

## Arsenic, Cadmium, Copper and Lead Accumulation in Water, Sediments and Fish Species of Oueme River in Bonou

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**Abstract:** In order to evaluate the level of contamination of Oueme river with heavy metals and raise awareness of the local population regarding heavy metals pollution and its risks for health, assessment of toxic metals (cadmium, lead, copper and arsenic) was carried out in water, sediments and fish species samples of Oueme River in Bonou municipality located in the south of Benin. The study was carried out in 2011. Except for water, sediments and fish samples were mineralized before the analysis with atomic absorption spectrophotometer. Mean concentrations of heavy metals in water rose from ND to 1.0 mg/L in the case of lead and 4.41 to 10.23 mg/L for arsenic. In water, copper showed low concentrations in all locations and most of the values of cadmium were below the detectable limits. The mean concentrations in the sediments were: Cd (0.01 to 22.07 mg/Kg); Pb (2.73 to 20.12 mg/Kg); Cu (7.84 to 58.96 mg/Kg) and As (0.01 to 870.03 mg/Kg). In fish, the concentrations were expressed in mg/Kg. *Clarias gariepinus* is the most polluted species with high levels in Cd, Pb, Cu and As (2.31±1.44; 2.09±1.29; 15.10±6.34; 13.90±7.88), respectively. The mean concentrations of heavy metals recorded in *Parachanna obstura* are 1.34±0.65; 1.17±0.79; 2.72±2.19; 4.11±3.56, respectively for Cd, Pb, Cu and As, respectively. In *Tilapia guineensis* were recorded Cd: 1.53±0.97; Pb: 1.56±1.27; Cu: 0.91±0.58 and As: 7.56±2.41. The implication of this finding is that the consumption of water and fishes of Oueme River by man could lead to health hazards induced by heavy metals.

**Key words:** Fish species, heavy metals, Oueme River, sediments, water

### INTRODUCTION

A great variety of pollutants affect the majority of water course which receive domestic, industrial and agricultural effluents. Among the different contaminants, 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 contamination of freshwater with heavy metals such as cadmium, lead, arsenic and copper has become a matter of great concern over the past decades not only

because of their threat to public water supplies but also because of the damage caused to aquatic life, especially to fishes. Once they come into the aquatic environment, the heavy metals scatter among the various compounds (water, solids in suspension, sediments and biota).

It is necessary to impute these environmental problems to the fast population growth coupled with the rapid and great urbanization, the expansion of the industrial activities and the intensive exploitation of resources.

But this demographic and industrial bang did not spare Benin rivers and particularly Oueme River, the main in Benin.

In fact, the results of the investigation carried out by (Pazou and Boko, 2006; Guedenon, 2009) proved that

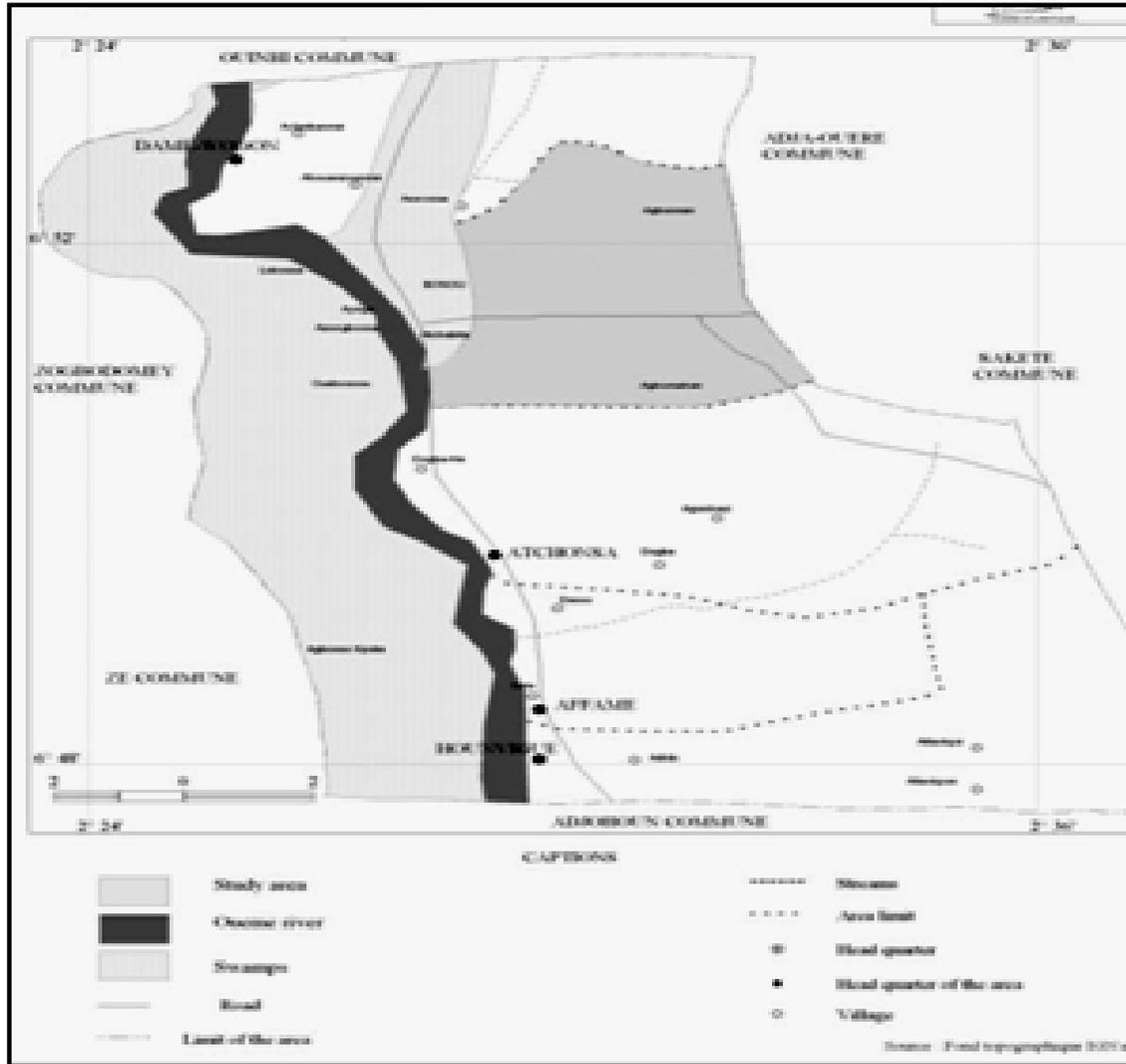


Fig. 1: Presentation of Oueme River and Bonou

Oueme River is polluted with chemicals such as pesticides and heavy metals. These pollutants that enter the river come from natural and anthropogenic sources. Their presence can be the result of either their direct immersion or an indirect process as in the case of the dry and humid dumps and of agricultural streaming (Conacher *et al.*, 1993).

As long as human-induced generation of heavy metals continues increasing 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 (Kaki *et al.*, 2011).

Thus our present investigation aims at renewing the assessment of heavy metal contamination in water, sediments and fish species in Oueme River in Bonou.

## MATERIALS AND METHODS

**Sampling area:** Figure 1 depicts the study area. From a hydrological point of view, Bonou is crossed from north to south by the Oueme River over a distance of about 40 km length. The main tributaries of Oueme River are: Gba, Djougoudou, Zou, Gnanhoui, and Wovi.

As every humid area, there is a high population concentration in Bonou, because of the advantages it abounds in. Thus it is more exposed to the destructive action of man. Very rich in natural resources, it is the centre of intense production activities. It offers local populations huge economical advantages in several fields out of which the most known are fishing, agriculture and water supply.

**Sampling:** Three kinds of samples were collected in July 2011 for this study: fish species, sediment and water in Oueme river in Bonou municipality. The top 20 cm of the bottom sediment samples were randomly collected to cover the sampling area using the Eckman bottom sampler device (Topouoglu *et al.*, 2002; ASTM, 1990) and kept in polypropylene containers (20 g) for metals analysis. Water samples were collected at various stations at a depth of 25 cm below the water surface in polypropylene bottles. As for the fish, fifteen samples of three most consumed species (*Clarias gariepinus*, *Tilapia guineensis* and *Parachanna obscura*) were purchased from fishermen and kept in polypropylene containers. 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).

**Heavy metal analysis:** Sediment samples and fish species 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. In terms of sediments, coarse materials were removed 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 or fish were weighed, and mineralized in 5 ml H<sub>2</sub>O<sub>2</sub> (32%) for 24 h and then in 5 mL HNO<sub>3</sub> (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 or fish sample was analyzed for trace elements 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 through Whatman filter papers 2 drops of Nitric acid were added and then aspirated directly into the flame Atomic Absorption Spectrophotometer (Thermo Electron Corporation with Solaar correction) for trace elements determination

Table 1: Concentrations of heavy metals in the water of Oueme River

Water	Cd	Pb	Cu	As
	ND	0.06	0.35	8.03
	ND	0.05	0.15	4.78
	ND	0.02	0.3	6.05
	ND	0.01	0.21	9.60
	0.2	0.07	0.18	6.81
	0.5	0.01	0.03	8.3
	ND	0.02	0.14	4.41
	ND	0.01	0.14	6.86
	0.1	0.01	0.03	8.03
	ND	1.06	0.24	5.75
	ND	0.05	0.23	5.97
	ND	ND	0.13	9.30
	ND	0.003	0.41	7.65
	ND	0.03	0.16	7.40
	ND	0.15	0.22	4.41
	ND	0.05	0.19	7.28
	0.3	0.10	0.18	7.45
	ND	0.11	0.26	8.28
	ND	0.10	0.24	7.78
	ND	0.10	0.11	8.04
	ND	0.03	0.16	8.45
	ND	0.08	0.25	8.02
	0.05	0.02	0.22	6.75
	ND	0.07	0.20	5.80
	ND	0.01	0.24	8.67
	ND	0.01	0.34	8.04
	ND	0.025	0.27	8.47
	ND	ND	0.16	10.23
	ND	0.10	0.30	6.29
	ND	0.03	0.25	8.02
Minimum	ND	ND	0.03	4.41
Maximum	0.5	1.06	0.70	10.23
Mean±SD	0.03±0.1	0.012±0.22	0.24±0.12	7.36±1.43

ND: not detectable

(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 using the same protocol.

**Statistical analyses:** Significant tests were carried out using the analysis of variance (ANOVA) of the statistical package for social sciences (SPSS Version 17) software. Statistical analyses (ANOVA) were used in order to show significant differences (p<0.05) in the values of cadmium, lead, arsenic and copper. The difference is regarded as highly significant if p value is lower than 0.01, statistically significant if pvalue is lower than 0.05, and non significant if p value is higher than 0.05. Student test was also carried out.

## RESULTS AND DISCUSSION

Cadmium (Cd), lead (Pb), copper (Cu) and arsenic (As) concentrations (mg/L) in water of Oueme River are given in Table 1.

The bioavailability tendency in the water was as follows: Cd<Pb<Cu<As. In most of the samples, Cd was

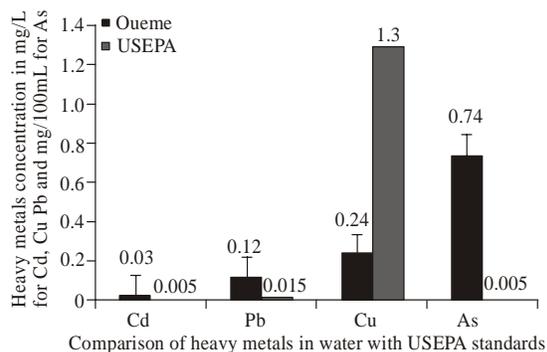


Fig. 2: Comparison of mean concentrations in heavy metals in the water of Oueme river with USEPA standards. Due to the alarming values of arsenic, its mean concentration in Fig. 2 is expressed in mg/100 mL.

not detectable for its levels were extremely low and below the detectable limit (0.01 mg/L). The concentrations of Pb ranged from ND to 1.06 mg/L with a mean concentration of 0.12 mg/L. The levels of copper were between 0.03 and 0.70 mg/L with a mean concentration of 0.24 mg/L. The concentrations of arsenic ranged between 4.41 and 10.23 mg/L with a mean concentration of 7.36 mg/L.

The different concentrations of heavy metals recorded in the water of Oueme River were compared to USEPA permissible levels (Cd: 0.005 mg/L; Pb: 0.015 mg/L; Cu: 1.3 mg/L; As: 0.005 mg/L) for drinking water as the trend showed in Fig. 2.

On all the sites the concentrations of arsenic were much higher (from 882 to 2046 times) than the safety limits set by USEPA ( $p = 0.000$ ). These values are the highest reported, exceeding the maximum value of 0.280 mg/L reported by Zandsalimi *et al.* (2011) in Bijar groundwater (Iran). For lead, the mean concentration recorded in Oueme water exceeded USEPA limit ( $p = 0.012$ ). In terms of cadmium, most of the sites presented levels below the detectable limit of the atomic absorption spectrophotometer used for heavy metals analysis-limit which is twice higher than USEPA standard and five times lower than WHO/FAO (2003) standard. Still cadmium mean concentration in water showed no significant difference ( $p = 0.177$ ). The concentrations of copper on all the sites were extremely lower than USEPA safety limit value ( $p = 0.000$ ). The values in the present study were higher than those reported by Ahmad *et al.* (2010) in the water of Buriganga River (Bangladesh) with respect to cadmium and lead (0.005 mg/L for Cd and 0.065 mg/L for Pb) but similar to that of copper (0.2 mg/L). According to USEPA standards, on one hand there was very little copper and little cadmium in the water of Oueme River. But on the other hand the water was

Table 2: Concentrations of heavy metals in sediments

Sediments	Cd	Pb	Cu	As
	20.14	3.67	57.46	705.53
	17.72	2.73	15.98	24.57
	18.93	3-2	36.72	365.05
	17.76	8.36	49.82	581.18
	5.55	6.56	23.42	7.93
	3.93	4.77	58.96	13.21
	1.04	6.65	11.93	0.01
	10.84	3.54	54.39	297.19
	0.09	5.12	16.43	0.01
	17.72	11.4	11.92	15.30
	0.56	5.88	14.18	0.01
	20.84	11.9	223.3	11.21
	22.07	7.77	51.04	782.06
	19.28	11.66	20.55	13.25
	0.01	20.12	10.57	9.93
	18.61	17.02	54.24	646.24
	10.80	9.03	28.36	13.4
	19.30	8.73	30.80	395.95
	11.11	3.37	21.53	16.43
	0.01	1.63	25.32	5.03
	19.37	5.62	53.61	2.33
	14.70	13.03	23.70	436.80
	6.67	5.57	7.842	870.03
	18.86	3.64	9.87	3.60
	11.11	2.73	8.11	14.90
	0.01	5.07	14.92	11.11
	12.75	1.43	11.9	401.5
	12.40	4.70	54.05	300.10
	5.55	3.25	11.51	13.00
	22.01	8.01	50.11	628.70
Minimum	0.01	2.73	7.84	0.01
Maximum	22.07	20.12	58.96	870.03
Mean±SD	12.11±7.77	7.39±4.46	28.74±17.99	220.41±286.64

polluted with lead and arsenic. All the aforementioned recorded results could often be attributed to contamination of the drainage water by the domestic municipal waste (Kaki *et al.*, 2011). The anomalously high values of As in all the places could be attributed to pressure treated wood, to pesticides used in the north of the study area for cotton cultivation and to lead-acid auto batteries discharged in the river by local population. These toxic metals could act as a slow but steady poison and adversely affect the ecology and thereby harm the flora, fauna and the local natural inhabitants.

In terms of sediments, the different heavy metals concentrations recorded (mg/Kg) are presented in Table 2. The bioavailability trend of heavy metals in the sediments was as followed:  $Pb < Cd < Cu < As$  which is slightly different from that of water.

The levels ranged [0.01; 22.07], [2.73; 20.12], [7.84; 58.96] and [0.01; 870], respectively for cadmium, lead, copper and arsenic. Heavy metals concentration in sediments compared with those of water showed that cadmium, lead, copper and arsenic in sediments were respectively 405, 62, 120 and 30 times higher than in water, respectively. Results observed accord with those of Cundy *et al.* (2003), Jha *et al.* (2003) and Kaki *et al.*

Table 3: Comparison of mean concentrations of heavy metals in sediments recorded in Oueme River with consensus based sediment quality guidelines CBSQGs of (MacDonald and Ingersoll, 2000)

	Cd	Pb	Cu	As
Oueme sediment	12.11	7.39	28.74	220.41
TEC	0.99	36	32	9.8
MEC	3	83	91	21.4
PEC	5	130	150	33

(2011) who explained that the elevation of metal levels highly concentrated in the bottom sediments is due to the fact that contaminating elements and compounds are transported by water and gather there. Therefore, sediments become “chemical archives” of heavy metal accumulations, which can provide valuable information in resolving the source and sink of heavy metal pollution. The case of cadmium was more remarkable since the quasi-quantity of cadmium seemed to be accumulated in sediments.

Mean concentration of cadmium recorded in our investigation was higher than those of Ahmad *et al.* (2010) and Kaki *et al.* (2011) respectively reported in sediments of Buriganga River (3.3 mg/Kg) in Bangladesh and in Nokoue lake sediments (6.37 mg/Kg) in Benin. Our value was similar to those of the authors cited above regarding copper but lower than Kaki *et al.* (2011) and Ahmad *et al.* (2010) when considering arsenic (256.56 mg/Kg) and lead (69.75 mg/Kg), respectively.

Müller *et al.* (2000) reported maximum values of 196; 37.5 and 465, respectively for Cu, Cd and Pb, in the sediment of Malter Reservoir in Germany.

Galán *et al.* (2003) reported the highest values of 846; 6.2 and 870 for Cu, Cd and Pb respectively in the sediment of Tinto River in Spain.

Audry *et al.* (2004) also recorded maximum values of 97.7; 125 and 523, respectively for Cu, Cd and Pb in the sediment of Lot River in France.

These maximum values concerning heavy metals were much higher than those found in the present studies with respect to copper, cadmium and lead.

Referring to arsenic, Zandsalimi *et al.* (2011) reported values ranging from 105.4 to 1500 mg/kg in the soils of Bijar (Iran). These arsenic levels are much higher than our findings.

The differences observed may be due to the period and the area of sampling.

In order to identify potential concern of toxic metals in the sediments of Oueme River, the results were compared to sediment quality guidelines standards established by the MacDonald and Ingersoll (2000) in Table 3. These guidelines provide concentrations of metals that have no effect on the majority of sediment-dwelling organisms, known as "Threshold Effect Concentration" (TEC), as well as concentrations that

Table 4: Heavy metals concentrations in *C.gariepinus*, *P.obstura* and *T.guineensis*

Fish species	Cd	Pb	Cu	As	
<i>C. gariepinus</i>	2.75	2.75	2.75	2.75	
	1.02	1.02	1.02	1.02	
	2.00	2.00	2.00	2.00	
	1.70	1.70	1.70	1.70	
	1.90	1.90	1.90	1.90	
	3.00	3.00	3.00	3.00	
	5.75	5.75	5.75	5.75	
	2.90	2.90	2.90	2.90	
	0.70	0.70	0.70	0.70	
	0.10	0.10	0.10	0.10	
	3.70	3.70	3.70	3.70	
	2.50	2.50	2.50	2.50	
	0.5	0.50	0.50	0.50	
	3.25	3.25	3.25	3.25	
	2.90	2.90	2.90	2.90	
	Minimum	0.10	0.50	1.70	0.70
	Maximum	5.75	7.70	24.90	30.05
Mean±SD	2.31±1.44	2.09±1.29	15.10±6.34	13.90±7.88	
<i>P. obscura</i>	1.22	1.30	5.95	1.22	
	0.5	0.70	3.01	0.50	
	0.35	1.05	1.45	0.35	
	2.5	0.80	0.90	2.50	
	1.23	1.25	2.01	1.23	
	0.9	1.01	1.95	0.90	
	1.47	0.90	2.00	1.47	
	0.5	2.10	0.74	0.50	
	1.20	2.50	0.84	1.20	
	2.32	0.01	5.10	2.32	
	1.47	1.35	4.25	1.47	
	1.30	2.90	0.05	1.30	
	1.57	0.19	7.30	1.57	
	2.30	0.80	0.87	2.30	
	1.30	0.75	4.50	1.30	
	Minimum	0.35	0.01	0.05	0.15
	Maximum	2.5	2.90	7.30	12.00
Mean±SD	1.34±0.65	1.17±0.79	2.72±2.19	4.11±3.56	
<i>T. guineensis</i>	3.27	1.42	1.92	7.01	
	2.10	0.90	0.01	12.01	
	1.90	0.50	1.03	7.85	
	1.08	1.01	0.80	4.50	
	0.78	1.30	0.82	7.80	
	3.24	0.90	1.45	3.70	
	1.20	2.00	1.32	8.90	
	0.93	1.70	0.20	9.20	
	0.90	1.02	0.05	10.01	
	1.02	0.50	1.24	9.45	
	2.90	2.07	0.70	8.75	
	0.01	1.20	1.80	6.80	
	1.90	5.80	0.67	7.50	
	0.82	1.08	0.50	7.05	
	1.01	2.01	1.24	3.01	
	Minimum	0.01	0.50	0.01	3.00
	Maximum	3.27	5.80	1.92	12.01
Mean±SD	1.53±0.97	1.56±1.27	1.91±0.58	7.56±2.41	

indicate polluted sediments. They are likely to affect organism health, defined as "Probable Effect Concentration" (PEC). The Midpoint Effect Concentration (MEC) is a midway concentration between the TEC and PEC concentrations.

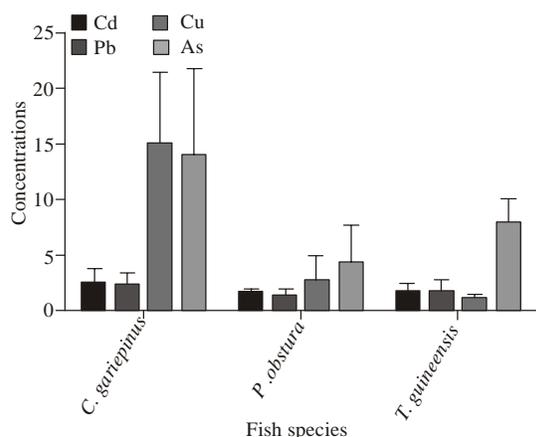


Fig.3: Comparison of the levels of heavy metals accumulation in fish species

Lead mean concentration in sediments was far below TEC ( $p = 0.000$ ). There was no significant difference between copper mean concentration and TEC value ( $p > 0.05$ ). Cadmium and arsenic concentrations highly exceeded PEC ( $p = 0.000$  and  $p = 0.001$ , respectively). Therefore, based on their heavy metal content, sediments must have been toxic.

Heavy metal contaminants in fish are of particular interest because of the potential risk to humans who consume them. Table 3 shows the concentrations of cadmium, lead, copper and arsenic in the three sampled species.

The patterns of heavy metals accumulation were  $Cd < Pb < As < Cu$ ,  $Pb < Cd < Cu < As$  and  $Cu < Pb$ ,  $Cd < As$ , respectively for *C. gariepinus*, *P. obtusa* and *T. guineensis*. It is clear that the accumulation of heavy metals varies according to fish species. Obasohan *et al.* (2006) find significant difference in heavy metals accumulation between *Malapterurus electricus* and *Chrysichthys nigrodigitatus*. Islam *et al.* (2010) also find significant differences in heavy metals accumulation among a large range of species such as *Thunnus thynnus*, *Salmo salar*, *Gadus macrocephalus*, *Theragra chalcogramma*, *Scomberomorus niphonius*, *Pampus argenteus* and canned fish including *T. tonggol* and *T. thynnus*. These authors reported that several factors such as pH and redox potential of the water, habitat species, age, size and trophic level of the fish are responsible for variation of trace elements content.

The comparison of heavy metals accumulation in the different species is depicted on Fig. 3.

In terms of heavy metals accumulation, *C. gariepinus* came in first position. It accumulated cadmium, copper, lead and arsenic at alarming levels far beyond maximum allowable limits in food fish set by USEPA ( $p = 0.000$ ).

This may be connected to the fact that being a bottom dweller species, *C. gariepinus* was probably more exposed to the metals in the sediments known as the archives of heavy metals (Cundy *et al.*, 2003; Jha *et al.*, 2003). Besides, the carnivorous feeding habits of the fish could also be a parameter. The levels of heavy metals concerning the two other species were also above USEPA standards ( $p < 0.01$  for Cd, Cu, and As, respectively). Only the level of Pb in *T. guineensis* showed no significant difference with USEPA value ( $p = 0.204$ ). Besides the aforementioned factors, the differences in the metals accumulation levels of the fish could be attributed to differences in their metabolic rates. It has been reported that different organisms have different metabolic rates and different food requirements and amounts. Organisms with high food intake tend to accumulate more metals (Ademoroti, 1996).

The presence of cadmium, lead, copper and arsenic in Oueme River had far-reaching implications directly to the biota and indirectly to man. The high metals levels may originate from anthropogenic activities. Actually in the last few decades, Benin witnessed a tremendous growth both in industrial and human developments. Most industries (cement, textiles, beer) and settlements are established along Oueme River so that the effluents from there are discharged directly or indirectly into the river.

Actually, 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). According to Neves (1985) the areas with high arsenic levels can be related to currents and a high sediment deposition rate. Cd is present as an impurity in several products, including phosphate fertilizers and detergents (Greaney, 2005).

Toxic effects on organisms resulting from trace metals pollution may alter community structure and in turn affect the aquatic ecosystem as a whole (Mendil and Uluözülü, 2007). Indeed copper-though essential for aquatic organisms and involved in biochemical processes such as enzyme activation-can be harmful when large single or daily intake occurs (Furnas, 1991). Others, such as cadmium, lead and arsenic have no known biological roles and are detrimental to essential life processes (Jones and Denton, 1984). In fact, cadmium interacts with the calcium metabolism, and in fish it causes abnormally low calcium levels (hypocalcaemia), probably by inhibiting calcium uptake from the water. Effects of long-term exposure can include larval mortality and temporary reduction in growth (AMAP, 1998). Lead is known as deadly and cumulative poison even when consumed in small quantities and is capable of deadening nerve receptors in man (Bodansky and Latener, 1987). Regarding arsenic, studies in animal laboratory have demonstrated that its toxicity is dependent on its form and its oxidation state. It is generally recognized that the

soluble inorganic arsenic is more toxic than the organic type. As for the trivalent forms [As (III)], they are more toxic than the pentavalent ones [As (V)]. There are multiple end-points, with several different organs and functions being affected, including the skin and the respiratory, cardiovascular, immune, genitourinary, reproductive, and gastrointestinal and nervous systems. Moreover Babel and Opiso (2007) have classified arsenic as group I carcinogens based on human epidemiological data (Hughes, 2002).

### CONCLUSION

The investigation showed that water, sediments and fish species of Oueme River in Bonou were contaminated by cadmium, lead, copper and arsenic. The levels of contamination of the river suggest that fish species and water consumption may induce health hazards to man. The potential harm from the studied metals leads to the conclusion that people not only should eat smaller quantities of *C. gariepinus* known to accumulate the highest levels of all the toxic metals but should also eat a diversity of fish to avoid consuming unhealthy quantities of these heavy metals.

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