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Case Study

Chemical characterization of metallic trace elements in aquatic plants: A case study of some plants in Porto Novo lagoon, South Benin

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Abstract

The lagoon of Porto-Novo is located in southern part of the republic of Benin. It covers average 30 km^2 in dry season and 50 km^{2}in wet season and represents the outlet which through the waters of the Ouémé River flows into the Atlantic Ocean by the Lagos Channel. The main objective of this study is to describe spatial distribution of copper and zinc in sediments but especially in aquatic plants in order to evaluate bioconcentration and to provide further information on heavy pollution by copper and zinc in the lagoon. Sediments, water and six aquatic plants (Typha domingensis, Eichhornia crassipes, Ipomea aquatica, Ludwigia abyssinica, Nymphaea lotus and Cyperus papyrus) samples were collectedat seven sites in the lagoon. The chemical analysis of the two heavy metals (Cu and Zn) was done using standardized spectrophotometer methods. The results were compared to standards and show that the concentrations in the lagoon exceed the recommended values. The pollution should have anthropogenic sources and need to be monitored to avoid damage to ecosystem of this important surface water of Benin.

Keywords: *Copper, zinc, pollution, bioaccumulation, biomonitoring*.

Introduction

Metal pollution is a global problem and concerns all regions with maintaining their high-quality water heritage[1]. Contamination of aquatic ecosystems by metals remains a serious environmental problem[2-4]. The problems associated with metal contamination were first identified in the industrially advanced countries because of their larger industrial spills and especially as a result of accidents due to mercury and cadmium pollution in Sweden and in Japan. The Africa case is more worrying because of the vulnerability of states that lack financial and sometimes technical means that would require the restoration of a polluted aquatic site. Metals are present in all compartments of the aquatic ecosystem (water, sediment, fauna and flora)[5]. The lagoon of Porto-Novo (southern Benin) regularly receives domestic liquid waste from the population through water collectors. It is an important source of fish products. Indeed, from the point of view of annual fish production, the Porto-Novo lagoon represents the third productive water body in southern Benin after Lake Nokoué and Lake Ahémé. It is a waterway very practiced by the populations of the village lake of the Aguégués and others.

Previous studies have shown that the waters and sediments of the lagoon are polluted by the Metallic Traces Elements (MTE)[6]. However, the literature searches do not reveal any studies relating to the use of aquatic plants to ensure a biomonitoring of the metal pollution of the Porto-Novo lagoon and the waters of Benin in general. In our study, we studied six (06) different aquatic plants species (*Typha domingensis, Eichhornia crassipes, Ipomea aquatica, Ludwigia abyssinica, Nymphaea lotus and Cyperus papyrus*), and sediment and water samples are collected at seven (07) sites on the lagoon.

The use of aquatic plants as pollution bioindicators, particularly, is studied by several researchers[7-9]. As results, many studies report that the use of plants for the removal of metals from contaminated sites[10-13]. But a few has focused on copper and zinc in lagoon of Porto-Novo, reason why we choose to study their accumulation in different components of this ecosystems. In fact, aquatic macrophytes have a certain ability to accumulate metals within their tissues (roots, stem, and leaves). Thus, there are an important link between trace metallic element and soil/ sediment[14].

The present study aims mainly to describe spatial distribution of copper and zinc in aquatic plants, sediments and water in order to provide in their concentration in water, sediment and plant components.

Material and methods

Sample collection: We carried out a site visit before the sampling campaign A total of seven (07) sites were chosen based on the specific criteria describe in Table-1 for each site., water, sediment and aquatic plants were collected and laboratory analysis were done to determine their copper and zinc concentration in plants, water and sediments. The criteria are described in the Table-1. The Figure-1 shows the distribution sampling sites map.

Determination of copper and zinc concentration in samples: Copper and zinc concentration in the water samples were determined using a colorimetric assay based on an atomic absorption spectrophotometer. The method used to determine the MTE concentration in water is the same for determining in distillates (sediments and plants after mineralization). Copper was determined by the Bicinchroninate method and zinc by the Zincover method. The method used for sediment mineralization is that of standard NF X31-147 and that used for the mineralization of plants is that of the NF standard EN ISO 15886. The Table-2 provides a summary of the mineralization of sediments and aquatic plants.

The analytical methods trace metal quantification in both sediment and plants are summarize in this chart represented by Figure-2.

Results and discussion

Physico-chemical analyzes: Table-3 shows the results of the physico-chemical analyzes carried out on the sampling sites.

Table-1: The different sampling sites.

Site	Name	Reasons of choice	Location
Site 1	Bouédomey center	Located in the middle of the lagoon this point constituted a source water supply of populations Aguégués, its waters are never salted according to the words of residents but rich in mercury and zinc from previous studies.	N06°29'81.6'' E002°34'22.1''
Site 2	Bouédomey 100m to the North	to the North To see the variation towards the North	N06°29'84.1'' E002°34'24.0''
Site 3	Bouédomey 100m towards the South	To see the variation towards the South	N06°29'77.8'' E002°34'20.5''
Site 4	Bouédomey 200m to the South	To see the variation towards the South	N06°29'75.9'' E002°34'19.5''
Site 5	The pier of Djassin	It will allow appreciating the influence of the transports of the goods and the people who leave this point towards the lacustrine village of Aguégués.	N06°28'38.1'' E002°35'42.3''
Site 6	Hotel Beaurivage	This is a resort located on the edge of the lagoon.	N06°28'22.3'' E002°36'23.6''
Site 7	Customs Tokpa	It allows measuring the contribution of the site of the National Assembly of Porto-Novo.	N06°27'94.5'' E002°37'42.6''

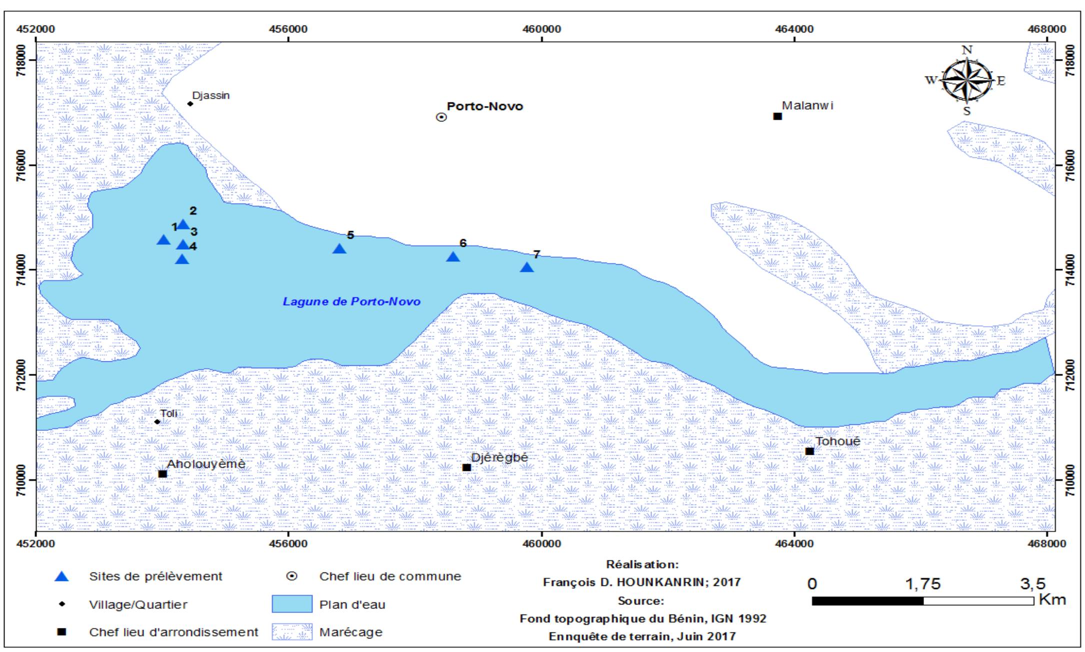

Figure-1: Distribution map of the sampling sites on the lagoon.

Table-2: Summary of Sediment and Plant Mineralization.

Samples	Quantity (g)	Regale water (ml)	Hydrochloric acid (HCl) in (ml)	Nitric acid (HNO_3) in (ml)	Mineralization temperature in (°C)	Mineralization time in (mn)
Sediment	0,5	8	6	2	95	75
Plant	0,5	10	7,5	2,5	100	60

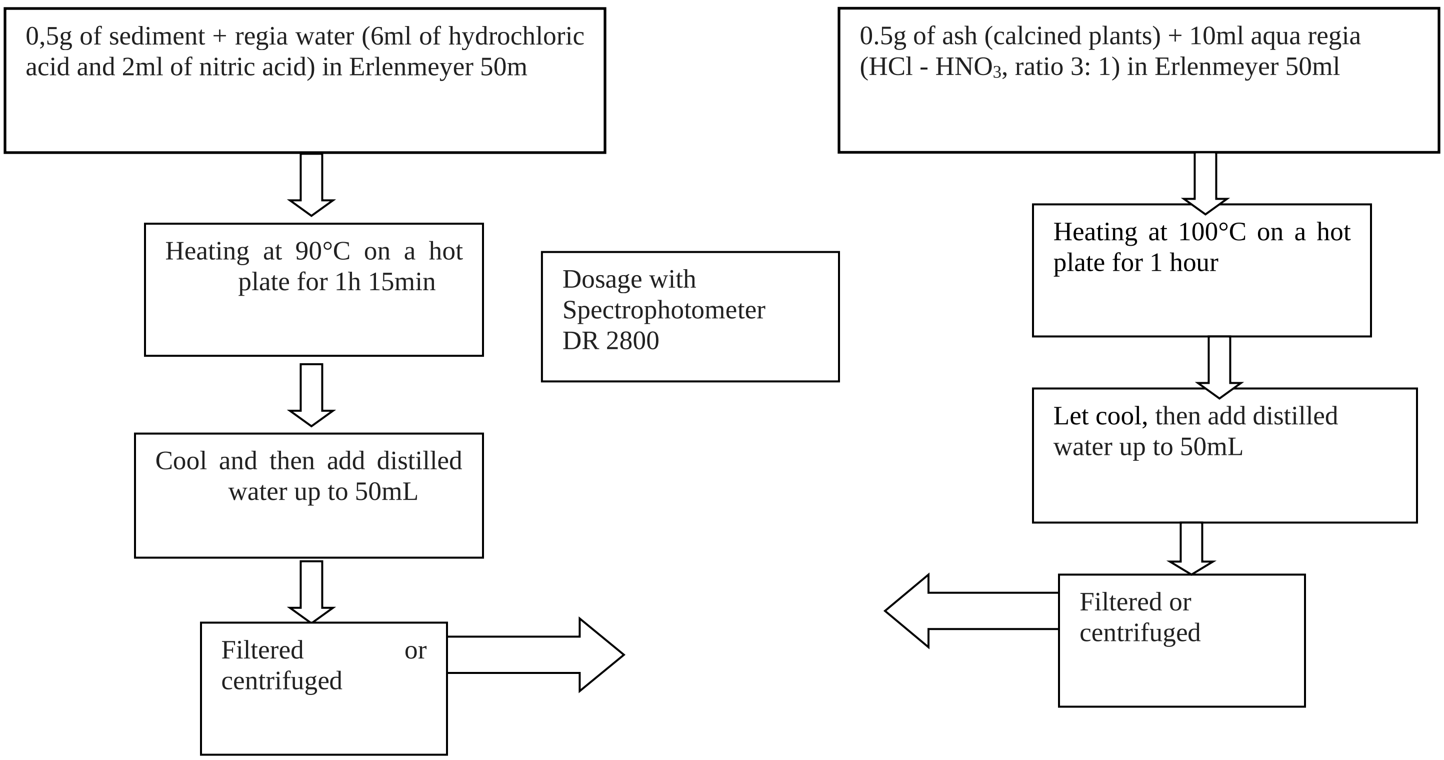

Figure-2: Trace metals measurements in sediments and plants methods chart.

Table-3: Physico-chemical analysis results of the waters sampled on the Porto-Novo lagoon.

Water	Temperature (°C)	pH	Conductivity (µs/cm)	TDS (mg/L)	Salinity (mg/L)	Redox potential (mv)
E1	27,3	5,9	67,9	68	00	94,5
E2	27,2	5,5	90,6	91	00	85,7
E3	27,3	5,3	79,1	79	00	95,7
E4	27,4	5,3	199,8	200	00	96,4
E5	27,7	5,2	205,8	212,6	00	107,2
E6	27,3	5,2	190,4	205	00	104,1
E7	27,1	5,4	154,3	154	00	88,4
Average	27,3	5,4	141,1	144,2	00	96

The pH of the waters of the Porto-Novo lagoon is between 5.2 and 5.9 with an average of 5.4. These values show acidic character of the waters. As conductivity is concerned the values range is between 67.9 and 205.8µs/cm with an average of 141.1 µs/cm. The positive values observed for the oxidation-reduction potential at all the sampling stations (85.7 to 107.2mv) indicate that the medium is oxidizing.

Analysis of trace metallic elements (copper and zinc): The results of the determination of copper and zinc in the waters of the Porto-Novo lagoon are shown in Figure-3.

The copper values obtained in the waters of the Porto-Novo lagoon are generally low and range from 0.001 to 0.006mg/L. Zinc values obtained in the waters of the Porto-Novo lagoon range from 0.05 to 0.13mg/L. The results of copper and zinc distribution in sediments taken from Porto-Novo lagoon are shown in Figure-4.

After the analyzes, we notice that the copper concentration is more concentrated in the studied sediments with an average content equal to 2.84mg/g than the zinc with an average content equal to 0.58mg/g.

Measured metal concentrations in sediments range from 2.10 mg/g to 4.55mg/g for copper and 0.45mg/g to 0.70mg/g for zinc. The highest value of copper concentration was found in the S3 sediment, while the lowest content was recorded in the S1 sediment and the highest zinc content was found in the S1 sediment while the minimum content was recorded in the S1 sediment S7.

The results of the copper and zinc determination in aquatic plants taken from the Porto-Novo lagoon are presented in Table-4.

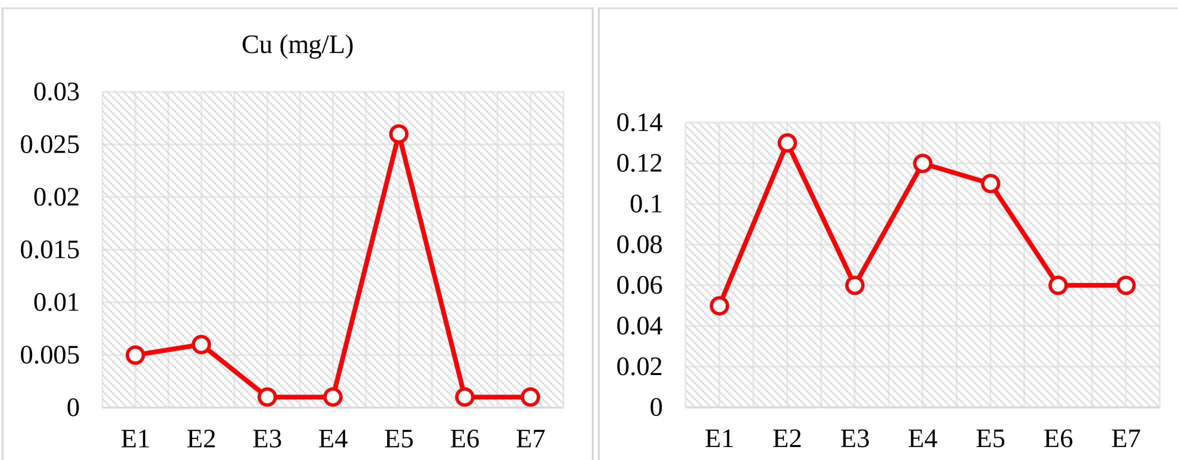

Figure-3: Copper and zinc contents in the waters of the Porto Novo lagoon.

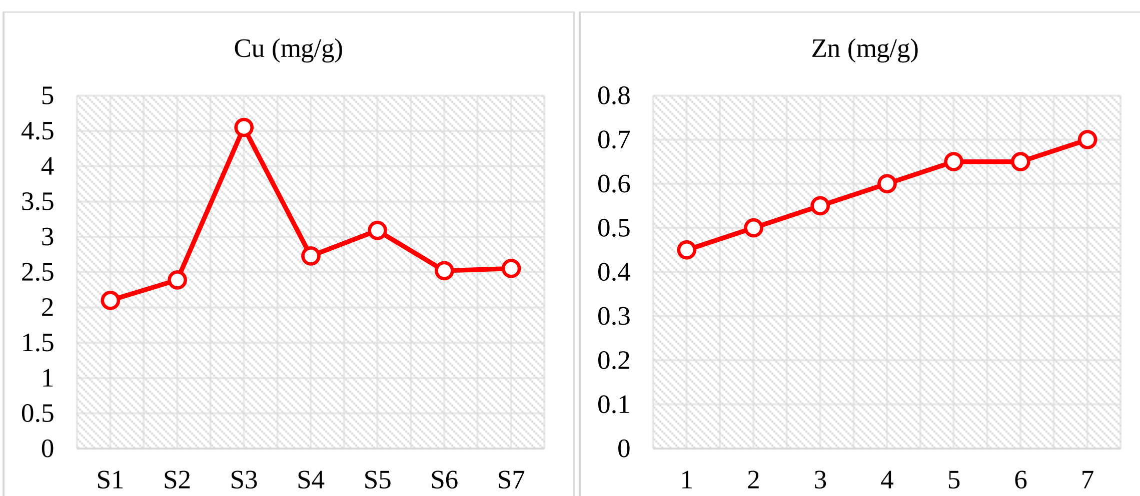

Figure-4: Copper and zinc contents in the sediments of the Porto Novo lagoon.

Table-4*:* Copper and zinc contents in aquatic plants of the Porto-Novo lagoon.

Parameters	Methods used	Samples of aquatic plants							Average
		P_1	P_2	P_3	P_4	P_5	P_6	P_7	
		Typha domingensis sp	*Eichhornia crassipes sp*	*Ipomoea aquatica sp*	*Cyperus papyrus sp*	*Ludwigia abyssinica sp*	*Nymphea lotus sp*	*Eichhornia crassipes sp*	
Copper (mg/g)	Bicinchroninate method	1,73	1,79	2,93	2,92	2,07	1,96	2,14	2,22
Zinc (mg/g)	Zincover method	0,60	0,80	0,70	0,80	0,50	0,50	0,55	0,54

Copper is more concentrated in the aquatic plants studied with an average content equal to 2.22mg/g than zinc with an average content equal to 0.63mg/g. The levels measured in plants vary between 1.73mg/g and 2.93mg/g for copper and between 0.50 mg/g and 0.80mg/g for zinc. The highest copper content was found in the P4 plant while the minimum level was recorded in the P1 plant. The highest zinc content was found in plants P2 and P4 while the minimum level was recorded in plants P5 and P6.

Bioconcentration factors is defined as the ratio of metal concentrations in plants and sediments for rooted species. The formula of bioconcentration factor is defined as:

$$FBC_{en} = \frac{[TM]_{en}}{[TM]_{sed}}$$

and ratios of metal concentrations in plants and water for floating species $FBC_{FL} = \frac{[\boldsymbol{TM}]_{\boldsymbol{FL}}}{[\boldsymbol{TM}]_{\boldsymbol{water}}}$

Where, TM is trace metal concentration

The results of bioconcentration factors are presented in Tables-5 and 6.

Table-5: Bioconcentration Factors (BCF) for copper and zinc for Ingrained Species Relative to Sediment.

Sampling sites	Species	Cu	Zn
Bouédomey center	*Typha domingensis*	0,82	1,33
Bouédomey 200m to the south	*Cyperus papyrus*	1,07	1,33
Hotel Beaurivage	*Nymphaea lotus*	0,78	0,77

For plants rooted species, these bioconcentration factors are varying from 0.78 to 1.07 for copper and from 0.77 to 1.33 for zinc. The highest bioconcentration factors were observed in the case of zinc accumulation by *Typha domingensis* and *Cyperus papyrus sp* and in the case of Cu accumulation by *Cyperus papyrus*. The lowest concentrations were observed for zinc and copper accumulation by *Nymphaea lotus*. The bioconcentration factor is presented in the Table-6.

Table-6: Bioconcentration Factors (BCF) for copper and zinc for floating plants species.

Sampling sites	Species	Cu	Zn
Bouédomey 100m to the North	*Eichhornia crassipes,*	298,33	6,15
Bouédomey 100m to the south	*Ipomoea aquatica*	2930	13,33
The jetty of Djassin	*Ludwigia abyssinica*	79,62	4,54
Customs Tokpa	*Eichhornia crassipes*	2140	9,16

For floating vegetables species, the bioconcentration factors range from 79.62 to 2930 for copper and from 4.54 to 13.33 for zinc. The highest bioconcentration factors were observed in the case of zinc accumulation as for copper by *Ipomoea aquatic*. *Eichhornia crassipes*, comes second and *Ludwigia abyssinica* thereafter.

Discussion: Aquatic plants pollution in Africa is often linked to population growth, which leads to increased anthropogenic activities resulting from different discharges. The bioavailability of MTE in sediments, aquatic plants and their mobility in water bodies increases the risks for aquatic organisms that live in these water bodies as well as for the man in charge of the food chain. It is therefore important to monitor water bodies by measuring chemical pollution parameters.

Water temperature plays an important role in the aquatic environment, for example the oxygen solubility of oxygen necessary for the equilibrium of aquatic life. It affects the chemical and biochemical reactions, the development and growth of living organisms in water, particularly microorganisms. It also influences the metabolic activity of aquatic organisms.

The average value of the recorded temperature recorded in Porto- Novo lagoon is 27.3 this value is slightly lower than that found (29°C) in 2011[6] on the same lagoon and in 2017 in the coastal lagoon (30°C)[15]; this decreasing may be due to the sampling time. This value does not disrupt the growth of aquatic plants species as it is in the range of 24°C to 35°C [16].

The pH is a parameter which gives information on the nature of water by the concentration of the H^+ ion. The average pH value of the waters of the Porto Novo lagoon is 5.4; this value is lower than that of natural waters and that found in 2011 on the same lagoon (6.28)[6].

The conductivity measurement is a good element to appreciate the degree of water mineralization. The average conductivity value recorded at the Porto-Novo lagoon is 141.1µS/cm so the water is weakly mineralized.

Previous studies have shown that the water and sediments of the Porto-Novo lagoon are polluted by metals including iron, manganese, chromium, lead, cadmium and mercury[17,18]. To these studies is added the present work showing that the Porto-Novo lagoon has an unusual concentration of copper and zinc in the sediments. For example, metallic trace element concentrations in lagoon waters range from 0.055mg/L to 0.13 mg/L for zinc; these values are lower than those found in 2011[6] in the same lagoon and in 2017 on the coastal lagoon (0.12 mg/L to 0.2mg/L)[15]. The copper concentration values obtained range from 0.001 to 0.006mg/L. This value is lower than those recorded in Sosiani River[19].

The average sediment MTE is 2840mg/kg for copper and 580 mg/kg for zinc. This value is higher than that found in 2010 in the same lagoon[18] and in 2017 in coastal lagoon (27.34mg/kg for copper and 64.64mg/kg for zinc)[15], in Ahémé Lake (sediment zinc concentrations areranged from 40.14mg/kg to 161.045mg/kg)[20]. According to the French recommendations for sediments quality of protection of aquatic life species, the maximum permissible concentrations for copper and zinc in sediments are 26 mg/kg and 88 mg/kg [21], respectively, the sediments of the Porto-Novo Lagoon are polluted by TME (copper and zinc). This confirms the research results of Chouti[6], which showed that the sediments of the lagoon are polluted by metals. This would be due to the presence of waste, the strong anthropic pressure on the resource, the installation of the “acadjas” and alsothe use of not suitable equipment for fishing.

From the results, it appears that copper is easily bioaccumulable by aquatic plants species studied than zinc with an average of 2.22mg/g compared to 0.64mg/g. This confirms the work of Marschner stating that plants can accumulate copper up to 400000mg/g dry matter in their root while the zinc content varies between 1 and 400mg/g dry matter in plants[22]. The bioconcentration factors (BCF) of floating species also have significantly higher values for copper than for zinc, thus supporting these results. On the other hand, for the rooted plants species, this factor is high for zinc than for copper, which allows us to affirm that the transport of zinc towards the plants accelerates more through the roots. Since zinc is absorbed by zinc influx transporters[23], we deduce that these influxes are more numerous in the roots of plant species.

These results confirm numerous studies already carried out around the world, including that of Ladislas revealing the ability of aquatic plants to accumulate metals in their tissues[24]. Then a self-purification of the lagoon would be possible by these plants. They can also tell us about the level of pollution of water bodies by metals, so they are bioindicators of metal pollution.

The various floating aquatic species sampled in the lagoon such as *Eichhornia crassipes Ipomoea aquatic sp* and *Ludwigia abyssinica* have a large capacity of accumulation of copper and zinc in the water column than rooted species such as *Nymphaea lotus sp*, *Typha domingensis sp and Cyperus papyrus* in sediments. The accumulation capacity of these floating plants for copper is greater than that for zinc and is close to rooted plants. These floating aquatic plants are therefore a good bioindicator of metallic contamination while at the same time having a high phyto-purifying power and can also be used to trap more copper than zinc in the water column. The bioindicator of metallic pollution of these plants has already been demonstrated[25-29].

Conclusion

The Porto-Novo lagoon is under the influence of metallic trace element pollution including copper and zinc, both in the water column and in the sediments. In this work, we show that of *Eichhornia crassipes, Ipomoea aquatic sp and Ludwigia abyssinica* can be used as complementary as phytopremediation water plants treatment of lakes and lagoons. Large fluctuations in metal pollution levels can also be observed if the hydrodynamic conditions changes in the lagoon. Given the various uses of public utility offered by the Porto-Novo lagoon, it is therefore essential to adopt a policy of control, monitoring and remediation of metallic pollution in these waters. This research work can help policy-makers to define strategies for sustainable management of the lagoon. Also awareness is necessary to populations which use ecological services of the lagoon.

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