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Pollution by Trace Metallic Elements in Groundwater around Lake Toho in Mono Department, Southern Benin

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Abstract This study aimed at assessing the level of contamination of groundwater around Lake Toho in Trace Metal Elements (TME) following two campaigns (one in the dry season and the other in the rainy season). A total of eleven (11) samples (two wells and nine boreholes) were analyzed by Spectrometry Microwave Plasma Atomic Emission (MP-AES). Measured parameters are Fe, Mn, Cu, Zn, Ni, Hg, Pb, Cd, As and Cr. Values obtained are compared with Benin and WHO recommendations for drinking water. It appears there are not Hg and Pb in waters during both seasons. Cu and Zn are non-existent in waters during the dry season but appear during the rainy season. Cd is absent in waters except in those of Vêha and Logbo which revealed it presence in the dry season, but disappeared in the rainy season. Such is also the behavior of As in the water of Goudohoué. Concentrations of Mn and Ni in dry season dropped in the rainy season. The waters of some sites revealed an increase in Cr in the rainy season compared to the dry season. Fe contents in all the waters increased in the rainy season compared to the dry season. The contamination factors as well as the degrees of contamination of water pollution were calculated and revealed a high contamination of waters in TME. This study shows that the groundwater around Lake Toho is under influence of anthropogenic activities that promote appearance of elements as Fe, Cr and Ni, representing health risks for populations.

Keywords Contamination, Groundwater, Metallic Trace Elements, Anthropogenic Activities, Lake Toho

Introduction

Fresh water is an essential food for human, animal and plant life [1,2]. Given its importance, it deserves special attention as it can be subject to serious threats due to human activities. All human activities involving the mobilization of natural resources lead to the production of waste (solid and liquid) and gaseous effluents capable of causing a transfer of pollutants [3]. These sources of pollution as well as the intensive use of chemical fertilizers in agriculture, etc. can be the cause of an increasing deterioration of the quality of water resources [4 ; 5]. The contamination of water by metallic trace elements (ETM) is nowadays one of the main difficulties facing the world [6 ; 7]. These authors have all deduced from their work that human activities are the main sources of ETM. Their presence in groundwater resources is of natural origin (chemical alteration of rocks and soils, wet and dry deposition of atmospheric particles) and/or anthropogenic (mining extraction, household materials, decomposition of animal

matter, pesticides) [8 ; 9 and 10]. In Benin, ETMs were also measured in the waters of Lake Toho [11 ; 12 and 13]. It was recognized as polluting in lead and cadmium. Agriculture is the primary activity carried out around Lake Toho, in the Mono department, in southern Benin. It is followed by fishing. They are developed on a large scale and with the use of uncontrolled quantities of fertilizers, for exponential yields. These products are rich in metals, with toxic consequences for plants, humans and animals [14 ; 15]. This represents a pollution problem for surface waters. In their interactions, groundwater could be contaminated by surface water and also by the infiltration of run off water saturated with residues of chemical fertilizers and pesticides used in agriculture. This contamination may be the cause of a growing deterioration in the quality of groundwater in the region, the main source of drinking water supply in the area. Thus, it is necessary to assess the content of MTEs in groundwater resources from the point of view of the health of populations. The ojective of this work is to evaluate the level of cotaminatio of groundwater around Lake Toho in trace metals (TMEs) in two campaigns (one in dry season and one in rainy season).

Material and Methods

Lake Toho is a lake in southwestern Benin. It covers 9.6 km^2 at low water and 15 km^2 during flooding with an average depth of 2.1 m [16]. It is surrounded by the districts of Kpinnou in the commune of Athiémé, Zoungbonou in the commune of Houéyogbé and Houin in the commune of Lokossa (Figure 1).

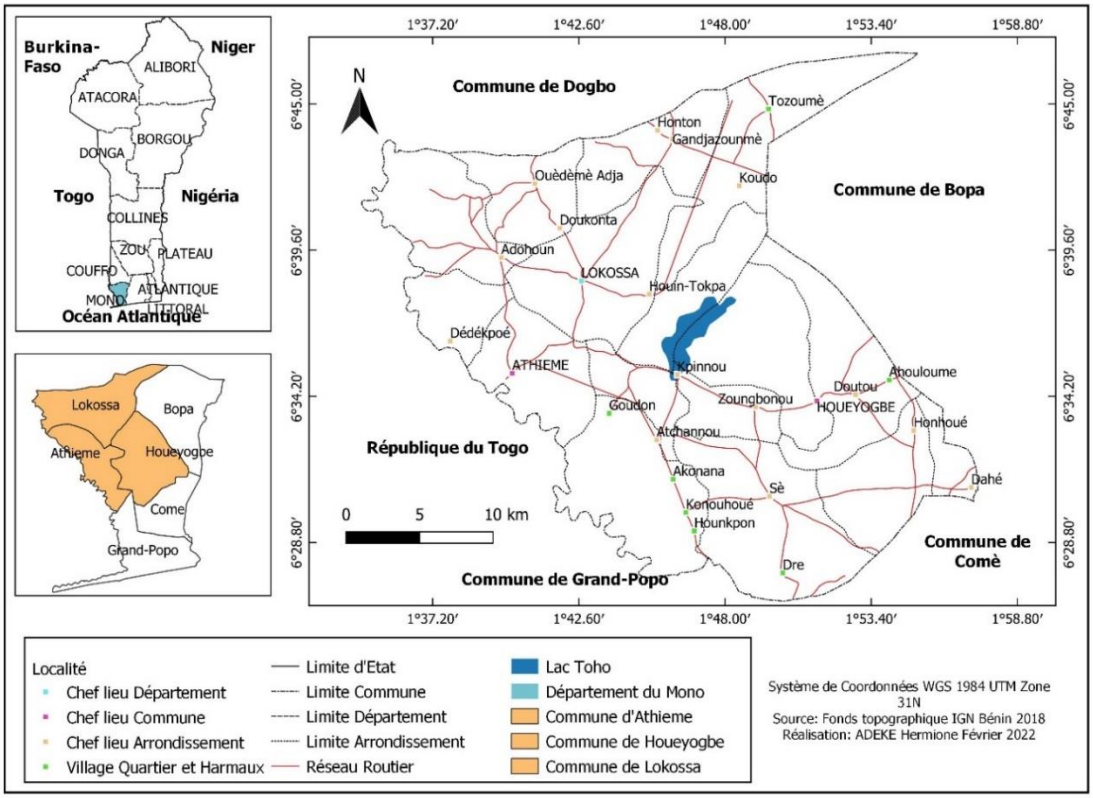

Figure 1: Lake Toho location map

Hydrogeology

According to the Hydrogeological map of Benin – 1/500000th scale of January 2012, the districts of Zoungbonou and Houin rest on units III and IV of the Coastal Sedimentary Basin (BSC), made up of kaolin clay and marl. The aquifer captured in these areas is Upper Paleocene and sometimes Middle Eocene. The depth of the boreholes varies from 50 to 280 m.

The district of Kpinnou rests on recent alluvium and old terraces of depressions of Ouémé and Mono. This region is made up of sands, clays, gravels and carbonaceous levels (PDC Athiémé, 2018-2022). The aquifer captured in this region is the quaternary. The depth of drilling in this zone varies between 20 and 400 m.

Soils

The physical environment of the district of Zoungbonou which is part of the study area is a valley area made up of black earth.

In Lokossa, the soils are ferralitic on the plateaus and hydromorphic:

- Ferralitic soils are subdivided into ferralitic soil on loose clay-sandy sediment and ferralitic soil on sandstone and sandy and clay-sandy colluvial materials. The latter erodes very quickly, not only because of its constitution, but especially because of the slope at (5 to 8%);
- The hydromorphic soils are of the alluvial and colluvial type in the valleys of rivers and lakes that are quite rich in organic matter, very fertile but seasonally flooded by the floods of the Mono River.

The soils distinguished in the Athiémé zone are predominantly Grey. The existence of bar soil and the absence of vertisols are noted.

Sampling

Groundwater samples were taken from 11 of the most used water supply structure in the three boroughs around Lake Toho (Table 1). Two sampling campaigns were carried out; in February during the dry season then in June 2022 during the rainy season, to check the variation in the quality of groundwater in the region between these two seasons representative of the 4 seasons in the region.

Table 1: Water sampling sites in municipalities

Types of samples	Website Number	Round-Sow	Locality	Type of work	Geographical coordinates	
					Latitude	Longitude
Water	1	KPINNOU	KPOCONDJI YOSSO	Drilling	06°35'10.453"	1°46'70.101"
	2		HAHAME	Well	06°35'26.405"	1°45'26.842"
	3	HOUIN	KPONOU DOUVO	Drilling	06°36'36.676"	1°45'16.836"
	4		WANKANMIN	Drilling	06°37'57.350"	1°45'13.153"
	5		VEHA	Drilling	06°39'50.196"	1°46'58.743"
	6		LOGBO	Drilling	06°37'70.654"	1°45'55.464"
	7		DON-KONDJI	Drilling	06°34'30.153"	1°45'42.014"
	8		AZONLIHOUE	Well	06°35'11.569"	1°45'26.060"
	9	ZOUNGBO-NOU	DADAHOUE	Drilling	06°36'23.501"	1°47'44.105"
	10		TOHONOU	Drilling	06°37'11.802"	1°47'26.332"
	11		GOUDOHOUE	Drilling	06°36'52.677"	1°47'21.705"

The geographic coordinates of each structure were obtained using a GPS and projected onto the location map of the study area. Figure 2 shows the different sampling points.

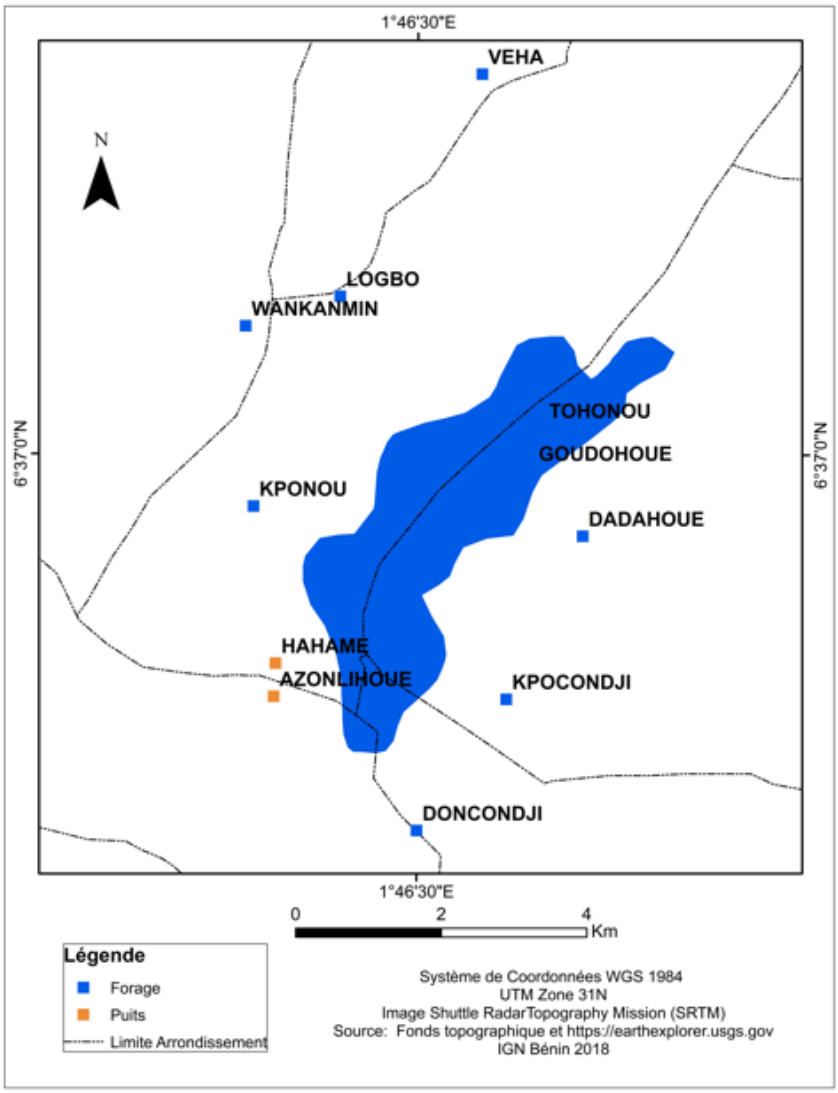

Figure 2: Distribution map of AEP points

Sample collection and processing

The groundwater samples were taken in 1.5 L bottles that were very clean and rinsed with distilled water. Tape and a marker were used to label the samples. They were kept with blocks of ice in a tightly closed cooler and transported by bus to the Agilent Technologies Laboratory in Lagos, Nigeria, where ten MTEs were analyzed in each water sample taken. Iron Fe, Manganese Mn, Copper Cu, Zinc Zn, Nickel Ni, Lead Pb, Cadmium Cd, and Chromium Cr were analyzed by the method of Spectrometry of Microwave Plasma Atomic Emission (MP-AES) using the standard Environmental Protection Agency 6010 (EPA 6010). Arsenic As and Mercury Hg were analyzed by the same method using the EPA 2008 standard.

Data processing

Histograms presenting the levels of variation of the MTEs (Fe, Mn, Ni, Pb, Cd, As, Hg, Cu, Zn and Cr in groundwater were carried out with Excel software. The assessment of the water quality was made on the basis of the

comparison of the values obtained experimentally with the threshold values set by the quality standard for water intended for consumption in the Republic of Benin (Decret-2001-094) and the WHO guideline (WHO 2017).

Water contamination by ETM was evaluated using pollution indices such as contamination factor (CF) and degree of contamination (Dc) of ETM.

All parameters were taken into account for this application except for zinc which has no standard according to the 2017 WHO recommendations used.

The contamination factor was calculated according to the following equation.

$$Fc = \frac{\text{Concentration of TME measured in water}}{\text{Standard value}}$$

The level of water contamination was determined according to the contamination classes [17 ; 18].

- FC < 1 = low contamination
- 1 < FC < 3 = moderate contamination
- 3 < FC < 6 = considerable contamination;
- HR > 6 =. Very heavy contamination.

The degree of contamination of water by metals was calculated according to the following equation [19]:

$\mathrm{Dc} = \sum_{i=n}^{n} Fci$

Where: Fci the contamination factor of the ith parameter, and n the normative value of the metal.

The degree of contamination was assessed based on the three classes of contamination [20 ; 21]:

- low for a Dc < 1,
- average for a Dc between 1 and 3,
- and high for a Dc > 3

Results and Discussion

- **Dosed Parameters**
  - **Iron content in water**

The iron contents obtained in the waters analyzed vary from 0.716 to 1.956 mg/L in the dry season and from 1.226 to 2.766 mg/L in the rainy season. The highest values are noted in the rainy season.

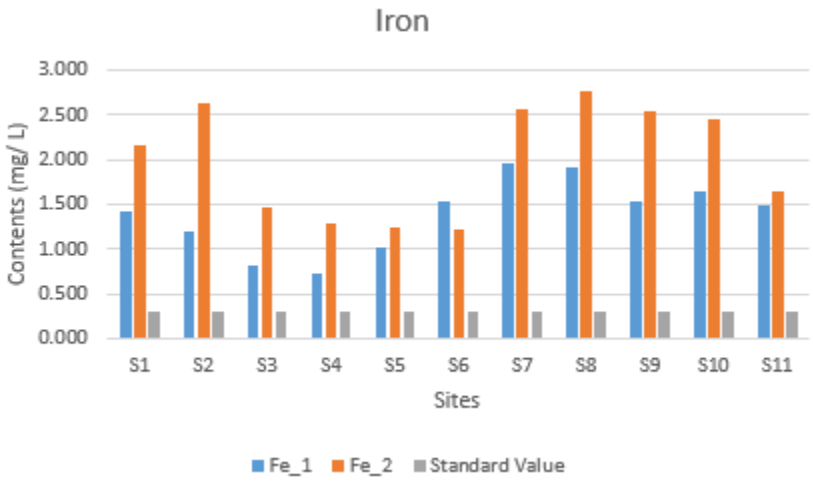

Figure 3: Spatio-temporal variation of iron in waters

- Manganese content in water

The manganese concentrations obtained vary from 0.026 to 0.244 mg/L in the dry season and from 0.008 to 0.039 mg/L in the rainy season. The highest values are noted in the dry season.

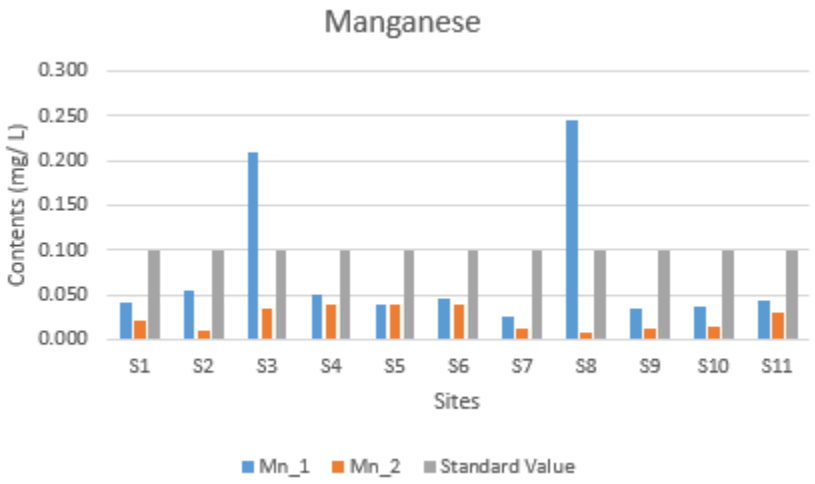

Figure 4: Spatio-temporal variation of Manganese in waters

- Nickel content in water

The high levels of Nickel in the waters are observed during the dry season. The concentrations of this element vary from 0.056 to 0.296 mg/L in the dry season and from 0.011 to 0.018 mg/L in the rainy season.

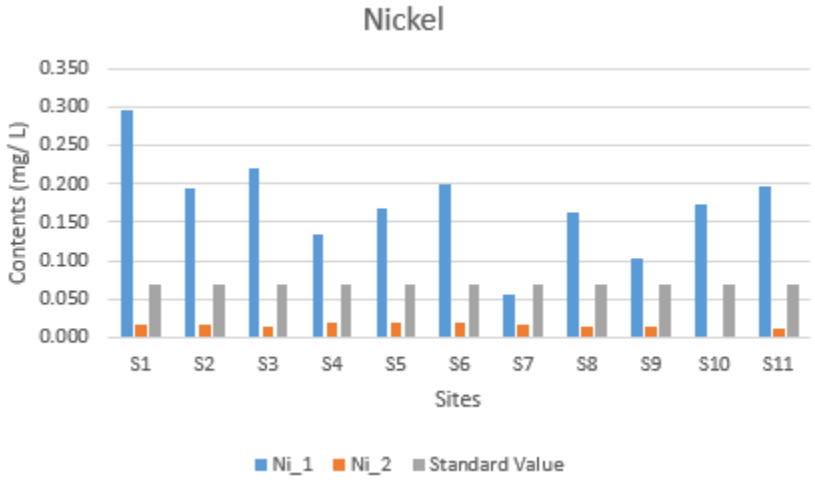

Figure 5: Spatio-temporal variation of Nickel in waters

- Chromium content in waters

The chromium concentrations obtained vary from 0.010 to 0.397 mg/L in the dry season and from 0.034 to 0.052 mg/L in the rainy season. The highest concentrations of this element are read during the dry season.

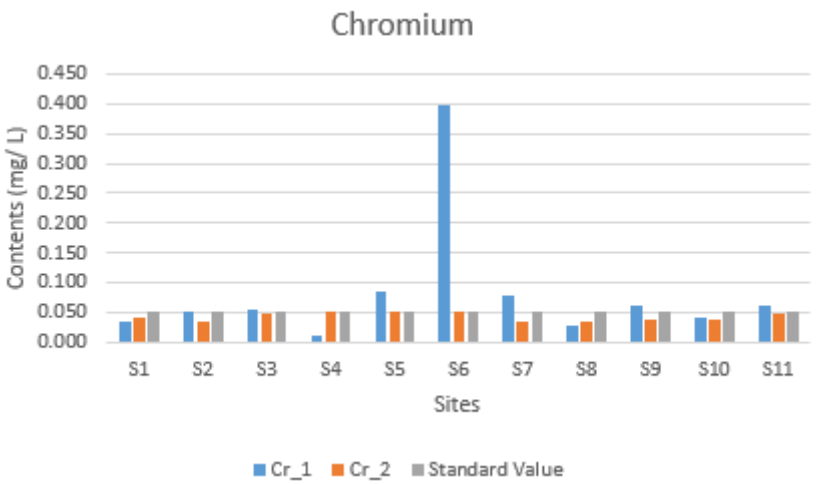

Figure 6: Spatio-temporal variation of Chromium in waters

- Copper content in waters

The presence of copper in the waters was observed only during the rainy season and its concentrations vary from 0.023 to 0.639 mg/L.

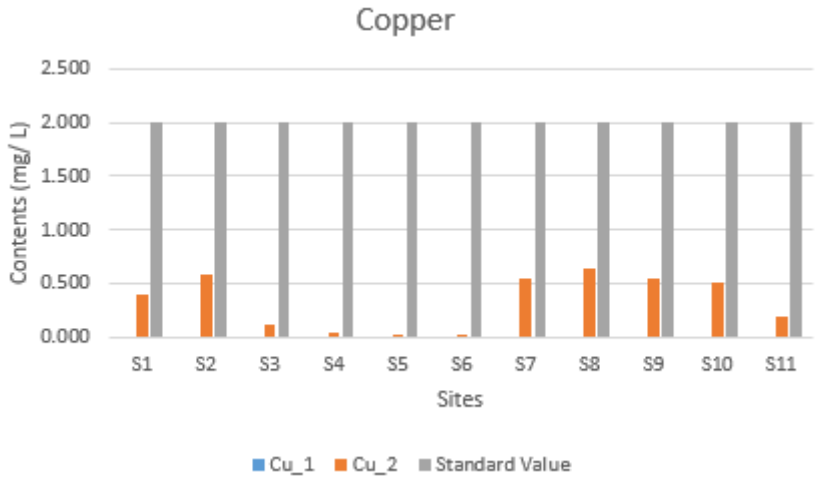

Figure 7 : Spatio-temporal variation of copper in waters

- Zinc content in water

Like copper in the analyzed waters, zinc was read only during the rainy season. Its contents vary from 0.010 to 0.140 mg/L.

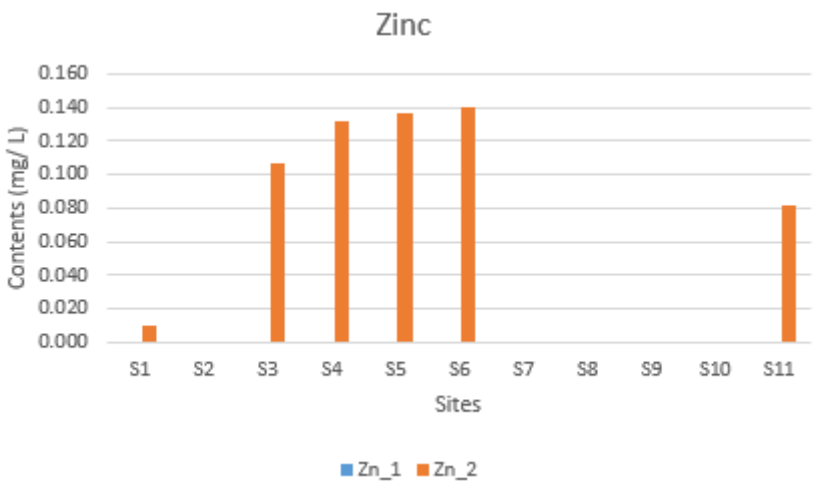

Figure 8: Spatio-temporal variation of zinc in waters

- Arsenic content in water

Of all the waters analyzed, only the sample from site 6, that of Logbo, which showed the presence of arsenic with a concentration of 0.349 mg/L in its water during the dry season.

- Cadmium content in water

Of all the samples analyzed, cadmium was found to be present in only two samples during the dry period.

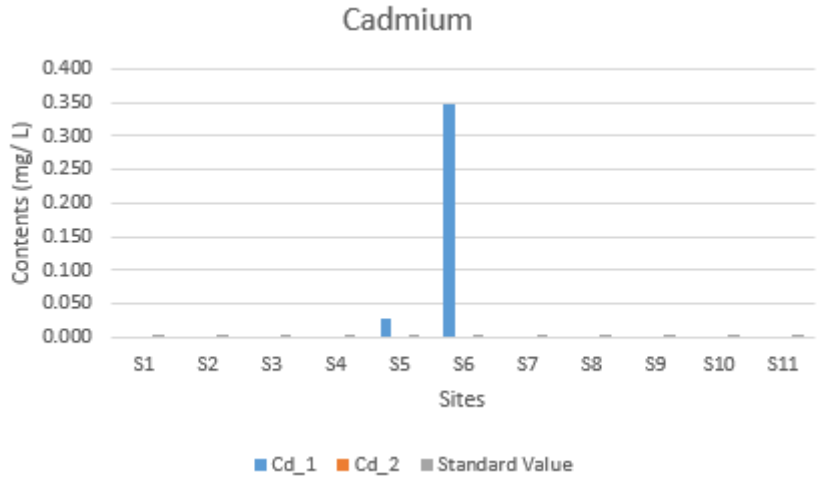

Figure 9: Spatio-temporal variation of Cadmium in waters

- Lead and mercury content in water

It should be noted that the concentrations of lead and mercury are absent in the waters.

- **contamination factor**

Mercury and lead contamination factors are zero. The contamination level indicators are grouped in the tables below.

Table 2: Metal contamination factor for each water in the dry season

		Metal Contamination Factor (SS)								
Site (s	No.	Fe	Mn	Cd	Ni	Cr	As	Cu	Hg	Pb
KPOCONDJI	1	CC	F c		CC	C m				
HAHAME	2				C m	C m				
KPONOU	3	C m			CC					
WANKANMIN	4				C m	F c				
VEHA	5	CC		T fc		C m				
LOGBO	6					CC				
SOCONDJI	7	T fc			F c	C m				
AZONLIHOUE	8		C m		C m	F c				
DADAHOUE	9	CC	F c			C m				
TOHONOU	10					F c				
GOUDOHOUE	11					C m	T fc			

With Cc: considerable contamination; Cm: moderate contamination; Fc: low contamination; Tfc: very high contamination

Table 3: Metal contamination factor for each water in the rainy season

		Metal Contamination Factor (SP)								
Site (s	No.	Fe	Mn	Cd	Ni	Cr	As	Cu	Hg	Pb
KPOCONDJI	1	T fc	F c		F c	F c		F c		
HAHAME	2									
KPONOU	3	CC				C m				
WANKANMIN	4									
VEHA	5									
LOGBO	6									
SOCONDJI	7	T fc				F c				
AZONLIHOUE	8									
DADAHOUE	9									
TOHONOU	10									
GOUDOHOUE	11	CC								

With Cc: considerable contamination; Cm: moderate contamination; Fc: low contamination; Tfc: very high contamination

- **Degree of contamination**

Considering the values obtained, and their classifications of the level of contamination of the waters, it is noted for all the waters, a high degree of contamination.

Discussion

The results of the analyzes obtained during the two sampling campaigns revealed a total absence of Pb and Hg in the waters. The zero values of lead agree with those of [22 ; 14]. The measured Cu and Zn showed their non-existence in the waters in the dry season but appear in the rainy season. Cu and Zn are among the trace elements found in

chemical fertilizers, pesticides and domestic waste [7]. The Cu values obtained following the second campaign vary from 0.023 to 0.639 mg/L. They are similar to the values of [23] (90.25 µg/L to 573.9 µg/l). These values are all in line with or below the standard values of Benin and the WHO. Zn values vary from 0 to 0.140 mg/L. They remain nil in some waters (Hahamé, Doncondji, Azonlihoué, Dadahoué and Tohonou). The WHO also recognizes these metals (Cu and Zn) as being trace elements for the human body. Of all the waters studied, only two samples (Vêha and Logbo) from the first campaign showed the presence of cadmium in their waters. These values are 0.027 mg/L and 0.348 mg/L respectively. They are all higher than the WHO recommendations which is 0.003 mg/L. These values tend towards those obtained by [23] in the groundwater of the Hahotoe-Kpogame phosphate mining area (South-Togo) whose maximum value is 0.02474mg/L. As was also found in the water of Goudohoué (site 11) in the dry season but disappeared in the rainy season. This water is heavily polluted with As because its noted content is equal to 0.349 mg/L instead of 0.001 mg/L which is the value recommended by the WHO for drinking water. Contamination of groundwater by arsenic is due to contact between rock and the groundwater table, which through erosion and soil alteration phenomena cause the release of minerals into the water. This contamination can also be due to the infiltration of agricultural wastewater which contains various metallic trace elements contained in chemical fertilizers and pesticides.The concentrations of Mn, Ni and Cr measured in the dry season dropped considerably in the rainy season. This finding may be due to dilution or precipitation caused by the increase in the volume of water in the rainy season. This increase in the volume of groundwater, boreholes in good condition and wells protected, in the rainy season is done by filtration, while that of open wells and boreholes not in good condition is done directly by runoff water, which explains the increase in Cr recorded in the rainy season compared to the dry season in Kpocondji, Wankanmin and Azonlihoué. The Mn present in the waters during the dry season varies from 0.026 mg/L to 0.244 mg/L. The concentrations recorded almost all comply with the WHO standard being 0.1 mg/L except for those in the waters of Kponou and Azonlihoué. In the rainy season, all the waters showed a tolerable presence of this element. These values obtained from the two campaigns are lower than those obtained [14] in the groundwater of the Hahotoe-Kpogame phosphate mining area (South-Togo). Manganese, iron and cadmium are MTEs found naturally in the earth's crust at varying concentrations depending on the nature of the soil. The study area is characterized by ferralitic soil [24] which is therefore rich in iron. In addition, these TMs are part of the additives of chemical fertilizers and pesticides used in agriculture [15]. Since the study area is not industrialized, the high levels of manganese, iron and cadmium observed in the water would come from the geological formations of the area on the one hand and from the agricultural activities carried out by the populations on the other. Concerning the element Ni, all the waters exept the one of Doncondji showed values higher than WHO recommendations (0.07 mg/L) in the dry season. In the rainy season, analyzes showed that all values complied with said standard. These values obtained in different seasons are lower than the values obtained by [25] in the waters and sediments in the vicinity of the Tighza mine in eastern central Morocco. Fe levels in all waters, in both seasons, exceeded WHO recommendations and Benin standards. They vary from 0.716 to 1.956 mg/L in the dry season and from 1.226 to 2.766 mg/L in the rainy season. There is an increase in concentrations during the rainy season. High levels were also observed in the groundwater of Dêkin by [26]. They are higher than the values of Okoundé in 2022 (0 to 1.25 mg/ L). Excess iron could be the cause of the changes in color of Lake Toho observed in places in 2018 and recently again in 2021. According to the circle of aquarists in 2015, excess iron is manifested by the proliferation of algae and respiratory difficulties of aquatic animals, hence the asphyxiated fish seen on the shores of the said lake, the subject of our work. Water contamination would be due to the infiltration of rainwater through polluted soil into groundwater. Indeed, the main activity conducted around Lake Toho is agriculture. In order to obtain an exponential yield, the populations use fertilizers and pesticides such as capizard and sunpyrifos, while exercising their activity. These products release trace metals into soils and waters, thus degrading their qualities [6 ; 7]. The contamination factors as well as the degrees of contamination of water pollution were calculated and revealed a high contamination of waters in ETM in general. In the dry season, the presence of ETM was observed in all waters. FC calculations revealed in the dry season, a very high cadmium contamination in the waters of Vêha and

Logbo. The same observation was made for the FC of arsenic in the water of Goudohoué. Significant contamination was observed in certain waters for certain parameters; Fe in the waters at seven sites, Ni in the waters at two sites. Except for Logbo water which gives a FC of moderate contamination, the other waters show a weak contamination or an average Cr contamination. CFs indicating medium contamination were obtained for Iron in the waters of Kponou and Wankanmin, Mn in Azonlihoué, Ni in Hahamé and Azonlihoué, in the districts of Houin and Zoungbonou. In the rainy season, there is a quantitative rise in iron in the water compared to the dry season. The FCs of this parameter which led to contamination considered at the levels of four sites indicate very high contamination; the average contamination of sites 3 and 4 testifies to the contamination considered. On the other hand, the FCs of the sites of Vêha, Logbo, Doncondji, Azonlihoué and Goudohoué remained in the same class as in the dry season. Mn and Ni FCs now show low contamination. Copper appears in the rainy season, unlike the dry season when it was completely absent. Its calculated FC indicates that all the waters analyzed are weakly contaminated. With the exception of the waters of the district of Houin (Lokossa), whose FCs show average contamination, the FCs of the waters of Kpinnou and Zoungbonou indicate low Cr contamination. The elements Cd, As, Hg and Pb are totally non-existent in the rainy season in the waters. We deduce from the values of the contamination factors calculated by metal and by sample that in the rainy season, all the waters are contaminated by iron and at different rates. The other existing parameters (metals) show moderate or very low contamination. The values of the degrees of contamination calculated from the FCs for all the waters are greater than 3; the waters analysed, if not all very highly contaminated, are considerably contaminated with various elements. The lowest value of Dc is 5.01 and the highest 132.15. These two values are obtained in the dry season. It emerges that all the waters studied have their Dc greater than 3; they all indicate high metal contamination. This study shows that the groundwater around Lake Toho is under the influence of anthropogenic activities that promote the appearance of certain elements such as Fe, Cu, Cr and Ni on the one hand and natural activities on the other. Part, thus representing health risks for the population.

Conclusion

The objective of this study was to assess the level of contamination of groundwater around Lake Toho in ETM namely Iron Fe, Manganese Mn, Copper Cu, Zinc Zn, Nickel Ni, Mercury Hg, Lead Pb, Cadmium Cd, Arsenic As and Chromium Cr following two campaigns (a dry season and a rainy season). The comparison of the concentrations of these elements was made between the values obtained from the two seasons and then with the normative values of the WHO and Benin for water intended for consumption. Pollution indices such as FC and Dc calculated revealed that overall, the waters of Kpocondji, Kponou, Vêha, Logbo and Goudohoué are of very poor quality. Kpocondji and Kponou are toxic in Ni, Vêha in cadmium, Goudohoué in Arsenic and Logbo in cadmium and chromium. However, all the waters studied are contaminated with iron. Thereby, the consumption of these waters by the populations exposes them to the risks of intoxication by the various elements resulting from anthropogenic activities. This water therefore deserves a minimum of treatment before consumption.

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