

Fish Contamination on Artisanal Gold Mining Area and Health Risks in Hiré, Côte D'Ivoire

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Received: October 5, 2018

Accepted: November 30, 2018

ABSTRACT

The present study aim at assessing the contamination of fish from rivers where chemicals used in gold extraction by artisanal miners are discharged. The study was conducted on in the town of Hiré in the south of Côte d'Ivoire. This town is dominated by the artisanal gold mining activities. Furthermore, the health risks associated with this contamination were also be assessed. The samples of two fishes (*Tilapia zillii* and *Oreochromis niloticus*) were collected along three rivers course (Agbalé, Tchebi and Akississo). These fishes are the most consumed by the population. Samples were persevered and taken to the laboratory for analysis. Muscles and gills were used for analysis. The sample fish tissues were analyzed by inductively coupled plasma mass spectrometry (copper and zinc); by cold vapor atomic fluorescence spectrometry (mercury) and by ultraviolet digestion (total cyanide). The results obtained showed in the organs of the fish, a strong accumulation of pollutants (copper, zinc, total cyanide), preferentially in the gills, on all sites. The content of these pollutants generally exceeds the threshold value tolerated for fish but also for humans. This is a limiting factor in the protein of the population of Hiré. Long-term consumption risks expose the population to contamination and therefore to the effects of these pollutants.

KEY WORDS: artisanal gold mining, fish contamination, health risks, heavy metals

INTRODUCTION

Development of economics activities of Côte d'Ivoire to the mining sector has led to the increased of artisanal gold mining. These activities are frequently accompanied by extensive environmental degradation and deplorable socio-economic conditions, both during operations and well after mining activities have ceased [1]. Indeed, artisanal miners employ rudimentary techniques for mineral extraction and often operate under hazardous, labour intensive, highly disorganized and illegal conditions. Human health impacts resulting from chemicals (mercury, cyanide, zinc, copper, etc.) use to extract gold. These chemicals polluted water and soils around sites and subsequently the food chain [2]. These pollutants are thus found in the tissues of plants and aquatic organisms. These fish, when ingested by man, contaminate it and expose it to the effects of the said pollutants. Trace elements (copper and zinc) play a biological role at low concentrations but become toxic at high levels. Others (cyanide and mercury) are considered to be trace pollutants of the environment and have deleterious biological effects even at low concentrations on human health [1-3].

In Côte d'Ivoire, few studies have been carried out concerning the characterization of environmental pollution and the health impacts of artisanal and small-scale gold mining activities. The present study aim at assessing the contamination of fish from rivers where chemicals (copper, mercury, zinc and total cyanide) used in gold-washing are discharged. Furthermore, the health risks associated with this contamination will also be assessed. In order to achieve these objectives, the town of Hiré was chosen because of the intensity of artisanal and small-scale gold mining activities in this zone compared to the other mining zones [4]. Specifically, measurements of copper, mercury, zinc and total cyanide concentrations in the gills and muscle tissues of *Tilapia zillii* and *Oreochromis niloticus*, which were the most consumed fishes, and analysis of the risks associated with their consumption.

MATERIALS AND METHODS

Study area

The study was carried in the town of Hiré (06°15'08.6 and 06°10'00.0 N and 05°23'44.8 to 05°16'32.1 W) [5]. The sampling stations are the streams bordering gold mining sites of Tchebi, Agbalé and Akississo (Figure 1).

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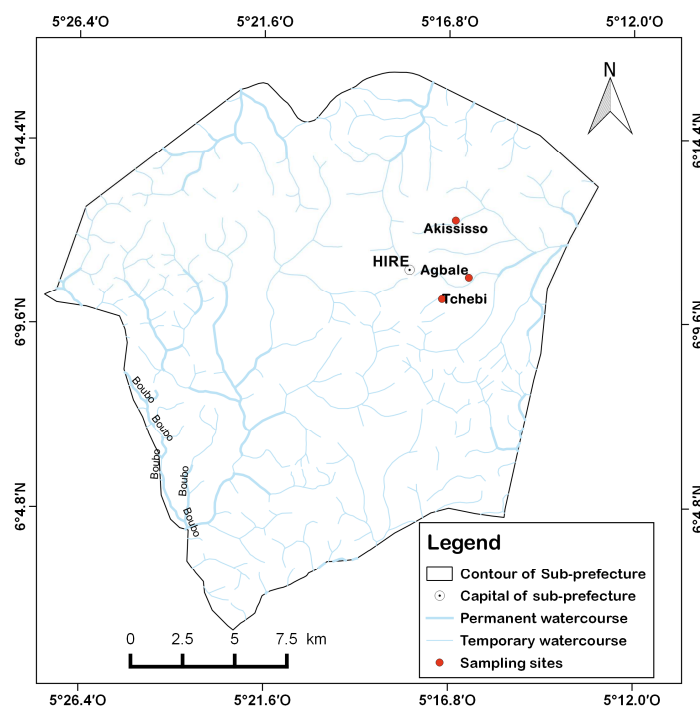


Figure 1. Sampling sites

Collection and preparation of fish samples

Three specimens of *Tilapia zillii* and *Oreochromis niloticus* were fishing from each sampling stations. They were considered as representative of fish species commonly consumed in the area under study. Fish were then identified according to the identification keys of [6-7] and were preserved in an ice box and transferred to the laboratory, where the samples were frozen. At laboratory, each specimen was weighed and measured by total length.

Chemical parameters concentration in fish tissues analyses

Preparation of samples and analysis were made according to FAO technical paper [8]. For metal analysis, frozen fish were partially thawed, and each fish was dissected using stainless steel instruments. Muscles and gills were taken out; composite samples of 25 to 100 g, respectively for small-size and large-size individuals, were used for analysis. The sample fish tissues were analyzed by inductively coupled plasma mass spectrometry (copper (Cu) and zinc (Zn)); by cold vapor atomic fluorescence spectrometry (mercury (Hg) and by ultraviolet digestion (total cyanide (CNT)).

Statistical analysis

The normality of the data was verified using the Shapiro-Wilk test (software R) and homogeneity was verified by Levene's test (STATISTICA 7.1). The variation of the chemicals parameters measured between organs fishes was compared using ANOVA of Kruskal-Wallis. The Mann Whitney test was employed to indicate significant differences between both organs fishes. The statistical program used for both tests was R software 3.1.1. The significance level was $p < 0.05$.

Method for assessing the health risks

The evaluation of the health risk to local people in the area of study posed by the consumption of fishes was based on the data from the muscle samples. The contents of the pollutants contained in the muscular tissues have been used for risks assessment.

Health risks of exposure of the population

Daily Dose of Exposure (DDE)

The daily dose of exposure (DDE) to chemical pollutants following consumption of fresh fish per individual was determined according to the equation 1 [9-10].

$$\text{DDE} = \frac{\text{CP}}{\text{BW}} = \frac{\text{CCP} * \text{R}}{\text{BW}} \quad (1)$$

Where

DDE (mg/kg/d): daily dose of an individual's exposure to chemical pollutants from fish consumption ;

CP (mg/kg/d): chemical pollutant intake per day after the consumption of fish by an individual ;

BW (kg): body weight of the fish consumer (60 kg) over the entire lifetime also estimated at 60 years [11] ;

CCP (mg/kg): concentration of chemical parameter in fish ;

R: yearly fish consumption per person, which is 14.45 kg for Côte d'Ivoire [12].

Hazard quotient (HQ)

The methodology of estimating hazard quotient (HQ) provides indications of the human health risk level due to exposure to pollutants [10]. HQ is the ratio between daily dose of an individual's exposure to chemical pollutants from fish consumption and tolerable daily dose. If the $\text{HQ} > 1$, there is a potential risk related to the studied metal [13]. The following equation was used to estimate risk:

$$\text{HQ} = \frac{\text{DDE}}{\text{TDD}} \quad (2)$$

Where

HQ: Hazard quotient

DDE (mg/kg/d): daily dose of an individual's exposure to chemical pollutants from fish consumption;

TDD (mg/kg/d): tolerable daily dose

Quantity of fish (QF) to be consumed for exposure to chemical pollutants

QF is the maximum quantity of fish can be eating to attack tolerable dose [14]. The equation (3) was used to estimate QF.

$$\text{QF} = \frac{\text{TDD} * \text{BW} * \text{FBM}}{\text{CCP} * \text{R}} \quad (3)$$

Where

QF (kg): Maximum quantity of fish can be eating by day without risk;

TDD (mg/kg/d): tolerable daily dose;

BW (kg): body weight of the fish consumer (60 kg) over the entire lifetime also estimated at 60 years [11] ;

FBM: Fish body mass (kg);

CCP (mg/kg): concentration of chemical parameter in fish;

R: yearly fish consumption per person, which is 14.45 kg for Côte d'Ivoire [12].

RESULTS

Concentration of mercury, copper, zinc and total cyanide in fish organs

The concentrations of mercury, copper, zinc and total cyanide in the gills and muscular tissues of the species *Tilapia zillii* and *Oreochromis niloticus* caught in the Agbalé, Tchebi and Akississo rivers are illustrated in Table 1.

Whatever the organ, fish and sampling site, mercury concentrations are well below the recommended threshold (0.5 mg/kg) for any organ, fish and sampling site. In fact, mercury concentrations are between $1.1 * 10^{-5}$ and $6 * 10^{-5}$ mg/kg. For *Tilapia zillii* from Akississo and Agbalé, and *Oreochromis niloticus* from Agbalé, the results indicate that Hg accumulates preferentially in the gills comparatively to *Tilapia zillii* and *Oreochromis niloticus* from Tchebi. The Kruskal-Wallis test showed no difference ($p > 0.05$) between the concentrations of mercury obtained in the gills and in muscle.

The concentrations of copper are above the threshold value (0.3 mg/kg) at any site. These concentrations recorded in the gills are higher to those of the muscle excepted *Oreochromis niloticus* from Akississo. In the gills, the minimum concentrations (0.53 mg/kg) of copper are recorded at Agbalé in *Oreochromis niloticus*, while the maximum concentrations (12.27 mg/kg) of copper in the same organ are recorded in *Tilapia zillii* from Tchebi. At the muscle, the low concentrations (0.36 mg/kg) of copper in both fish species are recorded at Agbalé. Unlike in the Tchebi *Tilapia zillii* muscles, where the highest concentrations (0.82

mg/kg) of copper are noted. The Kruskal Wallis test shows a difference ($p < 0.05$) between copper concentrations in gills and muscle.

The Zn concentrations in the two organs of the different fish exceeded FAO and WHO limit (0.5 mg/kg). It is also noted that the zinc concentrations recorded in the gills are significantly higher than those of the muscle tissues for all sites (Mann-Withney: $p < 0.05$). In the gills, the maximum Zn concentration observed was 40.99 mg/kg at Akississo in *Tilapia zillii* and the minimum of 7.93 mg/kg for *Oreochromis niloticus* collected at Akississo. At the muscle, the concentration of zinc is lowest (6.75 mg/kg) of *Tilapia zillii* from Tchebi, but, highest (9.40 mg/kg) of *Tilapia zillii* at Agbalé.

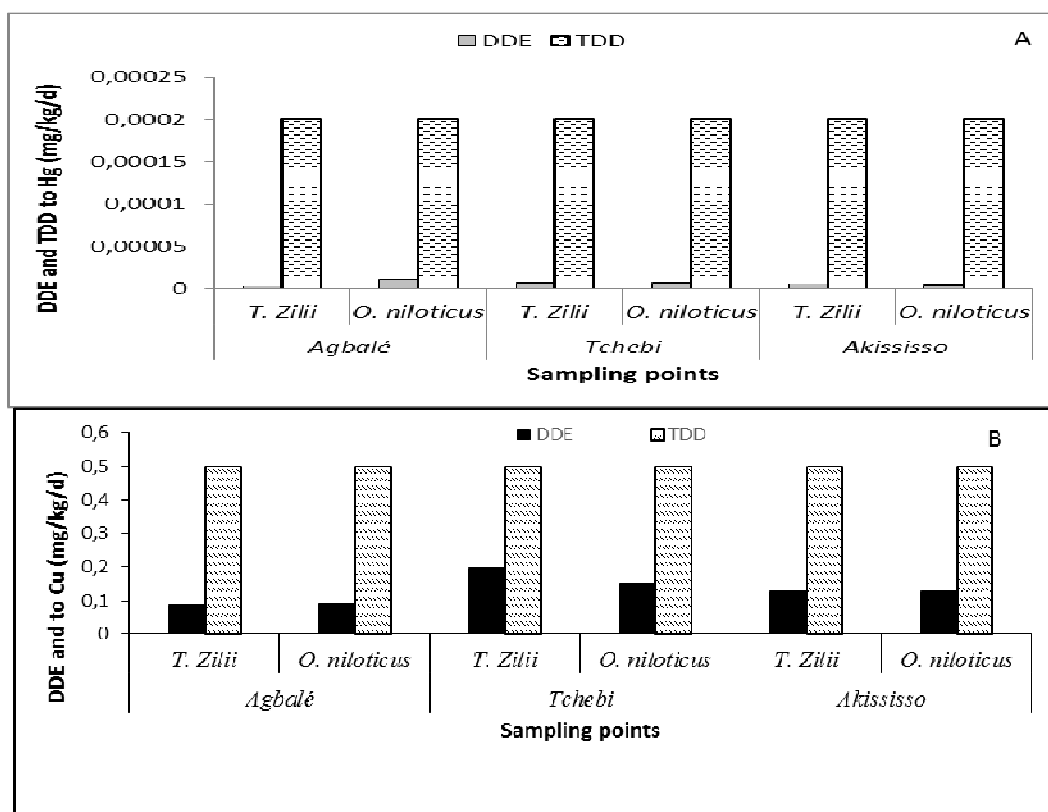
The total cyanide concentrations at the two organs of the different fish are above the threshold value (0.05 mg/kg). The total cyanide concentration accumulates preferentially in the gills than muscle. The low concentrations of total cyanide (0.72 mg/kg) are recorded at the muscle of *Tilapia zillii* from Agbalé, and the highest CNT concentrations content of *Oreochromis niloticus* from Tchebi was (4.81 mg/kg). The Kruskal Wallis test showed no difference ($p > 0.05$) between the total cyanide concentrations obtained in the gill and muscle.

Table 1. Heavy metals concentration in fish organs

Fish species	Sampling sites	Fish organs	Hg (mg/kg)	Cu (mg/kg)	Zn (mg/kg)	CNT (mg/kg)
<i>Tilapia zillii</i>	Akississo	Muscle	2,2*10 ⁻⁵	0.54	7.39	1.71
		Gill	6*10 ⁻⁵	3.03	40.99	3.22
	Tchebi	Muscle	2,9*10 ⁻⁵	0.82	6.75	2
		Gill	2,3*10 ⁻⁵	12.27	30.73	4.79
	Agbale	Muscle	1,6*10 ⁻⁵	0.36	9.40	0.72
		Gill	5,8*10 ⁻⁵	2.49	24.45	3.56
<i>Oreochromis niloticus</i>	Akississo	Muscle	1,9*10 ⁻⁵	0.53	7.93	2.16
		Gill	1,9*10 ⁻⁵	0.53	7.93	2.16
	Tchebi	Muscle	2,9*10 ⁻⁵	0.64	7.58	1.98
		Gill	1,1*10 ⁻⁵	6.28	15.38	4.81
	Agbale	Muscle	4,4*10 ⁻⁵	0.37	6.88	1.07
		Gill	5,8*10 ⁻⁵	2.49	24.45	3.56
Norm FAO/WHO			0.5	0.3	0.5	0.05

Daily dose exposure (DDE) to chemical pollutants

The DDE to Hg (Figure 2A), Cu (Figure 2B) are well below tolerable daily dose 0.0002 mg/kg/d, 0.5 mg/kg/d respectively. But the DDE to CNT (Figure 2C) were higher than tolerable daily dose (0.056 mg/kg/d).



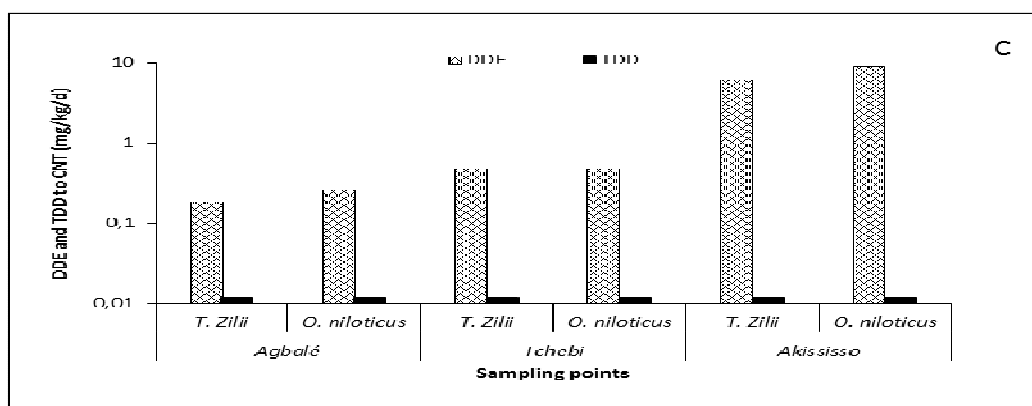


Figure 2. Daily dose of exposure (DDE) and tolerable daily dose to Hg (A), Cu (B) and CNT (C)

Hazard quotient (HQ)

In the present study, the results of HQ calculated for each of the heavy metals (Hg, Cu and CNT) in two fish species (*Tilapia zillii* and *Oreochromis niloticus*) are given in Table 2. The HQ to fish consumption is generally below 1 for Hg and Cu in all fish at sampling points. Unlike HQ values for CNT in Akississo fish's exceeds 1.

Table 2. Hazard quotients (HQ) for individual metals caused by the consumption of fish

Parameter	Havy metals	Sampling points						Threshold value
		Agbalé		Tchebi		Akississo		
		<i>T. zillii</i>	<i>O. niloticus</i>	<i>T. zillii</i>	<i>O. niloticus</i>	<i>T. zillii</i>	<i>O. niloticus</i>	
HQ	Hg	0.05	0.05	0.03	0.03	0.02	0.02	1
	Cu	0.17	0.18	0.40	0.28	0.26	0.26	
	CNT	0.32	0.46	0.86	0.86	11	15.96	

Quantity of fish (QF) to be consumed for exposure to chemical pollutants

The QF recorded from Agbalé site ranged from 0.59 for CNT to 539.31 (kg/day) for Hg with *T. zillii* (0.0085 kg), and from 0.35 for CNT to 162.22 (kg/day) for Hg with *O. niloticus* (0.0075 kg). The two fish species from Tchebi site presented high QF (803.02 kg/day) for Hg with *T. zillii* (0.0152 kg) and low QF (0.34 kg/day) for CNT with *O. niloticus* (0.00135 kg). *T. zillii* (0.00306 kg) and *O. niloticus* (0.00278 kg) showed higher QF (41.4 and 50.09 kg/day for Hg) and lower QF value (0.639 and 1.02 kg/day for CNT) on Akississo site.

Table 3. Maximum quantity of fish to be consumed by day without risk (QF)

Parameters	Heavy metals	Agbalé		Tchebi		Akississo	
		<i>T. zillii</i>	<i>O. niloticus</i>	<i>T. zillii</i>	<i>O. niloticus</i>	<i>T. zillii</i>	<i>O. niloticus</i>
FBM (kg)	Hg	0.0085	0.0075	0.0152	0.00135	0.00306	0.00278
QF (kg/day)	Hg	539.31	162.22	803.02	32.82	41.4	50.09
FBM (kg)	Cu	0.0085	0.0075	0.00152	0.00135	0.00306	0.00278
QF (kg/day)	Cu	2.44	2.097	1.764	2.217	5.972	5.426
FBM (kg)	CNT	0.0085	0.0075	0.0152	0.135	0.306	0.278
QF (kg/day)	CNT	0.59	0.35	0.38	0.34	1.02	0.639

DISCUSSION

Concerning the level of contamination of fish *Tilapia zillii* and *Oreochromis niloticus*, analyzes of pollutants in the organs (muscular tissues and gills) showed strong accumulations of copper, zinc and total cyanide in these organs. What would mean that the fish would have accumulated these pollutants follows a contamination. Fish gills accumulated more pollutants than muscle tissue. These same observations were noted by [15-16]. These authors showed that an accumulation of chemical pollutants in fish organs, especially at the

gill, was indicative of the high presence of these pollutants in their living environment or in their diet. However, the concentrations of Hg, Cu, Zn and CNT in fish organs differ markedly from site to site and from species to species. The difference between sites is due to the frequency of use of chemicals to extract gold [17].

Concerning the degree of accumulation of pollutants in fish species, *Tilapia Zillii* accumulated more pollutants than *Oreochromis niloticus*, irrespective of the sampling site and the analyzed organ. This could be explained by the fact that these fish not the same feeding mode. The fish studied belong to trophic levels in a food chain. According to [18], this chain includes primary consumers who directly harvest food from primary producers (vegetation, etc.) and secondary consumers who feed on primary consumers (invertebrates and small crabs, etc.). Indeed according to a study conducted by [19], *Oreochromis niloticus* feeds mainly on phytoplankton. He filters these seedlings into the water column. As for *Tilapia zillii*, it has a larger diet in that it feeds on insects, molluscs, zooplankton, fish, macrophytes [20]. As a result, the variety of the diet of *Tilapia zillii* is one of the factors contributing to a strong accumulation of chemical pollutants by this fish. Furthermore, [21-22] showed that the accumulation of chemical pollutants in fish organs also depended on factors such as the level of water and sediment contamination, diet, size, sex, Behavior, eating habits and the reproductive cycle. Moreover, according to [23-24], benthic species accumulated more pollutants because they live in the sediments that are the reservoirs of many chemical pollutants.

The results indicate that the risk of danger from fish consumption is less than 1 for Hg and Cu, but is very critical regarding total cyanide. Contamination of the consumer by polluted fish should be taken seriously. According to [25], fish remains an important source of protein for populations. It should be recalled that feeding populations is the source of their exposure to chemical pollutants [26]. For [27], due to their resistance to biodegradation, their persistence and toxicity, chemical pollutants can be concentrated in the muscular tissues of living organisms and cause considerable ecological and public health damage.

The quantities of *O. niloticus* from Tchebi and the two fish species caught in Akississo have the lowest amount in relation to the estimated quantity of fish to be consumed per day per individual regarding to mercury. Those small amounts are related to the fact that those fishes have accumulated high concentrations of mercury. As for contamination by copper, all fishes caught in Tchebi and Agbalé have the lowest quantities of fish to be consumed. This would mean that the fish in these sites were more impacted by copper, so an uncontrolled feeding of fish from these sites would expose the consumer more. For total cyanide contamination, fishes from the Tchebi and Agbalé streams have the lowest amounts of fish to be consumed. That quantity might be due to the accumulation of total cyanide in the fish muscles. For [3], these small amounts of fish to consume reflect the high toxicity of these pollutants to which consumers are exposed. There is then a relationship between the exposure of the populations and the heavy metals concentration in the flesh of the fish to be consumed [28]. Moreover, those maximum quantities of fish are higher than the total national average daily consumption in Côte d'Ivoire. These quantities of fish that should not be exceeded in consumption are a limiting factor to the consumption of the Hiré population, even if the probability of consuming such a quantity of fish per day is low.

CONCLUSION

Chemical pollutants preferentially concentrate in the gills than the muscle. In addition, *Tilapia zillii* concentrated more pollutants of *Oreochromis niloticus*. The hazards quotient determined clearly shows that the daily consumption of fish exposes consumers to high health risks because the levels of these metals are above standards. The risk of accumulation of these pollutants in the body is real and the adverse effects to be feared. In view of all the above, we recommend that the Hiré population not consume *Tilapia zillii* and *Oreochromis niloticus* fish from Tchebi and Akississo, to the competent authorities in this area, to regulate gold-washing activities in order to preserve the water and the fishing resources of the pollution of the chemicals used in this activity.

Acknowledgements

This study has been supported by Sida-UNESCO project on abandoned mines in sub-Saharan African countries. We are very grateful to the Minister in charge of Mines for data, permission to access and sampling. We thank the Sanitation and Environmental Engineering research team members for their help during the field data collecting.

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