



Assessment of heavy metals contamination in sediments at the lake of Ahémé in southern of Benin (West Africa)

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Abstract

This research is carried out in order to assess the pollution level of metal in the sediments from the lake of Ahémé. The physico-chemical parameters (pH, KCl , total organic matter, cation exchange capacity) and heavy metal concentrations (Fe, Zn, As, Pb and Cd) of surface sediments deduced from fourteen stations during two seasons has been measured by the absorption spectrophotometer DR 2800. The Enrichment Factor (FE) and the index of geo-accumulation (Igeo) methods is used to assess the led origins and its contamination of the sediments. The results show that the quantities of Zn, Pb and Cd are higher according to the GESAMP standards for surface sediments. The FE and the Igeo show that the Cd is the most enriched of all the elements studied and reveal a very high contamination in sediments of all the sampled stations during the two periods. The metal elements are predominant in the lake and from the anthropogenic sources.

1. Introduction

The coastal hydrosystems such as the Lakes, the estuaries and the lagoons, are nowadays submitted to high anthropogenic pressures, especially urbanization, tourism, agriculture, fishing, industrial expansion and mining exploitation [1]. These activities lead to imbalance of the ecosystems and generate polluting elements that affect the quality of frail and precious areas.

Among these polluting substances, the heavy metals are considered as dangerous for the aquatic environment, due to their persistence and their trend to the bioaccumulation of the aquatic organisms [2]. Some heavy metals like the iron and the zinc are necessary to the growing and the well-being of the living organisms, including human being. They have toxic effects when the organisms are exposed to higher level of concentration than what is normally required. Other elements like lead, cadmium, arsenic are not necessary to the metabolic activities and reveal a poor measure of toxic properties [3].

The charge of metallic trace elements in the coastal hydrosystems gains in these last years an increasing interest and a high concern. The behavior of these elements in lagoon area has broadly been discussed by scientists [4]. The aquatic ecosystems have a very important biological interest as they constitute shelter and vital feeding ground for migratory birds and a breeding ground for the fishes as well [4].

The Lake of Ahémé, one of the largest surface water in Benin, is registered for Ramsar 1017 site because of its extraordinary assets are used not only for its wealth in halieutic resources but also for tourism and commercial transactions [5]. Thus, it abounds of a variety of halieutic species (fishes, crabs, shrimps...) and constitutes an important water reserve for the hydric uses of the surrounding people.

Since several years, the quality of the Lake waters has serious been spoiled, result of the discharge of some untreated pollutants in this Lake [6-7]. Firstly, these discharges come from different sources whose agricultural activities like cash crop (peanut, palm tree, cotton, etc.) in the north of the basin, the culture of cereal, tubers (maize, rice, cassava, ...) in the south of the basin, and the market gardening (tomato, okra, eggplant, carrot, etc.)

developed in these sloping [6]. These agricultural activities require important quantity of fertilizer and pesticides responsible of the water enrichment in nutritive elements (zinc, phosphorus) and in heavy metals [5, 6, 8]. Secondly, the rejections results from the mismanagement of the solid and liquid wastes related to the fast growth of the waterside people [7]. These wastes are directly rejected in the water plan and contribute to the enrichment of the aquatic area in pollutants (heavy metal) and other undesirable or potentially dangerous elements for health [5-7]. Some studies diagnoses have been carried out on waters and sediments and have seriously put into evidence the high rate in heavy metal [5-7]. The metal contamination of sediments is a danger for the water, the living species and for the health of human being [9]. In the aquatic ecosystems, the heavy metal can be associated to the sediments and are susceptible to be released in the water [10-11]. The sediments are like micro-pollutants trap that give indication of the historic pollution of the river [9-12]. The objective of this work is to assess the level of pollution of surface sediment in Lake of Ahémé by iron, zinc, arsenic, lead and cadmium. It mainly aims not only at the preservation of water resources but also to the protection of aquatic ecosystem ant its biological potentialities.

2. Materials and methods

2.1. Study area

Located in the south West in Benin, the Lake of Ahémé is limited between the parallel of 6° 20 and 6° 40 North latitude and the meridians of 1° 55' and 2° 00' East longitude (Figure 1). It extends on an orientation of North East and South West between Tokpa – Domè and Guézin, and an orientation of North South between Bopa and Tokpa Dome. Its surface is 8 500 ha and it is the second largest river of Benin after the Lake Nokoué (15 000 ha). This Lake communicates in its upstream with the river Couffo and in its downstream with the Atlantic Ocean through Ahô channel, the later links the lagoon of Ouidah and Grand-Popo. The riverside communities of the Lake of Ahémé are the township of Comè, Bopa in the department of Mono and the township of Kpomassè in the department of Atlantic (Figure 1).

Generally the environment of the Lake of Ahémé benefits a subequatorial climate which marked by two rains seasons and two dry seasons in the year. The temperature of the area doesn't change much. It oscillates between 25.84 °C and 29.26 °C. The annual average is of 27.2°C in the south of the basin. The area study presents a low landscape relatively dominated by an area of plains sandy and clayey and some peneplain flooding areas. Fishing, agriculture, and breeding are the main economics activities developed around this water plan.

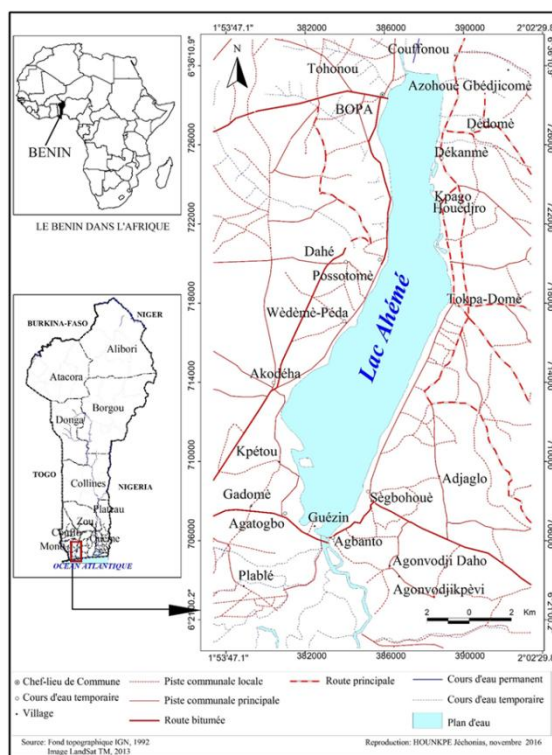


Figure 1: Geographical situation of the Lake Ahémé

2.2. Field works

Two sampling campaigns were conducted on Lake Ahémé for this study. The first one in July 2015, during high rain season and the second one in March 2016, during high dry season. The sampled stations have been chosen taking into account not only the villages where the anthropogenic pressure is present but also the areas of fluvial or marine inputs and the good geographical repartition (North, South, Center, East and west) in a way to cover the totality of the ecosystem and to have the reflection of true characteristics of water and sediments of the Lake. At the level of each predefined site, the sampling the surface sediments have been sampled at the level of each site with a barrow of Eckmann. The operation consists in scratching the bottom of the Lake with the Tipper opened and we close it once in the bottom with something which is against the weight; this quick closing brings the scratching of the sediment at least 10 cm deeper from the bottom of the Lake. The samples sediments have been packaged into new plastic bag and put in darkness and in a freezer at (4°C) before their transport to the laboratory.

Globally, 14 samples of sediment have been deducted from the Lake Ahémé. The different sampled sites have been codified and their geographical data have been taken with a GPS and placed on a map (Figure 2).

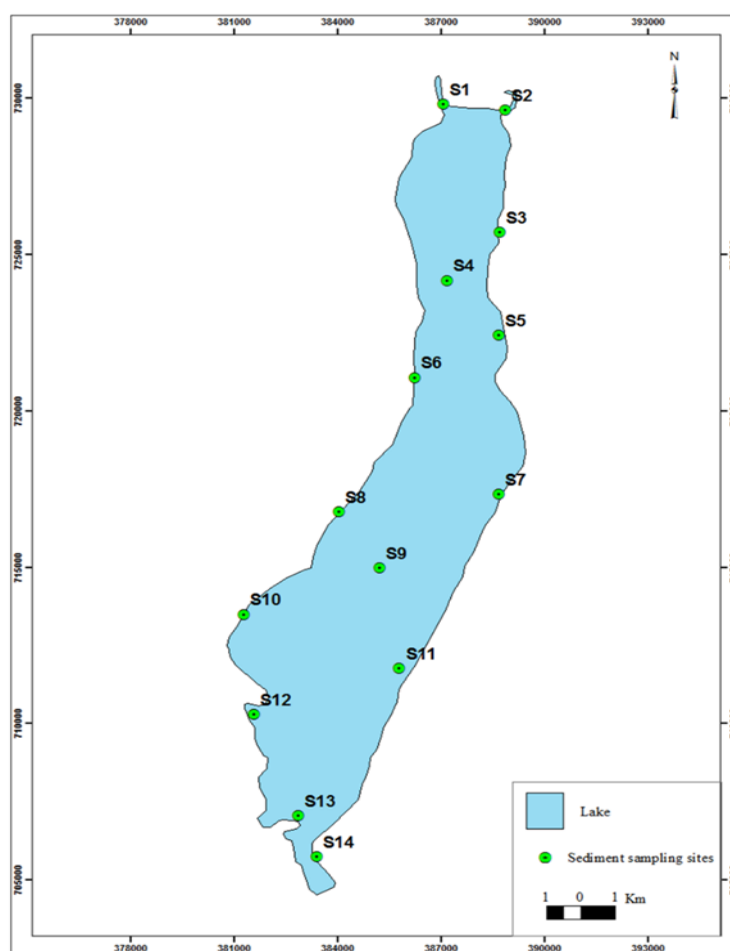


Figure 2: sediment sampling sites in the Lake of Ahémé

2. 3. Laboratory works

In the framework of this study, some chemical analyses have been carried out in the laboratory of control of quality of water and food at the National Direction of Public Health (DNSP).

The concentration metallic elements like iron, zinc, arsenic, lead and cadmium have been measured using absorption spectrophotometer after mineralization of the sediment samples by standardized HACH method. The mineralized obtained has been used for the dosing of different elements of metallic trace by the method described in the table 1 and put into the spectrophotometer of absorption DR2800 for the reading of the concentrations.

The Metson method and the loss-to-fire method are those used for the determination of the cation exchange capacity and the total organic matter, respectively. The pH was measured using a previously calibrated WTW

pH / Oxi 340i pH-meter. The concentration metallic elements like iron, zinc, arsenic, lead and cadmium have been measured with spectrophotometer of absorption after mineralization of samples sediment by the method of Hach. The mineralized obtained has been used for the dosing of different elements of metallic trace by the method described in the table 1 and put into the spectrophotometer of absorption DR2800 for the reading of the concentrations.

Table 1: Analysis methods of different heavy metal in sediments

Heavy metal	Methods of analysis	Reagent	Units	Sources
Lead	Dithizone method	DithiVer	mg/kg	
Cadmium	Dithizone method	DithiVer	mg/kg	Rodier <i>and al.</i> , 2009
Arsenic	Photométrique method	Diethyldithiocarbamate of argent	mg/kg	
Zinc	Zinconver method	2-carboxy-2-hydroxy-5'-sulfoformaziyl benzene	mg/kg	
Iron	Ferover method	1.10. phenanthroline	mg/kg	

2.4. Data analysis

In order to appreciate the quality of sediments, we compared the concentrations obtained at the different sampled points in the Lake with two different standards. The first is established by the Canadian council of ministers of environment in 1998 and the second is defined by the GESAMP (Group of Experts on the Scientific Aspects of Marine Pollution) established in 1982 (table 2).

Table 2: Standard of sediments used

Heavy metals	Standard of Sediments (mg/kg)		
	GESAMP, 1982	CCME, 1998	
		RPQS	CEP
Iron	41000		
Zinc	95	123	315
Arsenic	-	5.9	17
Lead	19	35	91.3
Cadmium	0.11	0.6	3.5

To evaluate the intensity of the contamination, the Enrichment factor (FE) and the index of geo-accumulation (Igeo) have been calculated. Their principle is based on the comparison of measured values in relation to the values of references such as the averages of the content of the elements of the earthy crust.

The Enrichment factor (FE) gives how many times an element is enriched related to the abundance of this element in the material of reference. The material of reference used in this study is the continental crust and is the one defined by [16], and world acknowledged like referring concentration (table 3) in non-polluted areas. The calculation of the FE has been defined by relating the content of a contaminated element of the sampling to the concentration of a reputed element relatively immovable of this sample, compared to the same report found in the referring material. The immovable element is exclusively from the source natural terrigenous. It is often chosen among Al, Li, Sc, Zr, Ti and Th or sometimes Fe or Mn [17].

The iron (Fe) has been chosen as immovable element of reference to make the calculation. This choice bases on the fact that the iron is naturally present in the waters and the sediments of the study area. Moreover, it is among the referring materials largely used in literature. There is no predefined rule for the choice of the referring element if it has not to be locally and mainly representative of terrigenous sources [18].

$$FE = \frac{[M]S/[Fe]S}{[M]RM/[Fe]RM}$$

Where FE = Factor of Enrichment; $[M]S$ = concentration in metal M in the sample; $[Fe]S$ = concentration of iron; $[M]RM$ = concentration of metal M in the material of reference and $[Fe]RM$ = concentration of iron in the material of reference. The values of FE have been interpreted in relation with the level of contamination defined by [19] and [20] (tables 4 and 5).

Table 3 : Concentration of heavy metal in the continental crust (Wedepohl, 1995)

Heavy metals	Iron	zinc	Arsenic	Lead	Cadmium
UCC (mg/kg)	30890	79	2	17	0.1

Table 4 : Level of contamination in relation with the values of FE (Acévédofigueroa *and al.*, 2006)

Value of FE	Level of contamination
$FE < 1$	No enrichment
$1 < FE < 3$	Weak / low enrichment
$3 < FE < 5$	Moderated enrichment
$5 < FE < 10$	Highlymoderatedenrichment
$10 < FE < 25$	High enrichment
$25 < FE < 50$	Very high enrichment
$FE > 50$	Extreme enrichment

Table 5 : Level of contamination in relation with the values of FE (Bilos *and al.*, 2001)

Value of FE	Source of contamination
$FE \leq 1$	Natural terrigenous sources
$FE > 1$	Other sources than the natural terrigenous sources
$FE > 2$	Beginning of the enrichment
$FE > 10$	Anthropical Source

A second criterion to evaluate the intensity of the metal pollution is the index of geo-accumulation (Müller, 1969). This index of empirical characteristic compared a given concentration to a value considered as a geochemical fund.

$$I_{géo} = \log_2\left(\frac{C_n}{1.5B_n}\right)$$

Where $I_{géo}$ = index of geo-accumulation; \log_2 = logarithm of base 2; n = considered element, C = measured concentration in the sample; B = geochemical background; 1.5 = background matrix correction in factor due to lithogenic effects. Moreover, Müller has defined a scale of values with six classes in function with the intensity of the pollution (table 6).

Table 6: Level of contamination in relation with the values of $I_{géo}$ (Müller, 1969)

Value of the index ($I_{géo}$)	Types $I_{géo}$	Intensity of the pollution
$I_{géo} > 5$	6	Extremely contaminated
$4 > I_{géo} > 5$	5	strongly to extremely contaminated
$3 > I_{géo} > 4$	4	Strongly contaminated
$2 > I_{géo} > 3$	3	Moderately to strongly contaminated
$1 > I_{géo} > 2$	2	Moderately contaminated
$0 > I_{géo} > 1$	1	uncontaminated to moderately contaminated
$I_{géo} < 0$	0	uncontaminated

3. Results and discussion

3.1. Physico-chemical parameters

The figure 3 shows that the values of the pH, the total organic matter and the cation exchange capacity vary from one season to another, from one site to another without taking into account a particular periodicity. The average measured pH value in sediments during the rainy season (6.7) is higher than that obtained in the dry season (6.68). These low pH values show that the sediments of Ahémé Lake are acidic and promote the release of trace elements and cationic species, in this case the heavy metals trapped in the sediments. This is the reason for the high average CEC values (19.78 meq / 100g in the rainy season and 18.20 meq / 100g in the dry period) observed in the sediments of Ahémé Lake. Since the cation exchange capacity is related to the presence of organic matter, we note that the CEC have high concentrations at the stations where the organic matter content is high. This observation is clearer at the S1 and S2 sites during the rainy season and the S9 site during the dry season. The organic pollution in the Ahémé Lake is partly due to the importance of continental intakes (plant debris) from the Couffo river as indicated by the level at the stations S1 and S2 during the rainy season. It may also be associated with a high level of domestic releases, as well as the agricultural and fishery activities practiced by neighboring populations at the Lake of Ahémé. According to [13], organic materials are true supports for biological beings, and trace elements of metal. These MOT contents predispose sediments and constitute a source of heavy metal pollution in the Lake of Ahémé.

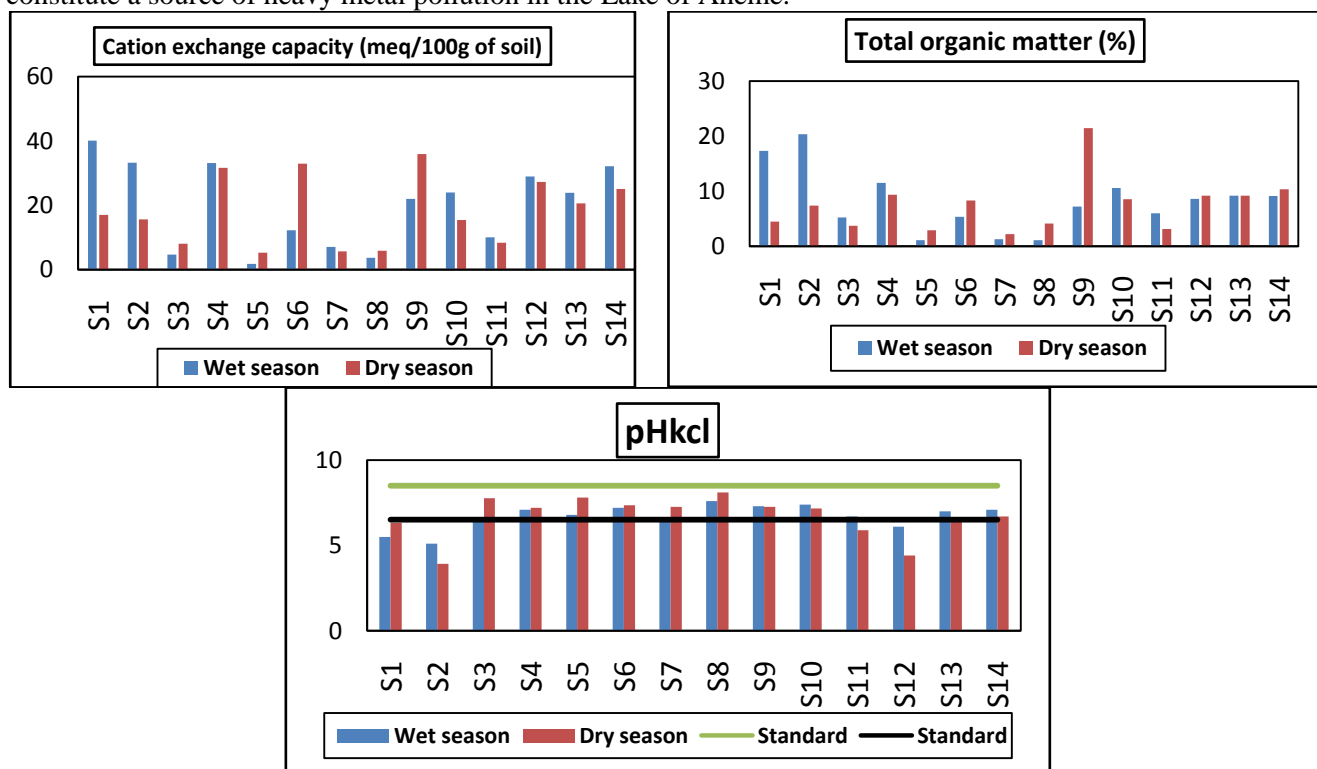


Figure 3: Seasonal and spatial variations of physico-chemical parameters of sediments of Lake Ahémé.

3.2. Heavy metal Concentration in sediments of the Lake Ahémé.

The results of the analysis of the heavy metals of sediments of the Lake Ahémé obtained during the two (02) sampling campaigns, are recorded in table 7.

Table 7: Content of heavy metal in the sediments of the Lake Ahémé.

Heavy metal (mg/kg)	Wet period			Dry period			GESAMP,1982	CCME, 1998	
	Max	Min	Average	Max	Min	Average		RPQS	CEP
Fe	10526.78	691.55	3689.17	12762	721	6224.92	41000		
Zn	137.1	40.41	67.18	614	71	275.57	95	123	315
As	3.1	0	0.70	10.5	0	2.49	-	5.9	17
Pb	92.6	8.36	44.46	45.63	2.78	28.76	19	35	91.3
Cd	3.5	0.53	1.22	3.27	0.33	1.42	0.11	0.6	3.5

Among the sediments and during the dry season, the Zn is the only element that shows an average content higher than the standard of GESAMP. No matter what the season is, the average tenor in lead and cadmium are always higher than the standard of GESAMP. The content in iron and arsenic are lower than the guide values of metal contents of non polluted sediments [14] and than the standards of Canadian heavy metal for the sediments of smooth waters [15]. The sediments of the Lake of Ahémé are then polluted in zinc, lead and cadmium. Compared with the average contents in heavy metals obtained in the Lake of Bini (table 8), a tropical ecosystem influenced by the farming activities, the rejections of domestic waste waters and uncontrolled rubbish dump [2], and the Lake of Ahémé looks less polluted in cadmium, lead and iron.

Table 8 : Comparison of average contents in metal (mg/kg) in the sediments of the Lakes Ahémé and Bini.

Aquatic ecosystems	Zn	Cd	Pb	As	Fe	References
Lake Bini (Cameroun)	43,52	5,12	65,43	-	87033,56	Oumar and <i>al.</i> , 2014
Lake Ahémé (Benin)	171,37	1,32	36,61	1,59	4957,04	Ongoing study

3.3. Enrichments factors

Table 9 shows the results of the FE of heavy metals in the sediments at the Lake of Ahémé in rain and dry season.

Table 9: Seasonal variation of enrichment factor of heavy metal in sediments of the Lake Ahémé.

Station	FE(Zn)		FE(As)		FE(Pb)		FE(Cd)	
	R S	D S	R S	D S	R S	D S	R S	D S
S1	3.12	25.00	6.22	0.00	14.24	16.2	101.31	107.37
S2	3.92	7.26	8.25	4.38	8.71	4,39	69.23	36.61
S3	42.27	26.53	19.43	18.22	102.00	29.26	357.34	99.92
S4	27.90	63.72	13.24	0.00	184.93	66.81	40741	970.6
S5	10.07	46.96	0.00	0.00	6.35	12.92	68.43	248.52
S6	15.14	85.00	0.00	0.00	34.80	2.75	403.39	256.7
S7	35.06	21.93	20.09	11.77	139.57	1.54	406.11	298.54
S8	0.05	41.00	6.49	0.00	19.99	5.78	191,29	694.16
S9	17.70	27.52	2.09	0.81	10.33	6.58	102.04	146.23
S10	4.57	20.18	0.00	14.05	12.82	7.18	26.11	191.59
S11	8.85	277.66	2.43	85.68	20.85	95.01	184.30	1328.1
S12	2.89	2.88	1.10	2.85	14.80	5.88	154.2	139.17
S13	4.04	5.65	0.00	4.52	24.35	3.89	33.2	147.51
S14	4.58	17.71	1.35	8.33	25.3	4.75	80.28	85.93

R S: Rain Season, **D S:** Dry Season

The analysis of this table shows that:

- The metal element zinc is enriched in numerous stations at the level of the Lake Ahémé. Beyond the stations S8 and S12 that are respectively no and lowly enriched and the stations S1, S2, S10, S11, S13, S14 that are moderated enriched in rain seasons, and the stations S12 lowly enriched and S2, S13 moderated enriched in dry season, all the other stations are highly and extremely enriched. Only these last stations are in majority anthropic sources of zinc element.
- Whatever the season is, the arsenic is by no means lowly enriched by the sediments of the Lake Ahémé, except at the level of stations 3, 4 and 7 in rain season and 3, 7, 10, and 11 in dry season. The anthropic sources of the metal is dominant at these stations.
- The lead stays globally more enriched in the sediments of the Lake Ahémé as well in rain season as in dry season. Apart from the stations S2 and S5 in rain season, all the other sites are highly enriched in lead. On the other hand, in dry season, only the sites S1, S3, S6, are very highly enriched and S4, S8 et S11

extremely enriched. The highly extremely enriched sites show clearly anthropic sources of the metal element lead in the sediments of the Lake Ahémé.

- The cadmium is enriched in the quasi-totality of sediments at the Lake of Ahémé. The level of enrichment of this element vary from an enrichment whatever high or extreme in rain season or in dry season. The anthropic source of this element is in majority in the aquatic ecosystem at the Lake of Ahémé.

These different observations allows us to classify the elements per order of enrichment as follows: Cd>>Pb>Zn>As in rain season and Cd>>Zn>Pb>As in dry season. It is well known that various anthropic activities can change the dynamics of a stream and add a variety of heavy metals [22]. Moreover, the Zn, the Pb and the Cd are metal elements that metallic characteristic an urban pollution type [3]. This high enrichment of these metal elements in the sediments at the Lake of Ahémé can be explained by the anthropogenic activities especially through the use of chemical inputs, the forbidden fishing methods with the use of the tire of car to constitute some trap for fishes, the liquid wastes made of waste waters directly flowed into the Lake by the riverside people, the solid wastes not well managed with the consequence of the development of uncontrolled rubbish dump on the bank of the Lake and finally the atmospheric deposit resulted from the combustion of fuels related to the road traffic.

3.4. The geo accumulation index

The table 10 shows the result of the index of geo accumulation during the rain and dry periods at the level of the different sampling stations of the Lake Ahémé.

Table 10 : Geo-accumulation Index of sediments in Lake Ahémé.

Station	Igeo (Fe)		Igeo (Zn)		Igeo (As)		Igeo (Pb)		Igeo (Cd)	
	R S	D S	R S	D S	R S	D S	R S	D S	R S	D S
S1	-3.19	-3.49	-1.55	1.15	-0.55	0.00	0.63	0.52	3.46	3.25
S2	-2.99	-2.4	-1.02	0.46	0.04	-0.27	0.12	-0.26	3.11	2.79
S3	-6.06	-4.19	-0.66	0.54	-1.78	-0.01	0.60	0.67	2.41	2.45
S4	-5.67	-5.91	-0.86	0.07	-1.94	0.00	1.86	0.14	3.00	4.01
S5	-4.27	-4.71	-0.94	0.84	0.00	0.00	-1.61	-1.02	1.82	3.24
S6	-5.44	-2.25	-1.52	-0.74	0.00	0.00	-0.31	-0.79	3.21	5.75
S7	-5.98	-3.82	-0.85	0.63	-1.66	-0.26	1.14	-3.19	2.67	4.4
S8	-5.67	-5.12	-1.28	0.24	-2.98	0.00	-1.35	0.66	1.90	4.32
S9	-3.93	-2.41	0.21	2.37	-2.87	-2.70	-0.56	0.31	2.73	4.78
S10	-2.14	-2.00	0.05	2.33	0.00	1.81	1.54	0.84	2.56	5.57
S11	-4.46	-6.00	-1.32	2.11	-3.18	0.41	-0.08	0.56	3.06	4.37
S12	-2.72	-2.09	-1.19	-0.56	-2.58	-0.58	1.16	0.46	4.54	5.02
S13	-2.9	-2.17	-0.92	0.32	0.00	0.00	1.66	-0.22	2.11	5.02
S14	-3.1	-1.86	-0.91	2.28	-2.67	1.19	1.55	0.39	3.22	4.56

R S: Rain Season, **D S**: Dry Season

From the analysis of the table 10, it results that from the five elements with metallic spots analyzed in the sediments, only the iron does not show a contamination in any period.

Globally the zinc does not show at all a slight contamination in rain and in dry season it varies from no contamination to a highly moderated one. Most of the southern stations of the Lake (S9, S10, S11 and S14) are those that show a high contamination in Zinc in dry season.

As in a rain or dry season, the arsenic shows a no slight contamination, except for the station S10 and S14 that show a moderated contamination in dry period.

The lead globally shows a high contamination as in a dry as rain period. This contamination varies from weak to moderate.

The cadmium shows a high to extreme contamination of these sediments during the two periods except for the station S8 which shows a moderated contamination.

These results confirm the previous observations with the factors of enrichment.

Similar results have been obtained by [2] in Dang Lake in Cameroon where cadmium has a geoaccumulation index which varies from high contamination to extreme contamination.

Conclusion

The results show that the sediments at the Lake of Ahémé are slightly acidic with high organic matter levels. The concentrations of heavy metal in the sediments showed high level for zinc, lead and cadmium. The value of the FE show an enrichment going from no to extreme during the two seasons for the whole metal, excepted the cadmium that oscillates between a very high enrichment to an extreme. The levels of contamination obtained by Igeo suggest that the iron does not show any contamination whereas the cadmium shows very high to extreme contamination during two seasons. The other metal elements (Zn, As, Pb) show levels of no contamination to moderate. The main sources of degradation of this ecosystem should be related to the anthropogenic pressure marked by the demographic growth and all the environment issues her generate. These data on the pollution of the Lake Ahémé are identified to as guide of assistance to the decision-making and fitting arrangements by the national and local actors, in order to preserve qualitatively the water resources, and to guarantee the social, economic and environmental wellbeing.

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