



Monitoring of Heavy Metals in the complex "Nokoué lake - Cotonou and Porto-Novo lagoon" ecosystem during three years in the Republic of Benin

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Available online at: www.isca.in

Received 22nd February 2013, revised 27th March 2013, accepted 19th April 2013

Abstract

Agricultural discharges and human activities affect complex "Nokoué lake, Cotonou and Porto-Novo lagoon ecosystems. This complex lagoon received effluent, sewage, municipal solid waste coming from neighboring cities. The present study aims to monitor heavy metals levels contamination in water, sediment and in aquatic species such as fish, oysters and shrimp during three years in twelve areas along the complex lake and lagoons. An atomic absorption spectrophotometer was used to measure heavy metals such as lead, cadmium, zinc and mercury. Analyses were done every year during three years. Water, sediment and aquatic species collected in the complex ecosystem are contaminated by zinc, cadmium, mercury, and lead with various levels varying according to years. It is important to take appropriate measures to limit the input of pollutants from human activities.

Keywords: Heavy metals, complex lake ecosystem, Benin.

Introduction

Lakes and lagoons situated along Atlantic Ocean have various aquatic species eaten by local population. In Benin, the complex lagoon (Nokoué lake - Cotonou and Porto-Novo lagoon) is one of the largest lake in West Africa with high productivities and exploitation. The biodiversity of this freshwater ecosystem is very high, with a large diversity of fish, molluscs, shellfishes, birds and amphibians¹. Because of its geographical position, the complex lagoon became a receptacle in which are rejected water from gutter, sewage, wastewater from surrounding cities such as Cotonou, Abomey-Calavi, So-Ava. Also, urban concentrations of population due to increased urbanization, anthropogenic activities and garbage deposits along the lagoon banks are the main causes of the complex pollution by heavy metals and other toxic substances. This situation is easily illustrated when visiting some municipalities such as Ladji, Minonchou, Dédokpo, Ahouansori. In lacustrial village such as Ganvié, and Sô-Tchanhoué, house garbage, sewage, and solid waste were directly put into the lake by the population. Toilets were hanged on top of garbage. Chemical products such as fertilizers, pesticides used in agriculture were drained into the lake². The complex lagoon is used for commercial transport and business between the neighbouring countries such as Nigeria. Those activities contributed to the complex lake pollution.

In Benin, fishing is one of the main activities carried out by lacustrial people. Fish collected from this complex contribute to

about 75% of the national fish production³. In year 2000, the complex lagoon production was between 65 and 70% of the continental waters production of Benin³. The complex lagoon was the most productive lake of West Africa with a fish production of over two tonnes per acre⁴. Fishes are also source of high proteins, micronutrients (trace elements, vitamins or provitamins) with high levels of biological values. The importance of fish to ensure food security of populations in need was announced in the Bangkok Declaration⁵.

Diversity, abundance and performance of aquatic resources depend on the habitat quality, natural, biophysical and human activities that affect the physico-chemical regimes of water bodies, water quality and biological communities⁶. Also, to assess environmental degradation risks and to ensure good water quality for aquatic life, Biney et al. suggested the need a monitoring system establishment, based on surface water chemical monitoring, bioassays, ecological studies and toxicological evaluation of substances⁷. So, to preserve aquatic ecosystems and human health, special attention should be paid to water quality and aquatic biodiversity. Various research works were carried out on heavy metals contamination of the Nokoué lake but very few studies have focused on the heavy metal contamination of water, sediments and aquatic resources such as fish, oysters and shrimp.

The aim of this study is to evaluate over a period of three years the contamination level of the complex lake by heavy metals

(lead, cadmium, mercury and zinc). Specific objectives are to identify heavy metals in water and in sediment different and to determine the bioaccumulation of heavy metals in aquatic species such as fish, oysters and shrimp.

Material and Methods

Study area: Located in the South-East of the Republic of Benin (6° 25'N, 2° 26'E), Nokoué lake has a surface area of 150 km² (figure1).

The lake measures 20 km in the East-West and 11 km in the North-South direction. In the east, Nokoué lake is linked to Porto-Novo Lagoon and forms a freshwater lake with a surface area of about 180 km². Nokoué lake is connected with the Atlantic Ocean by a channel named Cotonou lagoon, which has a total length of 4.5 km. The hydrological regime of Nokoué lake is characterized by a low flood from May to June, which is the main rainy season in southern Benin and a major flood from September to November because of water supply from the Ouémé river.

Sampling locations: Sampling locations were selected according to three criteria: i. good geographical distribution of locations through the complex lagoon; ii. shrimp and oysters fishing locations; iii. lacustrial village and residential houses locations of the complex lagoon.

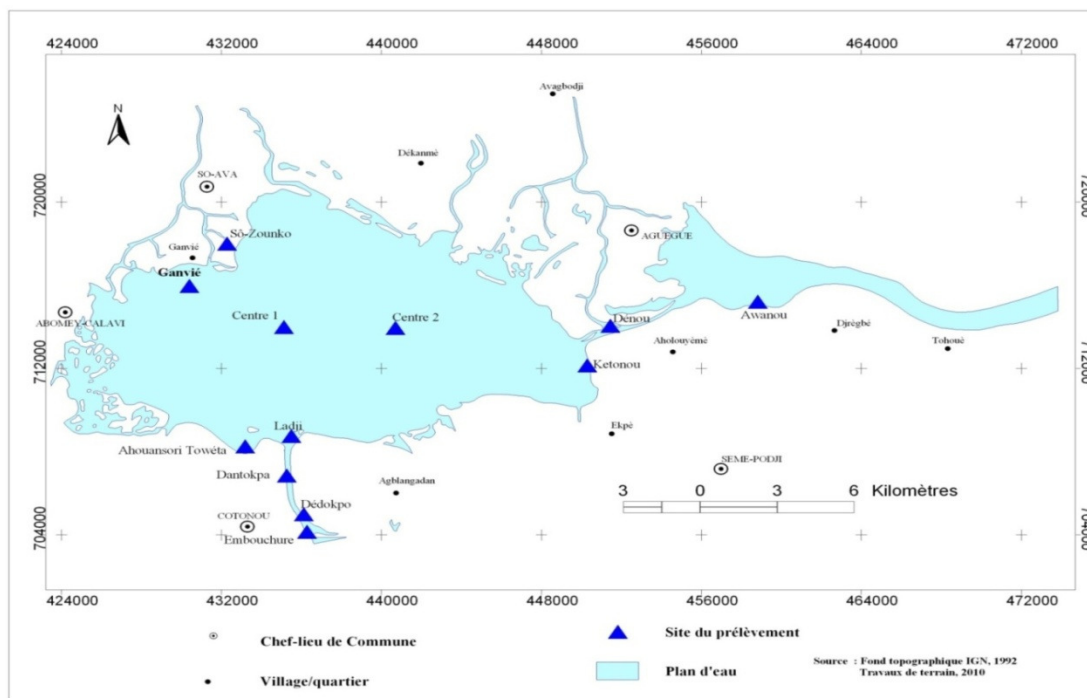
A total of twelve locations within four municipalities surrounding the complex lagoon were chosen: Ladji, Dantokpa, Embouchure, Dédokpo and Ahouansori-Towéta in the

municipality of Cotonou; Awanou and Kétonou in the municipality of Sèmè-Kpodji, Dénou in the municipality of Aguégués; Sô-Zounko, So-Tchanhoué in the municipality of Sô-Ava; Ganvié and two locations in the center of the Nokoué lake. Geographic coordinates of all locations were taken.

Water, sediment and aquatic species were taken in all localities except Oysters and shrimps which weren't found everywhere. Oyster species used in this study is *Ostrea edulis* Linnaeus, 1758 identified by the identification key proposed by FAO⁸. Shrimp sample is penaeidae identified by the identification key proposed by LB Holthuis in FAO⁸. *Tilapia guineensis* (Cichlidae) was chosen because of its abundance and its high consumption by the local population.

Sampling: Sampling was done in March 2010, repeated in March 2011 and in March 2012. Water samples were collected directly with glass bottles previously sterilized and rinsed with 10% nitric acid and distilled water.

Few cm layer of sediment sample were collected from the top with a grab sampler and placed in glass vials treated in the same way as water bottles. Aquatic species were caught using nets. Samples were kept at 4°C in ice box during transportation to laboratory. Aquatic species were dissected and lyophilised. Toxic substances analyzed in this study are zinc, lead, cadmium and mercury because the consumption of these metals are dangerous for human health and hold international community attention.



Figures-1
 The complex Nokoué lake and its sampling locations

Methods: Heavy metals analysis in water was done with spectrophotometer using specific reagents kits. Heavy metals in sediment and in aquatic species were measured by atomic spectrophotometer absorption (ASA). Fish, shrimp and oysters samples were dried and ground in a ceramic mortar. 5 g of each sample were weighed in a quartz crucible. 5 g of distilled water in another crucible to serve as blank. The crucibles containing samples and water as blank were put in a programmable oven. Initial temperature was lower than 100°C. The temperature increased to 450°C at a rate of 50°C/hour. After this calcinations step, crucibles were removed and allowed to cool down. 1 to 3 ml of water was added and was evaporated in a water bath. 5 ml of hydrochloric acid were added to each crucible and were evaporated. Residue were dissolved in a volume of 10 to 30 ml of nitric acid 0.1 mol / L. Crucibles were stirred thoroughly to dissolve the ashes for 1 to 2 hours then filtered in a 50 ml flask. The resulting solution was then analyzed by atomic spectrophotometer absorption.

Statistics analyses: To assess heavy metals variability between localities, from 2010 to 2012 and between heavy metals, multi-factor variance followed by multivariate linear regression were used⁹. Heavy metals variability in the complex water and sediment were assessed using multivariate analysis of variance followed by Wilks vector test¹⁰. The variability of lead concentration between aquatic species is assessed using nonparametric test for comparison of Kruskal Wallis¹¹. Analyzes were done with R-2.15.2 software¹².

Results and Discussion

Heavy metals in water: Results are discussed according to international standards values of WHO and EEC Directive which are 0.1 mg / L for lead, 1.5 mg / L for zinc, 0.005 mg / L for cadmium in water; 1.5 mg / kg for lead, 1 mg / kg for cadmium in oysters and 0.5 mg / kg for lead and cadmium in shrimp^{13,14}. Table 1 shows lead, cadmium, zinc and mercury averages in waters collected along the complex lagoon during three years.

Three factors variance analysis (years, locations and toxic substances) of heavy metals in waters collected in the complex lagoon localities have significantly changed. It has also experienced a significant variation between complex lagoon

localities between types of heavy metals and between localities by type of heavy metal in the complex with ($p < 0.00001$). Multiple linear regression analysis of heavy metals levels in water taking into account years, localities and various toxic substances (table 1) were done. This analysis done by taking 2010 as year reference and Awanou as locality reference and mercury as heavy metals reference showed that: i. by referring to 2010 year, heavy metals concentration in complex water raised significantly from 2010 to 2012 (estimate (2011) = 5.66, p (2011) = 0.050382 and estimate (2012) = 7.60, p (2012) = 0.010270) (table II); ii. by referring to Awanou locality, Ganvié, So-Tchanhoué and Ahouansori are the localities with high accumulation of heavy metals (table 2); iii. by referring to mercury, lead and Zinc are the most abundant metals in the complex water (table 2). These results are illustrated by figure 2.

Toxic metals levels varied from year to year and between localities. The highest concentrations are obtained in lacustral villages such as Ganvié and So-Tchanhoué and other residential areas where large amounts of discharged waste containing metal materials and batteries. The highest levels of lead are identified in water collected at Ganvié and Sô-Tchanhoué where values exceed standards (0.1 mg / l). The minimum values are observed at Porto-Novo lagoon. Zinc levels are also higher in all residential areas and especially along the Nokoué lake and Cotonou lagoon. Concentrations obtained are higher than those of lead. At Porto-Novo lagoon especially in Kétonou and Awanou area, the rates of heavy metals (lead, zinc, mercury and cadmium) are relatively low. These results could be justified not only by the lack of waste along the banks contrary to what is observed along Nokoué lake and Cotonou lagoon. Mercury levels identified remains low throughout the complex lagoon. According to cadmium; the values are 12 to 24 times higher than normal value which is 1 mg / l except mercury which is slightly higher except Dantokpa, Ahouansori, and Center of the lake levels and are three times higher than standards value.

When analyzing year by year metals rate in the complex lagoon, only lead levels showed a slight decrease in its concentration compared to years 2011 and 2012 and cadmium, mercury and zinc rate showed slight increases at all localities.

Table-1

Averages of lead, cadmium, zinc and mercury in waters collected along the lagoon complex (Nokoué lake, Cotonou and Porto-Novo lagoons) during three years

Heavy metals		2010	2011	2012	Mean of the measurement
Cadmium	Mean	14.42	14.53	15.48	14.81
	CI-95%	[08.53-20.30]	[08.60-20.45]	[09.17-21.78]	[11.68-17.94]
Mercury	Mean	01.41	01.40	01.39	01.40
	CI-95%	[00.65-02.17]	[00.61-02.19]	[00.62-02.16]	[01.00-01.80]
Lead	Mean	21.13	25.42	23.67	23.40
	CI-95%	[06.89-35.37]	[11.74-39.09]	[11.49- 35.84]	[16, 45-30.36]
Zinc	Mean	37.33	55.58	64.33	52.42
	CI-95%	[19.04-55.63]	[34.62-76.54]	[43.40-85.26]	[41.33-63.51]

Table-2
Summary of linear regression of heavy metals in water

Variability data	Estimate	Std.Error	Pr (> t)
Years			
2010	00.00	00	00
2011	05.66	2.86	0.050382
2012	07.65	2.93	0.010270
Localities			
Awanou	00.00	00	00
Ahouansori	26.70	3.53	<0.00001
Centre du lac	12.99	3.85	0.000988
Dantokpa	11.90	5.01	0.019082
Dédokpo	08.45	4.07	0.040044
Dénou	00.84	4.06	0.835473
Embouchure	08.48	3.74	0.025141
Ganvié	40.98	7.95	<0.00001
Kétonou	07.38	4.03	0.069955
Ladji	14.35	3.82	0.000266
Sô-tchanhoué	40.65	7.24	<0.00001
Sô-Zounko	13.15	6.52	0.045967
Heavy metals			
Mercury	00.00	00	00
Cadmium	13.41	2.69	<0.00001
lead	22.00	2.79	<0.00001
Zinc	51.01	4.11	<0.00001

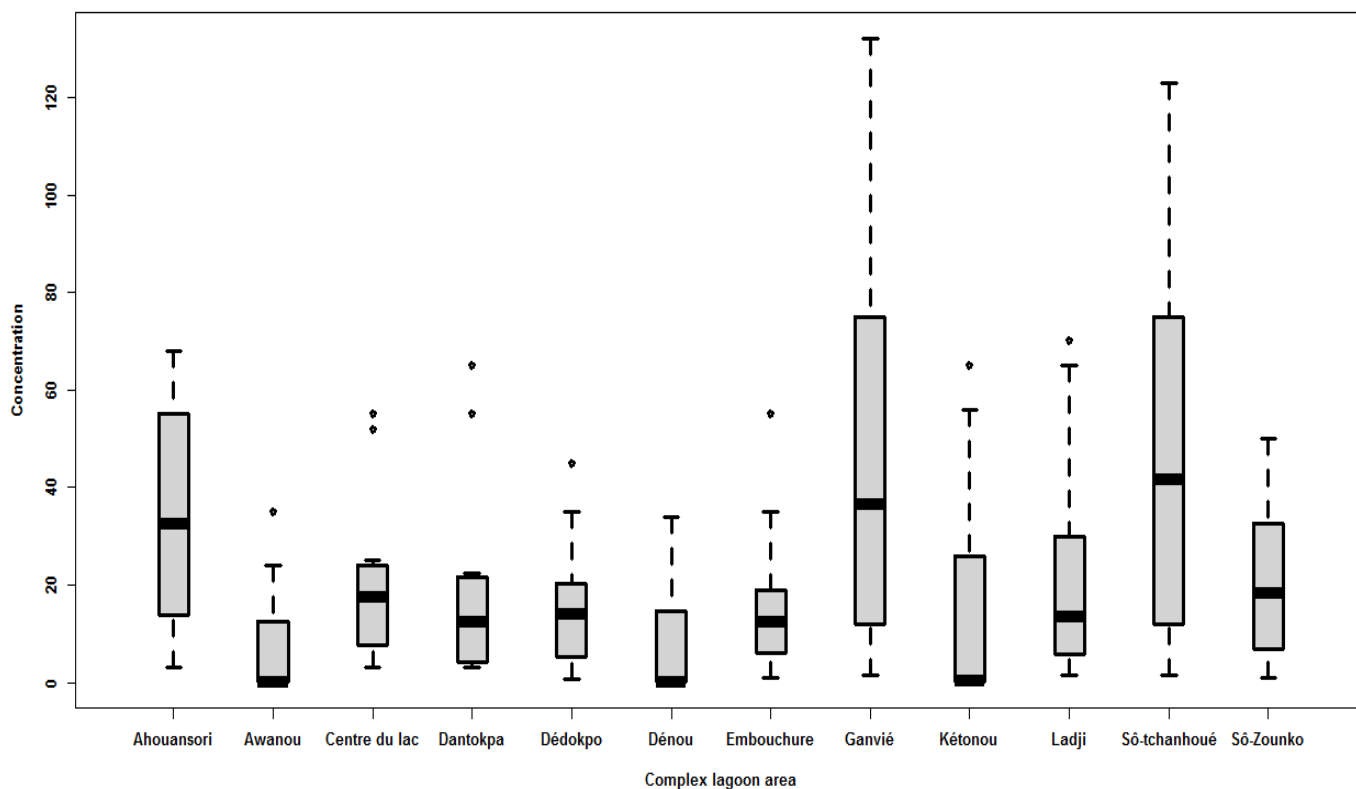


Figure-2
Variability of heavy metals levels in water collected from localities

Heavy metals in sediments: Three variance factors analysis (years, locations and toxic substances) of heavy metals levels in the complex lagoon sediments are represented in table 3.

The concentration values were transformed by Box-Cox family transformation before analysis. We notice that concentration had a significant change during the three years 'study, between the complex localities, between toxic and between localities by type of metal in sediments with $p < 0.05$.

Multiple linear regression analysis of the heavy metals concentration in sediments, taking into account years, localities

and various toxic substances and also taking 2010 as year reference, Awanou as locality reference and mercury as heavy metals reference showed that: i. by referring to 2010 year, heavy metals concentration in the complex sediments raised insignificantly from 2010 to 2012; ii. by referring to Awanou locality, Ganvié and Sô-Tchanhoué are the localities with high heavy metals accumulation; iii. by referring to mercury, lead and Zinc are the most abundant metals in the complex sediments (table 3). These results are illustrated in figure 3.

Table-3
 Summarize results of linear regression of heavy metals in sediments.

Variability data	Estimate	Std.Error	Pr (> t)
Years			
2010	0.00	00	00
2011	0.02	0.06	0.702686
2012	0.07	0.06	0.283370
Localities			
Awanou	0.00	00	00
Ahouansori	0.72	0.12	<0.00001
Centre du lac	0.87	0.15	<0.00001
Dantokpa	0.97	0.11	<0.00001
Dédokpo	0.75	0.11	<0.00001
Dénou	-0.03	0.17	0.848498
Embouchure	0.39	0.12	0.001669
Ganvié	1.10	0.14	<0.00001
Kétonou	0.09	0.13	0.491103
Ladji	0.95	0.12	<0.00001
Sô-tchanhoué	1.07	0.13	<0.00001
Sô-Zounko	0.78	0.15	<0.00001
Heavy metals			
Mercure	0.00	00	00
Cadmium	1.02	0.06	<0.00001
Plomb	1.24	0.06	<0.00001
Zinc	5.29	0.07	<0.00001

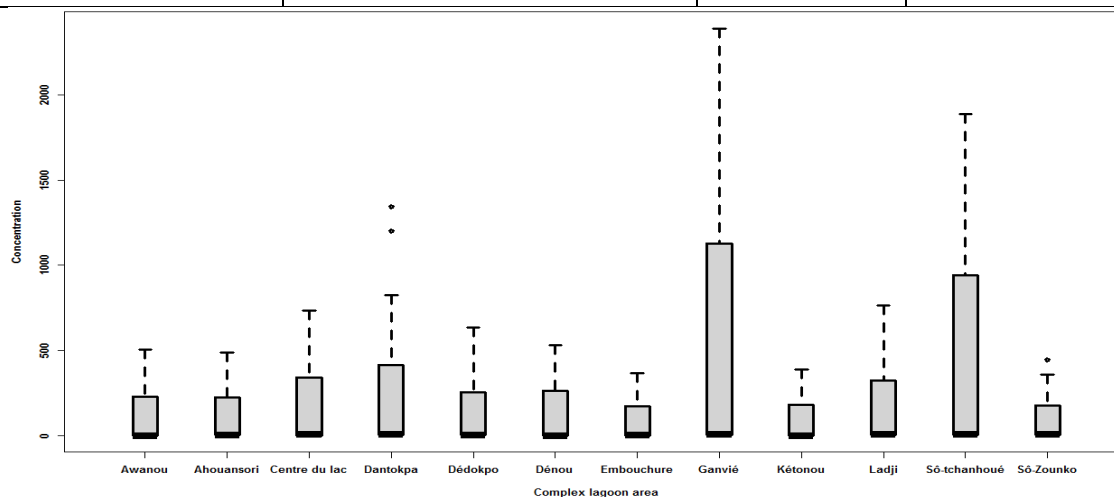


Figure-3
 Variability of heavy metals in the complex sediment collected in each locality

Heavy metals concentrations in sediment exceed those obtained in water. Inhabited populations areas' values are higher and are sometimes double of those found in uninhabited areas. These results could be explained by human activities causing heavy metals accumulation in the lake Ecosystem. Cadmium values are above the accepted norm which is 0.11 mg / kg in sediment and have a significant risk of bioaccumulation in fish resources¹⁵. Lead concentrations are below 19 mg / kg in sediment reported by Lawani¹⁵. Lead levels in sediments annually collected over a period of three years (12 to 12.5 mg / kg) are below the maximum values obtained by Gnandi in Bè Nyékomakpoé lagoons in Lomé (Togo)¹⁶. Minimum and maximum values of cadmium and zinc identified from complex lagoon in Bénin are higher than Bè Nyekonakpoe lagoon in Togo.

Multiple emission coming from Dantokpa market, plastics incineration, discharges originate from engines placed in the boats are the main contamination sources of the complex lake.

Comparative analysis of water and sediments shows that heavy metals levels are not uniform from one locality to another, from one year to another and from water to sediment $p < 0.0001$.

Heavy metals are more abundant in waters than in sediments ($P < 0.05$). Zinc is higher in sediment than in water.

Heavy metals in aquatic species: Cadmium was detected in oysters with an average of 0.78 mg / kg, mercury is below detection limit in all species analyzed. Zinc was found in tilapia. Table 4 shows the average concentrations of heavy metals found in the species. Anova factor analysis shows that lead does not risen significantly during the three years ($p = 0.0697$) but no significant reducing in each species. According to Kruskal Wallis' nonparametric comparison test, variability of lead and zinc levels in aquatic species was assessed using zinc level in shrimps and in oysters (zinc was not detected in tilapia). Results show that lead levels varied significantly between species (chi-squared = 7.4949, $p = 0.02358$).

Lead level in oysters (1.11 mg / kg) is higher than in shrimp (0.924 mg / kg) and in *Tilapia guineensis* (0.749 mg / kg). Oysters accumulate more lead than the other species.

According to the results of the same test, zinc is more abundant in oysters (1566.23 mg / kg) than in shrimp (49.94 mg / kg) (chi-squared = 5.4, $p = 0.02014$) (figure 4).

Table-4
Mean concentrations of heavy metals in aquatic species

Heavy metals		Shrimp	Oysters	Tilapia guineensis
Cadmium	Mean	<DL	00.78	<DL
	CI-95%	<DL	[00-01.99]	<DL
Mercury	Mean	<DL	<DL	<DL
	CI-95%	<DL	<DL	<DL
Lead	Mean	00.92	01.11	00.67
	CI-95%	[00.79-01.05]	[0.00-2.03]	[00.57-00.77]
Zinc	Mean	49.94	1566.23	<DL-
	CI-95%	[46.98-52.90]	[831.21-2301.25]	<DL

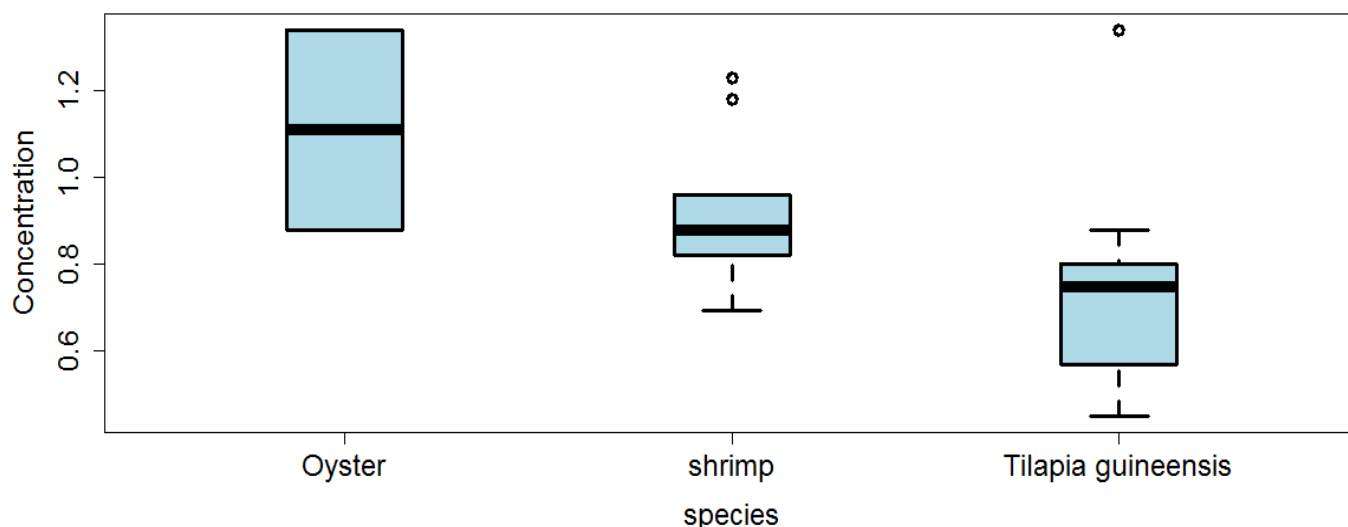


Figure 4
Variability of lead level in aquatic species

The average concentrations of lead identified at Sô-Zounko, Dédokpo and Kétonou during this study are higher than WHO's value¹³. These high levels could be explained by various reasons depending on localities. At Sô-Zounko and Kétonou this high increased levels could be explained by waste discharged into the lake, acadjas use to catch fish and especially petroleum traffic throughout the lake. The complex Nokoué-lake Porto-Novo and Cotonou lagoon is used as a communication channel to carry not only people but also goods from Nigeria. Lead containing in gasoline certainly contaminated the lake ecosystem and consequently aquatic resources. At Dédokpo locality the superiority of lead content could be explained not only by large quantities of waste discharged into the lake. These garbage and waste may contain lead, battery. Lead levels identified by Lawani in shrimp collected in the same Nokoué lake (5.17 mg / kg) are higher than lead levels recorded in this study¹⁵. Lead levels decreased from 2007 to 2010 but are still higher than the accepted values. Cadmium identified in oysters collected in Ahouansori Towéta exceeds the standards values of European Union. This superiority is due not only to large amounts of metal waste discharged into the lake but also to fertilizers in agriculture.

Conclusion

The assessment of heavy metals over a period of three years showed that the complex (Nokoué lake - Cotonou and Porto Novo lagoons) is polluted by heavy metals followed by bioaccumulation in aquatic species (shrimp, oysters and fish). This pollution is largely anthropogenic and constituted a real risk to flora, fauna as well as man through food chain.

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