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Health Risks Associated with Eating Fish Contaminated by Pesticides

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Abstract **Original Research Article**

In agriculture, pesticides play an essential role in increasing production yields. However, alongside the considerable benefits of these substances lie harmful effects on the environment and human health. The objective of this work was to assess the health risks associated with the consumption of fish contaminated with pesticide residues. Fish samples were taken from two hydroelectric dams and analysed using gas chromatography coupled with mass spectrometry (GC/MS). Aldicarb, chlorpropham, crimidine and vinclozolin were quantified with levels ranging from 0.034 mg/kg to 0.162 mg/kg. All these molecules had hazard ratios well below 1, ranging from 0.003 to 0.62. The population is therefore not exposed to any potential risk from pesticide residues. However, it is important to monitor the use of extremely hazardous pesticides and the effectiveness of risk mitigation measures.
Keywords: Health risk, Pesticides, Jawfish, Hydroelectric dams.

INTRODUCTION

Pesticides are chemicals used to prevent, control or eliminate unwanted organisms. In agriculture, they serve multiple purposes: eliminating weeds and harmful insects, protecting crops and harvested produce, inhibiting mould during storage and transport, etc. (Aubertot *et al.*, 2005). With the population growing rapidly, the use of these products has increased, as they play a key role in boosting production yields (Yadav and Devi, 2017). In fact, global pesticide consumption amounts to four million tonnes per year (Atlas des Pesticides, 2023). Alongside the considerable benefits of pesticides lie harmful effects on the environment and human health (Kalogridi *et al.*, 2014, Ezenonze *et al.*, 2015). In fact, plant protection products are toxic and some of them can persist in the environment (water, soil, air) and in food in the form of residues (Tawaye *et al.*, 2021; Yapo *et al.*, 2021). The harmful effects of pesticides on human health have been widely discussed by several researchers, including INSERM (2021), which, in a study, confirmed the strong presumption of a link between pesticide exposure and six diseases: non-Hodgkin's lymphoma (NHL), multiple myeloma, prostate cancer, Parkinson's disease, cognitive disorders, chronic obstructive pulmonary disease, and chronic bronchitis.

In Côte d'Ivoire, several authors have reported widespread contamination of aquatic ecosystems by pesticide residues (Traoré *et al.*, 2015; Diarra *et al.*, 2016; Gnonsoro *et al.*, 2016; Konan *et al.*, 2023). Most of these studies have focused on the contamination of surface waters and sediments. However, the organisms found in these environments deserve special attention as they are also exposed to chemicals. The present study aims to assess the health risks associated with the consumption of fish contaminated with pesticide residues.

MATERIALS AND METHODS

Presentation of study areas

The work was carried out in the Kossou and Taabo dam lakes (Figure 1). The Kossou dam Lake is located in the centre of Côte d'Ivoire in the department of Yamoussoukro. It was built on the Bandama River, between 05°30'25.1'west longitude and 07°03'12.5' north latitude (Koukougnon *et al.*, 2022). The Taabo hydroelectric facility is also located on the Bandama River, specifically on the watershed, between 05°04'57.4

'west longitude and 06°15'46.6' north latitude (Koukougnon *et al*., 2022). It is located approximately 120 km downstream from the Kossou dam (Groga, 2012) and is regulated by the latter (Aliko *et al*., 2010).

Biological material

The biological material consisted of fish caught in Lake Kossou and Lake Taabo.

Reagents and solvents

The pesticide standards used were of high purity (> 99%) and were supplied by Dr Ehrenstorfer GmbH (Germany). All extraction and analysis solvents were of analytical grade and were sourced from Fluka.

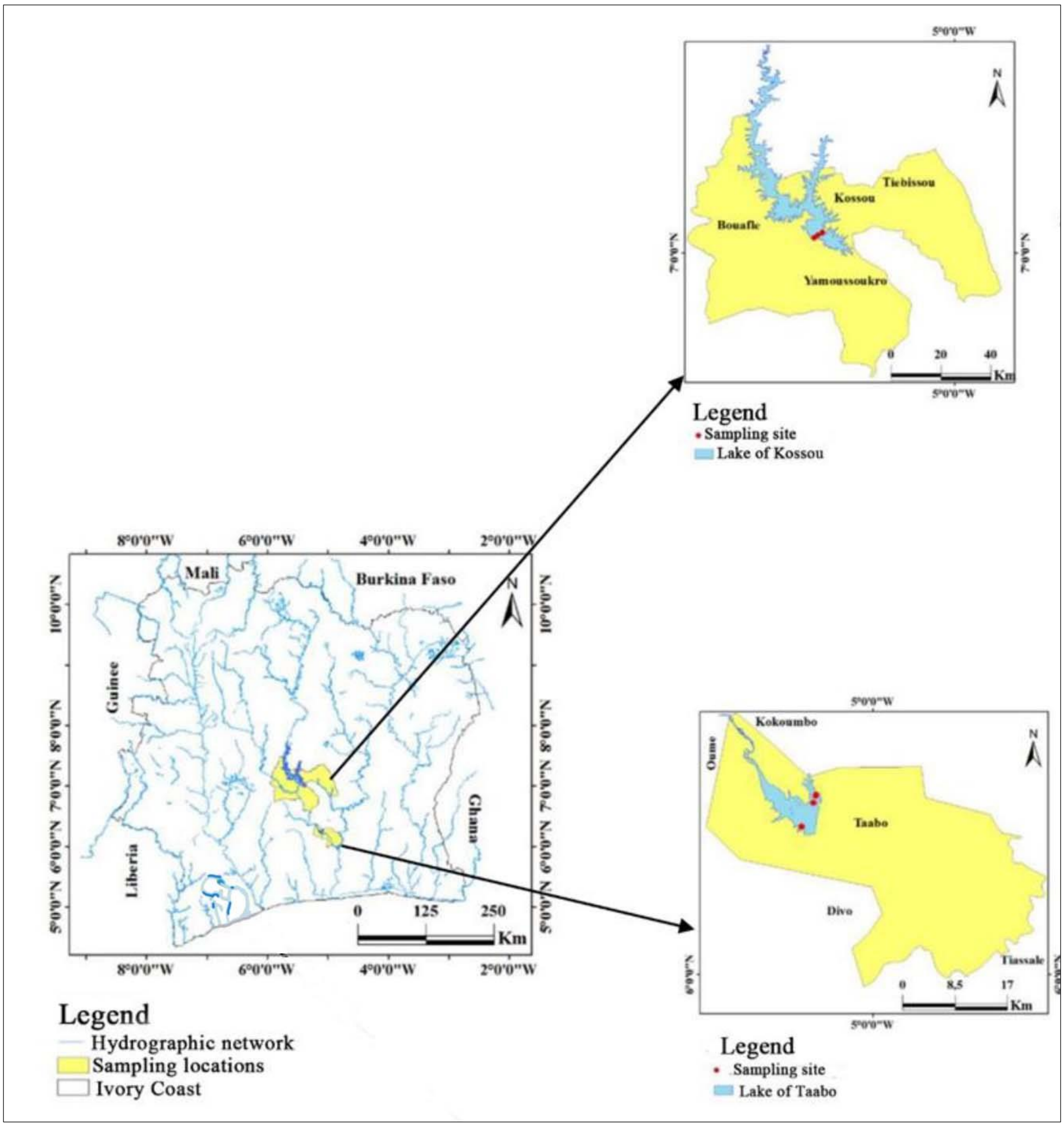

Figure 1: Study area

METHODS

Food survey

In Côte d'Ivoire, data-t-on food consumption is virtually non-existent. A survey of households and restaurants was therefore conducted to identify the most commonly consumed fish and eating habits. During this survey, a questionnaire was sent to people aged 18 and over to find out not only about their diet but also their general eating habits (IFN, 1996). The daily quantity consumed was obtained by calculating the average individual quantities of fish consumed per day.

Level of contamination

Sampling

Fish were collected during eight campaigns. After collection, the specimens were measured and weighed. The fish weighed between 100 g and 400 g. They were then placed in food bags, stored in a cooler at 4°C and transported to the laboratory where they were stored at -18°C until analysis.

Pesticide analysis

2 g of muscle tissue is homogenised for 5 minutes in 8 ml of acetone and centrifuged four times ;

the supernatant is then placed in separate tubes, and this extraction procedure is carried out twice. The samples are then evaporated under nitrogen, and the dry residue is recovered in a solution of acetone and methanol (50:50). The extract is then purified using a 500 mg C18 SPE column, conditioned with 2 ml of acetone and 2 ml of methanol. The column is dried by suction and the purified samples are collected in 3 ml of acetone. After evaporation under nitrogen, the samples are collected in 1 ml of methanol. The concentrations of the molecules measured are determined by GC/MS. A 5973N mass spectrometer coupled with a 6890 GC gas chromatograph (Agilent®, 30 m HP5-MS column, 0.25 mm ID, 0.25 µm fineness) are used. For each sample and each standard, 2 µL are injected. The temperature programme starts at 85°C, maintained for one minute, then rises by 6°C/minute to 170°C (maintained for 12 minutes), then rises again by 20°C/minute to 280°C, maintained for 4.33 minutes. The total analysis time is 37 minutes. The injector temperature is 250°C and is in splitless mode. Each sample is identified according to retention times (Lemarchand *et al*., 2013).

Quality control and statistical methods

Quality assurance and control were carried out using blanks and standard reference materials. Samples were analysed in triplicate. The limit of detection (LOD) for pesticides (chlorpropham, vinclozolin and crimidine) was 0.010 mg/kg and the limit of quantification was 0.032 mg/kg. Those for aldicarb were 0.007 mg/kg and 0.022 mg/kg, respectively. Microsoft Excel 2007 software was used for statistical analyses.

Food risk assessment

The risk we have considered stems exclusively from exposure through the ingestion of foods such as fish. According to the World Health Organisation (WHO), food risk assessment is a science-based process involving four main steps: identification of potential hazards, characterisation of hazards or toxicological reference values (TRVs), exposure assessment and risk characterisation (IPCS, 2009; FAO/WHO, 2014). Exposure assessment is based on combining data from dietary surveys (quantity of fish consumed and average body weight of individuals) with the concentrations of pesticides detected in samples. In practice, exposure estimation is based on the calculation of the theoretical maximum daily intake (TMDI) and the estimated daily intake (EDI) (Nougadère, 2015). The theoretical maximum daily intake (TMDI), which is a safe method, is calculated using the following formula:

$TMDI = \sum (MRL \times Qj)$, where MRL is the maximum residue limit for pesticides in fish, Qj is the amount of fish consumed per day (g/day). The theoretical daily exposure dose (TDED) is obtained by dividing the TMDI by body weight. Considered a realistic method, the estimated daily intake (EDI) is given by the formula below: $EDI = \sum (Ci \times Qj)$, where Ci is the average concentration of pesticide residues in fish (mg/kg) and Qj is the average quantity of fish consumed daily (g/day). The daily exposure dose (DED) is the quotient of the EDI divided by body weight. For molecules with threshold effects, such as pesticides, a hazard ratio (HR)is calculated.

If $HR < 1$, then the population is not exposed to any potential risk in principle.

If $HR > 1$, then toxic effects related to pesticides are likely to occur within the exposed population (Host *et al*., 2006).

RESULTS

Food survey

The average consumption of fish among respondents in Kossou and Taabo was 114.80 g per day per person and 110.44 g per day per person, respectively. The average body weight of respondents was 67 kg in Kossou and 66 kg in Taabo.

Level of contamination in fish

Minimum, maximum and average values (mg/kg) of pesticides detected in fish sampled from the lakes of Kossou and Taabo

The results presented in Table I show the level of pesticide contamination found in fish at the two dams. These results indicated that all fish samples were contaminated and that the levels varied depending on the pesticide and the study area. Aldicarb was the only molecule with the highest average concentration in fish from both lakes. Its concentration was 0.155 ± 0.015 mg/kg for fish from the Kossou dam and 0.162 ± 0.035 mg/kg for fish from Lake Taabo. Next comes crimidine, with an average value of 0.147 ± 0.024 mg/kg in fish from the Kossou hydroelectric dam. The other molecules showed relatively low levels regardless of the study site.

Table I : Minimum, maximum and average values (mg/kg) of pesticides detected in fish sampled from Kossou and Taabo lakes

Molecules		Aldicarb	Chlorpropham	Crimidine	Vinclozolin
	Min	0,046	0,042	0,064	0,034
Kossou	Max	0,198	0,107	0,235	0,042
	Average	0,155 ± 0,015	0,089 ± 0,011	0,147 ± 0,024	0,039 ± 0,002
	Min	0,083	0,051	0,037	0,033
Taabo	Max	1,112	0,091	0,078	0,036
	Average	0,162 ± 0,035	0,068 ± 0,001	0,058 ± 0,012	0,034 ± 0,002

Frequency of pesticide detection in samples analysed at the two dams

Figure 2 shows the frequency of detection in fish samples. Aldicarb was detected in 80% of samples at the Taabo dam and 66.66% at Lake Kossou. Crimidine was found in 66.66% of fish from both dams. For all molecules, the detection frequency was higher in samples from Taabo, at 58.33%.

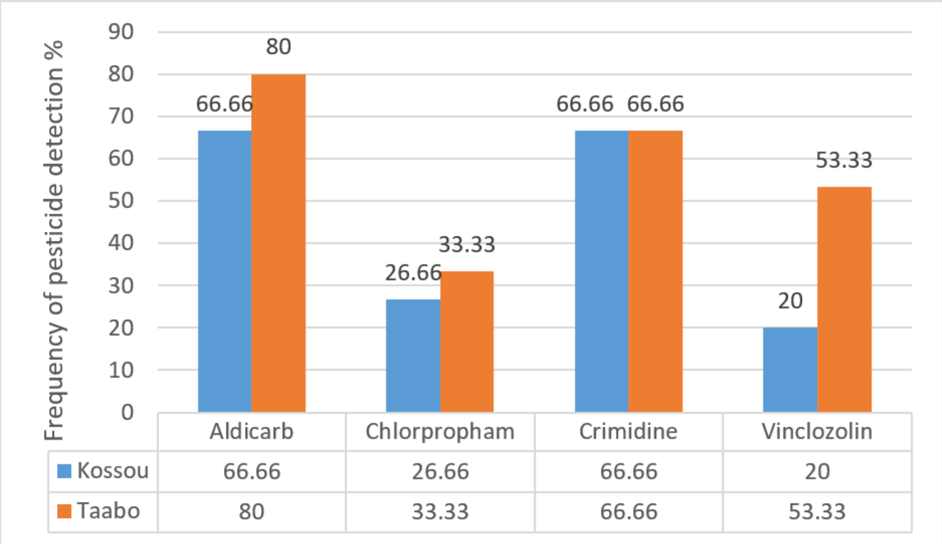

Figure 2: Frequency of pesticide detection in fish samples

Comparison of total pesticide loads in the two dams

The results showed that the total pesticide load was higher in Kossou than in Taabo (Figure 3). The total pesticide load was 57% in Kossou compared to 43% in Taabo.

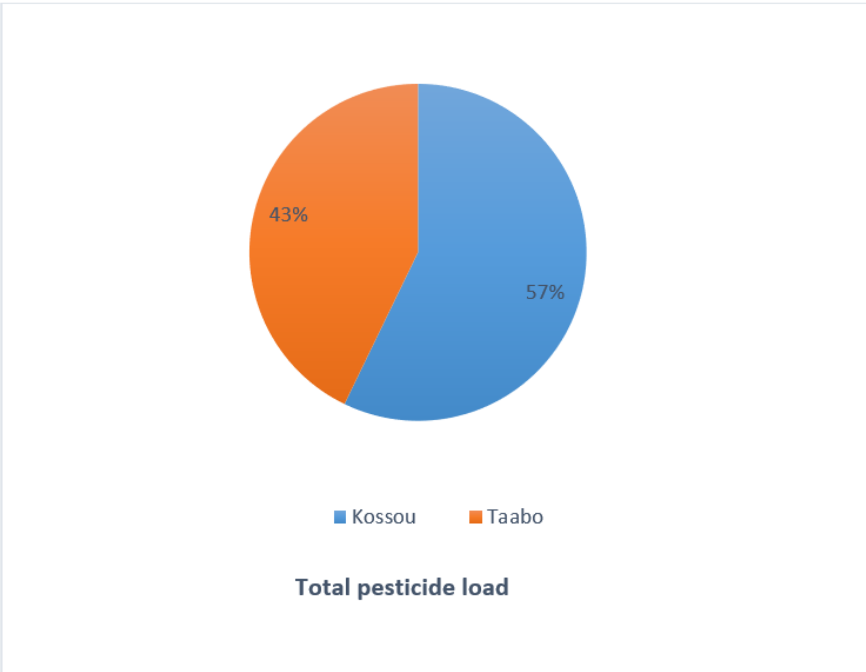

Figure 3: Total pesticide load in Lake Kossou and Lake Taabo

Comparison of pesticide residue levels in fish with Maximum Residue Limits (MRLs)

The results shown in Table II indicate that the concentrations of pesticides quantified in fish samples are mostly above the Maximum Residue Limits (MRLs), with the exception of vinclozolin.

Table II: Comparison of pesticide residue concentrations in fish with Maximum Residue Limits (MRLs).

	Kossou	Taabo	
Pesticide molecules	Average concentration (mg/kg)	Average concentration (mg/kg)	Maximum Residue Limit de Résidus (MRL) (mg/kg)
Aldicarb	0,155	0,162	0,01
Chlorpropham	0,089	0,068	0,05
Crimidine	0,147	0,058	0,01
Vinclozolin	0,039	0,034	0,05

The cumulative effect of pesticides and the exceeding of MRLs for most of the molecules studied led to an assessment of the risks associated with fish consumption.

Food risk assessment

Hazard identification and characterisation

The pesticides detected in fish can have harmful effects on human health. They have adverse effects on the endocrine system and are suspected of causing cancer. All of these substances were found in concentrations exceeding the maximum residue limits (MRLs), with the exception of vinclozolin.

Exposure assessment

The maximum concentrations of the molecules will be taken into account in the exposure calculation so as not to underestimate the risk.

Calculation of the theoretical maximum daily intake (TMDI) and the percentage of the acceptable daily intake (%ADI)

Tables III and IV show the TMDI and percentage of ADI for the molecules at the Kossou and Taabo dams.

Table III: Theoretical maximum daily intake (TMDI) and percentage of theoretical acceptable daily intake (%TADI) at the Kossou dam

Kossou		**Aldicarb**	**Chlorpropham**	**Crimidine**	**Vinclozolin**
Fish	Amount of fish consumed per day/person (g/person/day)	MRL (mg/kg)	MRL (mg/kg)	MRL (mg/kg)	MRL (mg/kg)
	114,80	0,01	0,05	0,01	0,05
	TMDI (mg/pers/j)	$11{,}48.10^{-4}$	$57{,}4.10^{-4}$	$11{,}48.10^{-4}$	$57{,}4.10^{-4}$
TDED = TMDI/BW (mg/kg pc/j)		$17{,}13.10^{-6}$	$85{,}67.10^{-6}$	$17{,}13.10^{-6}$	$85{,}67.10^{-6}$
% TADI		0,571	0,171	0,171	1,713

Table IV: Theoretical maximum daily intake (TMDI) and percentage of theoretical acceptable daily intake (%TADI) at the Taabo dam

Taabo		**Aldicarb**	**Chlorpropham**	**Crimidine**	**Vinclozolin**
Fish	Amount of fish consumed per day/person (g/person/day)	MRL (mg/kg)	MRL (mg/kg)	MRL (mg/kg)	MRL (mg/kg)
	110,44	0,01	0,05	0,01	0,05
	TMDI (mg/pers/j)	$11{,}04.10^{-4}$	$55{,}22.10^{-4}$	$11{,}04.10^{-4}$	$55{,}22.10^{-4}$
TDED = TMDI/BW (mg/kg pc/j)		$16{,}73.10^{-6}$	$83{,}67.10^{-6}$	$16{,}73.10^{-6}$	$83{,}67.10^{-6}$
% TADI		0,557	0,167	0,167	1,673

Based on these results, the percentages of the theoretical acceptable daily intake (%ADI) for all pesticides are less than 100 at all study sites. Consequently, the estimated daily intake (EDI) should not be calculated. However, given the abnormal presence of molecules in fish, it is essential to calculate this intake in order to better assess exposure.

Calculation of the estimated daily intake (EDI) and daily exposure dose (DED)

This calculation took into account the maximum levels detected in fish during the analysis and the body weight (BW) of the individuals surveyed.

Table V: Estimated daily intake (EDI) and daily exposure dose (DED) in fish from Lake Kossou

Kossou		**Aldicarb**	**Chlorpropham**	**Crimidine**	**Vinclozolin**
Fish	Amount of fish consumed per day/person (g/person/day)	Maximum concentration (mg/kg)	Maximum concentration (mg/kg)	Maximum concentration (mg/kg)	Maximum concentration (mg/kg)
	114,80	0,198	0,107	0,235	0,042
	EDI (mg/person/day)	$22{,}73.10^{-3}$	$12{,}28.10^{-3}$	$26{,}98.10^{-3}$	$4{,}82.10^{-3}$
DED = EDI/BW (mg/kg bw/day)		$3{,}40.10^{-4}$	$1{,}83.10^{-4}$	$4{,}03.10^{-4}$	$0{,}719.10^{-4}$

Table VI: Estimated daily intake (EDI) and daily exposure dose (DED) in fish from LakeTaabo

Taabo		Aldicarb	Chlorpropham	Crimidine	Vinclozolin
Fish	Amount of fish consumed per day/person (g/person/day)	Maximum concentration (mg/kg)	Maximum concentration (mg/kg)	Maximum concentration (mg/kg)	Maximum concentration (mg/kg)
	110,44	1,112	0,091	0,078	0,036
	EDI (mg/person/day)	$122{,}81.10^{-3}$	$10{,}05.10^{-3}$	$8{,}61.10^{-3}$	$3{,}97.10^{-3}$
DED = EDI/BW (mg/kg bw/day)		$18{,}6.10^{-4}$	$1{,}52.10^{-4}$	$1{,}30.10^{-4}$	$0{,}60.10^{-4}$

With regard to fish from Lake Kossou, aldicarb and crimidine have the highest daily exposure doses, which are 3.40×10^{-4} mg/kg bw/day and 4.03×10^{-4} mg/kg bw/day, respectively. These values are significantly lower than the ADIs set by international bodies at 0.003 mg/kg bw/day for aldicarb and 0.01 mg/kg bw/day for crimidine. As for the Taabo hydroelectric dam, the results showed that a daily intake of 122.81×10^{-3} mg/person/day of aldicarb resulted in a daily exposure of 18.6×10^{-4} mg/kg bw/day, which is lower than the ADI set at 0.003 mg/kg bw/day.

Hazard characterisation

The hazard ratios for the different molecules are shown in the table below

Table VII: Hazard ratios

Sites		Aldicarb ADI= 0,003 mg/kg bw/day	Chlorpropham ADI= 0,05 mg/kg bw/day	Crimidine ADI= 0,01 mg/kg bw/day	Vinclozolin ADI= 0,005 mg/kg bw/day
Kossou	HR= DED/ADI	0,113	0,004	0,040	0,014
Taabo	HR= DED/ADI	0,620	0,003	0,013	0,012

The hazard ratios for the molecules found in fish from both dams were less than 1, so the risk was acceptable.

DISCUSSION

The fish analysed were all contaminated with aldicarb, chlorpropham, crimidine and vinclozolin molecules. The highest concentrations were observed for crimidine and aldicarb. These substances are banned worldwide (FAO/UNEP, 2011; PAN, 2024). Their presence in the samples indicates fraudulent use. The same finding was made by Gnonsoro *et al.,*(2016) in a study conducted in 2016 in Akouédo Bay, where they detected residues of aldicarb and crimidine in surface waters and sediments. Another study led by Traoré *et al.,*(2015) also mentions the presence of these molecules in the waters of the Aghien and Potou lagoons in south-eastern Côte d'Ivoire.

Due to its toxicity (category Ia (extremely hazardous) in the World Health Organisation classification), aldicarb poses enormous risks to humans and the environment, particularly aquatic species (FAO/UNEP, 2011). Crimidine, meanwhile, is obsolete (PAN, 2024). Furthermore, the frequency with which these two molecules are detected is significant at both dams. This could be explained by recent misuse. In addition, the concentrations of the substances found in fish are higher than the MRLs for most of them. This could be attributed to poor agricultural practices. The uncontrolled use of plant protection products has been documented by several authors (Doumbia and Kadjo, 2009; Ahouangninou *et al*., 2011; Kanda *et al*., 2013). In fact, farmers who do not have a good level of education are unable to comply with good agricultural practices (Wognin *et al*., 2013; Son *et al*., 2017). Despite the high concentrations of these substances, the daily exposure doses are below the acceptable daily intake limits. Moreover, the hazard ratios of all molecules are less than 1. Such observations were made by Yapo *et al.,*(2022) during a study conducted on the health risks associated with the consumption of market garden produce in Korhogo, Côte d'Ivoire. In contrast, Yaya *et al.,*(2020) showed that the ratios of metals detected in offal and meat are well above 1. This high contamination is probably linked to the bioaccumulation coefficients (log kow > 3) of these metals, which are above 3 and explain their persistence in biological matrices.

CONCLUSION

The molecules quantified in fish were aldicarb, chlorpropham, crimidine and vinclozolin. The results revealed that the MRL was exceeded for all pesticides except vinclozolin. The dietary risk assessment showed that all substance ratios were well below 1. The risk is therefore considered acceptable for humans. Even though the hazard ratios are below 1, monitoring systems must be put in place to control the use of extremely hazardous pesticides and the effectiveness of risk mitigation measures. Since these substances are banned from use.

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