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Impact of Glyphosate and 2,4-D used in agriculture on the quality of *Chrysichthys nigrodigitatus* (Lacépède, 1803) from the Sassandra River in Guessabo (Côte D'ivoire)

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Abstract

The objective of this study is to evaluate the impact of glyphosate and 2,4-D contamination in the water, sediments, organs (gills, liver and muscles) of *Chrysichthys nigrodigitatus* and the health of the population related to the consumption of this fish from the river at Guessabo. The analysis of the different samples was done using HPLC. The results showed that the annual concentrations of the active ingredients (glyphosate and 2,4-D) varied in the water from 1.26 to 1.65 µg L^{-1}, and in the sediment from 0.06 to 0.23 mg.kg^{-1}. The concentrations of these active ingredients in fish muscle ranged from 0.14 to 0.36 mg kg^{-1}. The bioconcentration factors for fish organs range from 5994.1 to 14413.2 and the bioaccumulation factors range from 0.7 to 2.8. Then the highest hazard quotient (HQ) values related to fish contamination are ranked in the order of 0.044 for children and 0.018 for adults. In sum, consumers do not face major risks from 2,4-D and glyphosate when consuming *Chrysichthys nigrodigitatus* from the river at Guessabo. However, children under the age of eighteen do accumulate contaminants from the fish in this locality.

Keywords: 2,4-D; Glyphosate; Sassandra River; *Chrysichthys nigrodigitatus*; Guessabo; Côte d'Ivoire

1. Introduction

Agriculture is one of the main sources of income for the population in sub-Saharan Africa. In Côte d'Ivoire, the agricultural sector accounts for a quarter of the gross domestic product and employs nearly one in two people of working age [1]. In the large cities, agriculture is focused on market gardening and is a source of fresh produce for the population. This agriculture is very often practiced in swampy areas of the cities and uses pesticides to improve yields [2]. This agriculture is practised around rivers and lagoons to meet all the water needs of the crops [3]. In Guessabo, in the Haut-Sassandra, market gardeners and other farmers rush to the banks of the Sassandra River during the dry season to plant short-lived crops such as maize, rice, potatoes, okra, chilli peppers etc. Faced with the weediness of plots, the pressure of crop diseases and pests, these farmers resort to phytosanitary products (herbicides, insecticides and fungicides) to limit agricultural losses [4]. Thus glyphosate and 2,4-D, which are systemic foliar herbicides, respectively total and selective, are very popular for weeding pre-seeding and post-seeding plots. However, the abusive use of these pesticides in high and uncontrolled doses can have severe repercussions not only on the health of farmers and consumers, but above all on the balance of the ecosystem that is the Sassandra River. This contamination is effective through volatilisation, infiltration and runoff [5 ; 6]. The toxicity of pesticides has been demonstrated by several toxicological and ecotoxicological studies [2 ; 7 ; 8]. In addition, a high production of fish is recorded in this part of the Sassandra River at Guessabo. The species *Chrysichthys nigrodigitatus* is heavily fished and highly valued by the population [9]. Several studies have shown the exposure of aquatic environments to the effects of pesticides. These include Lévêque *& al*. [10], who assessed the level of contamination of aquatic fauna by pesticide residues in the

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Bandama, and Hampoh *& al*. [11] and Togbe *& al*. [12], who examined the exposure of the lagoon environment to chemical inputs, thus compromising the quality of the aquatic fauna. Very few studies have focused on the sanitary quality of fish from the Sassandra River on the mainland, in this case the Guessabo area, which is an area of high fish production and is also subject to stresses due to intense agricultural activities in its vicinity. This study aims to assess the impact of contamination with glyphosates and 2,4-D used in agriculture in the water, sediments, organs (gills, liver and muscle) of *Chrysichthys nigrodigitatus* in the Sassandra River at Guessabo and the health risks related to the consumption of the fish.

2. Material and methods

2.1. Material

2.1.1. Study areas

The sub-prefecture of Guessabo is located in west-central Côte d'Ivoire, in the Haut Sassandra between latitudes 6 ◦ 570 and 7 ◦ 2 0 N and longitudes 6 ◦ 450 and 6 ◦ 460 W. Its population is estimated at 36302 (NSI, 2015). The branching of the Sassandra River in this locality greatly favours inland fishing and agricultural development. During the dry season, due to the lowering of the river level, agriculture is intensified in its vicinity. Ten water and sediment sampling points were selected. These points are distributed to cover areas of high fishing and transport activity on the water body. They are also chosen according to the agricultural activities in the vicinity of the river (Figure 1).

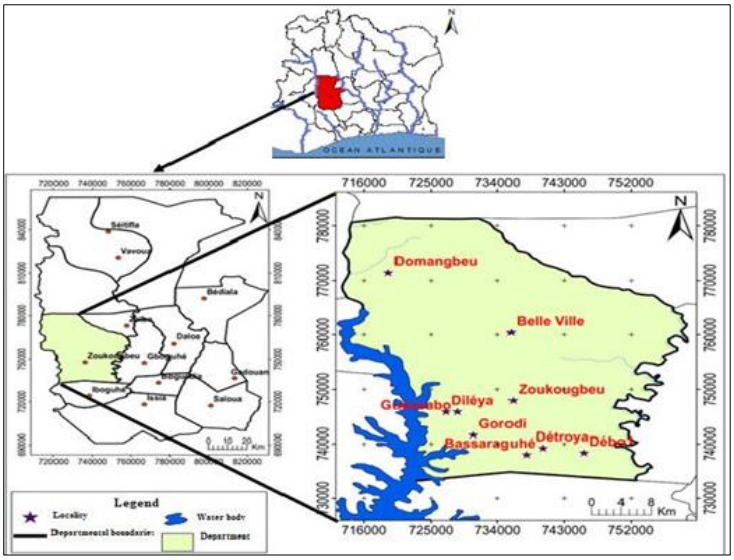

Figure 1 Map of the Sassandra River branch at Guessabo

2.1.2. Biological and analytical material

The study material consisted of specimens of *Chrysichthys nigrodigitatus* (Lacepède, 1803), water and sediments sampled in the Sassandra River at Guessabo.

Analytical standards of glyphosate and 2,4-D of 98% purity, acquired from Dr. Ehrenstorfer, were used to prepare the calibration solutions.

The glyphosate derivatization reagent glyphosate-MOCF of purity ≥ 99% was purchased from SIGMA-ALDRICH.

The reagents consist of acetonitrile, dichloromethane, methanol, ammonia (28 %), formic acid, glacial acetic acid, ethyl acetate, triethylamine, ammonium hydroxide (2 %), potassium hydroxide to 0, 5 M hydrochloric acid, 6 M hydrochloric acid, EDTA (sodium salt) and 9-fluorenylmethoxycarbonyl (FMOC) of purity ≥ 99%, all of HPLC grade and double distilled water were also used for the extraction and determination of glyphosate and 2,4-D. The equipment consisted of an electronic balance with a precision of ± 0.001g for weighing the fish and sediment samples and the reagents. A plastic beaker was used to measure the volume of water. A porcelain mortar, hand sieves with pore diameters ranging from 2 mm to 62 µm, an oven, a rotary evaporator, a centrifuge, a conical separating funnel, plastic tubing, a pasteur

pipette were used for sample conditioning. A high performance liquid chromatography line (SHIMADZU) and a computer with LC solution software were used for the quantification of pesticide residues in water, sediment and fish organs.

2.2. Methods

2.2.1. Sampling

Fish were collected at the landing sites from local fishermen. The fishermen use plank and motorised canoes. The fishing gear used was gill nets (mesh size: 14 and 20 mm) and hawks. The water and sediment samples were taken using a hydrological bottle with a capacity of one litre and a steel Van Veen type bucket with a surface area of 250 cm^2 respectively. The water was transferred into amber plastic bottles, wrapped with aluminium foil. The sediment was then transferred into food bags. After sampling, the fish, water bottles and sediment bags were placed under ice in a cooler and transported to the laboratory for analysis.

2.2.2. Determination of active ingredients

Extraction into water

The slightly modified MA 1 (AQUAREF) method described by Nhu-Trang *& al.* [13] was used to extract glyphosate and 2,4-D residues from water samples. A 50 mL sample of water was filtered through a polypropylene (pp) conical separating funnel with a single-use syringe having a cellulose membrane filter. Then 0.5 mL of aqueous solution (glyphosate or 2,4-D) at 20 µg. L^{-1} as tracers prior to derivatization and 1 mL of Borate-Na buffer were added. The whole set was shaken. Then 1 mL EDTA-Na_2 was added before being shaken again and left to stand for 5 minutes. After this step, respectively 4.5 mL acetonitrile and 0.6 mL fluorenylmethoxycarbonyl (FMOC) of purity ≥ 99% were added and shaken well each time, then allowed to react for 30 minutes in the dark at room temperature. After the derivatization phase, the sample was concentrated under nitrogen to a volume of 5 mL. A deposit of reaction by-product (FMOC) formed on the walls of the tube. The resulting solution was transferred to another 15 mL tube. The plastic tube was subsequently rinsed with 500 µL of ultrapure water. The extraction was carried out with 3 times 1.5 mL of ethyl acetate, then centrifuged for 20 seconds after each extraction to separate the two phases. The supernatant (ethyl acetate) was removed with a pasteur pipette. The aqueous phase was then concentrated under nitrogen for 15 minutes to remove the remaining ethyl acetate, with the tubes being shaken every 5 minutes. The final volume was approximately 5 mL. The sample was acidified (pH=3) with 100 µL of formic acid added to the aqueous phase and then made up to 5 mL with ultrapure water. The whole was homogenised. After these steps, the Oasis HLB SPE cartridges were conditioned with 2 x 500 µL of methanol and then 2 x 500 µL of 0.1% aqueous formic acid solution. This was followed by percolation of 5 mL of the acidified sample (pH=3) at a flow rate of approximately 1 mL.min-1. The tube was rinsed successively with 1 mL of 0.1% aqueous formic acid solution and 2 x 500 µL of ultrapure water. Then the adsorbent was dried briefly under vacuum for 1 minute. This was followed by the elution of a mixture (3 x 700 µL) of methanol and ammonium hydroxide (2 %) in the proportions (70 : 30 ; v/v). The eluate was collected in a 20 mL glass tube and concentrated under nitrogen for evaporation of the methanol. The residual volume after evaporation was approximately 0.3 mL. It was made up to 1 mL with ultrapure water and stored in a vial for HPLC analysis.

Sample preparation and extraction in sediments

The sediment samples were dried at room temperature on a bench top for seven to ten days, depending on their water content as proposed by Kpan Kpan *& al*. [14]. Once dried, the samples were sieved before being ground in a porcelain mortar. They were sieved again and the fine fraction (100 µm) was dried again in the oven at 60 °C for one hour to obtain a constant weight. The extraction was performed according to the technique proposed by Gery and Mazzella [15]. A 10 mL solution of 0.5 M potassium hydroxide (KOH) was added to 3 g of the sieved crushed material in a 50 mL conical bottom tube. The mixture was homogenised for 30 minutes on a shaker and then centrifuged at 3500 rpm for 10 minutes. After this step, the supernatant was removed (2.5 mL) and transferred to a 50 mL conical tube. Then 2.5 mL of ultrapure water was added and homogenised again. The pH was adjusted to 9 with a 6 M hydrochloric acid solution (approximately 160 µL). Prior to derivatisation, the Oasis HLB SPE cartridges were conditioned with 2 mL of methanol and 2 mL of ultrapure water. The homogenised extract (5mL) was percolated and collected in a 50 mL conical tube. Pesticide derivatisation was performed by first adding 50 µL of aqueous solution (glyphosate or 2,4-D) at 20 µg. L^{-1} as internal standards were added to the 5mL of the conical tube prior to derivatisation. Then Borate-Na buffer (325 µL) was added and the whole set was shaken. 1 mL EDTA-Na_2 was added before being shaken and left for 5 minutes. After this step, 4.5 mL acetonitrile and 0.6 mL fluorenylmethoxycarbonyl (fmoc) were added respectively and the mixture was shaken well each time and left to react for 30 minutes in the dark at room temperature (20 - 25 °C). The sample was then concentrated under nitrogen to a volume of 5 mL. A deposit of reaction by-product (FMOC) formed on the walls of the tube. The resulting solution was transferred to a 15 mL plastic tube. The plastic tube was then rinsed with

500 µL of ultrapure water. The extraction was carried out with ethyl acetate (3 times 1.5 mL), then centrifuged for 20 seconds after each extraction to separate the two phases. The supernatant (ethyl acetate) was removed with a pasteur pipette at each extraction. The aqueous phase was concentrated under nitrogen for 15 minutes to remove the remaining ethyl acetate. The tubes were shaken every 5 minutes. The final volume was approximately 5 mL. Formic acid (100 µL) was added to the aqueous phase (preconcentration) and then made up to 5 mL with ultrapure water. The whole mixture was homogenised. After these steps, the Oasis HLB SPE cartridges were conditioned with 2 x 500 µL of MeOH and then 2 x 500 µL of 0.1 % aqueous formic acid solution. This was followed by percolation of 5 mL of acidified sample (pH=3) at a flow rate of approximately 1 mL.min-1. The tube was rinsed successively with 1 mL of 0.1% aqueous HCOOH solution and 2 x 500 µL ultrapure water. Then the adsorbent was dried briefly under vacuum for 1 minute. This was followed by the elution of a MeOH mixture (3 x 700 µL). The eluate was collected in a 20 mL glass tube and concentrated under nitrogen allowing evaporation of the MeOH. The residual volume after evaporation of the methanol was approximately 0.2-0.3 mL. It was made up to 1 mL with ultrapure water and stored in a vial for HPLC analysis.

Extraction into fish organs

The extraction of pesticides from fish organs was performed by the Accelerated Solvent Extraction (ASE) technique, following the recommendations of Polard [16] and Yao [17]. The samples were ground in a mixture with hydromatrix in a 1/3 mass ratio. This grind (10 g) was loaded into the Dionex cell (ASE) and then supplemented with hydromatrix. Extraction with ASE was done using a mixture of acetone / dichloromethane solvents (75/25; v/v). The mixture was injected into the cell, held for 5 min at 50°C and 100 bar pressure. At the end of the 5 min, 60 % of the solvent volume is renewed. This sequence is repeated 3 times at this temperature, then 3 times at 100 °C. The solvent flushed from the cell is loaded with the extracted analytes. The volumes from the extractions at both temperatures are separated and placed in the freezer to remove the cold-frozen lipids. Using a rotary evaporator, the dichloromethane is removed and the filtrate volumes are reduced to 10 mL. Purification of the filtrates containing acetonitrile was done by adsorption chromatography on Oasis HLB Plus cartridges. The purified extract was dried using a rotary evaporator and then reconditioned in 1ml of ultrapure water and passed through an ultrasonic bath for 5min. Borate buffer (1ml) at pH 9 and fmoc solution (1ml) were added and allowed to drift for 45 min in the dark. After derivatization, 2 mL of dichloromethane was added and centrifuged for 10 min at 4000 rpm. At the end, 5 mL of supernatant was recovered and packed in a filter vial before injection into the HPLC.

Quantification of active ingredients in samples

Quantification of pesticide residues in water, sediment and fish organs was carried out using an HPLC chain consisting of a SIL-20A sampler, an LC-20AT, a TRAY tank, a DGU-20A5 degasser, a CTO-20A oven and a SPD-20A UV/VIS detector. Data acquisition, i.e. peaks and their areas, was possible using a computer with LC solution software. The HPLC chromatographic conditions were an injection volume of 5-20 µL, a flow rate of 0.45 mL/min. Mobile phase: A (acetonitrile) and B (0.1% triethylamine buffer adjusted to pH 9.5 with acetic acid). The elution mode was isocratic, with wavelengths 205 nm and 240 nm for glyphosate and 2,4-D respectively at the oven temperature of 45°C (Table 1). The peak areas of the standards and samples were used to calculate the active ingredient concentrations using the following formula.

$$Cp = \frac{Sech \times Ce \times V_2 \times V_f \times F}{Se \times Mech \times V_1}$$

With

- Cp: concentration of active ingredient (mg/L)
- Sech: peak area of the sample
- Se: peak area of the standard
- Ce: concentration of the standard (mg/L)
- V1 : volume to be purified (L)
- V2 : volume after purification (L)
- Vf: final volume (L)
- Mech : mass of the sample (Kg)
- F: dilution factor

Table 1 Chromatographic conditions for active ingredients in HPLC

Active substances	Wavelength (nm)	Mobile phase		Column	Injection volume (µl)
		Water (%)	Acetonitrile (%)		
2,4 D	240	20	80	Nucleosil 5C18	20
Glyphosate	205	20	80	Nucleosil 5C18	10

2.2.3. Processing the results

Bioconcentration factor

The bioconcentration factor (BCF) is defined as the ratio between the concentration of the chemical compound in the living organism and that in the living environment [18]. From the annual active ingredient values obtained, the bioconcentration factor of each ingredient is calculated according to the following expression:

$$BCF = \frac{C_o}{C_e}$$

With

- BCF: Bioconcentration Factor;
- C_o: Concentration of the active substance in the organism;
- C_e: Concentration of the substance in water.

Bioaccumulation factor

The bioaccumulation factor is the ratio of the concentration of the active substance in the organism to that in the sediment. The annual bioaccumulation factor for each active ingredient was calculated for all organs according to the formula used by Coulibaly [18].

$$BAF = \frac{C_o}{C_s}$$

with

- BAF: Bioaccumulation Factor;
- C_o: Concentration of the active substance in the organism;
- C_s: Concentration of the active substance in the sediment.

Expression of health risks related to the consumption of fish polluted by pesticides

The assessment of the health risks associated with the consumption of fish contaminated with glyphosate and 2,4-D will follow four main steps (Ouro-Sama *et al.,* 2014). These are to identify the hazard, select the Toxicological Reference Values (TRVs) or Acceptable Daily Intake (ADI) and assess population exposure. The Daily Exposure Dose (DEL) will be determined on the basis of chronic exposure of individuals. The average amount of fish assumed to be consumed by an Ivorian (child or adult) is 16 kg/year, approximately 0.044 kg/d [19]. The EDI is determined as follows;

$$DDE = C \times Q \times F/P$$

with:

- DDE : Daily Exposure Dose to pesticides (mg/kg/j)
- C: Pesticide concentration in fish (mg/kg)
- Q: Quantity of fish ingested per day, (kg/j)
- F: Frequency of exposure (F = 1), unitless
- P: Body weight of target (kg).

According to the US Environmental Protection Agency, the average body weight of children aged 0-15 years is 28 kg and that of an adult is 70 kg [20]. The hazard quotient (HQ) is used to characterise the risk for threshold effects.

For the oral route of exposure, it is calculated as follows:

$$HQ = DDE/ADI$$

ADI: Acceptable Daily Intake (mg/kg/j).

If HQ < 1, the occurrence of a toxic effect is unlikely. However, if HQ > 1, the occurrence of a toxic effect is likely.

2.3. Statistical treatment

Univariate analyses (one-way ANOVA) were used to process the data. The assumption of normality of the data distribution was tested. The Kolmogorov-Smirnov test was used to test the normality of the data distribution. This method of analysis concerned the study of the seasonal effect of active ingredient concentrations in water, sediment and fish organs. For these different tests the level is significant, if $p < 0.05$ and the level is not significant, if $p > 0.05$.

3. Results and discussion

3.1. Pesticide levels in the water of the Sassandra River at Guessabo

Glyphosate did not show a significant difference in concentration between the dry and rainy seasons (Table 2). In the dry season, its mean concentration was lower (1.04 ± 0.41 µg L^{-1}) than in the rainy season (2.31 ± 1.72 µg L^{-1}). The mean value of 2.4 D recorded in the dry season (0.78 ± 0.30 µg L^{-1}) was also lower than that recorded in the rainy season (1.74 ± 1.31µg L^{-1}). Statistical analysis showed a significant difference of 2.4 D between seasons ($p < 0.05$) (Table II)

Table 2 Annual and seasonal concentrations of active ingredients (mean ± standard deviation) in the water (µg L^{-1}) of the Sassandra River at Guessabo

Active substances	Seasons		Annual value
	Dry season	Rainy season	
Glyphosate	1.04 ± 0.41[a]	2.31± 1.72[b]	01.65 ± 0.02
2,4 D	0.78 ± 0.30[a]	1.74 ± 1.31[a]	01.26 ± 1.01

Concentrations with letters a and b in the same row are significantly different at the 0.05 level

3.1.1. Pesticide levels in the sediments of the Sassandra River at Guessabo

In contrast to 2,4-D, Glyphosate showed a significant difference in concentration between seasons ($p < 0.05$) (Table 3). In the dry season, the mean concentration of glyphosate was (0.09 ± 0.04 mg.kg^{-1}) lower than that of 2,4-D (0.10 ± 0.05 mg.kg^{-1}), while in the rainy season, the opposite effect was recorded. The average concentration of glyphosate (0.37 ± 0.19 mg.kg^{-1}) was higher than the concentration of 2,4-D (0.027 ± 0.01 mg.kg^{-1}) in the river sediments at Guessabo.

Table 3 Seasonal and annual concentrations of active ingredients (mean ± standard deviation) in the sediments (mg.kg-1) of the Sassandra River at Guessabo

Active substances	Seasons		Annual value
	Dry season	Rainy season	
Glyphosate	0.09 ± 0.04[a]	0.37 ± 0.19[b]	0.23 ± 0.19
2,4 D	0.10 ± 0.05[a]	0.027 ± 0.01[a]	0.06 ± 0.03

Concentrations with letters a and b in the same row are significantly different at the 0.05 level

3.1.2. Variation in the levels of active substances in the gills, liver and muscles of Chrysichthys nigrodigitatus

Table 4 shows the annual and seasonal concentrations of active substances in the gills, liver and muscles of *Chrysichthys nigrodigitatus* in Guessabo. The observation of this table shows a significant difference in concentration ($p < 0.05$) between the seasons with glyphosate and 2,4-D. Glyphosate (0.36 ± 0.29 mg.kg^{-1}) records the highest annual concentration in the liver of *Chrysichthys nigrodigitatus* caught in Guessabo. The low concentrations are recorded respectively in the dry season in the liver by glyphosate (0.03 ± 0.01 mg.kg^{-1}) and in the rainy season in the gills by 2,4-D (0.04 ± 0.02 mg.kg^{-1}). The observation of the different concentrations in the muscle of *Chrysichthys nigrodigitatus* shows higher concentrations of glyphosate and 2,4-D in the dry season than in the rainy season.

Table 4 Seasonal and annual concentrations of active ingredients in the gills, liver and muscle of *Chrysichthys nigrodigitatus* caught in the Sassandra River at Guessabo

Active substances		Seasons		Annual value
		Dry season	Rainy season	
Gills	Glyphosate	0.23 ± 0.11^a	0.07 ± 0.03^b	0.15 ± 0.11
	2,4-D	0.16 ± 0.05^a	0.04 ± 0.02^b	0.12 ± 0.07
Liver	Glyphosate	0.14 ± 0.07^a	0.59 ± 0.23^b	0.36 ± 0.29
	2,4-D	0.21 ± 0.04^a	0.14 ± 0.02^b	0.17 ± 0.05
Muscle	Glyphosate	0.23 ± 0.05^a	0.11 ± 0.04^b	0.17 ± 0.08
	2,4-D	0.18 ± 0.04^a	0.10 ± 0.01^b	0.14 ± 0.05

Concentrations with letters a and b in the same row are significantly different at the 0.05 level

3.1.3. Bioconcentration and bioaccumulation factor of pesticides in the organs of Chrysichthys nigrodigitatus

The cumulative annual bioconcentration factor of 2,4-D is higher than that of glyphosate (Table 5). In order of most to least accumulative organs, the gills are followed by the muscle and the liver. In descending order of accumulation of active ingredients, 2,4-D is followed by glyphosate. 2,4-D has the highest bioaccumulation factor in the liver (2.8) of *Chrysichthys nigrodigitatus*, while glyphosate (0.7) has a low value in the muscle (Table 5). 2,4-D has bioaccumulation factors higher than 2 in muscle and liver. However, glyphosate has bioaccumulation factors below 2. The bioaccumulation factors of the pesticides in ascending order are quite high in liver, muscle and gills. The order of increasing bioaccumulation factor of the active ingredients is 2,4-D followed by glyphosate.

Table 5 Bioconcentration and bioaccumulation factor of active ingredients in the organs of *Chrysichthys nigrodigitatus*

	Bioconcentration factors		Bioaccumulation factors	
Bodies	Glyphosate	2,4-D	Glyphosate	2,4-D
Muscle	6708.9	10693.9	0.7	2.2
Liver	14413.2	13580.2	1.6	2.8
Gills	5994.1	8045.5	0.6	1.6

3.1.4. Health risk related to the consumption of fish from the river in Guessabo

The results of exposure to active ingredients related to the ingestion of fish (*Chrysichthys nigrodigitatus*) as well as the corresponding hazard quotients (HQ) in adults and children are given in Table 6. The highest daily exposure dose (EDI) related to the consumption of *Chrysichthys nigrodigitatus* is held by Glyphosate in children (0.0027 mg/kg/j); with a hazard quotient (HQ) of the order of 0.0054. The different hazard quotients (HQ) for 2,4-D in children (0.044) are higher than those for adults (0.018). According to the report of the European Food, Environment and Occupational Health Safety Agency, for chronic threshold effects, 0.5 mg/kg bw/day is recommended for glyphosate and 0.05 mg/kg bw/day for 2,4-D.

Table 6 Daily exposure dose and hazard quotient in children and adults related to the consumption of *Chrysichthys nigrodigitatus*

Trace elements	C (mg/kg)	DJA (mg/kg/j)	DJE (mg/kg/j)		QD	
			Adult	Children	Adult	Children
Glyphosate	0.17	0.5	0.0011	0.0027	0.0022	0.0054
2,4-D	0.14	0.05	0.0009	0.0022	0.018	0.044

4. Discussion

The seasonal levels of active ingredients in the river water were much higher in the rainy season than in the dry season for glyphosate (2.31 µg. L^{-1}) and 2,4-D (1.74 µg. L^{-1}). These high concentration levels in the rainy season could be explained by intense agricultural activities in the vicinity of the river on the one hand and by rainwater runoff from agricultural fields and traffic on the river on the other. These results corroborate those of Yao & *al.* [17] in the Ebrié Lagoon. According to this author, seasonal concentrations of active ingredients are higher in the rainy and flood seasons than in the dry season. Furthermore, the results of the analysis of the different samples reveal that glyphosate and 2,4-D are present in the sediments. This observation is similar to that made by Pitrat *& al*. [21] and Toumi *& al*. [22] in sediments in Brazil and Senegal respectively. This accumulation could be justified by the fact that these pesticides have a hydrophobic character and being weakly soluble in water with a pH between 5.2 and 6.9 [23], they converge towards the sediments. Compared to their concentration in water, these pesticides have a high concentration in sediment [24 ; 21]. Differences in pesticide concentration in sediments were observed between seasons. Overall, the dry season is much more accumulative of active ingredients in sediments than the rainy season. This significant difference in pesticide concentration between seasons could be explained by the intensity of agricultural activities in the vicinity of the river or by the discharge of pesticide residues into the river in the rainy season. These contaminants observed in the river would expose organisms to acute or chronic contamination that could considerably influence aquatic life. The results of analyses of internal organs of fish in the river show that the species *Chrysichthys nigrodigitatus* does contain contaminants. These active substances are accumulated much more in the liver and gills overall. Contamination in the muscles of *Chrysichthys nigrodigitatus* is relatively low. According to Yapi [25], fish concentrate pollutants more in the liver than in the muscles. This is presumably due to the very important physiological role of the liver in the accumulation, metabolism and biotransformation of xenobiotics. The results obtained show a significant difference in the concentration of active ingredients in the organs between seasons. This difference in organ concentration could be justified by factors such as the availability of pesticides in the environment, the properties of the different active ingredients and their forms of absorption by the organism. From a general point of view, according to the analysis of the results, the chemicals are well concentrated in the species *Chrysichthys nigrodigitatus*. This would be justified by the greater affinity of these contaminants for sedimentary particles [26]. Furthermore, due to the hydrophilic nature of most of these substances, it becomes difficult to detect them in water [27]. A study conducted by Okonkwo *& al*. [28] in Nigeria to find out the level of contamination in the waters, sediments and fish of the Ogbakiri River in the Niger Delta region revealed high levels of pesticides in the sediments than in the waters. According to Osibanjo [27], the adsorption of these contaminants by sediments favours their movement into aquatic species. This makes living organisms in the benthic environment vulnerable. The species *Chrysichthys nigrodigitatus* lives almost on the muddy bottom and feeds mainly in the sediment [29]. This would justify the high concentration of active matter in *Chrysichthys nigrodigitatus*. In the dry season, the rate of pesticide accumulation is very high in fish organs. This would be due to the adaptation of the diet of *Chrysichthys nigrodigitatus*. During the rainy season, *Chrysichthys nigrodigitatus* feeds mainly on chirominids, oligochaetes and gastropods, whereas the prey is mainly fish. The most common fish species consumed in the dry season are chirominids and Odonata, mainly Neurogomphus sp. This observation is also made by Yao [30]. This author states that the seasons also influence the diet of fish. Furthermore, this variation in accumulation observed between seasons could be justified by variations in water properties and intrinsic factors such as the growth cycle and the reproduction cycle [31]. Significant differences in active ingredient concentrations are observed in different organs between seasons. This difference in concentration between seasons could be the result of seasonal pollution of waters and sediments that serve as habitat and food for fish. Bioconcentration factors are high in the organs of the species *Chrysichthys nigrodigitatus*. This result could be explained by the fact that the muscle of *Chrysichthys nigrodigitatus* is fatter. The results of Yao [17] show that bioaccumulation factors are higher in sector IV than in sector V in the jawfish in the assessment of the impact of pesticide contamination of fish in the Ebrié Lagoon. However, the results obtained in Guessabo are lower than those of Ibigbami *& al*. [32] and Lubna *& al*. [33] in Nigeria and Egypt respectively. However, this accumulation of pesticides in the body of the fish would expose the higher consumer to chronic intoxication by ingestion. Knowledge of the hazard quotient (HQ), the potential risk of exposure (human health) to pesticides through

ingestion, and the daily exposure dose allow an assessment of the hazard. This study gave DQs (DQ < 1) and EDIs calculated for *Chrysichthys nigrodigitatus* that are essentially harmless to the consumer.

5. Conclusion

The annual analysis of active ingredients in the river showed that 2, 4-D is less concentrated in the environment than glyphosate. The rainy season shows high concentrations of active ingredients, while the dry season does not. Sediment analysis revealed the presence of glyphosate and 2, 4-D in the Sassandra River at Guessabo. These concentrations of active ingredients vary from season to season. The levels of contamination recorded in the sediments are high compared to those recorded in the river water at Guessabo. The rainy season records more pesticide in the sediments than the dry season. In fish, the results of gill, liver and muscle analysis of Oreochromis niloticus and *Chrysichthys nigrodigitatus* caught in the Sassandra River at Guessabo, showed the presence of 2,4-D, and glyphosate in the different organs. With this fish, the muscle concentrates less pesticides than the liver. The gills are relatively more contaminated than the muscle. Furthermore, the bioconcentration factors are high in the organs of *Chrysichthys nigrodigitatus*. These contaminations are quite accentuated in the liver, justifying a chronic contamination by ingestion. The study of the potential risk of exposure of Oreochromis niloticus and *Chrysichthys nigrodigitatus* to pesticides shows that these fish are essentially harmless to the consumer.

Compliance with ethical standards

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Disclosure of conflict of interest

The authors declare that there are no conflicts of interest in this article.

Statement of ethical approval

This research work does not contain any animal studies conducted by any of the authors that require appropriate ethical approval.

Statement of informed consent

Informed consent was obtained from all participants included in this study.

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