



Zinc toxicity and sequential extraction in water and sediments of tropical lake: A case study of Ahémé Lake in Benin

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Abstract

The presence of trace metals in surface water at concentrations above natural standards becomes a situation of increasing concern. Lake Ahémé, the second lake in Southern Benin with an area of 78km² during the dry season and 126km² during floods with a maximum depth of 2.35m did not remain on the fringe of this crucial situation. In fact, over half a century, we witness poor management of this ecosystem through activities that ensure little its ecological health. To understand this situation, water and sediment sampling work was carried out on four stations to characterize the chemical-toxicological standpoint Lake Aheme-Guezin. In order to better characterize the pollution degree of the ecosystem, we also evaluated the risk of toxicity in the water by the seeding method of Onion roots. Meanwhile, a study on the chemical speciation of zinc in sediment was carried out by the sequential extraction method of Tessier. Data processing was performed by the spreadsheet Microsoft Office Excel 2013; the collection card has been completed and digitized through the Google Earth and Arc-Gis software. Geographic coordinates were determined through Geodata conversion software. The toxicity tests results indicate a high toxicity degree in water and those of speciation gives much higher concentration standards on all the sampling points. These results show that human activities around the lake and within the complex asphyxiated by toxic metals from household waste with waste water (domestic and valves).

Keywords: Speciation, lake sediment, sequential extraction, zinc toxicity, Guezin.

Introduction

Water is a vital natural resource, essential to all life on the earth and one of the most vulnerable between natural resource. It is an economic and social development factor which has no substitute. Indeed, the sustainable development of a country, a region, a site or even an activity depends on the establishment of a good management and policy for natural resources and environmental protection. Benin has a strong potential in natural resources¹ of which 13 billion cubic meters of surface water on average per year. These natural resources are highly threatened due to the rapid growth of population and increasing of waste production.

Various anthropogenic pressures on the environment caused over the years an advanced degradation of these resources which are remarkable at all ecological perception stages (biosphere, biome, population, ecosystem)². Most of these human activities lead to accumulations of Metallic Trace Elements (MTE) in soils with a risk to the terrestrial and aquatic environment³. Among the different types of pollution (organic and/or inorganic), contamination of aquatic ecosystems by metals is quite unique and remains a serious environmental problem of increasing concern⁴ thereby the trace metals are present in all compartments of the aquatic ecosystem (water, sediment, fauna and flora)⁵.

Lake Ahémé, the second lake in Southern Benin has not remained on the sidelines of this critical situation. Studies have assessed the state of degradation of this lake following the chemistry (inorganic and organic). Most of these studies mostly based on pollution by trace metal elements while emerging link between water, sediment and fish resources. These studies have already made the determination of trace elements (mercury, lead, copper, zinc and cadmium) in sediments and the waters of Lake Ahémé taking care to highlight the risk of toxicity^{6,7}. Now the evolution of ETM in the environment is not only based on their total content, insofar as their mobility and/or bioavailability depend primarily on the forms in which they are present in the environment^{8,9}. Otherwise, it is therefore the chemical forms, it's mean the speciation of a metal, which governs its toxicological properties, its future and its transfer modes in the environment. It is therefore important to consider their volatility (organic forms), their solubility in water (varying from one metal to another but also according to different forms of a given metal) and especially the metal partition coefficient water and particles, which is crucial to both become, transport and interactions with other ecosystem compartments^{10,11}. Therefore, to estimate the risk due to long-term pollution, it is urgent to understand that presence, otherwise normal, metals in an aquatic environment is not a problem but rather the fact that they can be mobilized and reach an exposed population.

Knowledge mobilization and transfer mechanisms in this regard play an equally important role as the identification of the presence of a contaminant in a given location. This therefore means identifying how a site is hazardous (or potentially hazardous) rather than polluted. Indeed, anxious to supplement existing studies, our work is part of this overall theme and relates in particular to the study of chemical transformations of zinc in the sediments and waters of Lake Ahémé. Meanwhile a measurement approach of trace metal toxicity to aquatic organisms is assessed by sowing onion roots.

Materials and methods

Sampling: Water and surface sediments samples were collected at the most representative points Guezin (East, West, North, South) with a pearl instead of the bucket of Heckman for sediment and water sampler in regarding water. In this study, four samples of 25 liters of water were collected as well as sediments following the four stations mentioned in Table-1.

Table-1: Sites of samples of water and sediments from Lake.

Stations	Reasons choice	Coordinates
North	Region with many houses and direct contact with every kind of wastes. It allows to appreciate pollution by domestics wastes and valves	N 06°23'50.204" E 001°56'23.82"
South	This point will help to quantify and evaluate the impact of old methods used by fishermen as "acadjas" and palm branches on the ecosystem.	N 06°23'22.333" E 001°56'23.78"
East	The East point is near a mangrove just to specify its effects on the ecosystem; it will help to quantify the contributions in the water coming from mangroves.	N 06°23'12.833" E 001°56'27.64"
West	Located just under the bridge, the West point allows to appreciate and to quantify the effect of the construction of this bridge on the aquatic environment	N 06°23'18.38" E 001°56'34.789"

Methods: The developed methodology is based on two aspects of the study: the speciation of zinc and toxicity testing. To better understand environmental issues and especially the toxicity of the lake Ahémé. We used research methods in relation to the results of the Canadian study office work. Roche International made an environmental diagnostic of the waters of the South of Benin⁶.

The preparation of the sediments before their analysis is essential and provides a representative sample in which the

concentration of pollutants is close to that present in the sediment. It comprises drying in the open air in the laboratory, in order to remove moisture and prevent damage before mineralization and sieving. It is a necessary step for the removal of large solid fragments that are usually not considered as part of the sediment. The fraction that is less than 2 mm is generally retained for analysis. Sieving is dry for the sediment whose elements are greater than 80 µm and by sedimentation. After the sediment preparation phase, the samples are subjected to sequential extractions. Chemical speciation analyses of zinc were carried with Tessier technic¹² following five different fractions, namely: i. fraction (F1) characterizing the exchangeable zinc; ii. acid-soluble fraction (F2) from carbonates; iii. fraction (F3) from oxides of iron and manganese (Fe and Mn); iv. fraction (F4) bound to the organic phase; v. fraction (F5) represents the residual fraction.

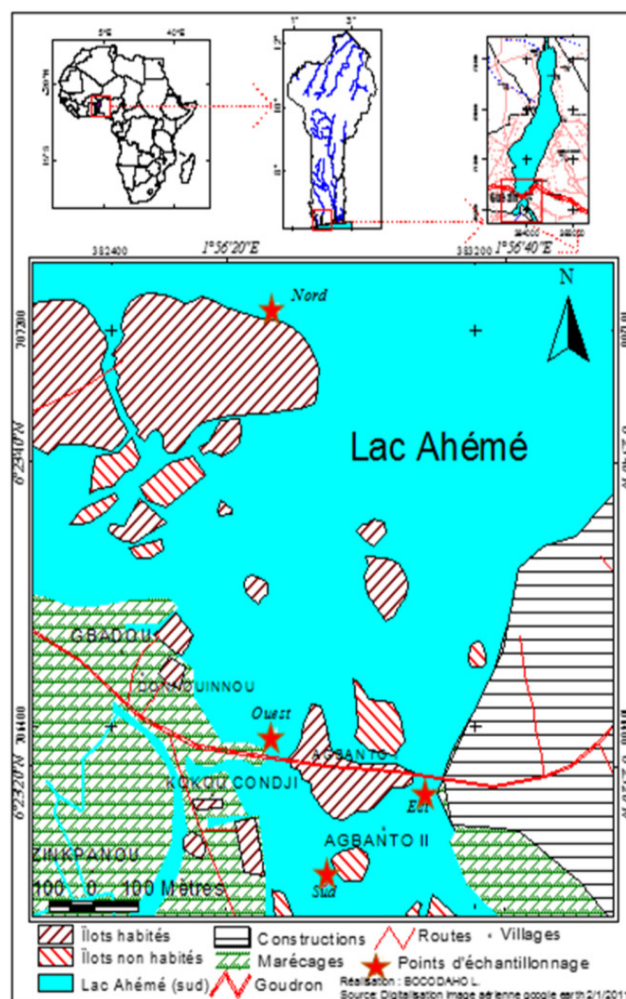


Figure-1: Location of sampling stations.

The method used for the toxicity testing is natural and is based on the inoculation of onion roots in water sampled at various proportions data. Carrying out a toxicity test requires a certain amount of distilled water and sampled water.

Procedure: (a) It has five tube of each sampling station containing respectively: i. 100% distilled water as a control; ii. 25% of lake water and 75% distilled water; iii. 50% of lake water and 50% distilled water; iv. 75% of lake water and 25% distilled water; v. 100% lake water to be analyzed; (b) Peel the roots and dry skin of the onions; (c) Cultivate an onion in each tube; (d) Change the water according to the proportions admitted every 24 hours for 72 hours;

Daily basis, there was a steady increase of onion roots under different aspects in each tube. i. After 72 hours, measure the root of each onion with the ruler; ii. The tube that has atrophied roots indicates acute toxicity.

Results and discussion

The concentration of zinc sediment is between 40.14 and 161.04 mg.kg⁻¹ with an average of 77.07 mg.kg⁻¹. Lake Aheme is subjected to metallic zinc contamination precisely at Guezin.

Analytical results of the extraction of chemical forms of zinc in the sediments of Lake Aheme-Guezin complex helped to draw histograms and graphs for all the stations studied. This shows a

fluctuating concentration following a change given by each station. The highest zinc levels are increased in the North station level in all geochemical fractions.

Table-2: Distribution of zinc in different fractions Guezin.

Chemical forms of Zinc	North	South	East	West	Average
	Weight (mg/kg) or (µg/kg)				
Exchangeable	7.9	1.2	1.24	2.24	3.145
Acid-soluble	46.84	6.88	5.52	2.48	15.43
Reducible	31.42	19.36	14.7	6.86	18.08
Oxidizable	58.42	11.37	10.32	3.6	20.93
Residual	16.46	14.2	22.32	24.69	19.48
Total of Zn	161.04	53.01	54.1	40.14	77.07

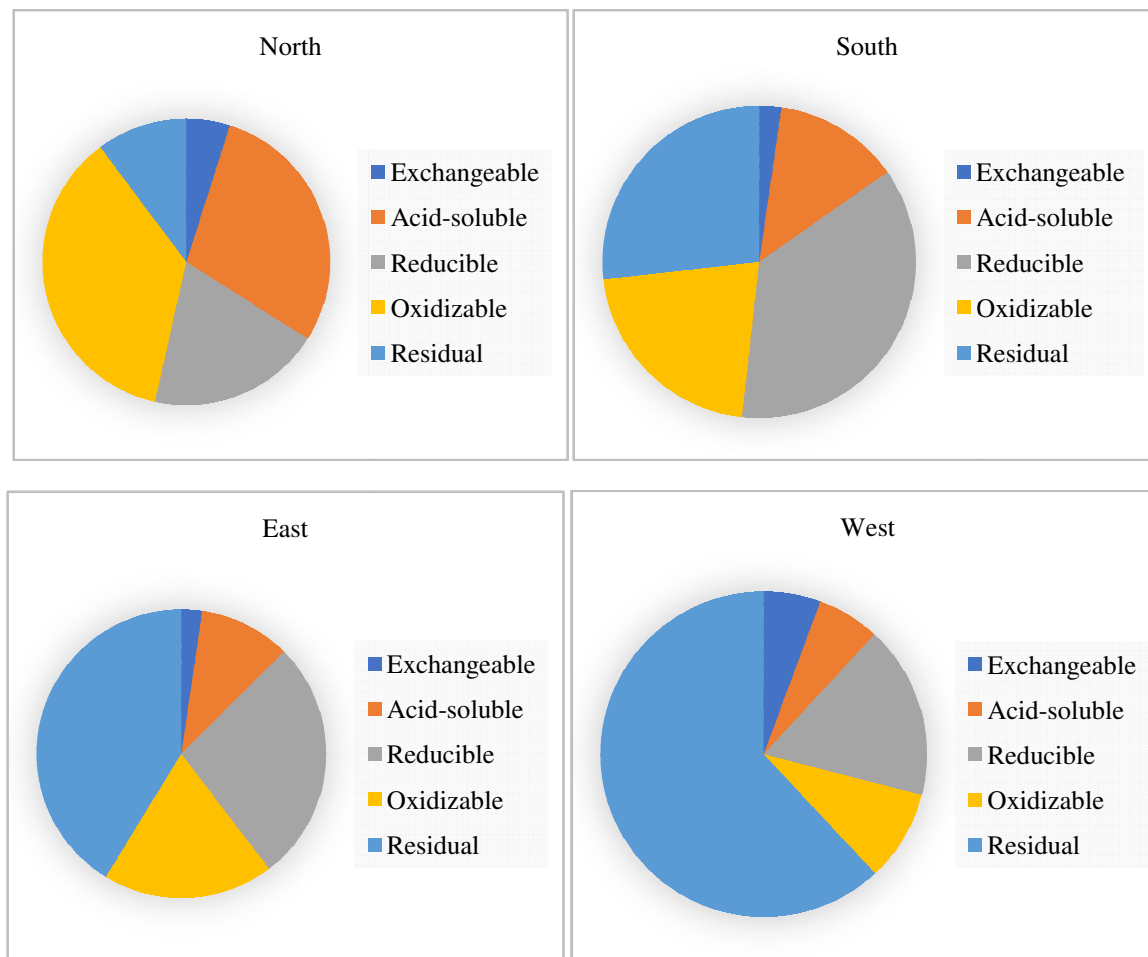


Figure-2: Distribution of Zinc chemical forms in sediments following each station.

Zinc is much more concentrated in the North in all chemical fractions for a total of 161. mg.kg⁻¹ (much higher than the standards). But, at the West Station, zinc has a low concentration. In fact, most of the population concentrated at the North Station, and then the high zinc content observed at this station is due to human activities that generate domestic waste, domestic sewage, latrine and others. Unlike in the West where the population is almost absent, the lowest concentration of zinc levels was noticed in almost all fractions.

Table-3: Percentage by mass zinc extracts and Risk Assessment Code.

Different fractions (%)	North	South	East	West
Exchangeable	4.91	2.26	2.29	5.58
Acid-soluble	29.08	12.98	10.2	6.18
Reductible	19.51	36.52	27.17	17.09
Oxydable	36.28	21.45	19.08	8.97
Residual	10.22	26.79	41.26	62.18
RAC	33.99	15.24	12.49	11.76

RAC = %Exchangeable +%Acid-soluble.

The North station is at high risk^{13,14} and all the other three stations (South, East, West) medium risk (between 11.8 and 18.4). In sum, the results of our research work in the area of the

lagoon complex Aheme-Guezin reveal zinc levels above the limit of detection because of the status of semi-lake village of the zone. This is largely due to the poor solid and liquid waste management without forgetting domestic and industrial wastewater generated by the lake and surrounding population without forgetting the contribution of thermal water plant Possotome^{7,15}.

Table-4: Onions roots lengths (cm) Average in waters at Guezin.

	0%	25%	50%	75%	100%
North	4.8	3.67	3.57	2.63	2.42
South	4.76	3.55	3.27	2.45	2.29
East	4.75	4	2.2	2	1.69
West	4.94	3.66	2.90	2.66	2.33
Average	4.82	3.72	2.99	2.44	2.18

Analytical results for the toxicity test gave an average of 4.82 cm to 2.18 cm and distilled water for the lake. There is a progressive decreasing of the root lengths as the concentration of the zinc in waters of the lake increases at each station (it means 4.94 cm at 0% to 1.69cm to 100 %). This decrease is due to the presence of pollutants in the lake that inhibit root growth. This testifies to the advanced state of the lake toxicity.

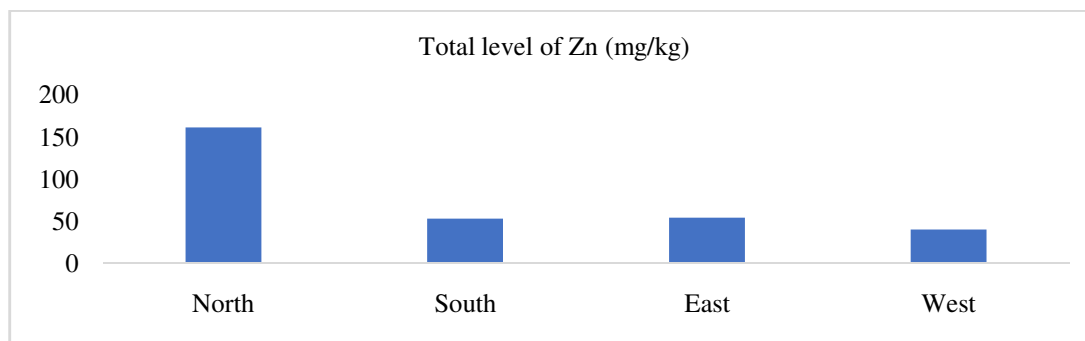


Figure-3: Total concentration of zinc in the sediments at each station.

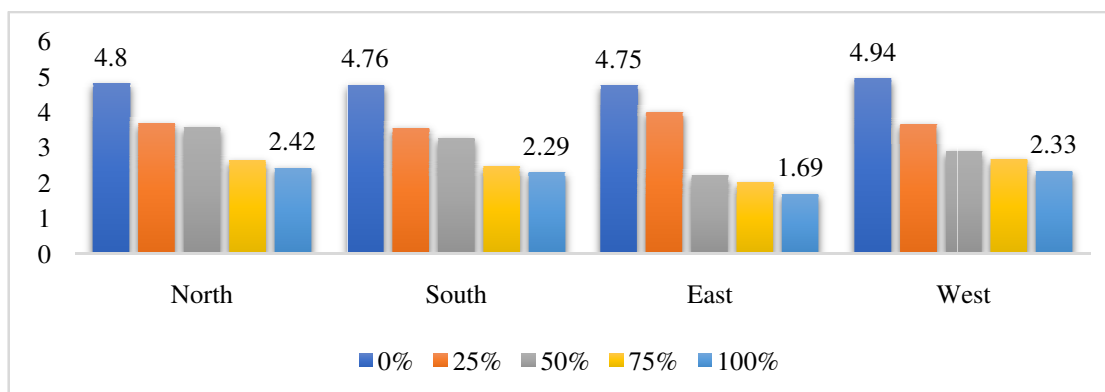


Figure 4: Length of onion roots (proportions 0% to 100%).

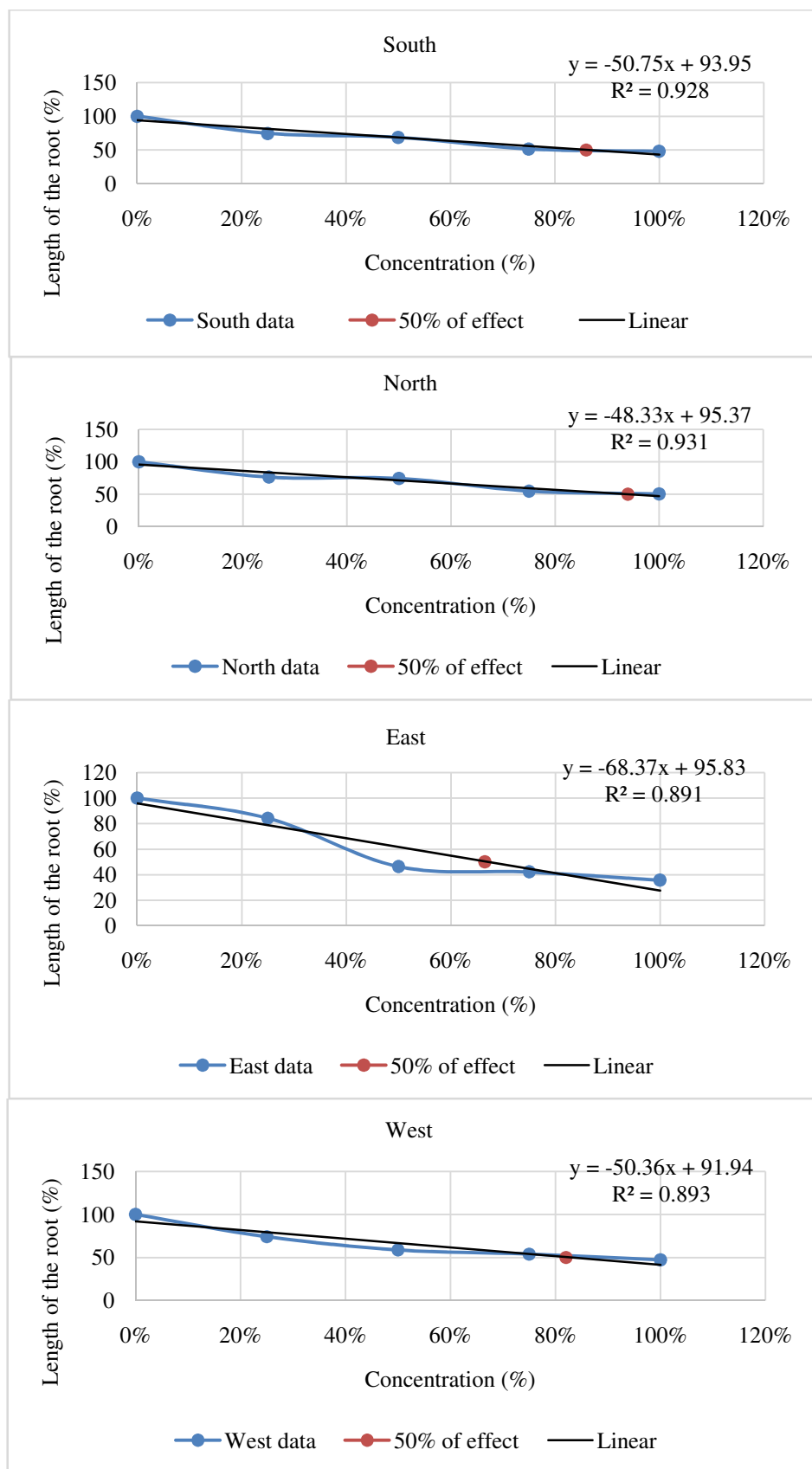


Figure-5: Dose-Reponses curves / Cytotoxicity test on the *Allium cepa*.

The Table-5 shows us that the waters of the Ahémé lake in GUEZIN present on the whole a level of toxicity in the least measures with a concentration efficient $CE_{50} = 81.5\%$. Nevertheless, we notice that these waters are more toxic to the East with $CE_{50} = 66.5\%$. Then come the toxicity in the west and to the South with respectively $CE_{50} = 82\%$ and $CE_{50} = 86\%$. The North of the Ahémé lake remains the less toxic site with the test of cytotoxicity on the *Allium cepa* ($CE_{50} = 94\%$). These results can be accepted with a coefficient of determination of 89 to 95%, what gives us elevated confidence degree.

Table-5: Classification of toxicity level in the waters of the Ahémé lake at GUEZIN.

	Concentration efficient: CE_{50} (%)	Coefficient of determination: R^2 (%)
East	66,5	89
West	82	89
South	86	93
North	94	93

Test of justification of the toxicity raised to the Eastern: i. The pH of water to the East is weaker than the one of the other sites that stretches toward the basicity. We can first underline that the weak value of the pH compared to the other, influence the thrust of the roots of onions. Mention also that it is not about an acidic pH. ii. The oxygen dissolved in the waters of this site is weak in relation to the other what favors manages the roots of onions. iii. From the potential of oxydoreduction, we can say that the waters of the lake are reducing. Nevertheless, the East is more oxidizer that the other sites. One will attend the reactions of reductions more in this zone of the lake that will tend to draw the oxygen of the middle. iv. The values raised of turbidity and MES are recorded at the Eastern what brings us to say that the waters of this site are more troubled and contain more chemical elements than the other sites, enter other the elements metallic traces. v. Seen the results on the speciation of zinc in the sediments of the lake, we notice that the strong quantity of acidosoluble zinc (fraction easily mobilizable in water) was record at the North. vi. We can deduct that the elements metallic traces that influenced the roots of onions more are apart from zinc and have not been taken in account in this survey.

Discussion: Solid and liquid wastes produced by human activities are dumped anyhow into the environment, loaded with scrap metal and / or chemical¹⁶⁻¹⁸. These trace metals leach into aquatic ecosystems and are a huge danger to aquatic organisms. For better protection of the aquatic ecosystem, standards not to exceed in the river sediments were laid down for trace metals by some States. The mean value obtained during this study is 77.07 mg.kg^{-1} . This value is lower than the Canadian Standards but upper than those obtained in sediments of Konkouré river

esturayin Guinea²⁰. In sediments, zinc is unevenly distributed along each geochemical fraction with high affinity for oxidizable fractions (27.15%), residual (25.28%, reducible (23.46%), acid-soluble (20%) and a very low affinity for the exchangeable fraction (4.08%). In the scientific literature, the normal concentration of zinc in clay sediments is of the order of 80 to 120 mg.kg^{-1} p.s. Zinc concentrations are high in the sandy clay sediments near releases²¹. Their distribution corresponds to the nature of the sediment with clay content and organic matter plays a crucial role. Moreover, Sericano and Pucci²² found that zinc is associated with sandy facies exposed to direct discharges. This high concentration of zinc in the sediments resulting from poor management of waste (solid and liquid) by the population and the use of biocides (pesticides, herbicides), fertilizers, composts by farmers around the lake by runoff, are found in the water retention²³.

Furthermore, this metal is assimilated by phytoplankton which grazed by herbivorous zooplankton is transferred mainly in the sediment. Hence our first conclusion is clear. The effect of zinc contamination linked to human activities. Zinc therefore is a threat to the life of aquatic organisms and human health. Referring to zinc concentrations in sediments on the north station ($161.04 \text{ mg.kg}^{-1}$), well above the norm, it follows that station that covers most of the population is heavily polluted by zinc with a high risk. Finally, reading the contamination indices of zinc revealed a higher rating to acceptable standards and class the complex lagoon Aheme-Guezin as a polluted area of class "B"²⁴. Observing the distribution of zinc contamination of the index values found in the lake leads to the conclusion that the surface sediment of the lake is heavily polluted by zinc with a high risk mainly at Nord station.

Meanwhile, the values from the toxicity test revealed atrophy at the root level in the lake compared to the roots of onions planted in distilled water; suggesting a high toxicity. This high risk of toxicity in the lake at different stations of Guezin suggests that the presence of pollutants in waters that inhibit root growth by toxic effects²⁵. In summary, this study shows that the waters and sediments of Lake Aheme-Guezin are contaminated with trace metals especially in zinc at the North station which is the living place of the majority of the study area population. Human activities around the lake and within the complex asphyxiated by household waste with waste water (domestic and valves).

Conclusion

Surface water are the primary vector of contamination by trace metals. These releases by various seep into the water and contaminate three biological matrices (water, sediment and aquatic) ecosystem. Over the time, these metallic elements transferred in surface sediments are partly metabolized by living aquatic organisms and circulated in the food chain.

In Benin, pollution from trace metals is an important factor for destruction of the ecosystem. The results of this study show that

the water and sediments of the lake Ahémé do not meet almost all acceptable standards for aquatic life. Ahémé Lake is under the influence of metal pollution and presents a high risk of toxicity. Likely sources of zinc in the lake are anthropogenic: the release of the thermal water plant Possotomè, solid and liquid waste directly communicating with the lake, not to mention the contributions of the Sea, the Channel and Aho Lagoon of Ouidah. All these actions lead to the greatest threat to the environment and the survival of the aquatic ecosystem. A national individual and collective awareness, followed by programs for wastes managements prove indispensable for the protection of the environment and preservation of our natural resources particularly Ahémé Lake is important for sustainable management of the Lake.

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