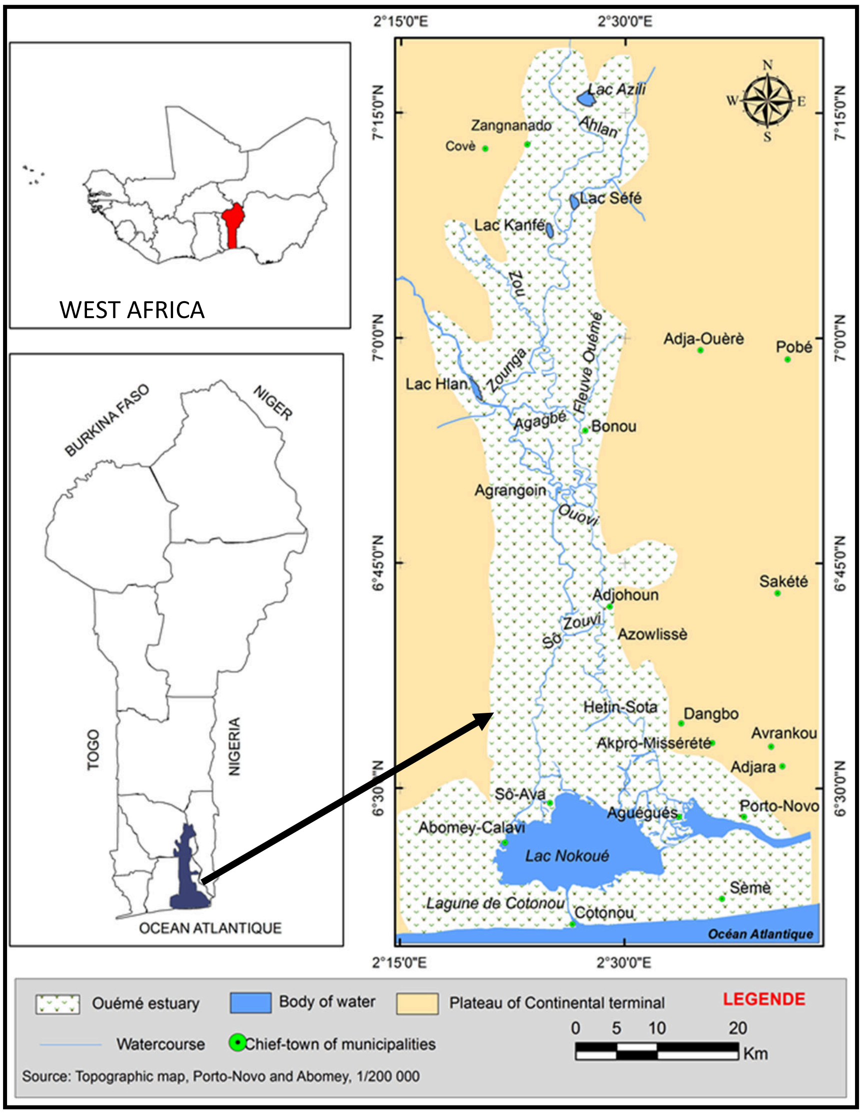

Fig. 1. Map showing Ouémé delta

2 LITERATURE REVIEW

Metal fate studies indicate that metals released into the aquatic environment in the particulate state readily sediment. Those arriving in the dissolved state react with organic and inorganic ligands thus forming complexes that attach to suspended particles and sediment [16]. The main components of these sediments are: interstitial water, organic matter and inorganic matter [17]. Organic matter consists of proteins, polysaccharides, lipids, humic and fulvic acids [18]. Humic and fulvic acids have a very high cation exchange and complexation capacity. These acids are negatively charged because of the carboxylic and phenolic groups in which a hydrogen can be replaced by metal ions [19]. Inorganic matter includes clays, carbonates and silicates. The more sediments are rich in fine particles (<150 µm), the more they are rich in organic matter and the greater their ability to complex with metallic contaminants [20]. This ability of the sediment component to complex metals is a function of the mineralogical nature of the sediment, since illites and montmorillonites are an excellent fixative. Sediment pH is, however, an important factor influencing the accumulation of metals. Its decrease is favorable to increasing the concentration of free metal cations in the soil solution [21]. PH values above 6 favor the precipitation of metal hydroxide, chelation by organic matter [22]. According to reference [23], the increase in Pb, Cu and Ni adsorption with pH could be attributed to a better ability to deprotonate oxygenated groups, which are better able to coordinate with metal cations. The mobility of metals at the sediment-water interface also seems to vary according to the salinity of the environment [4]. Sediment metals tend to be more mobile at low salinity. Decreased sediment salinity results in different partition coefficients Kd (metal to sediment and interstitial water concentration ratios) of the metals. In general, after accumulation of metals, the environmental risks will therefore depend on the physico-chemical conditions such as the nature of the sediment, the organic matter content, the pH, the salinity, the cation exchange capacity…

3 STUDY OBJECTIVES

Overall, this study aims to evaluate the influence of metallic trace elements on the sediment quality of the Ouémé delta. Specifically, it is a question of characterizing the physicochemical parameters of delta superficial sediments. Finally, it is necessary to determine the risk levels due to the accumulation of metallic trace elements in the delta sediments.

4 MATERIAL AND METHODS

4.1 DESCRIPTION OF STUDY AREA

Ouémé delta is located in the southern part of Benin, one of the West African countries (Fig. 1). Ouémé is the main river in the Benin hydrographic system with its tributaries Okpara and Zou. This delta is integrated into the coastal sedimentary basin of Benin, which consists of plateau, sandy cords, estuarial systems, foreshore and shoreface. The geological formations are made up of quaternary deposits which rest on a thick layer of sandstone, clays, limestone ... whose ages go up to the Cenomanian [24]. The lithology of quaternary deposits is composed of clays, sands, vases and peat. The climate is of the subequatorial type with average air temperatures of about 28.33 ° C in the great dry season and 27.46 ° C in the great rainy season. The warm months of February, March and April are hot (31-33 °C) followed by cool nights (24-26 °C) [25]. The relative humidity varies from 67.08 % to 71.83 %. From a morphological point of view, the Ouémé delta is divided into three sectors [26]. The upper delta starts from the confluence of Ouémé with the Zou up to the limit of Bonou. The medium delta goes from Bonou to Azowlissè in the commune of Adjohoun. The lower delta runs downstream from Azowlissè to the north of the complex Lake Nokoué-lagoon of Porto-Novo. From a hydrological point of view, in Bonou, after a period of recession that lasts from January to May, the flood wave arrives in June and the recession begins in November. When the flood level in Bonou is less than 7.50 m, the Ouémé River flows to Sô through Zounga and Agagbe tributaries are not significant [27]. Ouovi and Zouvi tributaries in the medium delta can flow from Ouémé to Sô Rivers when this level in Bonou exceeds 5.50 m. In the lower delta, overflows begin as soon as the water level in Bonou exceeds approximately 6.00 m. It is during this period of flood that Ouémé spreads in the delta sediments containing all sorts of toxic residues produced in the north and in the center of the country. At low water, salinity is close to 2 % at the mouth of the Sô and doesn’t exceed 1 % for Ouémé. During this last period, there is rise of lagoon waters which is about 25 km in Ouémé. Through this hydrodynamic inversion, the delta gets its supply of salt water, sediments, and pollutants from the littoral zone. The hydrosedimentary operation of the delta and its geographical position give it the quality of an excellent environment of deposit and transit of materials. Its specificity among all the depositional environments in the country justifies its choice in this study.

4.2 SAMPLING OF THE SEDIMENTS

A field survey was organized from 20 to 23 August 2015. Twelve (12) samples of surface sediments were collected by means of an Eckman bucket in twelve points. At each sampling point, three (3) to five (5) samples were taken and mixed. The sampling sites are located on the map (Fig.2). Sampling was done randomly. Two types of sampling sites were considered, namely sites close to areas of high pressure such as: Calavi loading dock (SCal), Cotonou Channel outlet (SCot), Ganvié (SGan), Sô-Ava loading dock (SSo-A), Ouédo-Aguékon (SOe-A) and Ahomey-Glon (SAh-G). The second type of site concerns areas where human presence is rare, such as Toché (SToc), Nokoué (SNok), Louho (SLou), Aguégué-Donoukpa (SAg-D), Dékanmè (SDek), and Ouédo-Gbadji (SOE-G).

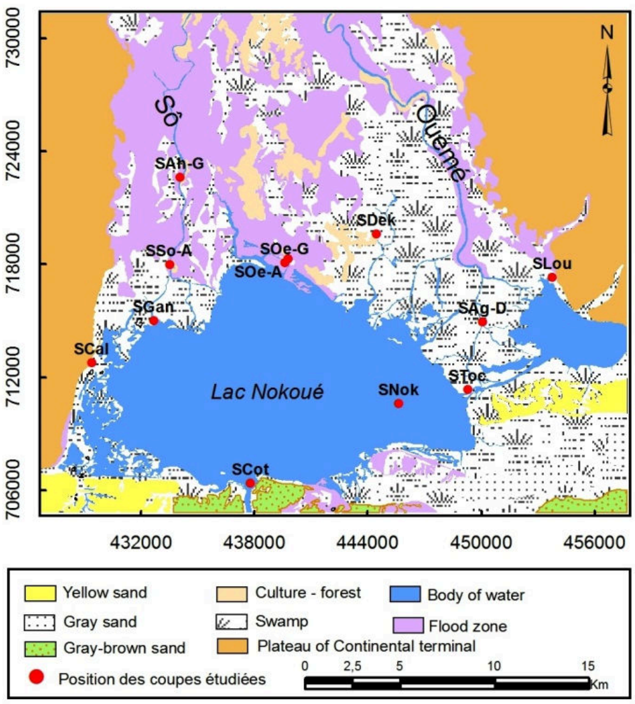

Fig. 2. Map showing the positioning of the sampling points

The sediments were then packed in plastic bags and labeled. Two (2) small drilling were taken using a 12 cm x 12 cm quadratic core sampler. The two cores were positioned within a radius of at least 200 m from human pooling points to minimize mixing and bioperturbation. A 4 cm pitch was observed for the sampling of the drilling. All samples were then transported to the laboratory as quickly as possible to be stored in a refrigerator at 3-4 ° C. All the physicochemical parameters were evaluated at the Laboratory of Mineral Chemistry of the Polytechnic School of Antananarivo (Madagascar). For the quantitative study of the dimensional classes of the particles, 200 g of dry sediment were collected, washed and then screened by series of nine mesh sieves between 400 and 40 µm of the AFNOR NFX 11504 module [28]. The pH assessment is based on the standard procedure. The CEC method of evaluation is the one of cobaltihexammine trichloride specified by ISO 23470: 2007. The percentages in OC of sediment are known according to the guidelines for analytical researches in Chemistry DR- 12-CSA-01 of the Center of Expertise in Environmental Analysis of Quebec. To determine the total metal contents, two grams of each sample were mixed with 20 ml of aqua regia. The dosage was done at ICP-MS of the National Mines and Strategic Industries Office (OMNIS / Madagascar). For the accuracy of the ICP-MS measurements, standard reference materials (Perkin Elmer 18-195 JB. N9300233) were used, three standards were carried out and a parallel control test was carried out on a sample of purified water HNO_3 5%. Environmental risk assessment is based on contamination (Igeo, CF, mDC) and ecological indices (ER, RI; Table 1). The Pearson correlation coefficients were used to test the significant differences with a 95 % confidence level in the R 3.3.2 software.

Table 1. Mathematical formulas of contamination and ecological risk indices

Name of index	Mathematical formulas	Classifications
Geoaccumulation index (Igeo): single-element contamination	$Igeo = log_2 \frac{C_n}{1.5B_n}$ [29] C_n is the measured concentration of the element n. B_n is a geochemical background value in the cores, the constant 1.5 to minimize the effect of background variations due to lithological differences and small anthropogenic influences	Igeo ≤ 0: uncontaminated sediment (I); 0 < Igeo ≤ 1: uncontaminated to moderately contaminated sediment (II); 1 < Igeo ≤ 2: moderately contaminated sediment (III); 2 < Igeo ≤ 3: moderately to highly contaminated sediment (IV); 3 < Igeo ≤ 4: highly contaminated sediment (V); 4 < Igeo ≤ 5: highly to extremely contaminated sediment (VI); 5 < Igeo: extremely contaminated sediment (VII) [30]
Contamination Factor (CF): single element contamination	$C_f^i = \frac{C_{0-1}^i}{C_n^i}$ [30] C_{0-1}^i is the average grade of each metal; C_n^i est is the reference value or the background or pre-industrial value	$C_f^i \leq 1$: Low contamination (I); $1 < C_f^i \leq 3$: moderate contamination (II); $3 < C_f^i \leq 6$: considerable contamination (III); $6 < C_f^i$: very high contamination (IV)
Modified Contamination Level (mDC): multi-element contamination	$\mathrm{mDC} = \frac{\sum_{n=1}^{i=n} (C_f^n)}{n}$ [30] amended by [31]. With n the number of elements analyzed. $i = i^{th}$ element (pollutant) and C_f the Contamination Factor	mDC < 1.5: zero with very low degree of contamination (I); 1.5 ≤ mDC <2: low degree of contamination (II); 2 ≤ mDC <4: moderate degree of contamination (III); 4 mDC < 8: high degree of contamination (IV); 8 ≤ mDC < 16: very high degree of contamination (V); 16 ≤ mDC <32: extremely high degree of contamination (VI); 32≤ mDC: ultra high degree of contamination (VII).
Potential Ecological Risk Factor (ER): single-element ecological risk	$E_r^i = T_r^i C_f^i$ [31]. The toxic response factor of the element i. T_r^i = 5 for Pb and Cu; 30 for Cd [32]	ER ≤ 40: low risk (I); 40 < ER ≤ 80: moderate risk (II); 80 < ER ≤ 160: considerable risk (III); 160 < ER ≤ 320: high risk (IV); 320 < ER: very high risk (V)
Risk index (RI): multi-element ecological risk	$RI = \sum_{i=1}^{12} = \sum_{i=1}^{12} T_r^i C_f^i$ [30]	RI ≤ 150: low risk (I); 150 < RI ≤ 300: moderate risk (II); 300 < IR ≤ 600: considerable risk (III); 600 < RI: high risk (IV).

5 RESULTS AND DISCUSSION

5.1 PHYSICO-CHEMICAL CHARACTERIZATION OF SEDIMENTS

From the sedimentological point of view, among the recognized sedimentary facies, are medium to coarse sands containing gravels in the Ahomey-Gblon sector (SAh-G, Fig.2). They contain 86.33 % of sand. The facies of Dékanmè (SDek), Ouédo-Gbadji (SOe-G) and Ouédo-Aguékon (SOe-A) sectors are made up of medium to fine sand with respectively 96.8 %, 96.28 % and 92.47 % of sand. In the mid to low-clay sands taken from Cotonou channel (SCot), Calavi pier (SCal) and Toché Channel (SToc). The sand proportions are respectively 90.2%, 82. 26% and 80.93 %. The fine clay sands are taken from Lake Nokoué (SNok) and Aguégué-Donoukpa (SAg-D) and contain respectively 79.53 % and 84.06 % of sand. The sediments of Ganvié (SGan) and Louho (SLou) sectors contain the lowest percentages of sand, which are 59.53 % and 53.46 %. For all of the twelve sites, the pH are slightly acidic and very little between 5 at Louho and 6.5 at the mouth of the Cotonou channel for an average of 5.50. CECs ranged from 65.25 meq/100g at Ouedo-Gbadji to 99.04 meq/100 g in Louho sediments with an average of 84.24 meq/100 g. The minimum of the OC (0.01%) was obtained in Ouédo-Gbadji (SOe-G) sediments and the maximum (3.33%) in the Ganvié sediments with an average of 0.84 %. The means of the Al_2O_3 and Fe_2O_3 contents are respectively 8.14 % and 3.9 %. The lowest Al_2O_3 content is measured in the Ouédo-Gbadji sediments (0.82 %) and the highest content (37 %) is obtained at Sô-Ava. Fe_2O_3 is also more concentrated at Sô-Ava (12.42 %) but its minimum content is determined at Ahomey-Glon (0.9 %). CaO shows a slight variation between 4.51 % (Ouédo Aguékon) and 7.81% (in Ganvié) for an average of 6.08 %, as shown in table-2, below;

Table 2. Physico-chemical parameters of sediments. CEC: Cation exchange capacity; OC: organic carbon; Fe_2O_3 : Iron oxide; Al_2O_3: Aluminum oxide; Aluminum oxide; CaO: Calcium oxide

Samples	pH	CEC	% OC	% Fe_2O_3	% Al_2O_3	% CaO
SNok	5.30	94.1	0.96	3.4	2.96	6.77
SToc	5.10	89.6	0.83	2.97	1.89	6.77
SLou	5.00	99	1.26	4.5	12.1	5.25
SAg-D	5.50	93.6	0.95	2.97	2.37	5.51
SDek	5.60	79.8	0.28	2.22	1.18	5.21
SOe-A	5.10	82.4	0.80	2.78	1.42	4.51
SOe-G	5.40	65.2	0.01	0.9	0.82	5.00
SAh-G	6.00	65.6	0.14	1.48	0.90	5.73
SGan	5.30	97.5	3.33	4.45	5.40	7.80
SSo-A	5.10	80.0	0.50	12.4	37.0	6.70
SCal	5.30	77.4	0.20	1.85	1.20	6.20
SCot	6.50	86.7	0.80	6.80	30.5	7.50

5.2 TOTAL METALLIC TRACE ELEMENTS (MTE) CONTENTS OF SEDIMENTS

Total content ranged from 11.078 ppm (SLou) to 149 ppm (SGan) for Cu; from 0.38 ppm (SOe-G) to 104.02 ppm (SCot) for Pb and from 0.001 ppm (SLou) to 4.604 ppm (SCot) for Cd. The average contents of the three metals are respectively 32.92 ppm; 23.63 ppm and 1.43 (Figure 3). The decreasing order of grades is: Cu > Pb > Cd. Considering the limit values for uncontaminated sediments from anthropogenic sources of 0.11 ppm according to the Directive 76-464 – EEC- 04/05/76 and 0.06-1.1 ppm according to the Agency for Toxic Substances and Disease Registry, it derives that the sediments SNok, SToc, Ag-D, SAh-G, SGan, SSo-A and SCot cross the standards and are therefore polluted in Cd. Regarding the Pb, limits values are exceeded in sediments SNok, SToc, SGan, SSo-A, SCal and SCot with reference to thresholds set at 19 ppm. Only SOe-A, SGan and SCot samples exceeded 33 ppm for Cu. From the spatial analysis of the above-mentioned contents, it appears that the polluted sites in Cd and Pb are distributed in the East-West and South sectors of Lake Nokoué. This distribution reflects the transit corridor for petroleum products from Nigeria, which is distributed to Sô-Ava, Calavi, Cotonou and Ganvié. Pollution at the outlet of the Cotonou Channel also highlights the contribution of solid waste from the Dantokpa market. Most of the Cu-polluted sediments have been collected in the vicinity of agglomerations or densely populated areas, including Ouédo-Aguékon, Ganvié and Cotonou. As a result, solid and liquid wastes generated by domestic activities and those from Dantokpa market would be the potential sources of Cu to these sites. In Lake Nokoué located downstream from the Ouémé delta, the average Cd content, estimated at 22.07 mg / kg by [12], is above the one determined for the present study area. Nevertheless, a slight increase is noted compared to the work of [13] which evaluated this content at 0.74 mg / kg. Superiority is also noted in relation to the Cu mean values of 28.27 mg / kg in Lake Nokoué [12], 26.42 mg / kg in Yangtze estuary (China) (Zhao *et al.*, 2012) and 28.7 mg / kg in Moulouya River (Morocco) [32]. As far as Pb is concerned, the present content is lower than the values determined for the latter two sites, which concentrated respectively 34.77 mg / kg and 2404.9 mg / kg. It is nevertheless higher than 6.88 mg / kg revealed by [12]. Details are shown in figure 3, below;

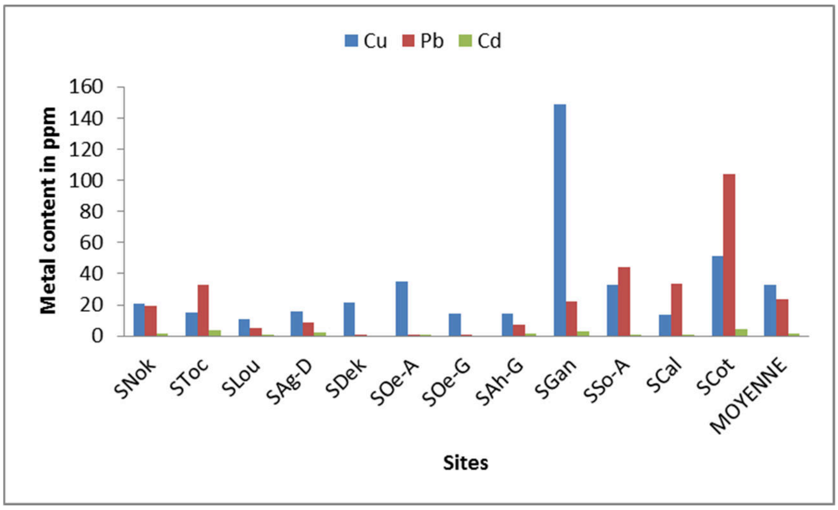

Fig. 3. Grades of metals analyzed in surface sediments

5.3 DETERMINATION OF THE GEOCHEMICAL BACKGROUND

For the determination of the geochemical background, the reference [1] on one hand considered the average of the concentrations in the deep layers of the cores and on the other hand the average contents in the earth's crust [33], [34]. In the two small cores positioned at points SSo-A and SAg-D, the Pb and Cd contents are below the detection limit of ICP-MS which is 10^{-5} ppm and that of Cu less than 10^{-4} ppm. Due to the context of our study environment, where occurred an important drainage process (which would justify these grades), we used elemental concentrations of earth's crust (Pb 20 ppm; Cu 25 ppm; Cd 0.098 ppm) [35].

5.4 RELATIONSHIP BETWEEN THE PHYSICO-CHEMICAL PARAMETERS AND THE TOTAL METAL CONTENT OF SEDIMENTS

To understand the physicochemical parameters and the different processes that would influence the distribution of metals in sediments, a correlation matrix has been established. A strong positive linear correlation (correlation coefficient $r > 0.75$, Table 3) is observed between the CEC, the fraction less than 63 µm of sediment and the OC. The first, established by the positive correlation between the percentages of the fraction less than 63 µm, the CEC and the OC percentage, is consistent with the results of the work carried out in the Ain Oussera region in the south of Algiers [19]. This bond is explained by the presence of humic substances capable of forming complexes with the clay minerals, which favors the increase of CEC and therefore the retention of metals in the sediments. CECs, OCs and fine percentages are high in sediments such as SLou, SGan SNok and SAg-D. This suggests a strong possibility for these sediments to create negative charges for metal retention [36]. The hydroxyl group that exists on the edges and outer layers of the clay minerals of these sediments can get rid of hydrogen which is replaced by other ions such as Ca^{2+}, Al^{3+}, Pb^{2+}, Cd^{2+} [22]. Of the three parameters, only the OC is strongly correlated with Cu ($r = 0.87$). The SOe-A, SGan and SCot sediments are more polluted with Cu and contain the highest levels of OC. Cu accumulated in these sediments is likely to form complexes with organic matter. The reference [33] have already confirmed that the complexation between organic matter and metals decreases from Cu^{2+} to Zn^{2+}. As for the major elements analyzed, only the percentages of Al_2O_3 and Fe_2O_3 indicate a strong correlation ($r = 0.93$). The positive bond established between Al_2O_3 and Fe_2O_3 shows a constant ratio between Fe/Al. According to [1], this ratio in the sediments of the former Touiref mining district (NW Tunisia) suggests a dominance of kaolinite and chlorite and reflects the processes of alteration and erosion that take place upstream.

Mean correlations are observed between Cu and CaO, between Pb, Al_2O_3 and CaO, and between Cd and CaO ($r < 0.72$). According to [37] in the Mahanadi estuarine basin (India), the similarity of the ionic radius of Cd (0.97Å) and Ca (0.99 Å) promotes the co-precipitation of Cd carbonates and its incorporation into the calcite network to form solid solutions of $Cd_{\alpha}Ca_{1-\alpha}CO_3$. Despite the possibility of such a post-accumulation process, the average relationship between CaO and these metals suggests that sediments have benefited from a seawater flow rich in Ca and releases from the vicinity of the Dantokpa market. PH isn't correlated with any of these parameters.

Table 3. Matrices of correlation between physicochemical parameters and the total contents of Cu, Pb and Cd

	pH	Fine	CEC	OC	Fe_2O_3	Al_2O_3	CaO	Cu	Pb	Cd
pH	1.00									
Fine	-0.35	1.00								
CEC	-0.29	**0.79**	1.00							
OC	-0.19	**0.77**	**0.75**	1.00						
Fe_2O_3	-0.04	0.12	0.24	0.17	1.00					
Al_2O_3	0.22	0.04	0.17	0.03	**0.93**	1.00				
CaO	0.25	0.22	0.38	0.53	0.46	0.44	1.00			
Cu	0.06	0.44	0.37	**0.87**	0.23	0.14	0.60	1.00		
Pb	0.55	-0.17	0.14	0.06	0.50	0.72	0.71	0.21	1.00	
Cd	0.50	0.06	0.33	0.33	0.22	0.30	0.72	0.34	0.69	1.00

5.5 EVALUATION OF CONTAMINATION AND ECOLOGICAL RISKS BY ELEMENT ANALYSIS IN SURFACE SEDIMENTS

The geo-accumulation indices are globally low to moderate for Pb and Cu. The Igeo of Cu vary between -1.76 at Louho and 1.99 at Ganvié. Those of Pb vary between -6.30 at Ouedo-Gbadji and 1.79 at Cotonou. Among sites with levels exceeding Cu standards, Cotonou is in the range of uncontaminated to moderately contaminated levels, while Ganvié site is moderately contaminated (Fig. 4). In the case of Pb, the contamination is moderate in Cotonou sediments, but covers the range of uncontaminated to moderately contaminated sites in Toché, Sô-Ava and Calavi sediments. The Cu contamination factors support Igeo. CF of Cu range from 0.44 at Louho and 5.96 at Ganvie. Those of the Pb vary between 0.02 at Ouedo-Gbadji and 5.20 at Cotonou. Compared to Igeo, which shows moderate contamination of sites contaminated with Cu and Pb, the CF shows a considerable level for the Cu accumulated in Ganvié and the Pb accumulated in Cotonou (Fig. 5). Although this range doesn't appear to be of great concern, the Ganvié site, where contamination is moderate (Igeo), allows domestic rejects to be associated. High Pb contamination suggests a contribution from municipal and wastewater [32]. Although this source is highly probable at the Cotonou site, the spatial distribution of polluted sites in Pb suggests a contribution from the old oil spills during transit along Lake Nokoué. However, minerals such as galena, cerusite and anglesite have been shown to probably be sources of high Pb concentration [38].

The Cd Igeos have more extreme values and oscillate between -7.20 in Louho and 4.97 in Cotonou. Cd-contaminated sites show a very critical range from moderately to highly contaminated (Sô-Ava) to highly to extremely contaminated (Toché and Cotonou) levels. CF of Cd oscillate between 0.01 at Louho and 46.98 at Cotonou. In the agricultural soils of Aswan (Egypt), the higher Cd CF were related to inputs of phosphate fertilizers, pesticides and manure [38]. Cd accumulation in the sediments of the Ouémé delta suggests a great contribution from the northern part of the country where agrochemicals are used extensively for cotton production. By way of illustration, a technical note from the Benin National Water Partnership "PNE" had already indicated that, at the end of the 2007-2008 season, in the 64.5 thousand tons of fertilizers and 1.2 million liters of pesticides used, more than 50 % of inputs wouldn't have been assimilated by plants. Furthermore, given the highly to extremely contaminated levels of Toché and Cotonou sediments, and because of the average relationship between Cd and CaO, it is very likely that these sites have benefited from a marine water transiting discharges from the Dantokpa market.

From an ecological point of view, the potential ecological risk factor indicates a low level of risk for Cu and Pb at all sites. The Cd, contrariwise, displays a very critical range ranging from high to very high in the polluted sites (Fig. 6). This state poses a threat to the aquatic organisms of Cotonou and Toché sites. Cd in the ionic state can easily integrate the trophic chain and then pass into the blood of living organisms. It can cause toxic effects through kidney failure and disruption of calcium metabolism in bone tissue. Cd is classified as a carcinogen because it contributes to bronchial cancers [39]. With regard to phytotoxicity, Cd can cause a decrease in nitrogen-fixing and production capacities as reported for *Brassica juncea* [40], [41]. However, [15] has indicated that only labile metal species are available and may be more toxic than complexed metals. Of this fact, the total metal concentration may be high while the amount of bioavailable metal is low In the case of Ouémé delta, the levels of risk involved will have to be confronted with the risks associated with the geochemical fractionation of the three metals in subsequent work.

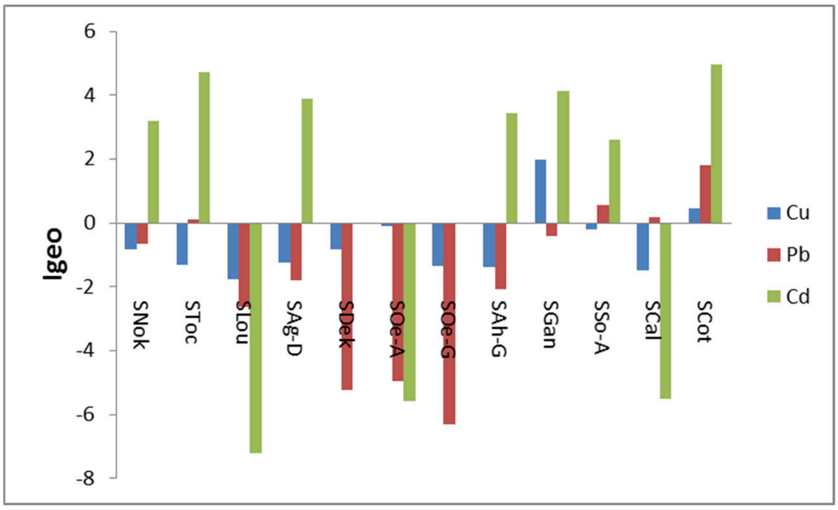

Fig. 4. Igeo in the superficial sediments of Ouémé

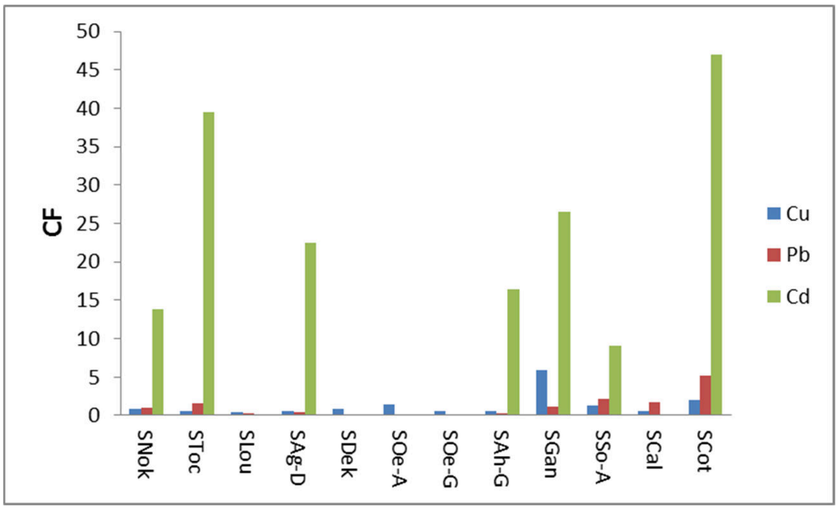

Fig. 5. CF in the superficial sediments of Ouémé

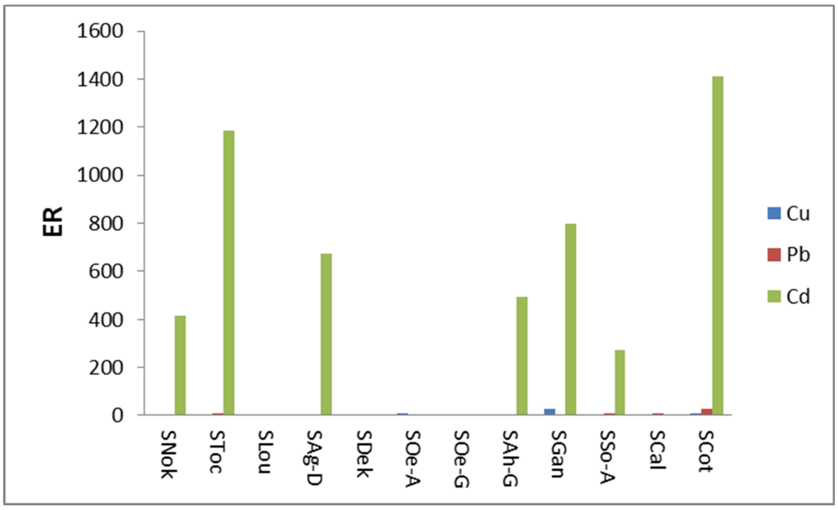

Fig. 6. ER in the superficial sediments of Ouémé

5.6 EVALUATION OF CONTAMINATION RISKS AND GLOBAL ECOLOGICAL RISKS BY SITE

The analysis of the results of the modified Degree of Contamination (mDC) and the Risk Index (RI) reveals three main groups according to levels of contamination and ecological risks. The first concerns the sites of Louho, Dekanmè, Ouédo-Aguékon, Ouédo-Gbadji and Calavi which are of zero to very low degree of contamination and therefore of a low ecological risk. The second group is represented by the Nokoué, Aguégué-Donoukpa, Ahomey-Gblon and Sô-Ava sites, which are characterized by a high degree of contamination and a considerable or even high ecological risk. The last group is the one of Toché, Ganvié and Cotonou, with a very high to extreme degree of contamination (case of Cotonou) and a high ecological risk. Cd-contaminated sites range from moderately to heavily contaminated to highly contaminated levels.

6 CONCLUSION

The present study made it possible to understand the influence of environmental parameters on the Pb, Cu and Cd fate of Ouémé delta superficial sediments and associated risk levels. Organic matter is revealed as a factor that can limit the availability of metals including Cu through the complexation process. Correlations between CaO and metals indicate a potential for metal dissolution if the environment becomes more and more acidic. The geoaccumulation indices provide information on the sediments analyzed that are not moderately contaminated with Cu and Pb, but reach extreme levels for Cd. The CF of Pb and Cu indicates a low to considerable level of contamination but these levels of contamination are strong for Cd. Potential ecological risk factors ER of Cu and Pb show low levels compared to Cd that reaches high to very high levels. Overall, the sediments of Louho, Dekanmè, Ouédo-Aguékon, Ouédo-Gbadji and Calavi sectors have a zero to very low level of contamination and therefore a low ecological risk. At Toché, Ganvié and Cotonou sectors, there is a very high degree of contamination and a high ecological risk. The high level highlights the direct or indirect contribution of the various anthropogenic activities without, however, obscuring the lithogenic sources which could generate very high concentrations. In any case, the toxicology of the contamination can raise major concerns only when the fraction of the bioavailable metal is important due the fact that only the latter is labile. Indeed, the evaluation of this bioavailable fraction will indicate whether, for high levels of contamination, biological resources are potentially exposed.

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REFERENCES

[1] M.A. Othmani, F. Souissi, E. Ferreira da Silva, A. Coynel, “Accumulation trends of metal contamination in sediments of the former Pb-Zn mining district of Touiref (NW Tunisia),” *Journal of African Earth Sciences*, vol. 111, pp. 231-243, 2015.

[2] T. Alharbi, A. El-Sorogy, “Assessment of metal contamination in coastal sediments of Al-Khobar,” *Journal of African Earth Science*s, vol. 129, pp.458-468, 2017.

[3] O. O. Olujimi, O. Oputu, O. Fatoki, O. E. Opatoyinbo, O. A. Aroyewun, J. Baruani, “Heavy Metals Speciation and Human Health Risk Assessment at an Illegal Gold Mining Site in Igun, Osun State, Nigeria,” *Journal of Health & Pollution,* Vol. 5, no.8, pp.19-32, 2015.

[4] H. K. Okoro, O. S. Fatoki, F. A. Adekola, B. J. Ximba, R. G Snyman, “A Review of Sequential Extraction Procedures for Heavy Metals Speciation in Soil and Sediments,” *Open Access Scientific Reports,* Vol. 1, no.3, pp.1-9 p, 2012.

[5] J. Wang, G. Liu, H. Liu, P. K.S. Lam, “Multivariate statistical evaluation of dissolved trace elements and a water quality assessment in the middle reaches of Huaihe River, Anhui, China,” *Science of the Total Environment,* Article in press*,* 2017.

[6] M. Zheng, L. Feng, J. He, M. Chen, J. Zhang, M. Zhang, J. Wang, “Delayed geochemical hazard: A tool for risk assessment of heavymetal polluted sites and case study,” *Journal of Hazardous Materials*, Vol. 287, pp. 197–206, 2015.

[7] J.B. Hounkpè, “ Environnement morpho-sédimentaire et géochimie des éléments en traces des eaux et des sédiments du lac Ahémé au Sud-Bénin,” Thèse de doctorat, Université d’Abomey-Calavi, 201p, 2017.

[8] S.A. Adechian, M.N. Baco, I. Akponikpe , I.I. Toko , J. Egah , K. Affoukou , “ Les pratiques paysannes de gestion des pesticides sur le maïs et le coton dans le bassin cotonnier du Bénin,” *VertigO*, vol. 15, no.2, pp. 1-15, 2015.

[9] INSAE, “Que retenir des effectifs de population en 2013,” Rapport du quatrième Recensement Général de la Population et de l’Habitation (RGPH4), 35p, 2015.

[10] D. Mama, “Méthodologie et résultats du diagnostic de l’eutrophisation du lac Nokoué (Bénin),” Thèse de doctorat de l’Université de Limoges, France, 177p, 2010.

[11] Organisation Internationale des Bois Tropicaux, " Cercle pour la Sauvegarde des Ressources Naturelles. Cartographie des forêts sacrées des sites Ramsar 1017 et 1018 du Bénin," Rapport, 81p, 2013.

[12] C. Kaki, P. Guedenon, N. Kelome, P. Edorh and R. Adechina, "Evaluation of heavy metals pollution of Nokoue lake," *African journal of Environmental Science and Technology*, Vol. 5, no.3, pp. 255–261, 2011.

[13] A.S. Hounkpatin, P. A Edorh, M. Sèzonlin, P. Guédénon, B. Elégbédé, G. Boni, V. Dougnon, S. Montcho, E. Kéké, M. Boko, "Pollution of aquatic ecosystems by heavy metals at Ganvié's lacustrine city (Benin) ," *International Research Journal of Biotechnology*, Vol. 3, no.6, pp. 81-87, 2012.

[14] A. Youssao, H. H. Soclo, C. Bonou, B. Fayomi, " Evaluation de la bioaccumulation du plomb dans les espèces animales marines et identification des sources de contamination métallique par une analyse multiélémentaire en métaux (Al, Cd, Cr, Cu, Pb) dans les eaux côtières du Bénin," *International Journal of Biological and Chemical Sciences*, Vol. 5, no.1, pp. 188-195, 2011.

[15] G. Daldoul, R. Souissi, F. Souissi, N. Jemmali, H.K. Chakroun," Assessment and mobility of heavy metals in carbonated soils contaminated by old mine tailings in North Tunisia,". *African Earth Sciences, a*ccepted manuscript, 2015. http://dx.doi.org/10.1016/j.jafrearsci.2015.06.004.

[16] S. Huo, J. Zhang, K.M. Yeager, B. Xi, Y. Qin, Z.HeZ, F. Wu," Mobility and sulfidization of heavy metals in sediments of a shallow eutrophic lake, Lake Taihu, China," Journal of environmental sciences, vol. 31, pp.1-11, 2015.

[17] C. Benoit, " Biogéochimie et enregistrement des composes organostanniques dans les sédiments du bassin d'Arcachon," Thèse de doctorat, Université Bordeaux I, 224p, 2005.

[18] C. Bonnet, "Développement de bioessais sur sédiments et applications à l'étude, en laboratoire, de la toxicité de sédiments dulçaquicoles contaminés," Thèse de l'Université de Metz, 2000.

[19] A. Bouzidi, A. Ararem, D. Imessaoudene, B. Yabrir, "Sequential extraction of Cs and Sr from Ain Oussera soils around Es-Salam research reactor facility," *Journal of environmental science*, Vol.36 , pp. 163-172, 2015.

[20] H. Li, A. Shi, X. Zhang, "Particle size distribution and characteristics of heavy metals in road-deposited sediments from Beijing Olympic Park," *Journal of Environmental Sciences*, Vol.32, pp.228-237, 2015.

[21] F. Wang, X. Lu, X.-Y. Li, "Selective removals of heavy metals (Pb^{2+}, Cu^{2+}, and Cd^{2+}) from wastewater by gelation with alginate for effective metal recovery," *Journal of Hazardous Materials*, pp. 1-28, 2016. http://dx.doi.org/10.1016/j.jhazmat.2016.01.021.

[22] N., Bolan, A. Kunhikrishnan, R. Thangarajan, J. Kumpiene, J. Park, T. Makino, M.B. Kirkham, K. Scheckel, "Remediation of heavy metal(loid)s contaminated soils – To mobilize or to immobilize," *Journal of Hazardous Materials,* vol. 266, pp. 141–166, 2014. http://dx.doi.org/10.1016/j.jhazmat.2013.12.018.

[23] C. Ding, W. Cheng, X. Wang, Z.-Y. Wu, Y. Sun , C. Chen , X. Wang, S.-H. Yu ," Competitive sorption of Pb(II), Cu(II) and Ni(II) on carbonaceous nanofibers: a spectroscopic and modeling approach," *Journal of Hazardous Materials*, pp.1-32, 2016. http://dx.doi.org/10.1016/j.jhazmat.2016.04.002

[24] IRB, "Etude de cartographie géologique et prospection minière de reconnaissance au Sud du 9ème parallèle," Rapport Istituto Recerche Breda. FED-OBEMINES, 80 p, 1987.

[25] A.B. Zannou, K.J.B. Vodounou ," Évolution des crues annuelles liées aux changements climatiques et adaptation des populations de la basse vallée de l'Ouémé ," Mélange Mac, ISBN 978-99919-867-2-2. Université d'Abomey-Calavi, pp. 233-244, 2011.

[26] F. Moniod ," Régime hydrologique de I'Ouémé (Dahomey) ," Cahier O.R.S.T.O.M., série Hydrologie, vol. 10, no. 2, pp. 1-13, 1973.

[27] L. Le Barbé, G. Ale, B. Millet, H. Texier, Y. Borel, R. Gualde, " Les ressources en eaux superficielles de la république du Bénin," Éditions de l'ORSTOM, Institut Français de Recherche Scientifique pour le Développement en Coopération, collection monographies hydrologiques, no. 11, Paris, 453 p, 1993.

[28] R.L. Folk, W.C. Ward, "Brazos River Bar: a student in the signifiance of grain size parameters*," Journal of Sedimentary Petrology,* no. 27, pp. 3-26, 1957.

[29] G. Muller, "Index of geoaccumulation in sediments of the Rhine River," *Geol* J., Vol.2, no.3, pp.108-118, 1969.

[30] L. Hakanson, "An ecological risk index for aquatic pollution control," A sedimentogical approach. *Water Research*, Vol.14, pp. 975-1001, 1980.

[31] G. M. S. Abrahim, R. J. Parker, " Assessment of heavy metal enrichment factors and the degree of contamination in marine sediments from Tamaki Estuary, Auckland, New Zealand," Environmental Monitoring and Assessment, Vol. 136, pp. 227-238, 2008.

[32] A. El Azhari, A. Rhoujjati, M.L. EL Hachimi, "Assessment of heavy metals and arsenic contamination in the sediments of the Moulouya River and the Hassan II Dam downstream of the abandoned mine Zeïda (High Moulouya, Morocco)," *Journal of African Earth Sciences,* 24p, 2016.

[33] S. Zhao, C. Feng, Y. Yang, J. Niu, Z. Shen, "Risk assessment of sedimentary metals in the Yangtze Estuary: New evidence of the relationships between two typical index methods," *Journal of Hazardous Materials,* Vol. 241– 242, pp. 164– 172, 2012.

[34] W.M. Badawy, E.H. Ghanim, O. G. Duliu, H. El Samman, M.V. Frontasyeva, "Major and trace element distribution in soil and sediments from the Egyptian central Nile Valley," *Journal of African Earth Sciences, a*ccepted manuscript*,* 2017.

[35] S.R. Taylor, S.M. McLennan, "The geochemical evolution of the continental crust," *Reviews of Geophysics,* no. 33, pp. 241–265, 1995.

[36] A. Dube, R. Zbytniewski, T. Kowalkowski, E. Cukrowska, B. Buszewski, "Adsorption and Migration of Heavy Metals in Soil," Polish Journal of Environmental Studies, vol. 10, no. 1, pp. 1-10, 2001.

[37] S. K. Sundaray, B.B. Nayak, S. Lin, B. Bhatta, "Geochemical speciation and risk assessment of heavy metals in the river estuarine sediments—A case study: Mahanadi basin, India," *Journal of Hazardous Materials,* Vol. 186, 2011.

[38] M.A.G. Darwish, H. Pollmann, "Trace elements assessment in agricultural and desert soils of Aswan area, south Egypt: Geochemical characteristics and environmental impacts," *Journal of African Earth Sciences*, Article in Press, 2015. http://dx.doi.org/10.1016/j.jafrearsci.2015.06.018.

[39] R.A.N. Lawani, " Impacts des activités agricoles sur la qualité des écosystèmes aquatiques du Haut-delta de l'Ouémé," Thèse de doctorat, Université d'Abomey-Calavi,246p, 2017.

[40] K.B. Balestrasse, S.M. Gallego, M.L. Tomara, "Cadmium-induced senescence in nodules of soybean (Glycine max L.) plants," Plant and soil, vol. 262, pp.373-381, 2004.

[41] L., Fatarna, A. Boutekrabt, Y. Arabi, A. Adda, Impact du cadmium, du zinc et du plomb sur la germination des graines d'*Atriplex halimus l.* (Amaranthaceae). Revue d'Ecologie (Terre et Vie), vol.72, no. 1, pp. 61-72, 2017.