

Full Length Research Paper

Evaluation of heavy metals pollution of Nokoue Lake

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Toxic metals (cadmium, lead, copper and arsenic) assessment was carried out in water and sediments samples of Nokoue Lake. 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 is from 6.5 to 8.5. Four kinds of textures were identified: mud, sand, sandy mud and muddy sand. Heavy metals mean concentrations in water rose from 0.01 to 10.1 mg/L for lead and 5.84 to 8.47 for arsenic. In water, copper showed low concentrations in all sites and the values of cadmium were below the detectable limits. The mean concentrations in the sediments 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 according to textures revealed that sandy mud and sand sediments recorded high concentrations of arsenic, mud registered high concentrations of cadmium and the sediment combining sand and mud registered high concentrations of copper. Besides, the correlation between heavy metal concentrations and pH except for arsenic.

Key words: Nokoue Lake, pollution, heavy metal, texture.

INTRODUCTION

Heavy metals are high pollutants because of their relative high toxicity and persistent nature in the environment. Therefore, knowledge of the changing concentrations and distribution of heavy metals and their compounds in various compartments of the environment is a priority for good environmental management programmes all over the world (Don-Pedro et al, 2004).

The enrichment of heavy metal in the environment can result from both anthropogenic activities and natural processes (Forstner and Wittmann, 1979; Nriagu, 1989; Veena et al., 1997). As long as human-induced generation of heavy metals continues in industrial and domestic activities, sustained measurements will be needed to assess the effectiveness of set limitation standards and facilitate the identification and quantification of the state of environmental degradation attributable to the discharged heavy metals. Contaminating elements and compounds are transported by water and gather in bottom and alluvial sediments. Thus there has been growing concern in recent years that certain anthropogenic trace metals released by industries and domestic effluents are incorporated into accumulating sediments. (Sokolowska, 1996; Zerbe et al., 1998). Their modes of transportation and levels in sediments and soils have been the topic of many researchers in connection with environmental problems arising from

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Abbreviations: ATSM, American society for testing materials; CBSQGs, consensus based sediment quality guidelines; MEC, midpoint effect concentration; EPA, environment protection agency; PEC, probable effect concentration; SPSS, social package for statistic software; TEC, threshold effect concentration.

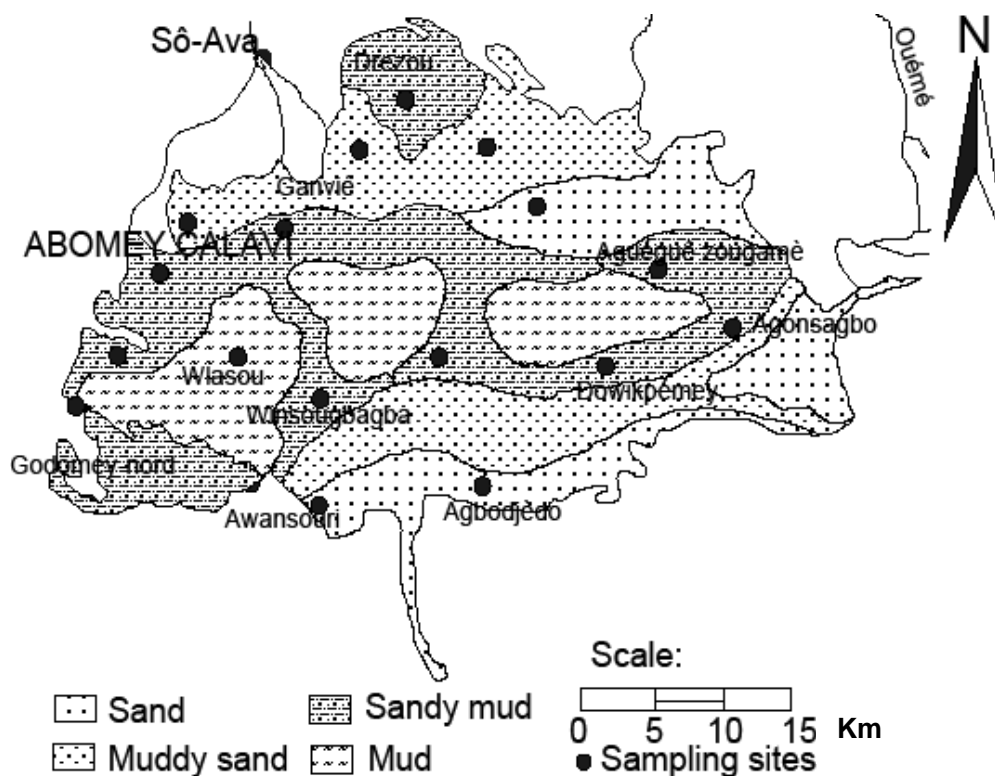


Figure 1. Study area with lithofacies repartition and the sampling sites.

contaminated materials (Kitano and Fujiyoshi, 1980; Ndiokwere, 1984). The elevation of metal levels often results in a high concentration in the bottom sediment. 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 (Cundy et al., 2003; Jha et al., 2003). Therefore the levels of input of the metals into the environment can be assessed by measuring the concentration in sediments above the natural background level.

Many studies revealed earlier the distribution of various heavy metal-geochemical complexes (Hickey and Kittrick, 1984; Forstner, 1989; 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 and moreover in West Africa.

Nokoue Lake in Benin is a good reference of a site 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 in the north of the town of Cotonou, where the proliferation of urban settlements and slum has meant increased human pressure and the generation of domestic and industrial effluents, which eventually find their way into the lake. The Nokoue Lake receives a complex mixture of domestic and industrial waste and has served as the ultimate sink for the disposal domestic

sewage for many years.

This study aims at assessing the heavy metal contamination of the Nokoue Lake water and sediment and on the other hand evaluating the correlation between the pH, the sediment texture and the heavy metals accumulation.

MATERIALS AND METHODS

The Nokoue Lake, a very variable surface according to the seasons, has an average depth of 3 m. The hydrodynamics of the Nokoue Lake shows three forms of contribution of waters: marine waters, meteorologically waters and continental waters (Houadéglá, 1991). In terms of sedimentology, the lake is characterized by four facies (Figure 1): sand, sandy clay, clayey-sand and mud (Oyede, 1991). That sedimentation is expressed by sand deposits at the outlet of Oueme River in the oriental and meridional area. The muddy sand deposited at the outlet of river Sô is the manifestation of the relative weakness of that river. The muddy sand and mud deposited in the central area evoke the decrease in the water current towards the central area.

Sampling

Two kinds of samples are used in the case of this study: sediment and water. 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; ATSM, 1990) 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

Table 1. Sampling sites with geographic coordinates and pH values.

Codification	Sites	Geographic coordinates	pH
Res 1	Awansouri	N 006°24'00" et E 002°28'48"	7.95
Res 2	Zogbo	N006°23'42" et E 002°22'55"	8.64
Res 3	Calavi south	N006°25'48" et E 002°23'24"	8.26
Nre 1	Agonsagbo	N006°26'13,2" et E 002°32'27"	7.6
Nre 2	Ahlangamey	N006°25'48" et E 002°28'12"	6.86
Emb 1	Calavi north	N006°27'00" et E 002°24'00"	7.97
Emb 2	Aguégué	N006°29'23" et E 002°27'02"	7.85
Nre 3	Drezou	N006°28'48" et E 002°28'48"	7.7
Res 4	Ganvié	N006°27'36" et E 002°25'48"	6.96

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 (Thomson et al., 1980; Bull and Williams, 2002; Langezaal et al., 2003; Simpson et al., 2004). Sample containers, sampling devices, glass and plastic material 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 by submersing the sensor in the water at the depth of 10 cm from the water surface. All parameters were displayed on the screen of the apparatus.

Heavy metal analysis

Sediment samples were oven-dried (5 to 7 g). Dry samples were to 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. Merch 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.

Texture analysis

The arenaceous index method used is to separate out the sand, mud, and clay sized particles from a sample by sieving it. Then particle size analysis of a sediment sample is reported as percent of sand, mud, and clay fractions.

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 show 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, $p \leq 0.05$.

RESULTS AND DISCUSSION

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

Heavy metal analysis results for water and sediment samples are presented and compared respectively with WHO norms and consensus based sediment quality guidelines. The statistical difference between two mean concentrations of heavy metals was evaluated by students' tests at 95%. So was the difference between our results and the international norms (WHO, 2003 and CBSQGs of MacDonald and Ingersoll, 2000). The different heavy metals mean concentrations in water were presented in (Table 2). The lowest lead mean concentration recorded was 0.01 mg/L at the site Res 1 and the highest lead mean concentration recorded was 10.1 mg/L at the 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 are low and varied from 0.16 mg/L (site Res 3) to 0.29 mg/L (site Res 2). In all the sites of the area, the mean concentrations of cadmium were extremely low and below the detectable limit (0.01 mg/L)

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

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

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

According to one way ANOVA the comparison of the different concentrations in water in the same column are significantly different ($P < 0.05$) at 5% except for the following cases whose P values are higher than 0.05 at 5% level.

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

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

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

According to one way ANOVA the comparison of the different concentrations in sediments in the same column are significantly different ($P < 0.05$) at 5% except Res 4 \approx Emb 2 and Emb 1 \approx Nre 3 for cadmium; Res 1 \approx Res 4 and Nre 2 \approx Emb 1 for lead; Emb 2 \approx Nre 3 for copper and Nre 1 \approx Res 4 for arsenic. For these cases, P values are higher than 0.05 at 5% level.

of the atomic absorption spectrophotometer.

The different heavy metals concentrations recorded in water of Nokoue Lake were compared to the limit values set by WHO (Cd: 0.05 mg/L; Pb: 0.05 mg/L; Cu: 1 mg/L; As: 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 the sites and the site Res 3 recorded the most elevated value thousand times higher than WHO norm. 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 norms, the lake water was polluted by lead and arsenic. All the aforementioned recorded 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 north 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.

In terms of sediments, the different heavy metals mean concentrations recorded are gathered in (Table 3). They were expressed in mg/Kg.

Maximum concentration of cadmium and lead usually occurred at site Nre 2 and minimum respectively 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.

To identify potential concern of toxic metals in the Nokoue Lake sediments, the results were compared to sediment quality guidelines established by the MacDonald and Ingersoll (2000) in Table 4.

These guidelines provide concentrations of metals that

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	Pb	Cu	As
Nokoué sediments	6.37		28.52	256.56
TEC	0.99	36	32	9.8
MEC	3	83	91	21.4
PEC	5	130	150	33

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.

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, sediment texture and hydro geological conditions.

The correlation of heavy metal concentrations with pH gave low values for Pearson coefficient for all the metals ($r \approx 0$) except for arsenic whose Pearson coefficient was negatively strong ($r \approx -0.7$); that 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. The (Figure 2) shows the repartition of different textures in Nokoué Lake and the concentration of heavy metals in different textures of sediments was assessed.

Sandy mud and sand register very higher concentrations of arsenic (roughly 32 times) than in 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 is 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 are high significant different for all the heavy metals studied, 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 imputed 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

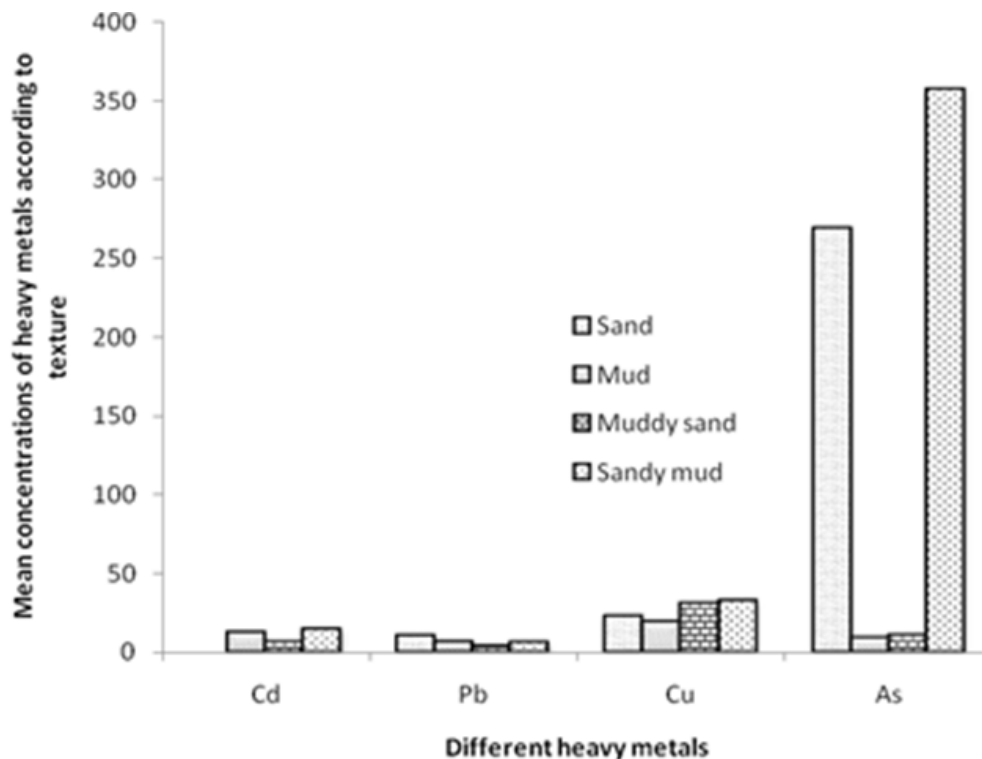


Figure 2. Heavy metals concentrations recorded in different textures.

the central business area of Benin's commercial capital. All that, trigger the alarming level of heavy metals in accumulating sediments of Nokoue 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 Nokoue 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 Nokoue 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 Nokoue 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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