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Evaluation of the state of pollution of complex Aheme Lake -lagoon of Ouidah by trace metals Zn, Cu, Cd, Pb and Cu speciation in sediment

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Abstract

The objective of this work is the evaluation of the state of pollution of the complex Aheme lake -Lagoon of Ouidah by trace metals elements (TME) such as zinc, copper, cadmium and lead, and speciation copper in sediments. This study reveals that the TME are much more concentrated in sediments [Cu: 46-356 mg/kg; Zn: 2.91 to 323 mg/kg; Pb: 1.53 to 4.17 mg/kg; Cd: 0 to 1.14 mg/kg], and in fish [Cu: 19 mg/kg; Zn: 10.36 mg/kg; Pb: 0.56 mg/kg; Cd: 0 mg/kg] and in the water column: [Cu: from 0.1 to 0.44 mg/L; Zn: 0.3 to 1.1 mg/L; Pb: from 0.013 to 0.33 mg/L; Cd: 0.067 to 0.009 mg/L]. Speciation of copper metal, the most abundant in sediments (average 171.44 mg/kg) for all sampling points, reveals that it is much more present in the oxide (29.83%) and the acid-soluble fraction (25.70%) at Guézin against 35.23% acid-soluble fraction and 30.92% in the reducible fraction Tohonou.

Keywords: Aheme lake, TME, speciation, sediment, water, fish.

Introduction

The Republic of Benin has tremendous potential in aquatic natural resources. Various anthropogenic pressures on the environment caused over the years, an advanced degradation of these resources[1]. Moreover, contamination of aquatic ecosystems by metals remains a serious environmental problem of increasing concern[2]. Water, fish species and sediments from Nokoue Lake and those of the lagoon of Porto-Novo in Benin are contaminated by heavy metals[3-5].

Sediments are micro traps; they give an indication of the historical pollution of watercourses[5,6]. Indeed, the contaminants are adsorbed to the particles in suspension and then accumulated in the sediments; most contaminants are on the clay, the hydroxides of Mn and Fe, carbonates, organic materials and biologic materials[7] and five fractions such as Exchangeable fractions, carbonates, oxides Fe and Mn, the organic matter and sulfides[8]. In the case of shallow lakes, resuspension of sediments enriched and leaching of nutrients help maintain high concentrations in the water masse.

The present study aims to assess the state of pollution of complex the lake Aheme and lagoon of Ouidah by trace metals (zinc, copper, cadmium, lead), and speciation of copper in sediments.

Material and Methods

Environment Study: The study was conducted on the periphery of the Aheme lake in Benin (West Africa). Aheme lake (78 km^2) is situated in a sub-equatorial climate. It connects the Couffo River and the coastal lagoon of Ouidah in the watershed Mono-Couffo. Around it is developed agriculture, livestock and especially fishing.

Methods: The pH and the sediment pH_{KCl}: The pH was measured in situ in the water with the pH/Oxi 340i WTW meter previously calibrated. Regarding pH_{KCl} we weighed 10 grams fine sediment sieved to 0.2 mm in a beaker. We added 25 mL of distilled water and was then stirred with a magnetic stirrer for 60 min at room temperature of 20 ± 2°C. This allows to suspend the whole of the sample and thereby to obtain a balance between the aqueous and solid phase. The mixture is then allowed to stand for two hours in airtight then pH_{KCl} is always measured in the supernatant using the pH meter WTW pH/Oxi 340i.

Total Organic Matter in Sediments: Determination of organic material by incineration. We followed the following steps: i. Drying of the sample of ground for 16 hours at 150°C., ii. Clean the crucible by heating to red, and then cool in a desiccator for 10 minutes. iii. Take the weight of the empty crucible. Add 10 g of dried soil. Record the final weight. iv. Calcine the soil in a mitten furnace at 375 °C for 16 hours. v. Allow to cool in a desiccator and weigh the crucible containing the ashes. vi. The calculation formula of MOT:

$$MOT = \frac{(P1-P0)-(P2-P0)}{(P1-P0)}$$

MOT: total organic material: P1: final weight, P0: the weight of the empty crucible P2: weight of the crucible containing the ashes.

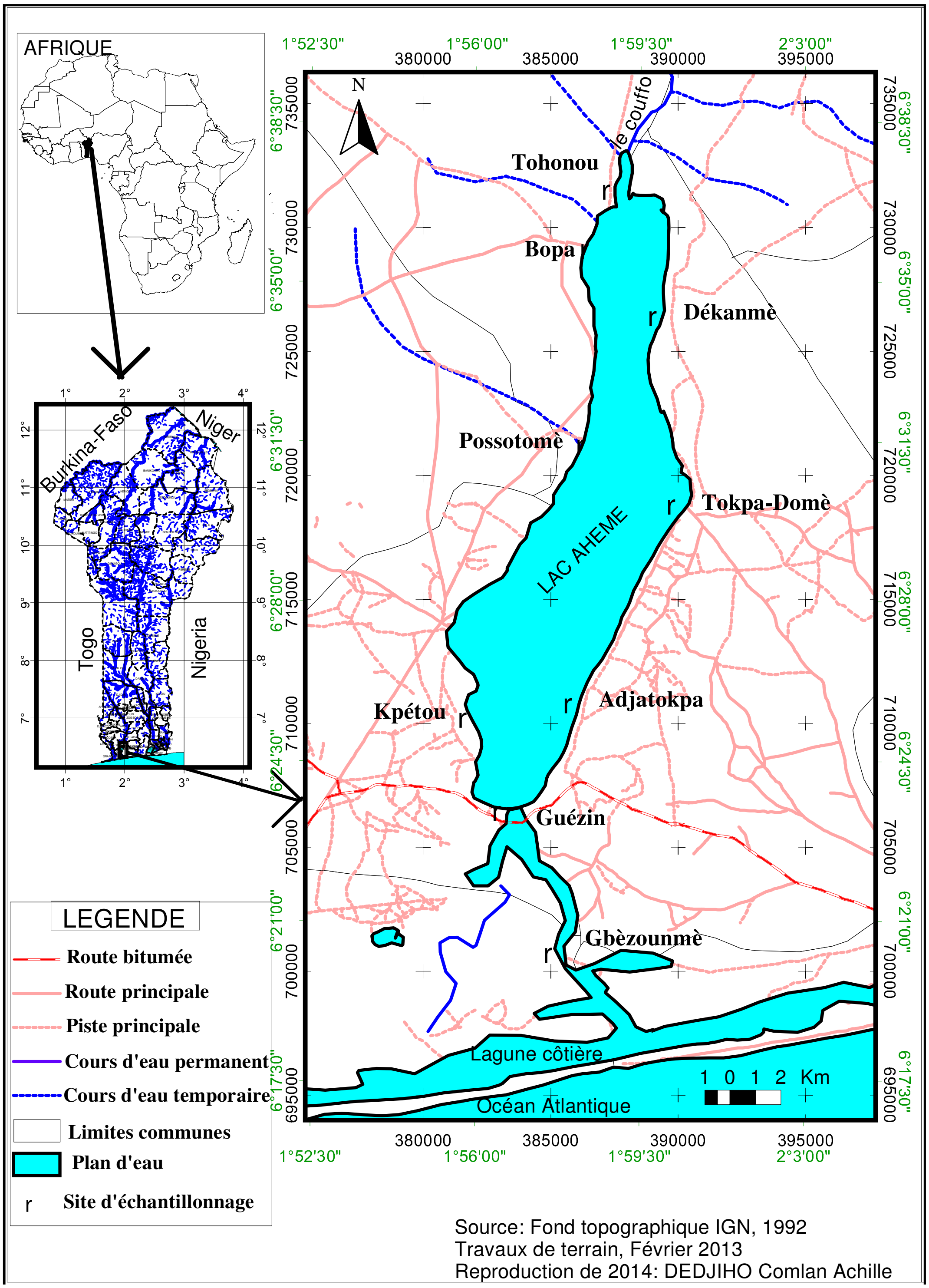

Figure-1
Location of the Environment study and sampling points

Cationic Exchange Capacity (CEC): The principle of this method is the titration with potassium hydroxide. During the titration, the protons attached are exchanged by potassium ions. The neutralization of the H^+ leached promotes displacement of the reaction. Monitoring of the concentration of potassium solution shows that it stays constant, until the time of saturation exchange sites. When the saturation point is exceeded, the potassium concentration of the solution increases with the bringing made. The CEC is then determined as the difference between the added potassium quantity and the potassium quantity remaining in the solution at the end of the titration[8].

Speciation: The method of speciation of copper is detailed in table 1 according to the work of Tessier[9].

Results and Discussion

Results: The pH_{water} measured (figure 2) are between 6.73 and 7.73, with an average of 7.16. The pH_{water} of Tohonou recorded and are weakly acidic Gbèzoumè among other sampling stations while those obtained Guézin are weakly basic. We also note that pH_{KCl} sediment vary between 3.69 and 7.85. Sediment samples collected Tohonou, Guézin Gbèzoumè and are very acidic, while the other samples are weakly basic.

Table-1
Sequential extraction of copper for 1,0 g of sample

Fractions	Extraction reagents	Volume (ml)	Times (h)
Exchangeable	1M $MgCl_2$, pH7, 20°C, continuous agitation	8	1
Acid-soluble (CO_3^{2-})	1M CH_3COONa/CH_3COOH, pH5, 20°C, continuous agitation	8	5
Reducible (Fe ; Mn)	0,04M NH_2OH, HCl + 25% CH_3COOH, 95°C intermittent agitation	20	6
Oxidizable Material (M.O.)	30% H_2O_2, 0,02M HNO_3, pH2, 85°C, intermittent agitation, 3,2M CH_3COONH_4, + 20% HNO_3	5 3 5	2 0,5
Remaining	40% HF + 60% $HClO_4$ (total Minéralization)	5	à sec
Total content	40% HF + 60% $HClO_4$ (total Minéralization)	10	à sec

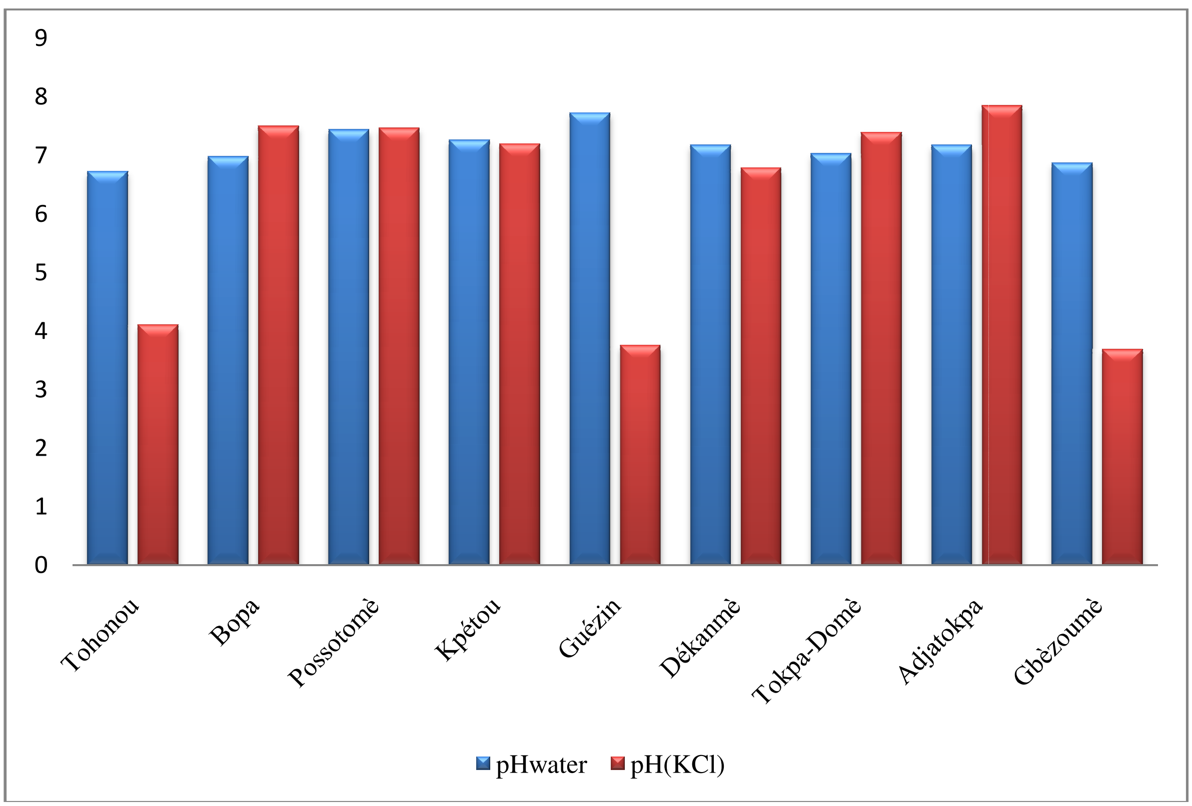

Figure-2
Change of pH_{water} and pH_{KCl} as a function of sampling stations

Total Organic Matter (TOM): TOM concentrations have varied from one sampling point to another (figure 4). In fact, high levels in TOM were recorded Tohonou (136.5 mg/g) at Kpétou (92.9 mg/g) and Guézin (130.3 mg/g). The lowest concentrations were recorded at Bopa (16.3 mg/g) and Adjatokpa (16.45 mg/g) compared to the average of all TOM sampling points is 67.73 mg/g.

Metal Trace Elements (TME): In water: On figure 5, we find that the Cu concentrations in the water vary from 0.10 to 0.44 mg/L with a mean of 0.34 mg/L. The highest concentrations were obtained at Tohonou, Adjatokpa and Gbèzoumè. The zinc is the metal most noticed: its concentration is in the range of 0.30 to 1.1 mg/L, with an average of 0.68 mg/L. The zinc is much more remarkable at Bopa, Guézin, Adjatokpa and Dékanmè. As far as the lead is concerned, its highest concentration was observed at Bopa and Adjatokpa. The average concentration of lead is 0.12 mg/L. The cadmium is the metal less present in the samples analyzed. The average is 0.007 mg/L.

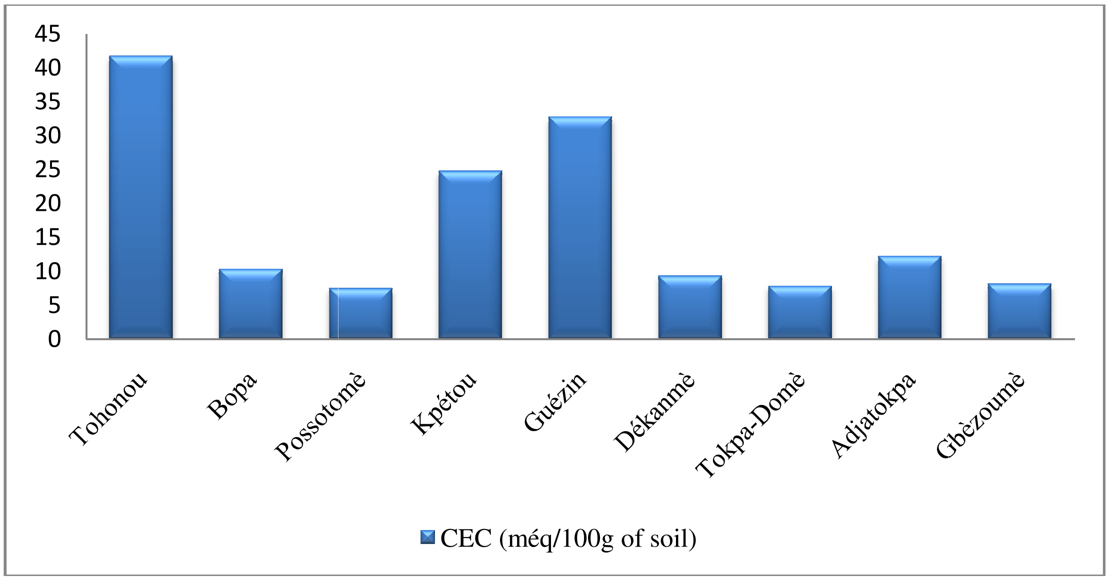

Figure-3
Measures of CEC of sampling stations

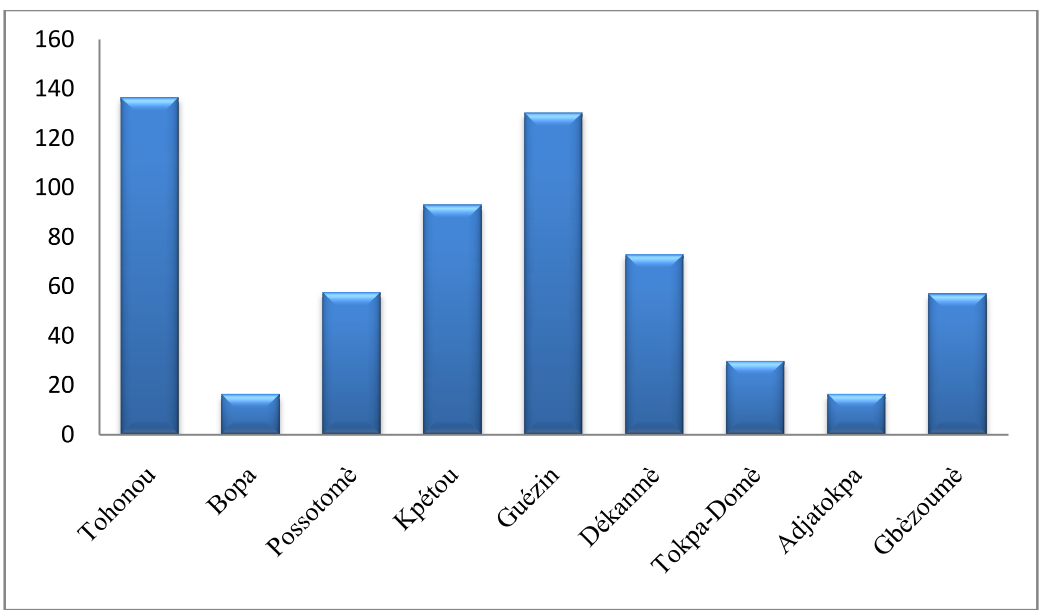

Figure-4
Total organic matter (TOM) of sediment samples

In Sediment: Figure 6 shows the metal concentrations in the sediments. Concentrations of copper are in the range 46 to 356 mg/kg with an average of 171.44 mg/kg. Zinc meanwhile is heavily concentrated in sediments Possotomé, Guézin and Gbèzoumè. The average concentration of zinc is 109.61 mg/kg. Lead concentrations in sediments are in the range of 1.53 to 4.17 mg/kg with an average of 2.97 mg/kg. Similarly, the concentrations of cadmium in the sediment in the range from 0 to 1.14 mg/kg with an average of 0.19 mg/kg.

In fish: We note that the copper concentration is 19.00 mg/kg, followed by the zinc (10.36 mg/kg) and lead (0.56 mg/kg). No trace of cadmium was found in Aheme Lake (figure 7).

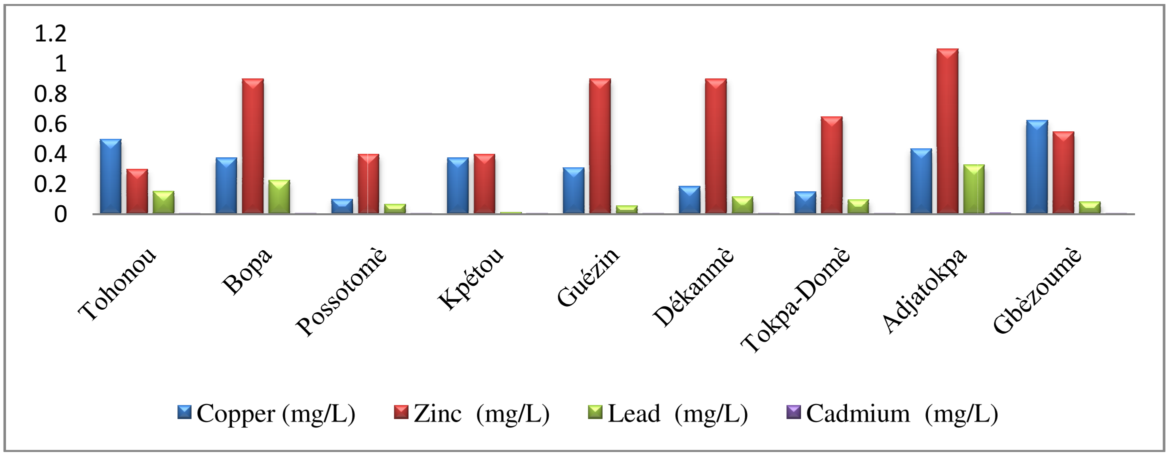

Figure-5
Levels of heavy metals in water

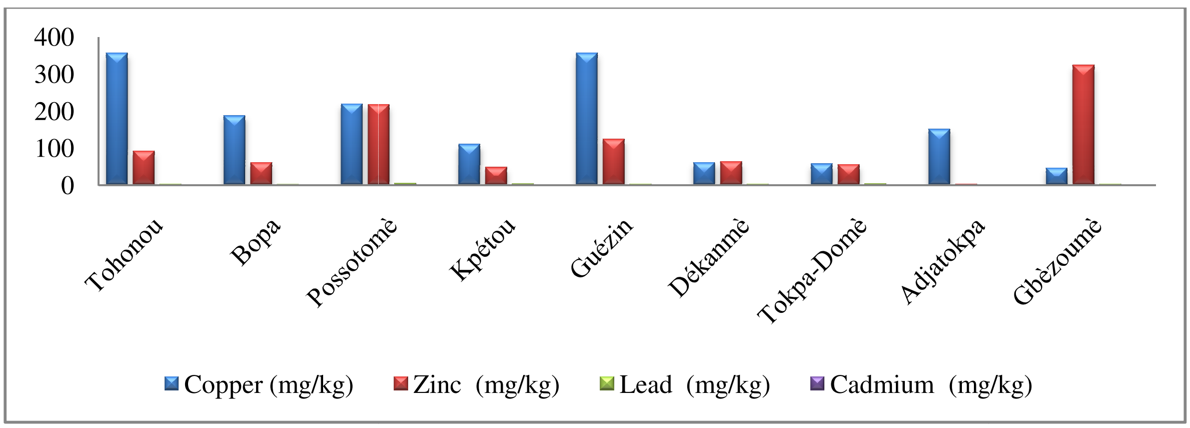

Figure 6: Levels of heavy metals in sediments

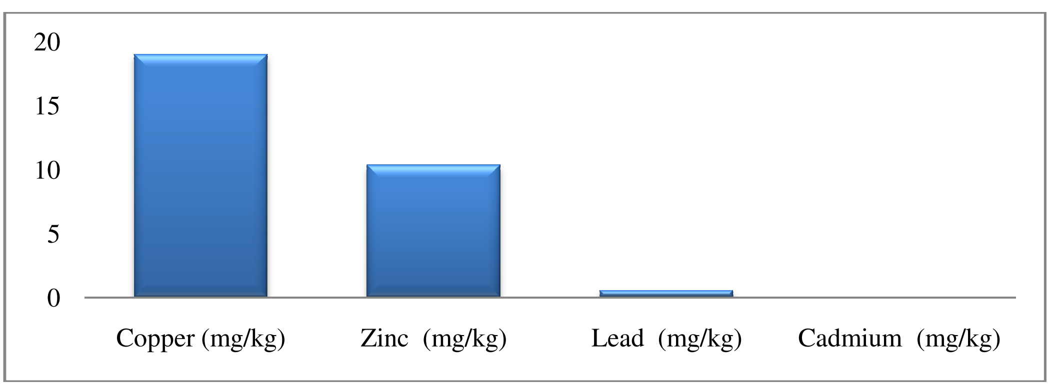

Figure-7
Levels of heavy metals in fish

Table-2
Standards of toxic metals

	Cd	**Pb**	**Cu**	**Zn**
Water lake and river (µg/L) GESAMP, 1982)	0,21	0,4	0,1	8,6
Sediments (Directive 76/464/CEE, 2000) in µg/g dry	0,11	19	33	95
Fish (Regulation CE 466/2001 en mg/kg for Hg, Cd, Pb, FAO (2001) in ppm for the remaining metals	0,01 à 0,05	0,2 à 0,4	3,0	1000

Speciation: Concentrations of each fraction on reading the atomic absorption spectrophotometer (AAS), flame being data in milligrams per liter, we have converted to milligrams per kilogram of sediment (table 3). These values were used to obtain the distribution diagrams according to the copper percentage associated with the various fractions (figure 8).

Figure 8 shows that in the sediments of Guézin and of Tohonou, copper is unequally distributed in different geochemical phases of sediments. Indeed, it is related to metal oxide to 29.83 %, 20.83 % to reducible fraction and 25.70 % in the acid-soluble fraction. In the same order, on sediments Tohonou, copper has a greater affinity for acid-soluble fractions (35.23 %), reducible (30.92 %) and oxidized (25.93 %).

Discussion: The measured pH_{Water} values flutuate hesitated between 6.73 and 7.73, with an average of 7.16. These pH_{Water}, ranged between 6.5 to 9, are good in aquaculture[10]. Moreover, the pH_{Water} is within the acceptable limit (5-9) for most plant and animal species, especially fish[11]. Indeed, for most aquatic species, the optimum pH_{Water} range for the reproduction is between 6 and 7.2. Beyond pH_{Water} = 9, there is mortality for many species[12].

It has been noticed that lower is pH_{KCl} (acid) higher is the CEC. This is justified by the fact that the acidic conditions favor the release of cations in the case of heavy metals trapped in the sediments.

Table-3
Results of sequential extractions of copper in masse (mg) and percentage (%)

		Guézin (mg/kg)	**Percentage (%)**	**Tohonou (mg/kg)**	**Percentage (%)**
The different fractions	Residual	66,80	21,37	25,12	7,25
	Oxidable	93,48	29,86	89,88	25,92
	Reducible	65,20	20,83	107,20	30,92
	Acid-soluble (carbonates)	80,45	25,70	122,13	35,23
	Exchangeable	7,15	2,28	2,38	0,69
	Total	313,08	100	346,71	100

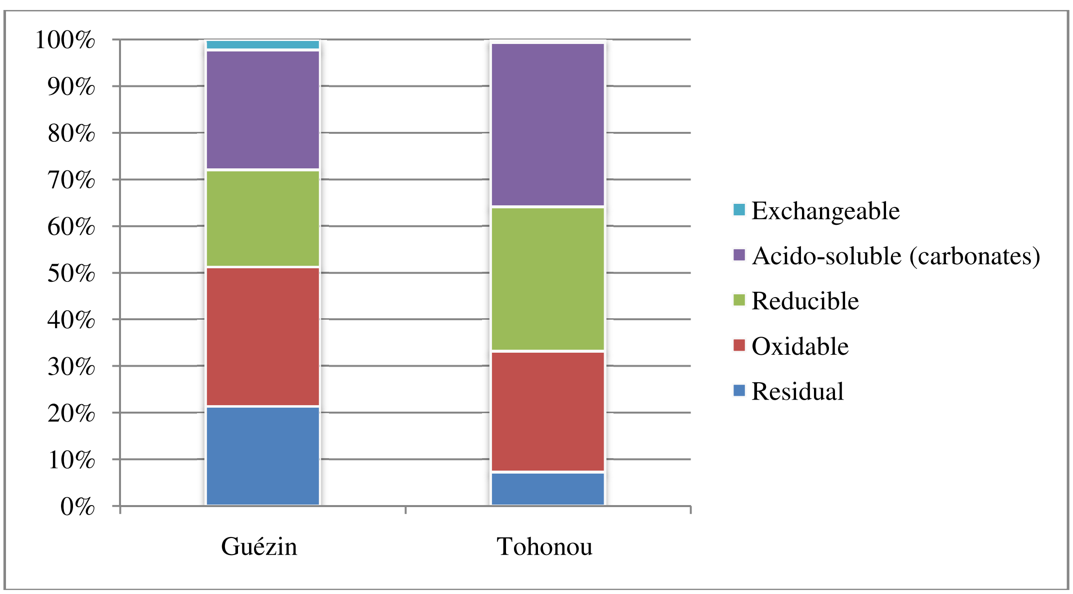

Figure-8
Relative content of copper in the different fractions

Table 2 presents the standards for different metals investigated. Comparing our results with standards, it is noticed that in the water, all the copper content is extraordinary. However in sediments, we note that the concentrations of TME such as copper, zinc and cadmium are beyond the standards. Moreover, in the fish, it is the content of copper and lead which are extraordinary. In general, the TME are more concentrated in sediments, fish in the water column. This is explained by the fact that the TME are not free in nature. They are fixed on the solid particles in suspension, which sometimes combine and within the scope of their weight settle to the bottom waters and sediments. The high concentration of metals measured is noticed at stations that are in the southern part (figure 1). Indeed, most of the time, the waters of the lagoon complex flow of the North (Couffo River) to the south draining everything they carry to the sea in the South. The bad solid waste management of riparian areas, the use of lagoon banks as garbage dumps and privies were the reasons for the high concentration of these metals in sediments. A comparison of results with those on the sediments of the lagoon Ebrié (Côte d'Ivoire)[13] and the work on sediments Maghrebian lake[14-16], reveal that our lagoon complex is less contaminated by metal trace elements.

Statistical Studies: The results of the principal component analysis of trace metals by the R 2.15.3 software, show that the first two axes explain 74.63 % for all the variability of the influence of these trace metals on the lake; which is sufficient for an unbiased interpretation of results. We therefore retain the first two axes for further interpretations. The correlation analysis of the TME with the axes (table 4 and figure 9) show that zinc and lead are strongly and positively correlated with the axis 1 as opposed to cadmium. Thus, environments rich in zinc and lead are poor cadmium and vice versa. Only the copper is strongly and positively correlated with the second axis.

The projection of different sampling points in the factorial axis plane (figure 10) shows that Tokpa- Dome, Gbèzoumè and Possotomé oppose to Adjatokpa on axis 1. Guézin and Tohonou oppose to Tokpa–Dome, Gbèzoumè, Adjatokpa, Kpétou and Dékanmè on axis 2. Bopa is less enriched in those metals. It thus appears that Tokpa - Dome, Gbèzoumè and Possotomé are very rich in zinc and lead versus to Adjatokpa which is highly enriched with cadmium and vice versa. Guézin and Tohonou are very rich in copper versus Tokpa Dome, Gbèzoumè, Adjatokpa, Kpétou and Dékanmè which are weak.

In conclusion, excepting Bopa, all other sample points contain high concentrations TME studied. This could be explained by the fact that the management of solid and liquid wastes that are occasionally conveyed into the lake by runoff.

Table-4
Correlation of variables with the axis

Metals	Dim.1	Dim.2
Copper	-0.21	0.98
Zinc	0.74	0.14
Lead	0.86	0.07
Cadmium	-0.82	0.06

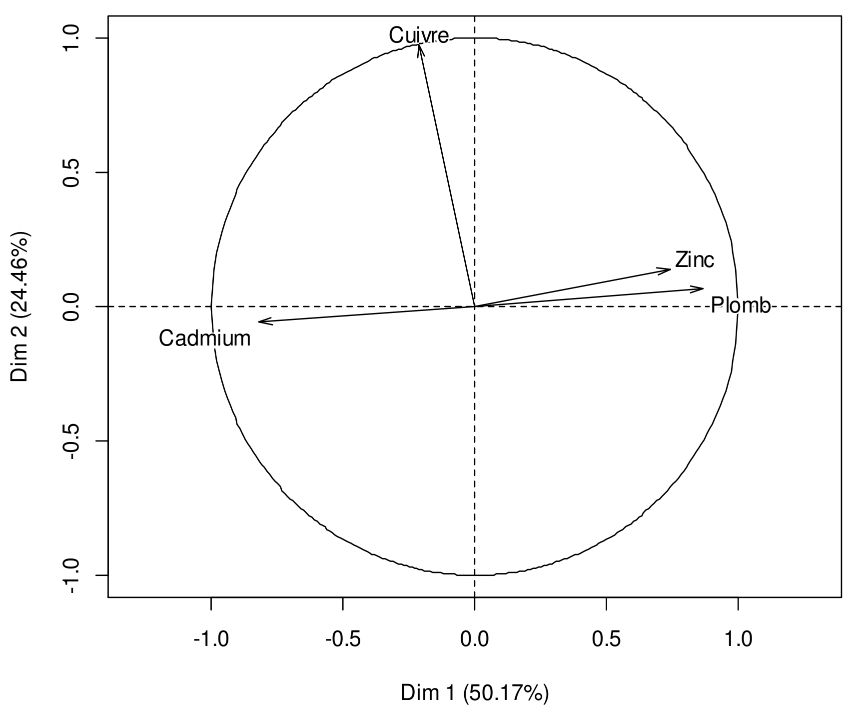

Figure-9
Correlation of TME with axis

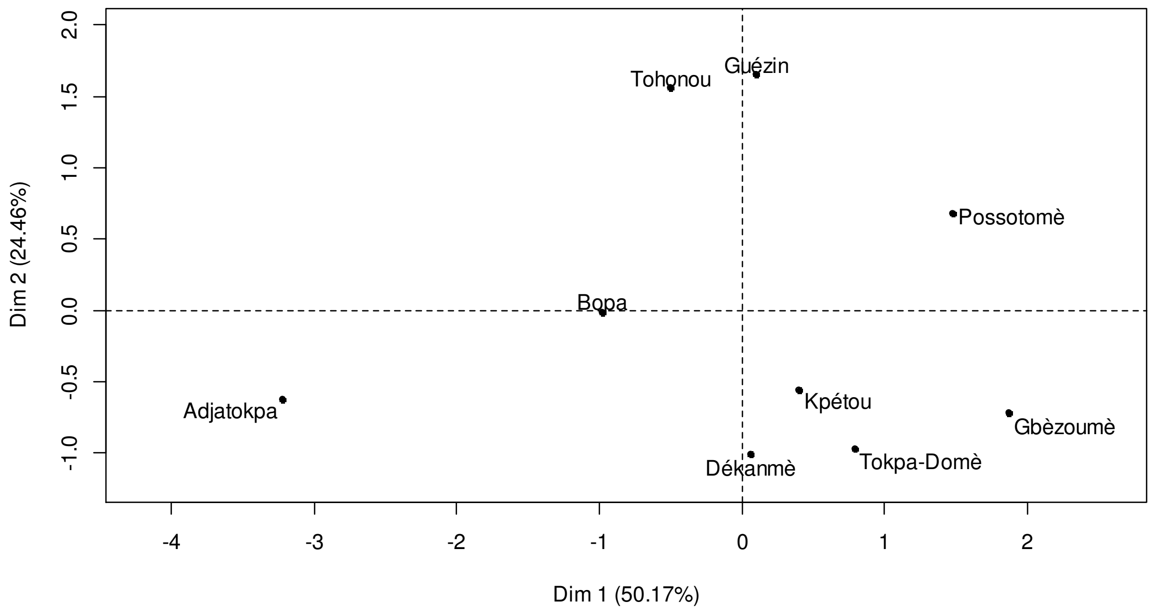

Figure-10
Projection of different sampling points in the factorial axis

Table-5
Bioaccumulation factors (BAF) of different metals

	Copper (mg/kg)	Zinc (mg/kg)	Lead (mg/kg)	Cadmium (mg/kg)
Fishs	19	10.36	0.56	0.00
Sediments	171.44	109.61	2.97	0.19
BAF	0.11	0.09	0.19	0.00

Table 5 shows the BAF of different TME inventoried. We find that the fish bioaccumulate more lead and copper than zinc and cadmium. On 100 % of copper present in the sediment, approximately 11% fall in the tissues of fish and on 100 % of lead, 19 % penetrate the flesh of fish. It thus appears that the aquatic ecosystem is in danger and in turn consumer health is threatened.

Conclusion

This study we have just completed the Aheme Lake and Lagoon of Ouidah has allowed us to have a scientific knowledge of the state of pollution by trace metals. It also help us to know the different fractions of copper metal in sediment. Policy management of wastewater and solid waste that polluate these water bodies is desirable in the management plans of neighboring municipalities.

References

1. Badahoui A., Fiogbé E.D. et Boko M., Les causes de la dégradation du lac Ahémé et ses chenaux, *Int. J. Biol. Chem. Sci.*, **4(4)**, 882-897 (**2010**)
2. Reyms-Keller A., Olson E., McGaw M., Oray C., Carlson O. and Beaty B., Effects ofheavy metals on Aedes aegypti Diptera, Culicidae) larvae, Ecotoxicol, *Environ. Saf.*, **39,** 41-47 (**1998**)
3. Lawani L., Etude de la pollution des eaux, des sédiments et des crevettes du lac Nokoué par les métaux (Pb, Cd, Cu, Zn, Fe) au Bénin. Mémoire de fin de formation pour l'obtention du diplôme d'Etudes Supérieures Spécialisées en aménagement et gestion des ressources naturelles (DESS/AGRN/UAC), Option: Aménagement rural et gestion des écosystèmes aquatiques, 94 (**2007**)
4. Houémènou H., Evaluation des déchets d'origine anthropique et leurs impacts potentiels sur les eaux du lac Nokoué. Mémoire pour l'obtention du diplôme de master en génie de l'environnement à EPAC/UAC, Bénin, 92 (**2012**)
5. Chouti W., Etude de la pollution chimique d'une lagune tropicale (eaux, sédiments, poissons) : Cas de la lagune de Porto-Novo (Sud Bénin), Thèse de doctorat à l'Université l'Université d'Abomey-Calavi au Bénin, 100 (**2011**)
6. Boucheseche C., Cremille E., Pelte T. et Pojer K., Guide technique n°7, pollution toxique et écotoxicologie : notion de base, Lyon, Agence de l'eau Rhône – Méditerranée – Corse, 83 (**2002**)

7. Eggleton E. and Thomas K. V., Areview of factors affecting the realise and bioavailability of contaminants during sediment disturbance events, *Environment International,* **30**, 973-980 (**2004**)

8. Nicolas-Simonot M.O., Fernandez Fernandez M.A. Chnevière P., Bailly M. and Grevillot G., Model for capacity variations of weak-acid and weak-base ionexchangers as a function of the ionic environment, *React.Polym,* (**17**), 39-59 (**1992**)

9. Tessier A., Campbell P.G.C. and Bisson M., Sequential extraction procedure for the speciation of particulate trace metals, *Analytical Chemistry*, **51**(**7**), 844-851 (**1979**)

10. Kanangire C. K., Effet de l'alimentaire des poisons avec Azolla sur l'écosystème agropiscicole au Rwanda. Dissertation présentée en vue de l'obtention du grade de Docteur en sciences. Faculté Universitaire Notre Dame de la Paix, Faculté des sciences. Namur-Belgique, 220 (**2001**)

11. Lamizana-Diallo M.B., Kenfach S. et Millogo-Rasolodimby J., Evaluation de la qualité physico-chimique de l'eau d'un cours d'eau temporaire du Burkina Faso – Le cas de Massili dans le Kadiogo, Sud Sciences et Tehnologies, (**16**), 23-28 (**2008**)

12. Zongo F., Contribution a l'étude du phytoplancton d'eau douce du Burkina Faso- Cas du barrage nº 3 de Ouagadougou. Thèse 3ème cycle, Université de Ouagadougou, 170 (**1993**)

13. Koffi Y., Métongo S., Trokourey A. and Yobou B., Assessment of Sediments Contamination by Heavy Metals in a Tropical Lagoon Urban Area (Ebrié Lagoon, Côte d'Ivoire), *Euro. J. Sci. Res.,* **34**(**2**), 280-289 (**2009**)

14. Ben M'Barek N., Impact des ouvrages sur l'équilibre de l'écosystème : Lac Ichkeul, Mémoire de DEA, Université de Tunis II, 97 (**1995**)

15. Ben Bouih H., Nassali H., Leblans M. et Srhiri A., Contamination en m étaux traces des sédiments du lac Fouarat (Maroc). *Afrique SCIENCE,* **01**(**1**), 109–125 (**2005**)

16. Azzaoui S., Géochimie de certains métaux lourds dans les sédiments de la lagune de Ghar el Melh (N-E, Tunisie), Mémoire de DEA, Université de Tunis II (1993) 100 (**1993**)