Heavy Metals Contamination of an Aquatic Environment and Health Risks Assessment in Two Fish Species: Case of the Guessabo Lake, Western Cote d'Ivoire

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ABSTRACT

The purpose of this study is to evaluate the contamination by heavy metals and the health risks of the residents of a watershed of the Sassandra river. Water and fish samples were taken from Guessabo Lake during the dry season and the rainy season. The average Hg, Pb, Cd and Zn concentrations in the water samples decreased during the rainy season by 20.51%, 80%, 18, 26% and 61.4%, respectively. In contrast, the average concentrations of As, Cu, Mn and Fe increased by 10%, 84.3%, 48.98% and 11.45%, respectively. The concentrations of heavy metals in water samples follow the trend: Fe> Cu> Mn> Pb> As> Zn> Hg> Cd. All metals except Fe were within permitted limits for drinking water quality at all stations during both seasons. The increase of As, Mn and Fe in water samples during rainy season was inversely proportional to their covalent index. The average heavy metal pollution index (HPI) for each sampling station showed higher pollution at the G2 station. The average Heavy metal evaluation index (HEI) of dry season (28) decreased relatively after the rainy season (21). Pearson's analysis showed that cadmium correlates strongly with HPI (r = 0.896) and HEI (r = 0.95) and iron is also highly correlated with HPI (r = 0.961) and HEI (r = 0.999). The concentration of trace metals obtained in the muscles of *Chrysichthys nigrodigitatus* (demersal) and Tilapia spp (benthopelagic) showed that Tilapia spp concentrated more non-essential metals (Hg, Cd and As) than *Chrysichthys nigrodigitatus*. Human health risks of trace metals in fish muscle and water were low, but among the selected metals, As and Hg are the non-essential elements contributing more to the cumulative hazard quotient of HI (0.845) for children and (0.39) for adults.

Keywords: Guessabo Lake, Water quality, Fish, Heavy metal pollution index, Heavy metal evaluation index, Health risks.

INTRODUCTION

The aquatic environment and water quality are considered to be the determining factor in the health and life of all organisms[1]. With the current mode of free disposal of agricultural products,

industrial, the flow of agricultural land and fishing techniques in Côte d'Ivoire, water bodies are increasingly vulnerable to pollution. Although industrial activities are relatively less important in the study area, environmental pollution, mainly from water sources, is significant because of the multiple sources of heavy metals. Sources of environmental pollution, including aquatic, come from mining effluents, domestic effluents and urban storm runoff. The leaching of heavy metals from rural areas such as those contained in pesticides are also potential sources in the area[2]. Ubiquitous and persistent heavy metals accumulate surreptitiously in nature and perhaps toxic to biota at low concentrations[3,4]. The consumption of impacted ecosystem products is a major source of contamination[5]. Heavy metals are non-biodegradable. Therefore, they cannot be eliminated by the self-cleaning process.

Fish contains proteins, vitamins, essential minerals and unsaturated fatty acids that are essential in human nutrition. It is also an important source of income[6]. According to Fair *et al.,*[7] human health is closely linked to dietary habits and dietary ingredients. The American Heart Society recommends consuming fish twice a week because it helps reduce the risk of heart disease[8]. However, if a healthy diet requires inputs of trace elements, vitamins and minerals it must also exclude pollutants. Also, Liu *et al.,*[9] states that vitamin C, iron and other nutrients stored in the body decrease with the consumption of food contaminated with Pb, Cd, As, Hg and other toxic elements. This leads to a decrease in immunity and a deterioration of human functions. The adverse health effects associated with bioaccumulation and biomagnification of heavy metals in the food chain are neurological, cardiovascular and renal disorders[10,11,12]. The fact that fish are also an important component of the diet raises serious concerns about health risks. Numerous studies have shown that humans could be significantly affected by the consumption of fish contaminated with heavy metals[13,14]. Pollution of fish by heavy metals has become a global concern, not only because of threats to fish, but also because of the public health risks associated with fish consumption[15,16].

The analysis of dissolved metals in water is useful for assessing pollution status and revealing the degree of contamination[17]. Guessabo Lake, one of the major lakes in western Côte d'Ivoire that supplies freshwater fish from Upper Sassandra

and surrounding areas, is subject to anthropogenic impacts in urban and agricultural areas. Small villages and settlements bordering the watercourse use this water resource without any prior treatment as drinking water. The interest aroused by this study stems not only from the importance of the natural resource but also from its vulnerability related to activities on its watershed. Therefore, this study should enable us to fill the gap of scientific data on this subject and can serve as a tool to help decision-making for development. To overcome the lack of literature in this area, this study describes an approach to determine the degree of risk of pollution. Due to the existence of more than one heavy metal absorption pathway, consideration should be given to the different routes of exposure in the health risk assessment process for residents living near these waters sweet. However, common routes of exposure to water are ingestion and skin absorption[18]. In this work, it will be mainly: (1) to explain the seasonal evolution of the concentrations of Hg, Cd, Pb, Zn, Cu, Fe, As and Mn in surface water and to compare them with the norms drinking water quality, (2) determine the heavy metal content in the muscles of the fish, (3) assess the potential risks to human health.

MATERIALS AND METHODS

Study area

Guessabo Lake object of our study has an area of 27 km[2]. It is located between 6° 57 'and 7° 2' and 5° 30' north latitude, and between 6° 45' and 6° 46' west longitude. It is located upstream of the dam of buyo built at the outlet of the Sassandra river. This latter drains a catchment area of about 75,000 km[2], including 62,000 km[2] in Côte d'Ivoire[19]. Stretching from the savannas of the north to the dense forest in the south, it undergoes the successive influence of the pluviometric regimes of the tropical transition climate and the equatorial transition climate. The shores of the lake are lined with cocoa plantations, rubber trees, forests and livestock farms. Its depths vary from 0.5 m to 20 m. The east bank is occupied by the sub-prefecture of Guessabo. Guessabo Lake is a permanent watercourse. The particularity of the study area is its mountainous landscape. The terrain is quite hilly with an average altitude of 300 m. However, the mountainous area does not cover the entire study area. However, the mountainous area does not cover the entire study area[20]. There are vast and high plateaus, plains and

hollows very extensive. The region enjoys a humid tropical climate with a dry season and a rainy season. Medium-fertility ferritic soils are favourable for the development of agriculture in this area[21]. There are also soils developed on basic rocks potentially rich in mineral salts and hydromorphic soils located in the lowlands. This regional advantage makes forests prone to human aggression during the dry season due to extensive agricultural slash-and-burn practices. The main activity on this lake is fishing with motorized gear.

Sampling, pre-treatment and analysis
Sampling

The map of the study area and sampling points is shown in Fig. 1. We collected 28 surface water samples seasonally from December 2017 to October 2018. We took care to take the samples at the same place during the four campaigns. The reagent used for sampling and filtration is HNO_3 pure

quality 48%. The goal is to stabilize the solutions at pH = 2 to minimize precipitation and adsorption on the bottle walls, as required by the standard procedure. The sample bottle is rinsed with a little sample before filling. All samples taken are stored in a cooler and within 24 h in a refrigerator at 4°C. The filtration apparatus is cleaned regularly with HCl 1N and rinsed with water to avoid memory effects on the collected water. The water samples were placed in clean polyethylene bottles. The fish, *Tilapia* spp and *Chrysichthys nigrodigitatus*, were chosen because of their socio-economic importance in catches and because of their diet. For this study,17 *Chrysichthys nigrodigitatus* and 11 *Tilapia* spp were dissected. The fish samples were washed several times with deionized water, cut into small pieces in the laboratory. It should be mentioned here that the fish were removed from their skin and the muscles located between the back and the tail were removed for analysis.
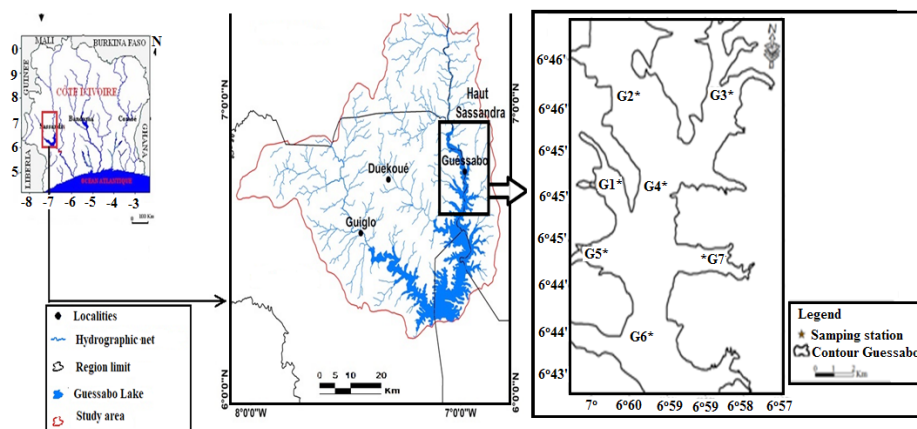

Fig. 1. Location of the seven sampling stations selected

Fish samples pretreatment

The metals taken into account in this work are two types: non-essential toxic metals (mercury (Hg), lead (Pb), cadmium (Cd)) and essential metals such as iron (Fe) and copper (Cu). After thawing at room temperature, the muscle samples were macerated into small pieces and mixed to obtain a homogeneous mixture. After mixing, approximately 5 g of each sample was quantitatively transferred to a Kjeldahl flask. The digestion of the sample was followed by the addition of 20 mL of concentrated nitric acid (HNO_3, pure 48%), followed by heating at a temperature between 210 and 350°C for about 10 to 20 minutes. Then 10 mL concentrated sulfuric acid (H_2SO_4, analytical grade) was added

to the sample. Boiling continued until the samples were digested. For portion separation, 5 mL of concentrated nitric acid was added gradually. The clear sample is cooled to room temperature and washed with distilled water. The samples were filtered using Whatman® filter (15 mm) in 50 mL volumetric flask and distilled water was used to adjust the volume. The same procedures were applied to blank samples without tissue. For recovery aims, control samples were prepared from fish tissue homogenate.

Samples analysis

Heavy metal concentrations were determined using atomic absorption spectrometry

(Perkin-Elmer, 3300/96, MHS-10) with a specific lamp for each particular metal. The heavy metal concentrations Pb, Cd, Fe, Zn, Mn and Cu were analysed by flame atomic absorption spectrometry. Arsenic and mercury were determined by atomic absorption spectrometry with hydride/cold vapor generation. Lead was determined by atomic absorption spectrometry in a graphite furnace. The following wavelengths were used: Pb (283.3 nm), Cd (228.8 nm), Fe (248.3 nm), Zn (213.9 nm), Mn (279.5 nm), Cu (324.8 nm), As (193.7 nm) and Hg (253.7 nm). The detection limits for trace elements and metalloids Mn, Fe, Cu, Zn, As, Cd, Pb and Hg are respectively 0.0002, 0.001, 0.0006, 0.002, 0.005, 0.0003 and 0.0001 mg kg^{-1}. The quality of the analytical data has been ensured through the implementation of quality assurance and laboratory quality control methods, including the use of standard operating procedures, calibration with standards, blank analysis reagents, recovery of known additions and replica analysis. All analyses were performed in triplicate and the results were expressed as an average. In order to minimize the variability among the sample results, we used the same analytical laboratory and this laboratory applied the same method of analysis for each chemical element searched during the study period.

Pollution index

The interpretation of water quality datasets for pollution assessment is quite difficult because of the simple elemental concentrations[22]. On the other hand, quality indices have a great deal of flexibility in analysing data sets for better interpretation of pollution[23]. In order to evaluate the quality of water by its heavy metal content in Guessabo Lake, two indices were used. The heavy metals pollution index (HPI) and heavy metals evaluation index (HEI) proposed by[24] are the ones used. The HPI and HEI methods are introduced to evaluate the overall quality of water by adding to heavy metals. The HPI index takes into account the relative toxicity of each metal by assigning a weighting factor or a rating (Wi) to each chosen parameter. The scoring system is an arbitrary value between 0 and 1 and its choice depends on the importance of individual quality considerations. It can be defined as inversely proportional to the allowed standard value[25]. In the calculation of HPI in this study, the concentration limits, that is, the allowed standard value (Si) and the highest desirable value (Ii) for each parameter, were extracted from the WHO standards. The Heavy Metals Evaluation Index (HEI) is used to synchronize the criteria for different pollution indices[26]. The HEI criteria for surface water samples are thus classified as low (HEI<40), medium (HEI = 40–80), and high (HEI>80). Different authors define for HPI a critical limit value 100 for water intended for consumption beyond which water is considered to be of poor quality. Thus, these different indices can be expressed by the following equations.

Table 1: Equations for the calculation of metal quality indices

Name of the quality indices	Equation	Reference
Heavy metals pollution Index	$HPI = \dfrac{\sum_{i=1}^{n} W_i Q_i}{\sum_{n=1}^{n} W_i}$ $Qi = \sum_{i=1}^{n} \dfrac{M_i - I_i}{S_i - I_i} \times 100$	(1)[24,26]
Heavy metals evaluation index	$HEI = \sum_{i}^{n} \dfrac{Hc}{H_{MAC}}$	(2)[26,27]

Where Qi: sub-index of the nth parameter, Wi: unit weighting of the parameter i, n: number of parameters considered. Mi: measured heavy metal content of the parameter i, Ii: ideal values of the parameter i, and Si: standard value of the parameter i, the sign (-) indicates the numerical differences between the two values, ignoring the algebraic sign. Hc: measured heavy metal content of parameter i, Hmac: maximum permissible concentration of parameter i.

Table 2 : HPI calculation parameters for lake water based on medium heavy metal concentration

Parameters	Wi	S	I	MAC
Cu	0,001	1000	2000	1000
Fe	0,005	300	200	200
Mn	0,02	100	500	50
Zn	0,0002	5000	3000	5000
Cd	0,3	5	3	3
Pb	0,7	100	10	1,5
As	0,02	50	10	50
Hg	1	1	6	1

Risk assessment methods

Liang *et al.,*[5] define health risk as the probability of adverse human health effects from environmental pollution. The health risk assessment model developed by the US Environmental Protection Agency[28] to assess the risk to human health of heavy metals is the one adopted in this work.

Calculations of daily intake

Strictly speaking, the consumption of pollutants in humans refers to the effective dose of pollutants that can enter in blood and have effects on human tissues and organs. However, because of some scientific constraints and taking into account

conservative principles, the calculation of absorption is expressed as the amount of pollutants absorbed by the body per body weight per unit of time based on the potential dose in general as 'have made several authors[29,30]. The intake of heavy metals is simply the exposure dose by ingestion of water (Exping, μg/L/day), fish (Expingp, μg/g/day) and the dermal exposure intake by absorption (μg/L/day) of harmful substances during the exposure period. The methods used to calculate the exposure intake vary according to the exposure pathways (Table 3). The definition and value of the exposure parameters are listed in Table 4.

Table 3: Equations of the absorbed daily intake via the different exposures

Exhibition routes	Exposure calculations	Reference
Water of Ingestion	$Exp_{ing} = \dfrac{C \times IR \times EF \times ED}{Bw \times AT}$	(3)[28]
Fish of Ingestion	$Exp_{ingp} = \dfrac{C_p \times IR_p \times ED \times EF}{BW \times AT} \times 10^{-3}$	(4)[31]
Skin absorption of water	$Exp_{derm} = \dfrac{C \times SA \times Kp \times ET \times EF \times ED \times 10^{-3}}{Bw \times AT}$	(5)[28]

Table 4: Calculation parameter of the daily exposure dose of heavy metals

Exhibition route	Basic Settings	Physical meanings	Values	References
Basic parameters	C (μl/L)	Concentrations of heavy metals and metalloids	Average values	This study
	Cp (μg/g)	Concentrations of fish metals	Average values	This study
	EF (days/year)	Frequency of exposure	180	This study
Exposure settings	ED (year)	Duration of exposure	6 (child)	[32]
			30 (adult)	
	Bw (Kg)	Average body mass	28 Kg (child)	[33]
			70Kg (adult)	
	AT (days)	Average exposure Time	2190 (child)	[32]
			10950 (adult)	
Hand-Mouth feeding	IR (L)	Amount of water ingested	1,5 (child)	[33]
			2L(adult)	
	IRp	Ingested fish rate	38,5g/ day / person	[34]
			28,9g/ day / person	
	Kp (cm/hr)	Dermal permeability coefficient of compound in water	(Cd, Cu Fe As and Hg (0,001)), Pb (0,0001), Zn (0,0006)	[32]
Skin exposure	SA (cm²)	Exposed skin surface	6600 (Child)	[32]
			18000 (adult)	
	ET	ET: Exposure Time	0,5h/day	This study

Health risk assessment

Populations that are regularly exposed include local residents, especially fishermen and

their families who consume fish and drink water from the lake at least once a day. However, fish can reach the table of any Ivorian, as no source

is indicated for fish sold on the market. This study focuses on the oral and dermal routes and concerns chronic exposures only. The non-carcinogenic risk is assessed by comparing a level of exposure over a specified period (eg, whole life) to a reference dose calculated for a similar exposure period. The non-carcinogenic risk may be characterized by a hazard quotient (HQ). The health risks caused by different contaminants entering the body through different routes of exposure are divided into carcinogenic and non-carcinogenic risks. Carcinogenic risk refers to the additional likelihood that an individual will develop cancer during his lifetime as a result of exposure to carcinogens. The hazard quotient is the ratio of chronic daily intake (Exp) to chronic reference dose (RFD). If HQ <1, the occurrence of a toxic effect is very unlikely and if HQ> 1, the occurrence of a toxic effect cannot be ruled out. The calculation equations of the different exposure hazards.

$$HQing = \frac{Exp_{ing}}{RfD_{ing}} \qquad (6)$$

$$HQ_{derm} = \frac{Exp_{derm}}{RfD_{derm}} \qquad (7)$$

RESULTS

Heavy metals in waters

The results of the descriptive analyses of heavy metals in the study period are given in Table 6. The seasonal and spatial evolution of the metallic elements is shown in Figure 2.

The Hg concentration is between 0 µg/L and 1.04 µg/L, with an estimated average of 0.347 ± 0.05 µg/L. That of Pb ranges from 0.02 µg/L to 5.44 µg/L, with an average value of 1.48 ± 0.85 µg/L. As for Cd, the values fluctuate between 0 µg/L and 0.35 µg/L, with an estimated average of 0.09 ± 0.02 µg/L. As concentrations range from 0.09 to 2.06, with an average value of 0.74 ± 0.11 µg/L. The Zn concentration is between 0.23 µg/L and 4.28 µg/L, with an estimated average of 1.37 ± 0.75 µg/L. As for Cu, its content varies between 0.02 and 5.46, with an average value of 1.89 ± 1.61 µg/L. The average concentration of Mn is 1.86 ± 1.06 µg/L. The minimum and maximum values are 0.65 and 5.45 µg/L, respectively. Regarding Fe, its content is between 2.27 mg/L and 13.54 mg/L, with an estimated average of 4.76 ± 1.11 mg/L.

The results of spatio-temporal variations in total Hg, Pb and Zn concentrations show that the highest concentrations are recorded during the dry season in the lake Fig. 2. With regard to cadmium, no clear trend is observed in the evolution of this parameter. The highest concentrations of Fe, As, Cu and Mn are generally obtained during the rainy season. In contrast, the lowest concentrations are measured in the dry season. Station 5 has the higher Pb content of the study period. The stations (1, 2 and 3) located on the right flank of the bridge recorded overall higher values of Hg, Pb and As. The total trace element content of the lake generally decreases along a gradient in concentration of upstream to downstream (station G1 to G6). All heavy metals recorded high concentrations at the G2 stations during both seasons. Mean concentrations of Hg, Pb, Cd and Zn decreased during the rainy season by 20.51%, 80%, 18.26% and 61.4% respectively. In contrast, mean concentrations of As, Cu, Mn and Fe increased by 10%, 84.3%, 48.98% and 11.45%, respectively. The abundance of these metallic trace elements in the waters of the study area follows the following decreasing order: Fe> Cu> Mn> Pb> As> Zn> Hg> Cd.

In this study, correlation between different metals and pollution indices were calculated. Statistical analysis shows both positive and negative correlation between different metals (Table 7). The results of the analyses show that Zinc is positively correlated with lead (r = 0.647) and arsenic (r = 0.914). On the other hand, Mn is negatively with lead (r = -0.673), arsenic (r = -0.777) and Zn (r = -0.833). Iron is strongly correlated with cadmium (r = 0.949).

Estimation of the intensity of water contamination by HMs

Table 6 presents the calculated HPI and HEI values for both seasons. The average value of HPI in Guessabo Lake during the dry season (94.87) and the rainy season (80.36) is lower than the critical limit 100. HPI values decreased significantly from the dry season to the rainy season at stations 2, 5 and 4. The HPI of the G2 (110) and G5 (104) stations are above the critical limit during the dry season. 100% of the sampling sites recorded HPI values below the critical value during the rainy season compared to 72% in the dry season.

The average HEI values for the dry season and the rainy season are 28.18 and 21.54, respectively. The Pearson correlation matrix shows that cadmium is strongly correlated with HPI (r = 0.896) and HEI (r = 0.95) and iron is also strongly correlated with HPI (r = 0.961) and HEI (r = 0.999). HPI and HEI methods show more or less similar trends for most of the samples (Table 7).
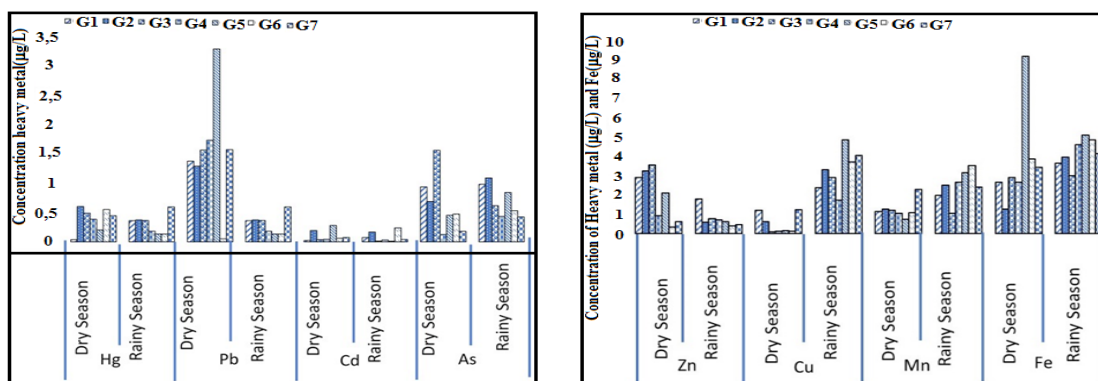

Fig. 2. Seasonal variation of heavy metal concentrations in Guessabo Lake

Table 5: Average Concentration of Heavy Metals in Guessabo Lake and reference doses of non-carcinogens

Parameter	Hg (µg/L)	Pb (µg/L)	Cd (µg/L)	As (µg/L)	Cu (µg/L)	Mn (µg/L)	Zn (µg/L)	Fe (mg/L)
Mean± S.D	0,347±0,05	1,48±0,85	0,09±0,02	0,74±0,11	1,89±1,61	1,86±1,06	1,37±0,75	4,76±1,11
Range	0-1,04	0,02-5,44	0-0,35	0,09-2,06	0,02-5,46	0,65-5,45	0,23-4,28	2,27-13,54
[36]	1	10	3	10	2000	500	3000	0,2
RfDing (Water)	0,1	1,4	0,5	0,3	40	-	300	700
RfDderm	0,007	0,42	0,025	0,123	8	-	60	140

Table 6: Guessabo Lake Heavy Metal Pollution Index (HPI) and Heavy Metal Evaluation Index (HEI) at each station in the dry and rainy seasons

Stations	HPI		HEI	
	Dry Season	Rainy Season	Dry Season	Rainy Season
G1	92,37	89,50	14,33	18,92
G2	110,11	90,37	64,76	20,56
G3	88,378	89,24	16,17	15,70
G4	88,72	11,86	14,87	23,41
G5	104,13	96,70	48,40	25,76
G6	90,53	94,48	19,96	24,66
G7	89,85	89,51	18,79	21,79
Mean	94,87±8,64	80,36±30,33	28,18±20,06	21,54±3,49
Water Mean	87,61±19,48		24,76±11,77	

Table 7: Pearson's correlations matrix between trace elements and pollution indices

	Hg	Pb	Cd	As	Zn	Cu	Mn	Fe	HPI	HEI
Hg	1									
Pb	-0,136	1								
Cd	0,063	0,251	1							
As	-0,046	0,525	0,266	1						
Zn	-0,155	0,647	0,140	0,914	1					
Cu	0,15	0,017	0,459	-0,080	-0,168	1				
Mn	0,16	-0,673	0,194	-0,777	-0,833	0,515	1			
Fe	0,03	0,240	0,949	0,091	0,078	0,399	0,280	1		
HPI	-0,23	0,220	0,896	0,061	0,079	0,343	0,272	0,961	1	
HEI	0,045	0,278	0,950	0,112	0,102	0,397	0,250	0,999	0,956	1
	Hg	Pb	Cd	As	Zn	Cu	Mn	Fe	HPI	HEI

Concentrations of heavy metals in fish muscles

The concentrations (average and range) of the non-essential metals (Pb, Cd and Hg) and essential metals (Fe and Cu) in the fish muscles analysed are presented in Table (8). The average concentration of Hg in Chrysichthys nigrodigitatus (demersal) muscle (0.056 µg/g w.w) is relatively high compared to the average Hg concentration of *Tilapia* spp (benthopelagic) (0.038 µg/g.w.w).

Mean Cd content in *Tilapia* spp muscle (0.01 µg/g w.w) was significantly higher than *Chrysichthys nigrodigitatus* content (0.004 µg/g w.w). However, no significant difference is observed between the Pb levels in the two species. The level of Cd found in *Tilapia* spp is 2.5 times higher than that found in *Chrysichthys nigrodigitatus* fish and the Pb level is 1.7 times higher than that of *Chrysichthys nigrodigitatus*.

Table 8: Concentration of heavy metals in fish muscle analysed in Guessabo Lake and norm according to[34], CE and EQs

Fish		Heavy Metals (µg/g w.w)				
		Hg	Cd	Pb	Cu	Fe
Chrysichthys nigrodigitatus	Mean±SD	0,056± 0,06	0,004±0,002	0,071±0,073	3,35±1,56	27,61±22,51
	Min-Max	0,01-0,24	0,001-0,012	0,013-0,325	1,23-6,54	3,00-65,08
Tilapia spp	Mean±SD	0,038±0,04	0,01±0,01	0,12±0,08	4,16±1,61	13,72±20,18
	Min-Max	0,02- 0,18	0,001-0,04	0,03-0,25	2,18-6,63	2,80-69,80
[34]		0,5	0,1	0,3	30	43
EC*			0,05	0,2-0,3		
EQS**		0,02				
RfD (µg/g /days)[35]		0,0003	0,001	0,004	0,04	0,7

*Commission of the European Communities, **Environmental Quality standard

Daily intake and Hazard Quotient

Daily intake of ingestion (Exping) and dermal exposure (Expderm) are calculated to evaluate the overall non-carcinogenic risk posed by certain metals when ingestion of water, fish and skin contact (Table 9). The non-carcinogenic (HQ) risk results for various heavy metals for the two exposure pathways are presented in Table (10). The results show that children are more exposed than adults at all levels. Of the two exposure routes, diet was the determining factor in the risk quotient. The risk quotient of ingestion of raw water is greater than the ingestion of fish. The metal HQ values of the estimated average HQing and HQderm

concentrations in the water samples are in the order of Fe> Hg> As> Pb> Cd> Cu> Zn and Fe> As> Pb> Cu> Zn, respectively. The results indicated that Fe, Hg, As and Pb are the main contributors to ingestion and Fe, As and Pb are the main contributors to skin penetration. The metal HQ values of the estimated average concentrations of HQing *Chrysichthys nigrodigitatus* and HQing *Tilapias* spp are about Hg> Cu> Fe> Pb> Cd and Hg> Cu> Pb> Fe> Cd, respectively. The results indicated that Hg and Cu are the main contributors to fish ingestion. The total value of the non-carcinogenic risk index (HQ) is for children (0.845) and adults (0.39).

Table 9: Daily ingestion dose (water and fish) and daily dermal exposure

Heavy Metals	Exposure by ingestion of water (µg/ L/day)		Dermal Exposure		Exposure by ingestion of fish *Chrysichthys nigrodigitatus*		Exposure by ingestion *Tilapia*		Total exposure by metals	
	Child	Adult	Child	Adult	Child	Adult	Child	Adult	Child	Adult
Hg	$9.18.10^{-3}$	$4.87.10^{-3}$	$2.02.10^{-5}$	$2.20.10^{-5}$	$2.8.10^{-5}$	$1.52.10^{-5}$	$1.9.10^{-5}$	$1.03.10^{-5}$	$9.23.10^{-3}$	$4.89.10^{-3}$
Cd	$2.39.10^{-3}$	$1.27.10^{-3}$	$5.26.10^{-6}$	$5.76.10^{-6}$	$2.0.10^{-6}$	$1.08.10^{-6}$	$1.85.10^{-5}$	10^{-5}	$2.63.10^{-3}$	$1.33.10^{-3}$
As	$1.58.10^{-2}$	$9.31.10^{-3}$	$3.86.10^{-5}$	$4.22.10^{-5}$	-	-	-	-	$1.75.10^{-2}$	$9.71.10^{-3}$
Pb	$3.91.10^{-2}$	$2.07.10^{-2}$	$8.61.10^{-6}$	$9.40.10^{-6}$	$3.55.10^{-5}$	$1.91.10^{-5}$	6.10^{-5}	$3.2.10^{-5}$	$4.29.10^{-2}$	$2.16.10^{-2}$
Cu	$5.00.10^{-2}$	$2.65.10^{-2}$	$1.10.10^{-4}$	$1.20.10^{-4}$	$1.67.10^{-3}$	$9.08.10^{-4}$	$2.08.10^{-3}$	$1.13.10^{-3}$	537.10^{-2}	$2.97.10^{-2}$
Fe	125.74	66.88	0.27	0.30	$1.38.10^{-2}$	$7.48.10^{-3}$	$6.86.10^{-3}$	$3.72.10^{-3}$	125,76	67.18
Zn	$3.60.10^{-2}$	$1.91.10^{-2}$	$4.76.10^{-5}$	$5.19.10^{-5}$	-	-	-	-	$3.94.10^{-2}$	$1.99.10^{-2}$

Table 10 : Summary of Risk Quotients in different matrices (water and fish) for adult and child

Heavy Metals	Quotient of Water Ingestion Hazards (HQ)		Dermal Hazard Quotient		Risk Quotient of *Chrysichthys nigrodigitatus* Ingestion		Risk Quotient of *Tilapia* Ingestion	
	Child	Adult	Child	Adult	Child	Adult	Child	Adult
Hg	9.1810^{-2}	$4.87.10^{-2}$	$2.88.10^{-3}$	$3,14.10^{-3}$	9.10^{-2}	$5.07.10^{-2}$	$6.3.10^{-2}$	$3.43.10^{-2}$
Cd	$4.78.10^{-3}$	$2.54.10^{-3}$	$2.10.10^{-4}$	$2,30.10^{-4}$	2.10^{-3}	$1.08.10^{-3}$	$1.85.10^{-3}$	10^{-2}
As	$5.26.10^{-2}$	$3.10.10^{-2}$	$3.14.10^{-4}$	$3.43.10^{-4}$	-	-	-	-
Pb	$2.79.10^{-2}$	$1.47.10^{-2}$	$2.05.10^{-5}$	$2.2.10^{-5}$	$8.87.10^{-3}$	$4.77.10^{-3}$	$1.5.10^{-2}$	8.10^{-3}
Cu	$1.25.10^{-3}$	$6.62.10^{-4}$	$1.37.10^{-5}$	$1.5.10^{-5}$	$4.2.10^{-2}$	$2.27.10^{-2}$	$5.2.10^{-2}$	$2,8.10^{-2}$
Fe	0.18	$9.55.10^{-2}$	$1.93.10^{-3}$	$2.14.10^{-3}$	$1.97.10^{-2}$	$1.07.10^{-2}$	$9.8.10^{-3}$	$5.3.10^{-3}$
Zn	$1.20.10^{-4}$	$6.36.10^{-5}$	$7.93.10^{-7}$	$8.65.10^{-7}$	-	-	-	-
Total	0.360	0.190	$5.36.10^{-3}$	$5.89.10^{-3}$	0,163	0,089	0,162	0,085

DISCUSSION

Water pollution by heavy metals

Seasonal variation of heavy metals in water is potentially influenced by physicochemical properties such as dissolved oxygen, salinity, temperature and pH. The positive correlation found between Zn-Pb -As, indicates a possible common source of these three elements in this study. The high content of trace elements such as Hg, Pb, Cd and Zn during the dry season would be due to increased evaporation and lower rainfall[37]. Also, the concentrations of Zn and Cd are relatively high in the dry season could be explained by the acidity (pH = 6.3) of the medium and the redox potential (Eh = 37 mV) highly oxidizing in water and sediments that favour the solution of these elements[38]. This decrease during the rainy season is due to the dilution effect, whereas the increase in As, Cu, Mn and Fe concentrations could be attributed to the desorption of these metals in the sediments due to dilution. During the rainy season, heavy metals penetrate the lakes through leaching as inorganic complexes or hydrated ions, which are readily adsorbed on the surface of the sediment particles and constitute the labile fraction[39]. This desorption concerned both the elements Hg, Pb, Cd and Zn but the dilution prevailed over this phenomenon. The increase in the average concentration of As, Cu, Mn and Fe in the rainy season followed the following order: Cu> Mn> Fe> As was inversely proportional to their covalence index As > Fe> Mn. According to Pal *et al.,*[4], the increase in heavy metal adsorption is closely related to their covalent index. However, Cu which is in two different classes defined by[40] did not follow this order. Also, the strong increase in Cu and Mn during the rainy season is due to their use in the composition of pesticides carried in neighbouring fields. Moreover, in the sedimentary cycle, Cu is associated with clay minerals, and especially associated with manganese[38], this justifies the positive correlation Cu and Mn (r = 0.51).

The concentration of all heavy metals was higher at the G2 station because it is located downstream of the volume of water coming from the North of the country and from the neighbouring country, which carried the wastes discharged by most densely populated areas. Concentrations of Cd, Pb, Mn, Zn, Cu, As, Hg and Fe were determined in the waters of Guessabo Lake. Cd, Pb, Mn, Zn, Cu, As and Hg are present in the waters in low concentrations, with values below the JORF standards[41] for raw water intended for the production of drinking water. High concentrations of Fe above the norm for the production of drinking water are observed in lake waters. These high levels are related to the preponderance of ferruginous soils in the study area[42]. This high iron content in surface water was reported by[43] in the waters of Lake Wadi El-Rayan in Egypt and by[44] in the Aghien Lagoon in Côte d'Ivoire. Heavy metals come mainly from erosion of rocks, soils and sediments where they occur naturally. They come mainly from human activities[45]. Their anthropic origins are multiple. They come from the leaching of plant protection products and fertilizers used in plantations. Indeed, Calamari *et al.,*[46] noted the presence of elements studied in biocides and chemical fertilizers that are used at will in the study area. Leaching of domestic waste is a major source of heavy metals. These elements are found in all household waste compartments[47]. In addition, people cross the river using motorized boats that use fuel whose residues are dumped into the water. Also,

the fishermen also use these motorized boats as means of displacement during the fishing activities. Calamari *et al.,*[46] indicate that the fuels contain Hg, Cu, Fe, Mn, Pb and Cd. Field observations have shown that these fishing activities are more intense during the dry season and fishermen to increase the yield proceed to prohibited fishing techniques such as the establishment of Acadjas (implantation of clusters of branches planted on the plans of waters) to fish. These plants may contain high levels of heavy metals related to their emission by anthropogenic activities[48]. The decomposition of these causes a return of heavy metals in the lake. This could also explain the increase in the content of some during the dry season.

Cd and Fe show strong positive correlation (Table 7) with the indices (HPI et HEI) values indicating the metals are the major factors for the pollution in this region. In the Table 6, mean values of HPI and HEI indices were observed to be 87 and 24, respectively, which indicated that the water samples of this lake were contaminated with low degree of pollution by heavy metals. So, severe precautions must be taken at the anthropogenic input location to control the heavy metal influx. The low scores are found at the stations (G3, G4) part which suggests the existence of similar point sources.

Fish Pollution

Iron showed the highest content in the muscles of both species of fish followed by Cu, Pb Hg and Cd. The results show that the average heavy metal content in fish muscles differs from one fish to another. This shows that different species of fish from the same stream contain different levels of heavy metal content. The cadmium content is generally low in nature. The concentrations of Cd (0.004 µg/g w.w) and Cu (3.35 µg/g w.w) in *Chrysichthys nigrodigitatus* from Guessabo Lake are lower than those found in fish of the same species in the Ogba River in Nigeria by 49 indicating 0.085 µg/g w.w for Cd and 5.32 µg/g w.w for Cu. However, high concentrations of Cu (0.1- 43.3 µg/g w.w) were reported in this type of fish in Tshangalele Lake in Congo due to mining activity[50]. The same author reported high values of Fe in the same lake (2.75- 81.1 µg /g w.w). Alipour *et al.,*[51] found levels in the same order as ours in Miankaleh Lake in Iran (28 µg/g w.w). *Chrysichthys nigrodigitatus* fish from Guessabo Lake have Pb levels (0.07µg/g w.w) less than those from Ogba

River (0, 5 µg/g w.w). With regard to mercury, the European Directive of 008/105/EC of 16/12/2008 legislated on the Environmental Quality standard by setting the limit of 0.02 µg/g w.w content of fish in muscles for consumption. The mercury concentration in *Chrysichthys nigrodigitatus* ranged from 0.01 to 0.24 with an average of 0.056 µg/g w.w. This shows that grades are substantially higher than this standard. The Tilapia content (0.038 µg/g w.w) is also higher than this standard. However, these concentrations remain lower than that proposed by 34, except for one fish containing Pb content (0.325 µg/g w.w) higher than this standard (0.3 µg/g w.w). Cd concentration (0.01 µg/g w.w) in Guessabo Lake's *Tilappia* spp are lower than those found in fish of the same species in the Galas River (0.02 µg/g w.w) and Langat River (0.03 µg/g w.w) 52,53. On the other hand, the Pb content (0.12 µg/g w.w) in the Guessabo Lake's Tilapia is higher than that determined in the fish of the same species in the Galas River in Malaysia by the same author[52], which indicates 0.05 µg/g w.w for lead. This difference would be related to the state of metallic pollution of their respective biotope. In this study the most abundant elements in the fish were Cu and Fe and the weakest were Cd, Pb and Hg. The species that contains the maximum of toxic metals (Cd, Pb and Hg) is tilapia (0.168 µg/g w.w) against (0.131 µg/g w.w) for fish of the genus *Chrysichthys nigrodigitatus*. On the other hand, *Chrysichthys nigrodigitatus* fish (31.02 µg/g w.w) recorded the maximum of essential metals (Cu and Fe) compared to (17.88 µg/g w.w) for *Tilapia* spp and the tilapia spp recorded the mean higher in Cd, Pb and Cu. This difference in heavy metal concentrations between the two species may be due to the difference in their physiological capacity for assimilation and excretion of the ingested trace element and their anatomy, diet and habitat[54]. Indeed, *Chrysichthys nigrodigitatus* (demersal) has an omnivorous benthophagous diet[44]. Living on the bottom, it finds its food in the muddy bottoms and consumes mostly organic detritus and invertebrates, while Tilapia is a planctophagous and benthopelagic species. Our results are contrary to those of[55] who found that *Chrysichthys nigrodigitatus* concentrated more non-essential metals than tilapia. The species of benthopelagic fish has more concentrated trace element Cd than the demersal species and this could be due to the fact that tilapias although closer to the sediments and also bioconcentrates this element

trace metal present in the aquatic environment as well from the water. Indeed, some authors have shown that this element is more in aqueous phase than in sediments[56]. *Chrysichthys nigrodigitatus* (demersal) has concentrated more trace elements that are more present in solid phase because more benthic and feeding on benthic organisms or even muddy bottom.

Assessment of health risk related to metals

The hazard quotient of Hg was higher than other non-essential metals, mainly because of its low RfD value. The total value of non-carcinogenic risk index (HQ) for children (0.845) and for adults (0.39) for selected metals is less than unity, indicating that the selected metals are only little or no risk to residents through skin contact or ingestion. Children are most exposed to trace metals because of their low body weight and physiological fragility as contaminants are easily absorbed into their bodies[55]. The children's organism potentially absorbs more contaminants and remains unable to eliminate them as easily as adults, since their elimination systems are less developed.

CONCLUSION

The study shows that the water of Guessabo Lake exhibits low concentration of heavy metals like Cd, As, Pb, Hg, Cu and Zn. The heavy metal pollution index (HPI <100) and heavy metal evaluation Index (HEI<40) place water quality in low contamination level. However, Guessabo Lake heavy metals Poll shows that the stations (G2 and G5) were moderately polluted in dry season. Fluctuations in concentration of various heavy metals have been observed in different seasons. Pearson's correlation analysis has shown that it can be an effective tool for identifying the most contributing of trace elements to this Contamination. The results show that all the fish samples analyzed are not polluted by trace metals in comparison with the standards recommended by WHO/FAO. The health risk assessment of concomitant multi-pathway exposure has shown an absence or low risk for fishermen and their families live at the edges of this watercourse. However, some human activities are deplored in this zone. The revelations of this study call on the authorities to persevere in the control of fishing techniques and in management, conservation and sustainable development, in order to allow an optimal use of this resource.

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Conflicts of Interest

The authors declared that they have no conflicts of interest to this work.

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