

INFLUENCE OF PHYSICOCHEMICALS AND TEXTURES IN HEAVY METALS ACCUMULATION IN LAKE NOKOUE (BENIN)

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ABSTRACT

Toxic metals (cadmium, lead, copper and arsenic) assessment was carried out in water and sediments samples of Lake Nokoué. Except for water, a group of sediment samples was mineralized before the analysis with atomic absorption spectrophotometer. The second group of sediment samples was processed for texture analysis. The results revealed that for the physico-chemical characteristics, the pH ranged from 6.5 to 8.5 while identified textures were mud, sand, sandy mud and muddy sand. On the average, heavy metals concentration in water increased from 0.01 to 10.1 mg/L, while lead increases from 5.84 to 8.47 for arsenic. In water, copper showed low concentrations at all sites while cadmium was below the detectable limits. The mean sediments concentration ranges were Cd (0.56 to 22.07 mg/L), Pb (3.2 to 13.94 mg/L), Cu (11.51 to 54.39 mg/L) and As (ND to 436.81 mg/L). Besides, the pattern of trace elements accumulation in the textures revealed that sandy mud and sand sediments recorded high concentrations of arsenic with mud having high cadmium concentrations while sandy mud and muddy sand surfaces had high concentrations of copper. The result also shows no correlation between heavy metal and pH except for arsenic in Lake Nokoué (BENIN).

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KEYWORDS: Nokoue Lake, Pollution, Heavy Metal, Texture, Physicochemical Parameters

INTRODUCTION

Heavy metals are high pollutants due to their relative high toxicity and persistent nature in the environment. Knowledge on the changing concentrations and distribution of heavy metals and their compounds in various compartments of the environment is therefore priority for appropriate environmental management programmes and Sustainable Development all over the world (Don-Pedro et al., 2004). Thus, this work is essential to Sustainable Development. It should be noted that enrichment of heavy metal in the environment can result from both anthropogenic activities and natural processes (Nriagu, 1989; Veena et al., 1997). Hence, as long as human-induced heavy metals generation continues in industrial and domestic activities, sustainable measurements will therefore be needed to assess the effectiveness of set standards limit of such metals. Such assessment is also needful towards identification and quantification of degradable environmental state resulting from heavy metals discharge. Also, contaminating elements and compounds are transported by water with high concentration in water basins and alluvial sediments. This has resulted into growing concern in recent years of the need to estimate the concentration of anthropogenic trace metals from industries and domestic effluents in sediments (Sokolowska, 1996; Zerbe et al., 1998). As a result, sediments become “chemical archives” of heavy

metal accumulations, which can provide valuable information in resolving the source and sink of heavy metal pollution (Jha et al., 2003). Therefore, the levels of heavy metals input into the environment can easily be assessed by measuring their concentration in sediments.

Thus, research on heavy metals transportation modes and concentration with their associated environmental problems in sediments and soils have highly being carried out (Kitano and Fujiyoshi, 1980; Ndiokwere, 1984).

Many earlier studies revealed the distribution of various heavy metal-geochemical complexes (Belzunce-Segarra et al., 1997; Tsai et al., 1998). Unfortunately, the correlation between the sediment texture and the accumulation of heavy metals in sediments have seldom been explored on a quantitative basis, most especially in West Africa.

Lake Nokoue (Republic of Benin) is a good reference of location, where human pressures and natural values compete with each other and where the degree of metal contamination has not been subject to overall assessment. It is located north of Cotonou town, where the proliferation of urban settlements and slum has meant increased human pressure and domestic and industrial effluents generation, which eventually find their way into

the lake. Lake Nokoué receives a complex mixture of domestic and industrial waste and serves as the ultimate sink for the disposal domestic sewage for many years. This study assessed the heavy metal contamination of the Lake Nokoué water and sediment as well as estimated the degree of relationship between the pH, the sediment texture and the heavy metals accumulation in the lake.

MATERIALS AND METHOD

Sampling

Twenty-seven Water and twenty-seven sediment samples were carried out at nine stations in Lake Nokoué. For the sediment sampling, the top 20 cm of the bottom sediment samples were collected from each sampling station using the Eckman bottom sampler device (Topouoglu et al., 2002) and kept in polypropylene containers (20g) for metals analysis and in glass bottles (at least 150 g) for texture analysis. Water samples were collected at various stations at a depth of 25 cm below the water surface in glass bottles. At each site, three random sub-samples of water and sediments were collected whereas the sediments for texture analysis were mixed, to ensure that the sample was representative for this site. All the samples were kept cool on the study field. During their transportation to the laboratory, precautions (cold storage on ice, complete filling containers, use of plastic materials for storage, avoidance of undue agitation) were taken to minimize any kind of disturbances (Langezaal et al., 2003; Simpson et al., 2004). Sample containers, sampling devices, glass and plastic materials were carefully cleaned before use, by soaking in 10% nitric acid (USEPA, 2001). The different sites were located using the global positioning system (Garmin GPS 12 _ L). All the sampling sites can be classified into three categories: residential areas (Res), non residential areas (Nre) and the areas close to embouchures (Emb). The pH of the water was measured using Horiba multiparameter.

Heavy Metal Analysis

Sediment samples were oven-dried (5 to 7 g). Dry samples were ground into a homogenous mixture using a porcelain mortar and pestle and sieved through a 2 mm mesh screen to remove coarse materials because particles >2 mm may consist of shells, rocks, wood, and other detrital materials, and are usually not a source of bioavailable contaminants (Mudroch et al., 1997). Besides, large debris, shells and visible organisms were removed prior to grinding. For metal analysis, 2 g of dried and grounded sediment were weighed, and mineralized in 5 ml H₂O₂ (32%) for 24 h and then 5 ml HNO₃ (62%) for 30 min using Teflon container. The contents of the Teflon container were digested gently and slowly, by heating in a sand bath till the contents got to near dryness. They were then set aside for cooling. The digest was filtered into a 50 ml volumetric flask, specially made for using distilled water. Each digested sediment sample was analyzed for trace metals using a flame Atomic Absorption Spectrophotometer (Thermo Electron Corporation with Solaar correction). The digestion and analytical procedures were checked by E. Merck Darmstadt, Germany and BDH Chemical Limited with known concentration for heavy metals. The levels of trace

metals are expressed in mg/kg. Water samples were not subjected to further treatment. After filtration, they were added 2 drops of Nitric acid and then aspirated directly into the flame Atomic Absorption Spectrophotometer (Thermo Electron Corporation with Solaar correction) for metal determination (Obasohan, 2007). Values are expressed in mg/L. To confirm the coherence and accuracy of the results, sample analyses were performed at least three times with the same protocol. The measured value was compared with the international standards (WHO, 2003 and CBSQGs of MacDonald and Ingersoll, 2000).

Texture Analysis

Arenaceous index method was used to separate the sand, mud, and clay sized particles from collected sediment sample by sieving. Then particle size analysis was carried-out to ascertain the percentage distribution of sand, mud, and clay fractions in the sediment.

Statistical Analyses

Significant tests were carried out using the analysis of variance (ANOVA) of the statistical package for social sciences (SPSS Version 17) computer programme. Statistical analysis (ANOVA) was used in order to check if there are significant differences ($P < 0.05$) in the values of Cadmium, Lead and Copper. The difference is regarded as highly significant if P value is lower than 0.01, statistically significant if P value is lower than 0.05, and non significant if P value is higher than 0.05. The statistical relationship between pH and trace elements accumulation in sediment was determined by bivariate correlation using the Pearson coefficient in a two-tailed test, $p \leq 0.05$. The statistical difference between two mean concentrations of heavy metals was evaluated by students' tests at 95%.

To identify potential concern of toxic metals in Nokoue Lake sediments, the results were compared to sediment quality guidelines by MacDonald and Ingersoll (2000). These guidelines provide concentrations of metals that have no effect on the majority of sediment-dwelling organisms, designated as "threshold effect concentration" (TEC), and concentrations that indicate polluted sediment and are likely to affect organism health, designated as "probable effect concentration" (PEC). The midpoint effect concentration (MEC) is a concentration midway between the TEC and PEC concentrations.

RESULTS AND DISCUSSION

Heavy metal analysis results for water and sediment samples are presented in tables 2 and 3 and compared respectively with WHO safety limits and consensus based sediment quality guidelines. So was Heavy metals mean concentrations in sampled water were presented in (Table 2). The lowest lead mean concentration was recorded at site Res 1 with a value of 0.01 mg/L and the highest was 10.1 mg/L at site Res 3. Based on arsenic concentrations, site Emb 1 was the most contaminated and site Nre 2 was the least contaminated. The copper mean concentrations in water were low varying from 0.16 mg/L (site Res 3) to 0.29 mg/L (site Res 2). In all the sites, the mean cadmium

concentration was extremely low and below the detectable limit (0.01 mg/L).

Table 1 presents the sampling sites with their geographic coordinates and the pH values.

Codes	Stations	Coordonnées Géographiques	Températures (°C)	pH
Res 1	Awansouri	N 006°24'00" et E 002°28'48"	26	7,95
Res 2	Zogbo	N006°23'42" et E 002°22'55"	26,4	8,64
Res 3	Calavi sud	N006°25'48" et E 002°23'24"	26,2	8,26
Nre 1	Agonsagbo	N006°26'13,2" et E 002°32'27"	25	7,6
Nre 2	Ahlangamey	N006°25'48" et E 002°28'12"	26	6,86
Emb 1	Calavi nord	N006°27'00" et E 002°24'00"	25,7	7,97
Emb 2	Aguégué	N006°29'23" et E 002°27'02"	25	7,85
Nre 3	Drezou	N006°28'48" et E 002°28'48"	25	7,7
Res 4	Ganvié	N006°27'36" et E 002°25'48"	27,1	6,96

Table 2: Mean concentrations of heavy metals in water sample at the different sites. The different mean concentrations are in mg/L.

Means ± SD	Cd (mg/L)	Pb (mg/L)	Cu (mg/L)	As (mg/L)
Res 1	-	0.01 ± 0.01	0.23 ± 0.09	8.26 ± 2.78
Res 2	-	0.01 ± 0.01	0.29 ± 0.07	8.35 ± 0.44
Res 3	-	10.1 ± 0.00	0.16 ± 0.08	7.39 ± 0.91
Nre 1	-	0.08 ± 0.04	0.25 ± 0.01	8.03 ± 0.35
Nre 2	-	0.08 ± 0.10	0.20 ± 0.02	5.84 ± 2.03
Emb 1	-	0.05 ± 0.02	0.27 ± 0.20	8.47 ± 1.16
Emb 2	-	0.36 ± 0.60	0.20 ± 0.05	6.19 ± 0.59
Nre 3	-	0.04 ± 0.04	0.18 ± 0.03	6.94 ± 2.60
Res 4	-	0.05 ± 0.01	0.25 ± 0.14	6.40 ± 2.30

- : below the detectable limit which is 0.01 for cadmium, lead, copper and arsenic.

The one way ANOVA analysis revealed a significantly different ($P < 0.05$) at 5% in heavy metal concentration in water of the same column except for the following cases whose P values are higher than 0.05 at 5% level.

Res 1 ≈ Res 2; Nre1 ≈ Nre 2; Emb 1 ≈ Nre 3 ≈ Res 4 for lead. Nre 1 ≈ Res 4; Res ≈ Nre 2 ≈ Emb 2 ; Nre 2 ≈ Emb 2 for Copper. Res 1 ≈ Res 2 ≈ Emb 1 for arsenic.

Also, heavy metal concentrations in sediments of the same column are significantly different ($P < 0.05$) at 5% except Res 4 ≈ Emb 2 and Emb 1 ≈ Nre 3 for cadmium; Res 1 ≈ Res 4 and Nre 2 ≈ Emb 1 for lead; Emb 2 ≈ Nre 3 for copper and Nre 1 ≈ Res 4 for arsenic since the P values are higher than 0.05 at 5% level.

For these cases, as estimated using the atomic absorption spectrophotometer, the different heavy metals concentrations recorded in water of Lake Nokoué were compared to the WHO limit values set (Cd: 0.05 mg/L; Pb: 0.05 mg/L; Cu: 1 mg/L which is 0.05 mg/L, for drinking water. In all the sites the mean concentrations of arsenic were extremely higher (from 585 to 848 times) than the safety limits set by WHO ($p = 0.000$). For lead

the limits were exceeded for most sites and site Res 3 recorded the highest value which is thousand times higher than WHO limit. There was very little cadmium in the lake water and the concentration of copper in all the sites were extremely lower than the WHO safety limit value. According to WHO standards, the lake water was polluted by lead and arsenic and the aforementioned results could often be attributed to contamination of the drainage water by the domestic municipal waste. The anomalously high values of As in all the places could be attributed to pressure treated wood, pesticides used in the northern part of study area and lead-acid auto batteries discharged in the lake by local population. These toxic metals could act as a slow poison and adversely affects the ecology and thereby harming the flora, the fauna and the natural inhabitant.

Table 3: Mean concentrations of heavy metals in sediment samples at the different sites.

Means ± SD	Cd (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	As (mg/kg)
Res1	18.93 ± 1.71	3.2 ± 0.66	36.72 ± 7.33	365.05 ± 35.51
Res2	10.84 ± 9.77	6.56 ± 2.59	54.39 ± 6.46	297.19 ± 30.61
Res3	0.56 ± 0.67	5.86 ± 1.08	14.18 ± 3.18	-
Nre1	19.28 ± 2.20	11.66 ± 0.37	20.59 ± 3.83	13.25 ± 12.90
Nre2	22.07 ± 15.61	13.94 ± 8.73	30.80 ± 28.62	395.99 ± 37.98
Emb1	14.70 ± 5.52	13.02 ± 5.65	41.3 ± 18.30	329.82 ± 32.48
Emb2	11.11 ± 7.86	3.54 ± 2.00	23.42 ± 2.68	7.93 ± 5.48
Nre3	14.96 ± 7.19	3.98 ± 1.45	23.77 ± 40.66	436.81 ± 40.66
Res4	11.11 ± 7.86	3.25 ± 2.57	11.51 ± 2.68	13.00 ± 2.68

In terms of sediments, the different heavy metals mean concentrations recorded are expressed in mg/Kg and presented in Table 3. Maximum concentration of cadmium and lead occurred at site Nre 2 with minimum concentration at site Res 3 and Res 1. The highest concentration in copper and the lowest concentration in arsenic were recorded at the same site Res 2 whereas the lowest concentration of copper and the highest concentration of arsenic were respectively registered at sites Res 4 and Nre 3. The mean concentrations were compared to sediment quality guidelines (MacDonald and Ingersoll,2000) as shown in Table 4.

Table 4: Comparison of sediment heavy metal mean concentration recorded in Nokoué Lake with consensus based sediment quality guidelines CBSQGs of (MacDonald and Ingersoll, 2000)

	Cd (mg/kg)	Pb (mg/kg)	Cu (mg/kg)	As (mg/kg)
Sediments of Nokoué	6.37		28.52	256.56
TEC	0.99	36	32	9.8
MEC	3	83	91	21.4
PEC	5	130	150	33

Sites Res 1, Nre 1 and Nre 2 had the most cadmium concentrations exceeding PEC. Arsenic levels in sites Res

1, Res 2, Nre 2, Emb 1 and Nre 3 were in order of magnitude, nine to thirteen times higher than the acute value (PEC). Site Res 3 had no arsenic concentration exceeding TEC. Lead did not exceed TEC in any of the sediments. No concentration of copper exceeded PEC in any of the sediments but Sites Res 1, Res 2 and Emb 1 did have concentrations in copper exceeding TEC. Most sites had sediment concentrations of Cd, and As above the PEC. Therefore, based on their heavy metal content, sediments should have been toxic. The presence of these metals in the aquatic ecosystem had far-reaching implications directly to the biota and indirectly to man. Toxic effects on benthic organisms resulting from trace metals pollution may alter community structure and in turn affect the aquatic ecosystem as a whole (Mendil and Uluözlü, 2007). The presence of high metals levels may originate from diffuse anthropogenic inputs from agriculture wastes. Cu is used in construction materials and Pb was formerly used in paints, pigments and glass (Donze et al., 1990). One of the major sources of arsenic is pesticides and herbicides (Donze et al., 1990). The areas with high arsenic level can be related to currents and a high sediment deposition rate in the area according to Neves (1985). Cd is present as an impurity in several products, including phosphate fertilizers and detergents (Greaney, 2005). It is necessary to notice that many factors are involved in the accumulation of toxic metals among which are temperature, pH, and sediment texture and hydro geological conditions. The correlation between heavy metal concentrations and pH using the Pearson coefficient was low, for all the metals ($r \approx 0$) except for arsenic whose Pearson coefficient was negatively strong ($r \approx -0.7$); this implies that the decrease of pH triggers the increase of arsenic concentrations in sediments. According to Filipek and Owen (1979) and Basaham and Al-Lihaibi (1993), texture of sediment could be the most important parameter that influences metal concentration. Then sediment samples were sorted into four textural classes: sand, mud, sandy mud and muddy sand (Figure 1)

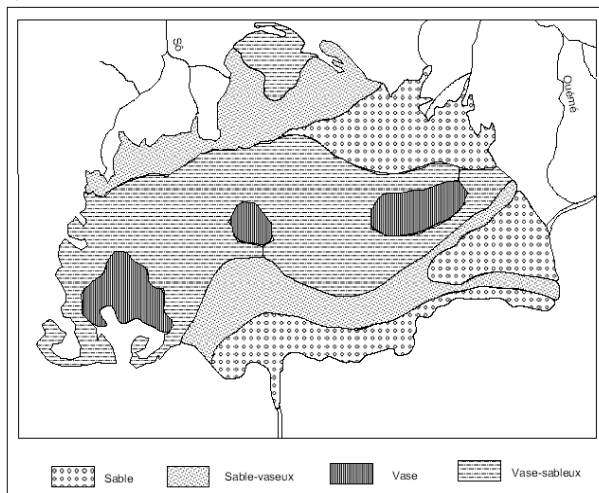


Figure 1: Study area with lithofacies repartition and the sampling sites.

Source: On-site study

Figure 2 shows the repartition of different textures in Nokoue Lake and the concentration of heavy metals in different textures of sediments was assessed.

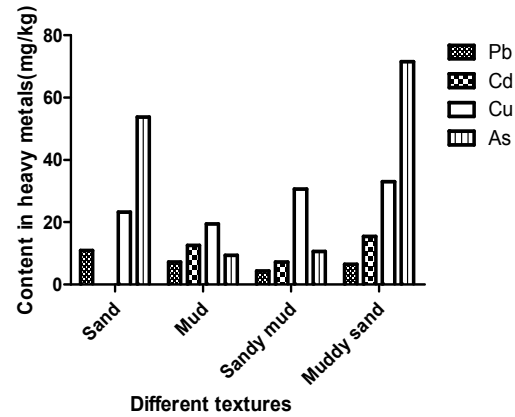


Figure 2: Heavy metals concentrations recorded in different textures.

Source: On-site study

In respect of texture, Sandy mud and sand had higher concentrations of arsenic (roughly 32 times) than mud and muddy sand. Contrary to Arsenic, higher concentration of cadmium was recorded in mud and sand registered the lowest concentration. But the highest concentration of cadmium was obtained in sandy mud sediment. Sandy mud and muddy sand (combination of sand and mud) registered higher concentrations of copper than sandy and muddy sediments. Though the concentrations of heavy metals recorded in different textures sediment were highly significant different for all the heavy metals in concern, it is difficult to predict the pattern of accumulation of trace elements according to sediment textures in our study. The highest concentration of lead was recorded in sand whereas the lowest in muddy sand sediment. Our research showed that the granulometric partitioning affirmed the role of particle size in enriching the trace metals. Lead and arsenic tended to accumulate more in sand sediment whereas copper accumulated higher in sediments made with mud and sand association. Cadmium did not accumulate at all in sand and tended to accumulate in mud-dominant sediments. Only the case of cadmium shows similarity with the findings of Filipek and Owen (1979), Tessier et al. (1985) and Basaham and Lihaibi (1993), who reported that heavy metals were largely associated with the clay fraction. In fact, the clay/silt fraction has a high surface area and because of its surface chemistry is more likely to adsorb organic and heavy metal contaminants. All the results could be attributed to anthropogenic sources. Actually in the last few decades, Cotonou witnessed a tremendous growth both in industrial and human developments. Most industries (cement, textiles, beer) and settlements are established around Cotonou harbour so that the effluents there from are discharged directly or indirectly into the harbour. Besides, the daily smog from the combustion of fossil fuel due to the great proliferation of cars and motorcycles blur the skyline of the central business area of Benin's commercial capital. All that,

trigger the alarming level of heavy metals in accumulating sediments of Nokoué Lake. As a result, the water largely exploited by local population for drinking and domestic use could engender public health problems. In fact, chronic hepatitis and hepatic cirrhosis have been related to arsenic intoxication (Reynold, 1901). Lead and cadmium are known as deadly and cumulative poisons even when consumed in small quantities and are capable of deadening nerve receptors in man (Bodansky and Latner, 1987). Copper in excess could induce hemolytic anemia and kidney damage (WHO). To tackle heavy metals pollution in Nokoué Lake that is causing negative impact on community health, more deterring waste management and control measures should be adopted to reduce the amount of pollutants discharged into the Lake by industry and domestic activities.

CONCLUSION

This study allowed measuring the level of pollution of Nokoué Lake with cadmium, lead, copper and arsenic. Either in water or in sediment, concentrations of some metals are high and sometimes exceed the standards. Preferential accumulation of metals in different textures (sand, clay, etc.) was also noticed. This pollution registered in the Nokoué Lake is connected to the domestic, agricultural and industrial activities and could affect the lake's fishery resources. Particular attention must then be put on the monitoring of water quality and fishery resources of the lake in order to safeguard the health of surrounding populations.

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REFERENCES

ASTM (1990). Guide for collection, storage, characterization and manipulation of sediments for toxicological testing. American Society for testing materials pH USAC 1-971.

Basaham AS, Al-Lihaibi SS (1993). Trace elements in sediments of the western Gulf. *Mar. Pollut. Bull.*, 27: 103- 107.

Belzunce-Segarra MJ, Bacon JR, Prego R, Wilson MJ (1997). Chemical forms of heavy metals in surface sediments of the San Simon inlet, Ria de Vigo, Galicia. Part A: Environmental Science and Engineering and Toxic and Hazardous Substance Control. *J. Environ. Sci. Health*, 32: 1271–1292.

Bodansky O, Latner AL (1987). *Advances in Clinical Chemistry*. Acad. Press. New York. 20 : 288.

Don-Pedro KN, Oyewo E O, Otitolaju AA (2004). Trend of heavy metal concentrations in Lagos lagoon ecosystem, Nigeria. *West Afr. J. Appl. Ecol.*, Vol 5.

Donze M, Nieuwendijk C, Boxtel A, Quaak M (1990). *Shaping the Environment: Aquatic Pollution and Dredging in the European Community*. Delwel Publishers, Hague, Netherlands. 184 p.

Filipek LH, Owen RM (1979). Geochemical associations and grain-size partitioning of heavy metals in lacustrine sediments. *Chem. Geol.* 26:105- 107.

Greaney KM (2005). An assessment of Heavy Metals Contamination in the Marine Sediments of Las Perlas Archipelago, Gulf of Panama. M.Sc. thesis, Heriot-Watt University, Edinburgh, 114p.

Houadégla WA (1991). Rythmes Climatique et Productions halieutiques au Bénin : cas du lac Nokoué, Mémoire de maîtrise, UNB : 196p, Annexes.

Jha SK, Chavan SB, Pandit GG, Sadasivan S (2003). Geochronology of Pb and Hg Pollution in a coastal marine environment using global fallout. *J. Environ. Radioact.* 69 :145–157.

Kitano Y, Fujiyoshi R (1980). Selective chemical leaching of cadmium, copper, manganese and iron in marine sediment. *Geochim. J.* 14:113-122.

Langezaal AM, Emst SR, Haese RR, Van Bergen PF, Van der Zwaan GT (2003). Disturbance of intertidal sediments: the response of bacteria and foraminifera. *Estuar. Coastal Shelf Sci.* 58: 249-264.

MacDonald DD, Ingersoll CG (2000). Development and evaluation of consensus based sediment quality guidelines for freshwater ecosystems. *Arch. Environ. Contam. Toxicol.*

Mendil D, Uluözlü OD (2007). Determination of trace metal levels in sediment and five fish species from lakes in Tokat, Turkey. *Food Chem.*, 101: 739-745.

Mudroch A, Azcue J M, Mudroch P (1997). *Manual of physicochemical analysis of aquatic sediments*. CRC press Boca Raton, FL, USA.

Ndiokwere CL (1984). A study of heavy metal pollution from motor vehicle emission and its effect on roadside vegetation and crop in Nigeria. *Environ. Pollut.*, 7: 35-42.

Neves RJJ (1985). Biodimensional model for residual circulation in coastal zones: application to the Sado Estuary. *Ann. Geophys.*, 3: 465–472

Nriagu JO (1989). A global assessment of the natural sources of atmosphere traces metals. *Nature* 338: 47–49

Obasohan E E (2007). Heavy metals concentrations in the offal, gill, muscle and liver of a freshwater mudfish (*Parachanna obscura*) from Ogba River, Benin city, Nigeria. *Afr. J. Biotechnol.*, 22. 6: 2620-2627.

Oyede LM (1991). Present sedimentary dynamic and signals recorded in the quaternary and neogene sequences in margino-littoral area of Benin. University of Bourgogne- National university of Bénin (Doctoral Thesis in Geol. Matine), p. 302.

Reynold ES (1901). In account of epidemic outbreak of arsenical poisons occurring in Beer drinkers in north of England and the Midland Countries in 1900. *Lancet*, 1: 166-170.

Simpson SL, Angel BM, Jolley DF (2004). Metal equilibration in laboratory-contaminated (spiked) sediments used for the development whole-sediment toxicity tests. *Chemosphere*, 54: 597- 609.

Tessier A, Rapin F, Carignan R (1985). Trace metals in oxic lake sediments: possible adsorption onto iron oxyhydroxides. *Geochim. Cosmochim. Acta*, 47: 1091–1098.

Tsai LJ, Yu KC, Chang JS, Ho ST (1998). Fractionation of heavy metals in sediment cores from the Ell-Ren river, Taiwan. *Water. Sci. Tech.*, 37(6–7): 217–224.

Topouoglu SC, Kirbasoglu O, Gungor A (2002). Heavy metals in organisms and sediments from Turkish coast of the black sea 1997- 1998. pp. 521- 525.

USEPA (2001). Methods for collection, storage and manipulation of sediments for chemical and toxicological analyses, U. S. Environmental protection Agency Technical Manual EPA- 823- B-01-002, office of water, Washington, DC, USA.

Veena B, Radhakrishnan CK, Chacko J (1997). Heavy metal induced biochemical effects in an estuarine teleost. *Indian J. Mar. Sci.*, 26: 74–78.

WHO / FAO (2003). Joint FAO/WHO expert committee on food additives. Sixty-first meeting. Summary and conclusions.

Zerbe J, Sobczynski T, Elbanowska H, Siepak J (1998). Speciation of Heavy Metals in Bottom Sediments of Lakes. *Polish, J. Environ.Stud.*, 20–25.