Status of contamination of the jawfish (*Chrysichthys nigrodigitatus*, (Lapécède, (1803)) by organophosphorus residues in the hydroelectric dams of Faé, Kossou and Taabo (Ivory Coast)

Abstract: The present study aims at determining the level of contamination of the jawfish (*Chrysichthys nigrodigitatus*) by organophosphate residues in the hydroelectric dams of Faé, Kossou and Taabo. Ninety (90) fish were collected from these three dams during eight sampling campaigns. Composite samples were formed, each for two fish. A total of forty-five (45) composite samples were formed. The detection of pesticide residues in the fish samples was determined by gas chromatography-mass spectrometer (GC/MS). The results show that the average total organophosphate residue load at the three dams is 0.184 mg/kg. The Faé hydroelectric scheme had the highest total load of 0.266 mg/kg in fish samples, compared to 0.197 mg/kg for Taabo and 0.089 mg/kg for the Kossou hydroelectric dam. The relatively high average total concentration is observed for parathion-methyl with a value of 0.130 ± 0.023 mg/kg. Chlorfenvinphos, with a total average concentration of 0.046 ± 0.007 mg/kg was the only molecule present in all the fish samples analyzed in the three hydroelectric dams. In addition, most of the molecules detected in the fish samples had concentrations that exceeded the Maximum Residue Limits (MRLs) for pesticides, whose values range from 0.01 to 0.05 mg/kg. Thus, the daily consumption of jawfish (*Chrysichthys nigrodigitatus*) from these dams could present a major health risk to the populations.

Key words: Organophosphates, Chrysichthys nigrodigitatus, Hydroelectric dams, Faé, Kossou, Taabo

INTRODUCTION

Organophosphate pesticides are second generation pesticides. They are the major groups of chemicals used for the protection of crops, livestock, human health and as warfare agents [1].

These compounds have gradually replaced organochlorines because of their high insecticidal properties. They persist little in the environment and accumulate less in organisms [2, 3]. However, studies show acute toxicity of organophosphates in non-target animals [3]. In addition to acute toxicity, they can cause various clinical effects such as endocrine disruption, immunotoxicity and cellular injury [4].

Organophosphates are neurotoxic substances that act on the nervous system of insects. Unfortunately, their action is not specific to insects and they can be neurotoxic to several animal species including humans [5].

There is growing concern about the long-term adverse effects of these chemicals. Studies on organophosphate insecticides, especially chlorpyrifos, show that children in the womb or in early life can suffer from neurodevelopmental disorders [6]. Thus, they are exposed to an alteration in cognitive performance such as a decrease in the intelligence quotient (IQ), i.e. the loss of memory capacity [7].

In addition, cases of poisoning are reported. According to the WHO, 3 million cases of pesticide poisoning, particularly organophosphate poisoning, are recorded each year, causing more than 250,000 deaths [8, 9].

Ivory Coast is particularly affected by this problem as it is one of the largest consumers of pesticides in West Africa with 13,000 tons of pesticides per year [10].

Previous studies report the presence of organophosphate residues in several foodstuffs including fruits, vegetables, cereals, onion and bean leaves and chillies [11, 12].

The present study aims to determine the level of contamination of the jawfish (*chrysichthys nigrodigitatus*) by organophosphate pesticides in the hydroelectric dams of Faé, Kossou and Taabo.

MATERIALS AND METHODS

Presentation of the study areas: The study was conducted in three localities (Faé, Kossou and Taabo) where export crops such as cocoa, coffee, rubber and banana are grown intensively. The hydroelectric dams in these areas are subject to strong anthropogenic pressures. The different study areas are presented in Figure 1.

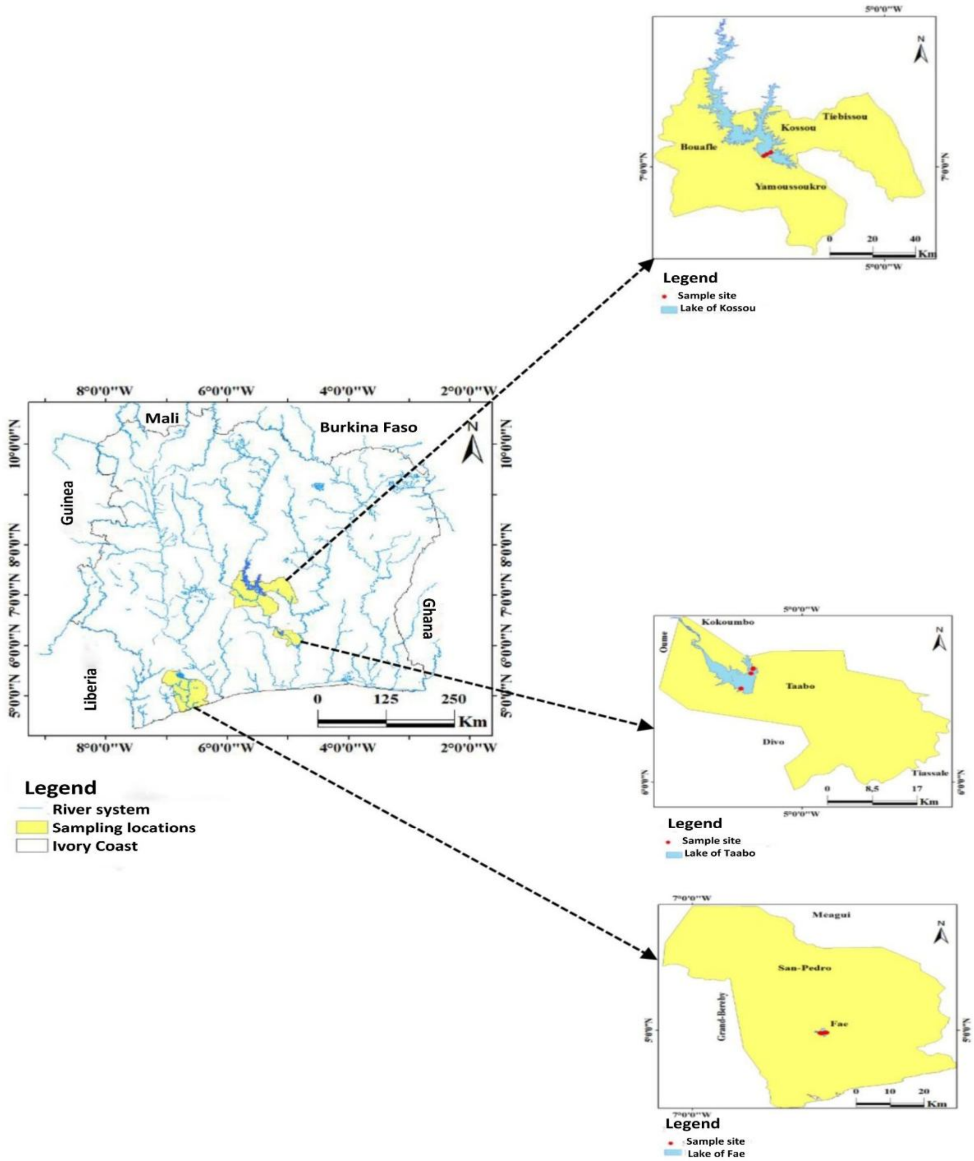

Figure 1 : Location of the study areas

Faé hydroelectric dam: Built in 1978, the Faé hydroelectric dam was commissioned in 1983. This lake is located on the San-Pedro River, between 06°38'40.2" W longitude and 04°59'27.2" N latitude, in the southwest of Ivory Coast, near the town whose name it bears

[13]. With an area of 16.28 km^2 [13], the Faé dam is located 35 km north of the town of San Pedro, at an altitude of 25 meters in the middle of an equatorial forest. Its watershed covers an area of 2424 km^2 [14].

Kossou hydroelectric dam: The Kossou dam is built on the Bandama River, between 05°30'25.1" W longitude and 07°03'12.5" N latitude. Lake Kossou is located 296 km from the mouth of the river [15]. It was commissioned in 1972 and covers a watershed of 32400 km^2 [14]. The hydrological regime of the lake is of the transitional equatorial type and is subject to the Baulean climate according to the United Nations Framework Convention on Climate Change [16].

Taabo hydroelectric dam: The Taabo hydroelectric dam was created in 1978 and is located in the Bandama River watershed, between 05°04'57.4" W longitude and 06°15'46.6" N latitude. It is located about 110 km downstream from the confluence of the Bandama White and Bandama Red (the Marahoué) and about 120 km downstream from the Kossou hydroelectric dam [17]. This water body covers an area of 69 km^2 and its volume of water stored at the normal flood level is 625,103 m^3 [17, 18]. It drains a watershed of 58700 km^2 and its average annual flow is 128.7 m3/s [19]. Lake Taabo has a tropical type of hydroelectric regime and is subject to the Sudanese climate. It is regulated by the Kossou hydroelectric scheme built upstream [18].

Fish Sampling: Sampling was conducted over eight campaigns (06 to 09 December 2017, 15 to 18 January 2018, 26 February to 01 March 2018, 16 to 19 April 2018, 04 to 07 June 2018, 16 to 19 July 2018, 03 to 06 September and 08 to 11 October 2018). After each collection, the fish are weighed. The mass of the fish varied between 100 g and 400 g. The fish were wrapped in aluminum foil and then placed in food bags and stored in coolers at 4°C. A total of ninety (90) fish were captured with thirty species per site. Composite samples were taken, each for two fish. Thus, forty-five composite samples were collected for the three sites. All the conditioned samples were frozen at -18°C until analysis.

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

The extraction protocol for pesticides in fish samples as well as the purification of the extracts was performed by the method described by [20].

Extraction of fish samples and purification of extracts: 5 g of ground sample (dorsal muscle) is mixed and homogenized in 60 mL of dichloromethane and 10 g of anhydrous sodium sulfate (Na2SO4). The mixture is then filtered through a phase separator filter (Whatman) and evaporated under vacuum at 40°C. The dry extracts are then taken up in 3 mL of ethanol, then undergo an ultrasonic passage. The mixture is then purified on a Sep-Pak R300 column (Silica Waters, 020810; 500 mg) which is preconditioned with 2 mL of methanol and 2 mL of ethanol. The next step which is elution was performed with 2 mL of dichloromethane. The purified extracts were evaporated to dryness and recovered in 3 mL of dichloromethane. The concentrations of organophosphorus pesticides (chlorfenvinphos, chlorpyrifos, parathion-ethyl, pararhion-methyl) were determined.

Instrumental analysis: For each sample and each element serving as standard, the injection volume is 2 µL. The temperature program is maintained for 2 minutes starting at 100°C and reaching 200°C at a rate of 55°C/minute. It is then maintained for 5 minutes, at a rate of 50°C/minute until 220°C. Finally 60°C/minute to 300°C for 3 minutes. At the end of the sample elution, the system is maintained at 300°C for 2 minutes. The injector is maintained at 250°C and the carrier gas flow (He) is 2.5 mL/minute. The detection temperature is 300°C. Each organophosphorus pesticide, is identified from its retention time.

Statistical treatment of the data: The Shapiro-Wilk normality test was performed on the variables. The result of this test showed that the data do not follow a normal distribution ($p < 0.05$). Thus, the non-parametric Mann Whitney and Kruskal-Wallis tests were performed on the variables ($p < 0.05$).

In addition, Principal Component Analysis (PCA), which is a descriptive method, was used. It allowed us to appreciate the relationships that exist between the different molecules studied and especially to access their structuring at the level of the three study areas. STATISTICA 7.1 software was used for the analyses.

RESULTS

Level of contamination of jaws with organophosphate pesticides at the Faé, Kossou and Taabo hydroelectric dams: The results presented in Figure 2 indicate the level of organophosphate residue impregnation in jaws (*Chrysichthys nigrodigitatus*) from the Faé, Kossou and Taabo hydroelectric dams.

Parathion-ethyl, parathion-methyl, and chlorfenvinphos were the only organophosphorus pesticides present in fish samples in the Lake Faé dam (Figure 2a). The mean concentrations of parathion-ethyl and parathion-methyl were 0.084 ± 0.002 mg/kg and 0.147 ± 0.009 mg/kg, respectively. The detection frequencies were 20% for parathion-ethyl and 26.66% for the parathion-methyl molecule. Chlorfenvinphos recorded the lowest average concentration which was 0.035 ± 0.004 mg/kg, with a detection frequency of 13.33%.

In fish from the Kossou hydroelectric dam (Figure 2b), only parathion-ethyl and chlorfenvinphos were detected in the samples analyzed. The average concentration of parathion-ethyl was 0.033 ± 0.004 mg/kg with a detection frequency of 26.66%, that of chlorfenvinphos was 0.056 ±0.005 mg/kg and its detection frequency was 20%.

At the Taabo hydroelectric dam (Figure 2c), parathion-methyl had a mean concentration of 0.114 ± 0.057 mg/kg, its detection frequency was 46.66%. The lowest average concentration was decelerated at chlorpyrifos (0.037 ± 0.001 mg/kg) with a detection frequency of 33.33%.

The average total organophosphate residue load at the three dams was 0.184 mg/kg. The Faé hydroelectric dam recorded the highest total load of 0.266 mg/kg in fish samples, compared to 0.197 mg/kg for the Taabo dam and 0.089 mg/kg for the Kossou hydroelectric dam. The relatively high average total concentration is observed for parathion-methyl with a value of 0.130 ± 0.023 mg/kg. Chlorfenvinphos, with a total mean concentration of 0.046 ± 0.007 mg/kg was the only molecule present in all fish samples analyzed at the three hydroelectric dams.

The mean concentrations of organophosphorus pesticides detected in fish samples ranged from 0.033 ± 0.004 mg/kg to 0.147 ± 0.009 mg/kg.

In Faé, 100% of the organophosphate molecules detected in fish have concentrations that are above the Maximum Residue Limits (MRLs).

In Kossou, 50% of the molecules were found to be above the MRLs, and in Taabo 66.66% of the organophosphates were found to be above the MRLs, ranging from 0.01 mg/kg to 0.05 mg/kg. Thus, it is clear that more than half of the organophosphorus pesticides found in fish have average concentrations that are above the Maximum Residue Limits.

The daily consumption of jawfish (*Chrysichthys nigrodigitatus*) from these hydroelectric dams could present a major health risk to the population.

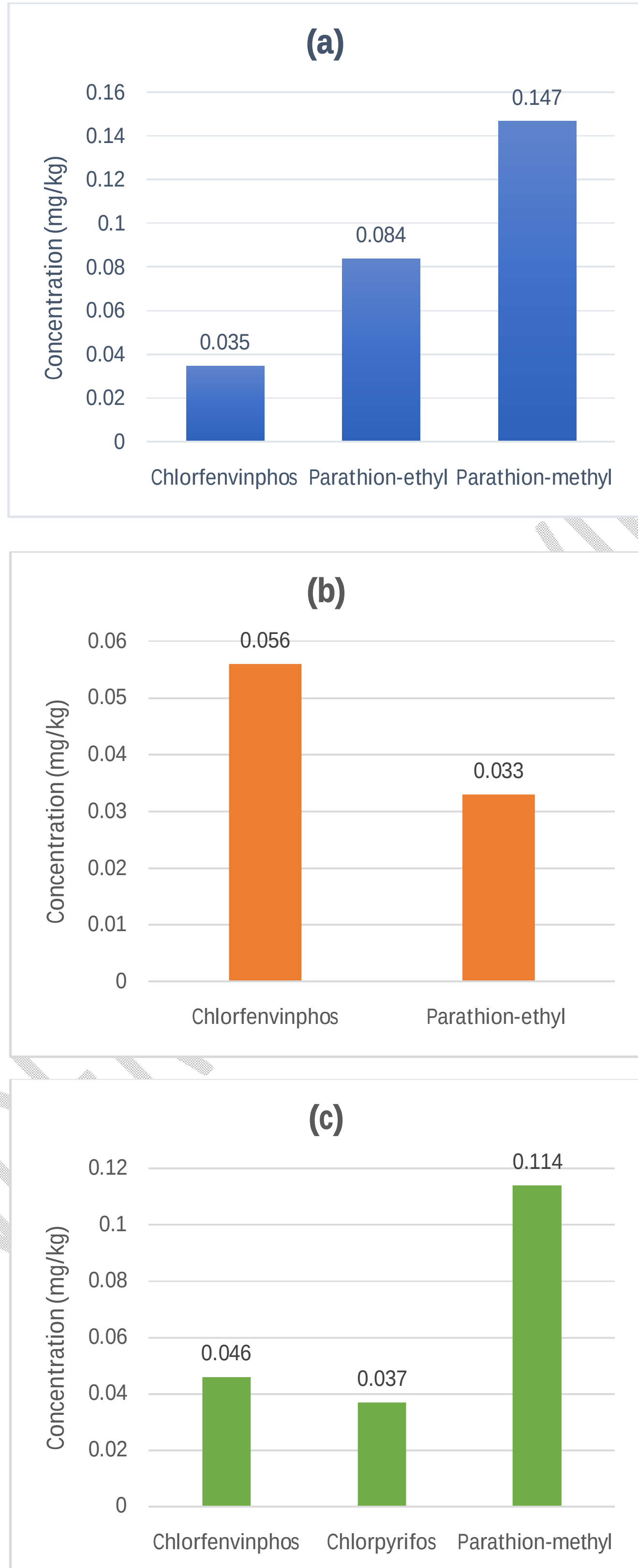

Figure 2: Average concentrations of substituted urea residues in jawfish (*Chrysichthys nigrodigitatus*) samples from Faé (a), Kossou (b) and Taabo (c) dams

Comparison of organophosphorus residues in jadefish (*Chrysichthys nigrodigitatus*) at the Faé, Kossou and Taabo dams

The evolution of chlorfenvinphos in the jawfish (*Chrysichthys nigrodigitatus*) at the three hydroelectric dams is shown in Figure 3.

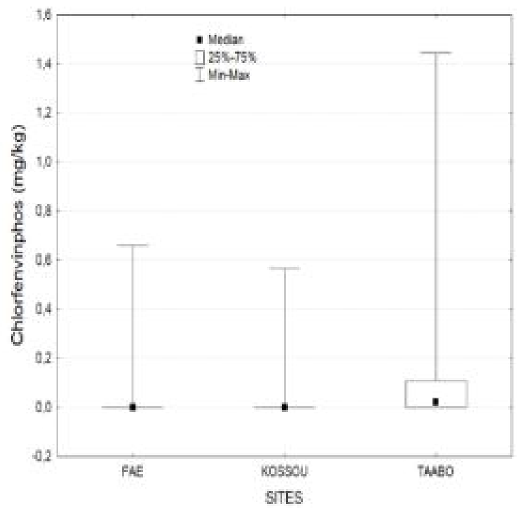

Figure 3: Comparison of chlorfenvinphos in jawfish (*Chrysichthys nigrodigitatus*) at the Faé, Kossou and Taabo dams

The Kruskall-Wallis and Mann-Whitney tests showed that there are significant differences between the levels of the chlorfenvinphos molecule in jawfish from the Faé and Taabo hydroelectric dams and between those from Kossou and Taabo ($p < 0.05$).

Principal Component Analysis (PCA) of organophosphate residues in jawfish (*Chrysichthys nigrodigitatus*) from the three dams (Faé, Kossou and Taabo)

Figure 4 shows the results of the Principal Component Analysis (PCA) of organophosphate residues in jawfish (*Chrysichthys nigrodigitatus*) at the three hydroelectric dams.

The first two axes represent 63.55% of the total variance. The first axis expresses 38.31% of the total variance and is negatively defined for parathion-methyl and parathion-ethyl. Axis 2 expresses 25.24% of the same variance, chlorfenvinphos is positively correlated to this axis. Chlorpyrifos is strongly and negatively correlated to this same axis. Fish from the Faé hydropower scheme are significantly more contaminated with parathion-ethyl and parathion-methyl. At Kossou, the highest average concentration was observed for chlorfenvinphos and finally at Taabo, the fish were more contaminated with chlorpyrifos.

Statistical tests showed that fish from the lake at Faé Dam are much more contaminated with organophosphate residues than those from Kossou and Taabo. These results are consistent with the higher total load of organophosphate pesticides detected in fish samples from the Faé hydroelectric dam compared to those from Kossou and Taabo.

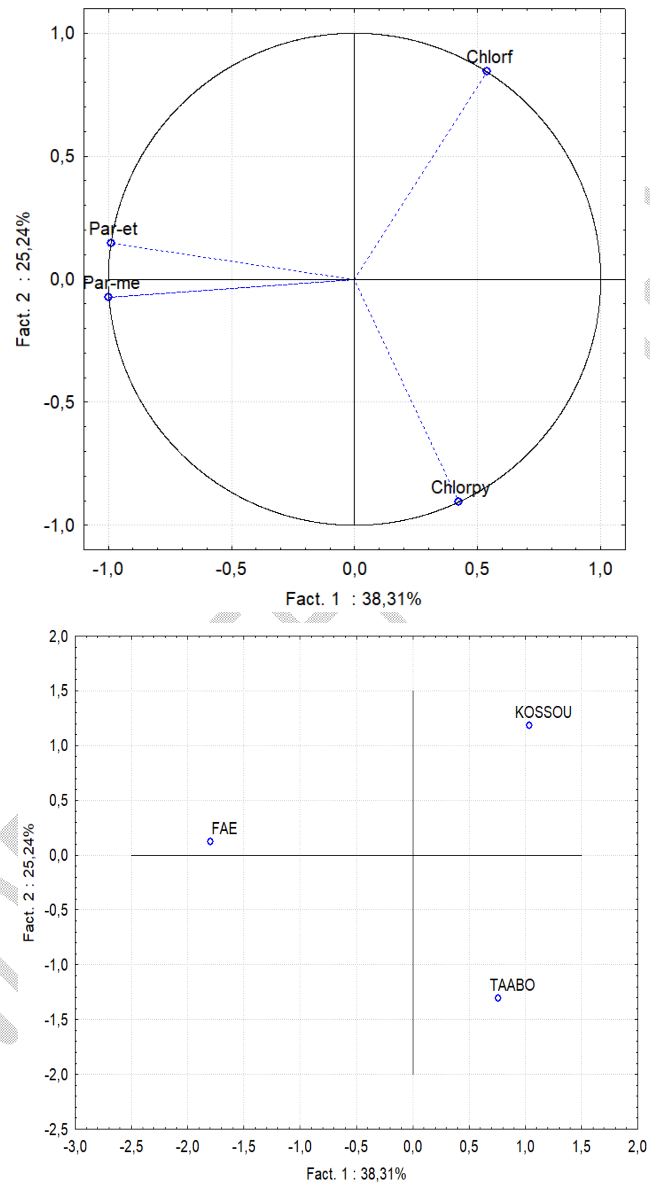

Figure 4: Principal Component Analysis (PCA) of organophosphate residues in jawfish (*Chrysichthys nigrodigitatus*) at the three dams

Chlorf: chlorfenvinphos; Chlorpy: chlorpyrifos; Par-et: Parathion-ethyl; Par-me: Parathion-methyl

DISCUSSION

The organophosphorus pesticides measured in this study are: chlorfenvinphos, chlorpyrifos, parathion-ethyl and parathion-methyl. The contamination of fish samples by organophosphorus residues appeared to be low for most of the molecules. This could be explained by the fact that these substances are banned from use because of their toxicity to humans and the environment [21; 22; 23]. Parathion-methyl showed a relatively high average concentration in all samples from the three sites. It is a molecule classified in category Ia (extremely toxic) by the WHO (World Health Organization) and as an insecticide of toxicity category I (most toxic) by the US Environmental Protection Agency [24]. Similarly, parathion-ethyl is one of the most dangerous organophosphate insecticides [25] and also classified in category Ia (extremely toxic).

Chlofenvinphos is the only molecule detected in the chewers at the three hydroelectric dams. It is a substance classified in category Ib (very toxic). As for chlorpyrifos, it is classified as moderately hazardous. In addition to being extremely toxic, organophosphate pesticides have adverse effects on human health. For example, exposure to parathion-methyl causes adverse effects on female reproductive organs with endometrial hemorrhage during pregnancy [26]. This molecule is banned in Ivory Coast.

As for parathion-ethyl, the EPA has classified it as a possible human carcinogen in group C and the IARC (International Agency for Research on Cancer) classifies it as a human carcinogen in group 3 [21; 25]. In addition, population-based studies have provided information on Parkinson's disease following parathion-ethyl exposure [27; 28]

The presence of these molecules with low concentrations remains a concern, since these substances can have adverse effects on aquatic fauna before degrading [29]. The average concentrations found in our samples are of the same order of magnitude as those found by [30] in Tono Reservoir (Ghana) where the average concentrations of chlorpyrifos in three fish species are 0.093 ± 0.074 µg/g (mg/kg) for C. anguillaris species, 0.087 ± 0.038 µg/g for S. intermedius and 0.050 ± 0.057 µg/g for the fish M. senegalensis. Statistical analyses revealed that the chlorfenvinphos molecule showed a significant difference ($p < 0.05$) at the three dams. This significant variation could be related on the one hand to the different sources of pollution in the study areas, and on the other hand to the amount of plant protection products applied on the crops. The Principal Component Analysis (PCA) showed that fish from Lake Faé are much more contaminated with parathion-ethyl and parathion-methyl, while those from Kossou and Taabo are rich in chlorfenvinphos and chlorpyrifos respectively. The high concentrations of parathion-ethyl and parathion-methyl recorded in the Faé dam samples are probably due to the fraudulent and intense use of formulations containing these substances.

CONCLUSION

The fish samples analyzed were all contaminated with organophosphate residues with levels varying from one dam to another. The average concentrations of pesticides detected in the samples range from 0.033 ± 0.004 mg/kg to 0.147 ± 0.009 mg/kg. More than half of the molecules detected in the fish samples have values that exceed the Maximum Residue Limits (MRLs), which are between 0.01 and 0.05 mg/kg. Thus, the daily consumption of jawfish (*Chrysichthys nigrodigitatus*) from these dams could present a major health risk for the population.

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