International Journal of Science and Technology Research Archive

ISSN: 0799-6632 (Online)

Journal homepage: https://sciresjournals.com/ijstra/

(RESEARCH ARTICLE)

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Contamination of the waters and fishery resources of Lake Nokoué by pyrethroid molecules

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International Journal of Science and Technology Research Archive, 2022, 03(02), 045–055

Publication history: Received on 01 September 2022; revised on 18 October 2022; accepted on 21 October 2022

Article DOI: https://doi.org/10.53771/ijstra.2022.3.2.0110

Abstract

The use of pesticides in agricultural activities near water bodies and fishing practices with the use of impregnated mosquito nets contaminate fishery resources. This is the case of Lake Nokoué in the Municipality of Sô-Ava, which for decades has become a receptacle for chemical pollutants such as pyrethroids. This observation prompted the present research which aims to determine the level of contamination of the waters and fishery resources of Lake Nokoué by pyrethroid molecules. The method used consisted of surveying the farmers working on the shores of Lake Nokoué, the different types of pesticides they use in the fight against pests on their crops. Then, the pyrethroid molecules (deltamethrin and cypermethrin) were looked for in water and fish samples taken, by the QuEChERS technique (Quick, Easy, Cheap, Efficient, Rugged an Safe) at the Laboratory of the 'International Institute of Tropical Agriculture (station) of Benin. At the end of the work, 13 types of pesticides were identified, of which only 26.31% are approved by the Sahelian Pesticides Committee (CSP). A wide range of unapproved pesticides representing 73.68% is also used in the study environment. Laboratory analyzes revealed the presence of the desired active ingredients at concentrations that greatly exceed the WHO standard in all water and fish samples. Non-repeat two-way proc ANOVA analysis of variance and the Student Newman Keuls test revealed that the concentrations of cypermethrin in the samples exceeded those of deltametrin.

Keywords: Contamination; Waters and Fishery Resources; Pyrethroid Molecules; Lake Nokoué

1 Introduction

Of all types of pollution, agricultural pollution receives attention because of its detrimental effects on the quality and functions of rivers. It represents a typical case of multiple and generalized pollution of the aquatic compartment [1]. The increasing use of agricultural inputs contributes dangerously to the degradation of water quality. The use of pesticides in agriculture has become systematic in Africa to optimize the yields of cash crops and market gardening [2].

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Pyrethroids are among the most widely used insecticides in Africa. The best known are bifenthrin, cypermethrin, esfenvalerate, lambda-cyhalothrin, cyfluthrin and permethrin. They are used in agriculture, forestry, fish farming, horticulture and the medical field (fight against mosquitoes / malaria), in textiles, wood storage, building protection (fight against termites) and professional and amateur gardening [3].

But the use of these pesticides in pest control is not without consequences for the environment [4]. The environmental consequences relate in particular to the quality of water and fishery resources.

In Benin, almost all bodies of water and rivers experience pollution problems linked to agricultural practices [5]. In the commune of Sô-Ava, agriculture and fishing, which constitute the main source of income, are very active around Lake Nokoué as it recedes. The populations, in order to increase their production, increase the sown areas, use phytosanitary products, thus accentuating the degradation of environmental components [5]. The main routes of emission of pyrethroids into the aquatic environment are entrainment by water (rain, irrigation) and wind. Discharges from wastewater treatment plants can also contain significant quantities [6]. Being very hydrophobic, pyrethroids easily bind to organic carbon and particles and accumulate in soil and sediments where they degrade within months. In the aquatic environment, they are bioavailable in dissolved form or bound to particles [7].

In order to protect and manage in a reasoned way the surface water resources of Benin, it is necessary to have an idea of the current state of the various water bodies and the effects of poor agricultural and fishing practices. This is what justifies the initiative of this research, the main objective of which is to determine the level of contamination of the waters and fish species of Lake Nokoué by pyrethroids.

2 Framework, materials and study method

2.1 Study framework

The Municipality of Sô-Ava lies between 6 ° 25 "and 6 ° 39" north latitude and 2 ° 21 "and 2 ° 30" east longitude. Covering an area of two hundred and eighteen (218) km2, it is limited to the north by the towns of Zê, Dangbo and Adjohoun; in the South by the Municipality of Cotonou; to the east by the Lacustrine Municipality of Aguégués and to the West by the Municipality of Abomey-Calavi.

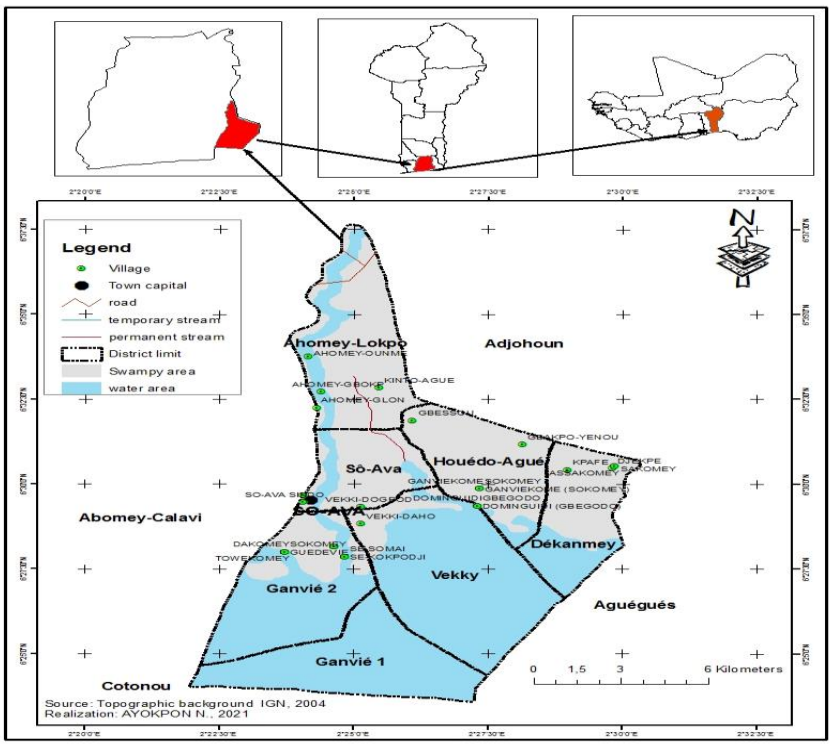


Figure 1 Geographical location of Sô-Ava

On the hydrographic level, the Municipality of Sô-Ava is crossed by the Sô river. This is the most important permanent waterway in the Municipality. 84.4km long.

The Municipality of Sô-Ava has its source in Lake Hlan and is linked to the Ouémé river by backwaters. Its highest flows are observed during floods and its lowest flows are observed during low water. The Municipality of Sô-Ava is characterized by its richness in water mass (65% of the territory) which has earned it the name of Lacustrine Municipality. It is drained by various permanent and temporary rivers. These rivers are located largely in the west of the town, and constitute an economic asset for the population, which engages in many income-generating activities. Thus, apart from the fishing practiced by a good part of the population, the Sô river also serves to facilitate the traffic of contraband petroleum products from Nigeria to a good part of southern Benin. Although it is an informal activity, the trafficking of contraband petroleum products has grown significantly in the Municipality of Sô-Ava and involves several actors. Some of these streams are sacred because they are used for ritual purposes. The rise of the Ouémé River, Lake Nokoué and the Sô River by flood water causes flooding in the town [8].

2.2 Study methods

2.2.1 Type of study

This is an analytical study that examines the contamination of water and fish species by pyrethroid molecules. It was a question of evaluating the eco-toxicological risks of Lake Nokoué related to the use of mosquito nets in fishing practices and pesticides in agriculture on the shore of the lake. The level of contamination of the lake was determined by measuring the content of two molecules of pyrethroids namely cypermethrin and deltamethrin in three species of fish and in the water of the lake.

2.3 Study data

The data used in the context of this study are the concentrations of deltametrine and cypermethrin molecules in the waters and fish of Lake Nokoué.

2.4 Data collection techniques and tools

2.4.1 Laboratory analysis

Sampling of water, fish and laboratory analyzes are the different data collection techniques used to assess the level of contamination of Lake Nokoué by pyrethroid molecules.

Assay protocol for cypermethrin and deltamethrin molecules

2.4.2 Sampling

Depending on the geographical location of Lake Nokoué, the surrounding habitat, the abundance of fishing activities and fishing dam sites with mosquito nets, the dynamics of pyrethroid molecules suspended in the water, agricultural activities developed near the lake and probable sources of pollution, a representative number of twelve (12) points from which samples were taken was selected from the entire lake site. Composite samples were taken in each arrondissement with the different samples.

2.4.3 Withdrawals

All samples were taken on the morning of December 28, 2020 and then stored at 4 ° C in coolers containing accumulators before being sent to the laboratory of the International Institute of Tropical Agriculture (IITA).

The water samples were taken in PVC bottles with a capacity of 1.5 liters. Prior to collection, the vials were thoroughly cleaned and rinsed with distilled water. At the time of collection, the previously washed vials were rinsed three times with the water to be collected. Samples were collected manually at fixed sampling points.

With regard to fish, the most frequent, mature and most consumed species of this lake ecosystem which were taken in the morning from the catches of artisanal fishermen (Plate 1).

Local name:	aboli	ahotoun	Akpavi
Scientific name	*Clarias gariepinus*	*Silurus glanis*	*Oréochronis niloticus*

Figure 2 Sample of fish taken

The carefully labeled fish samples were wrapped with aluminum foil as shown in photo 1, to avoid contact with sunlight and are placed in a cooler containing frozen accumulators and then transported to the laboratory.

Figure 3 Sample of fish taken **Shooting:** Landéou R., 2022

2.5 Analysis method

It consisted of assaying deltamethrin and cypermethrin in water and fish samples collected by the QuEChERS (Quick, Easy, Cheap, Efficient, Rugged an Safe) technique at the IATI Laboratory. Due to variations in the protocol depending on the chromatographic system used at the end of treatment, the preparation of fish samples by the QuEChERS method is presented in two separate sections for greater clarity. The first is devoted to the preparation of samples for analysis by liquid chromatography coupled with tandem mass spectrometry (LC / MS-MS) while the second deals with the preparation of those intended for analysis by chromatography in gas phase coupled with mass spectrometry (GC / MS).

3 Results

3.1 Phytosanitary products used in Benin and in the Municipality of Sô-Ava

In Benin, the most widely used types of pesticides are insecticides and herbicides. Water contamination by these pesticides is either occasional during the handling of products, filling or rinsing of sprayers, or diffuse, after the

application of the products by runoff to surface water [9] (Soclo, 2003; Yehouénou, 2005). Contamination of waterways also comes from the direct use during the low water period by fishermen of organochlorine pesticides, in particular endosulfan, dichloro diphenyl trichloroethane (DDT), endrin to capture fish. (Soclo, 2003; Yehouénou, 2005) [9]. Among the pesticides used, pyrethroids, aminophosphates and triazines also occupy a prominent place (Gbaguidi et al., 2011) [10]. The most common pesticide active ingredients in Benin are glyphosate, atrazine, flubendiamide, spirotetramate and pyrethroids (Emamectin, Cyfluthrin, Cypermethrin, Betacyfluthrin) (Adechian et al., 2015) [11].

3.2 Pesticides identified in the Municipality of Sô-Ava

As part of this research, a census was taken of the pesticides most used in the study environment by the population in their various activities. Table 1 presents the results of the survey work.

Among these thirteen (13) pesticides used, only 26.31% are approved by the Sahelian Pesticides Committee (CSP). A wide range of unapproved pesticides representing 73.68% is also used in the study environment. Unregistered pesticides are in principle prohibited from use. Their presence constitutes enormous health risks for Lake Nokoué and the surrounding population. The pesticides listed which have been classified according to the WHO toxicity scale generally belong to class II and III. Class II representing 26.31%, corresponds to moderately dangerous pesticides, which implies that these pesticides must be handled by educated and trained people. However, the population of the study environment, characterized by a low level of education and a lack of training in the use of pesticides, should in principle not use these pesticides. Class III representing 15.79%, for its part, corresponds to low-hazard pesticides that can be used by market gardeners.

Table 1 Pesticides used by farmers in the Municipality of Sô-Ava

Type of pesticide	Trade name	frequency	Active ingredients	Concentration	Chemical family
Insecticides	COTALM P 218 EC	5	Lambdacyhalothrine Profenofos	18 g/L 200 g/L	PYRÉTHRINOÏDE ORGANOPHOSPHORÉ
	DECIS 15 EC	6	Deltamethrine	15 g/L	PYRÉTHRINOÏDE
	CYPERCAL 50 EC	19	Cypermethrine	50 g/L	PYRÉTHRINOÏDE
	COTOFAN 350 EC	4	Endosulfan	350 g/L	CYCLODIÈNE/ ORGANOCHLORÉ
	CAPT 88 EC	12	Acetamipride Cypermethrine	16 g/L 72 g/L	NE PYRÉTHRINOÏDE
	CYPER-D	1	Cypermethrine	10 g/L	PYRÉTHRINOÏDE
	CYDIM C50	1	Cypermethrine	50 g/L	PYRÉTHRINOÏDE
	CYFLUTHRALM 318 EC	1	Cyfluthrine Profenofos	18 g/L 300 g/L	PYRÉTHRINOÏDE ORGANOPHOSPHORÉ
	DURSBAN	1	Chlorpyriphos-ethyl	300 g/L	ORGANOPHOSPHORÉ
Nematicides	DIAFURAN 5G	3	Carbofuran	50 g/kg	CARBAMATE
Fongicides	FOKO	6	Mancozèbe	800 g/kg	CARBAMATE
	TOPSIN M	3	Methythiophanate	800 g/kg	BENZIMIDAZOLE
	IVORY	2	Manèbe	800 g/kg	CARBAMATE

About 57.89% of the pesticides listed are intended for the treatment of cotton plants, however market gardeners use them for the treatment of market garden crops. The latter explain this by the fact that pesticides intended for market gardening taken individually are less dosed and effective in controlling pests on their crops. As a result, they proceed to mixtures of pesticides of which they do not control the dosage or the persistence or resort to pesticides intended for cotton plants. Thus, a market gardener can use on average 3 types of pesticides for the treatment of a crop (photo 2).

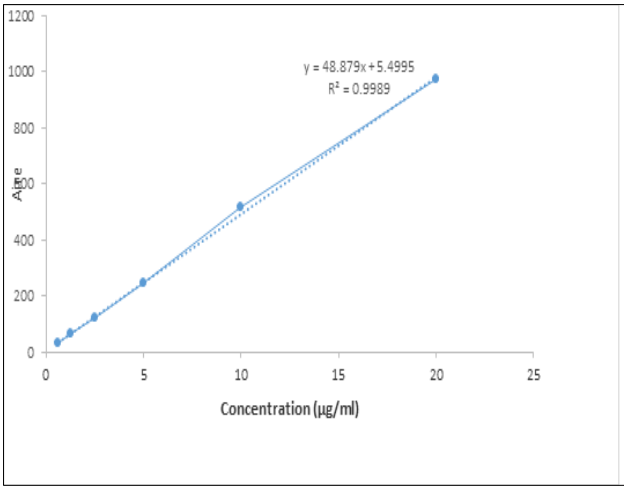
Figure 4 Pesticides used for crop treatment in Sô-Ava on the shore of Lake Nokoué **Shooting:** Landéou R., 2022

Depending on the targets, the farmers of the Municipality of Sô-Ava use a variety of pesticides. There is a dominance of insecticides with a percentage of 69.23%, followed by Nematicides (7.69%) and fungicides (23.08%).

3.3 Content of pyrethroid molecules in water and fish samples from Lake Nokoué

3.3.1 Characteristics of standard active ingredients

Two active ingredients (Deltamethrin, cypermethrin) are analyzed during the work. Dilutions of 20 µg / ml, 10 µg / ml, 5 µg / ml, 2.5 µg / ml, 1.25 µg / ml and 0.625 µg / ml were prepared for each active ingredient to calibrate the corresponding regression lines as shown in figures 1 and 2.



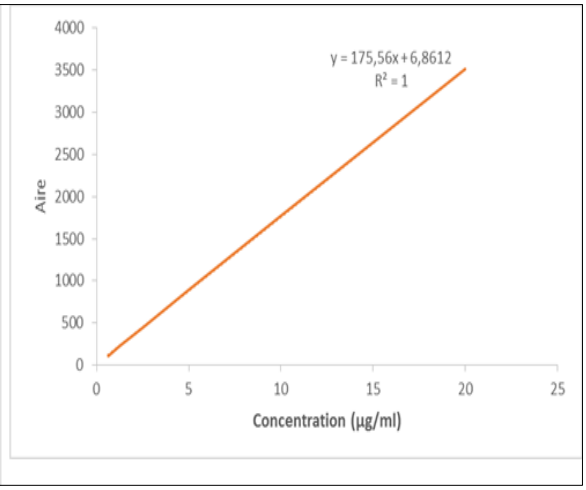


Figure 5 Regression lines of deltamtrin **Figure 6** Regression lines of cypermethrin

As in figures 5 and 6, the results of these regressions led to the following conclusions: the concentration of the pesticides sought follows a first order law of disappearance with correlation coefficients of the order of 48.69 for deltametrine and 175, 56 for cypermethrin.

The equation of the regression line, the correlation coefficient, the slope, the limit of detection and the limit of quantification of each active ingredient are reported in Table 2.

Table 2 Characteristics of standard active materials analyzed with the HPLC machine

Insecticides	Dilution scale(µg/ml)	Regression equation	r^2	Slope	Intercede
Deltamtrine	0,625-20	$y = 48{,}879x + 5{,}5$	0,99	48,879	5,5
Cyperméthrine	0,625-20	y=175,56x+6,86	1	175,56	6,86

As shown in the table, the concentration of each desired active ingredient in water and fish samples is determined by its regression equation. The variable x represents the area of the wavelength read during the operation.

3.4 Deltametrine and cypermethrin content in the water and fish of Lake Nokoué

3.4.1 Water

The water samples were directly assayed at the IITA laboratory for the search for the active ingredients studied (deltametrine, cypermethrin). The standard regression equations of these two active ingredients made it possible to determine the content of each water sample of deltametrine and cypermethrin, according to the areas of the wavelengths read on the chromatogram. The residue rates calculated and presented in FIG. 3 constitute the results of the analyzes.

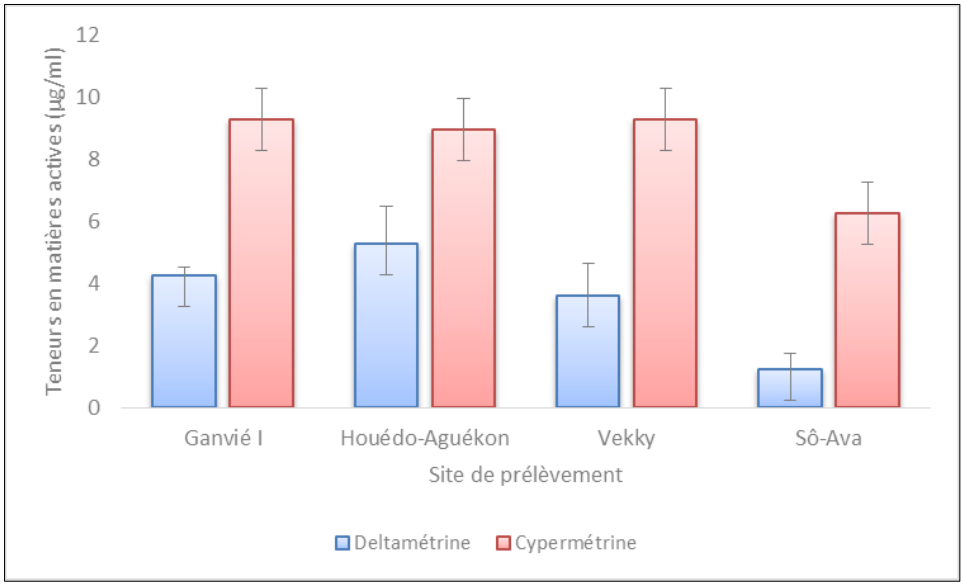


Figure 7 Concentration of deltametrine in the sampled waters

As shown in Figure 7, the two active ingredients (deltametrine and cypermethrin) sought in the context of the present study are present in the water samples at various levels. Cypermethrin is the active ingredient with the highest content in all the waters sampled. Its content varies from 6.26 (µg / ml) to 9.26 (µg / ml). The lowest level of 6.26 (µg / ml) is obtained at Sô-Ava and the highest level of contamination is found in the water sampled at Houédo-Aguékon and Ganvié. As for deltametrine, its content is lower than cypermethrin. This low concentration of this active material can be explained by its degradable nature in the face of sunlight. The water sampled at Houèdo-Aguékon is the most contaminated with deltametrine molecules with an average concentration of 5.29 (µg / ml), while the water sampled at Sô-Ava has the low rate of contamination with an average of 1, 24 µg / ml.

3.5 Determination of active ingredients in fish samples from Lake Nokoué

The varied range of fish abounding in the Sô-Ava lake ecosystem made it possible to select three (03) types of fish belonging to different families and having various diets. The pyrethroid molecules studied in the present work were therefore assayed at the level of these mature fish species and the results obtained are presented in Table III.

Table 3 Concentration of deltametrine in sampled fish

Sites	Species	Cyperméthrine (mg/kg)	Deltamétrine (mg/kg)
Standards OMS		3 mg/kg	0,7 mgKg
Ganvié	TP	6,29	2,57
	SN	9,42	4,29
	CG	11,09	6,09
Houèdo	TP	7,69	6,72
	SN	10,24	6,33
	CG	9,74	4,6
Vekky	TP	7,54	4,91
	SN	10,13	5,79
	CG	10,84	6,43
Sô-Ava	TP	3,28	1,65
	SN	5,17	3,39
	CG	5,41	4,63

It appears in Table 3 that all the fish sampled are contaminated with the pyrethroid molecules sought within the framework of this study. The concentrations found were above the Maximum Residue Limits (MRLs) established by WHO in all samples. The results of Table III reveal real contamination of the fishery resources of Lake Nokoué by pyrethroid molecules. This testifies to the strong pollution of Lake Nokoué by human activities.

The concentrations of the active ingredients obtained vary from species to species and from site to site. Thus, to determine the most accumulating species of pyrethroid molecules and the most polluted sites, the present study carried out an analysis of variances.

3.6 Comparison of Deltametrine and Cypermethrin Concentrations in Fish Samples

The comparison of the contents of the active substances sought in fish made it possible to determine the species of fish which accumulate the most pesticides and the most polluted capture sites.

The results of the two-way proc ANOVA analysis of variance (sites and species) with replication, carried out at the capture sites and by fish species are presented in Table 4.

Table 4 Results of the analysis of variances on the comparison of the levels of deltametrine and cypermethrin in the chairs of the sampled fish

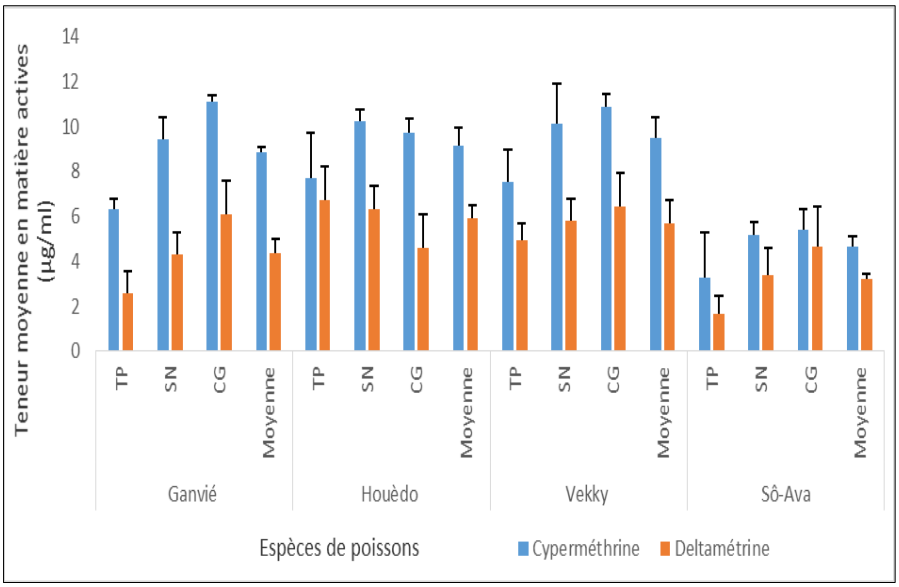
Source	DDL	Valeur de Ficher	
		Deltamétrine	Cyperméthrine
Site	3	3,38**	5,28***
Species	2	4,62***	3,75**
Site* Species	6	2,28 ns	4,58***

ns = no-significant relationship, * = significant relation to the threshold of 10 %, ** = significant relation to the threshold of 5 % admis, *** = significant relation to the threshold of 1%.Source: Fieldwork, Sô-Ava, 2022

Table 4 shows a significant effect ($p < 0.05$) of the two factors (sites and species) on the two molecules sought. This means that the concentration of deltametrine and cypermethrin in fish chairs varies according to the species and the

sampling sites. So, we can remember that the level of contamination of Lake Nokoué is not the same in all the districts of the Municipality of Sô-Ava. Likewise, some species of fish accumulate more pyrethroid molecules than others.

The Student-Newman-Keuls tests, the results of which are presented in FIG. 4, made it possible to determine the levels of the observed differences.



Source: Fieldwork, Sô-Ava, 2022

Figure 8 Results of the Student-Newman-Keuls tests on the comparison of the contents of deltamtrin and cypermethrin in the chairs of the sampled fish

Analysis of the figure shows that in fish samples, cypermethrin is the most dominant molecule. Its concentration greatly exceeds that of deltametrine. In addition, the average concentrations of pesticides are, in general, higher in the districts of Ganvié, Houédo-Aguékon and Vekky than in Sô-Ava. This testifies to the low contamination of Lake Nokoué at the level of Sô-Ava compared to the districts. Regarding fish species, Student-Newman-Keuls tests show that tilapia accumulate less pyrethroid molecules than other species collected. The pesticide concentrations found in the fish fairly well reflect the contamination of Lake Nokoué by the human activities of the riparian populations such as fishing practices, agricultural practices in terms of phytosanitary treatments. These active ingredient contents make it possible to deduce that the practices are relatively uniform in the areas of Ganvié, Houédo-Aguékon and Vekky with almost the same concentrations of active ingredients found at the different sites. The variations in levels observed from one site to another would lie in the frequencies of use of pesticides, which vary according to the crops cultivated with regard to agriculture at the level of the bank.

4 Discussion

This study looked at the contamination of Lake Nokoué and its fishery resources by pyrethroid molecules. So, the different types of pesticides used by the populations in the study environment were identified. The application of pesticides is the method of choice for the control of crop pests in the Municipality of Sô-Ava. All the market gardeners interviewed declared that they used these substances on their crops. A total of 13 types of pesticides have been identified with market gardeners, 26.31% of which are approved by the CSP. These results are similar to those of KOLIA, (2015) [12], which found 19 pesticides used by market gardeners on the Loumbila dam site in Burkina Faso. Of the 19 pesticides, the author found that only 20.69% are registered by the CSP. These results are also comparable to those reported by Ntow W. J., (2006) [13] in Ghana where all respondents used pesticides and to those of Sibanda, T., et al. (2014) [14] in Zimbabwe. Several reasons can explain this situation: availability of affordable products in single-dose sachets or packaged in bottles on the informal market, cultivation of vegetables susceptible to attack, perceptions of potential risks and yield losses by market gardeners, absence of others. Readily available pest management alternatives [15].

The excessive use of these pesticides in the immediate vicinity of Lake Nokoué accompanied by wild fishing practices with the use of impregnated mosquito nets strongly contaminate Lake Nokoué and its fishery resources. This is why

during the present study, some pyrethroid molecules (deltametrine and cypermethrin) were looked for in the water and fish of Lake Noukoué. Laboratory results showed that all water and fish samples contain concentrations of the desired active ingredients that exceed WHO standards. The two-way proc ANOVA analysis of variances with repetition and the Student-Newman-Keuls tests carried out on the comparison of the levels of deltamtrin and cypermethrin in the chairs of the sampled fish showed that throughout the study area, the levels cypermethrin in water and fish samples exceed those of deltametrine. This variation in the levels of the two active ingredients sought within the framework of this study can be justified by the use of pesticides such as CYPERCAL 50 EC, the main active ingredient of which is cypermethrin, CAPT 88 EC, of which the main active ingredients are 'Acetamiprid and Cypermethrin. The frequencies of use of these two pesticides rich in cypermethrin are in the respective order of 29.69 and 18.75% against 9.21% which is the frequency of use of DECIS 15 EC, the only pesticide whose active ingredient is deltametrine.

The impact of these active ingredients on fishery resources was demonstrated by Glin et al., (2006) [16] who reported the presence of residues of chemical synthetic pesticides in aquatic animal species in watercourses. areas of high cotton production. Yehouenou (2005) [8] underlines the contamination of four species and nine varieties of fish caught in the Ouémé River, Lake Nokoué as well as in the Cotonou lagoon downstream by around twenty pesticide residues. Analyzes on male Sarotherodon melanotheron tilapia captured along the Ouémé River showed the presence of lindane, dieldrin and heptachlor. In fish, crabs and amphibians that were collected from the Kiti River in the Zou department in the Republic of Benin, compounds like DDT and endosulfan reached high levels of 403 ng / g of lipids (Yehouenou et al., 2014) [17]. A study carried out by Imorou Toko et al. (2014) [18] on the effect of TIHAN 175 O-TEQ on the physiological parameters of reproduction of Clarias gariepinus broodstock exposed to chronic doses showed significant reductions in the rate of hemoglobin and hematocrit level in exposed broodstock. Plasma concentrations of Na +, K +, Cl-, P and Fe2 + in broodstock exposed to TIHAN for 45 days were also significantly affected, thus exposing the broodstock to an imbalance in the body's metabolism. In other West African countries, the same results were obtained. Residues of organochlorines have been detected in fish from lagoon and marine environments in Côte d'Ivoire, Zimbabwe, and Nigeria. Recent data show contamination of fish from Lake Nakuru with DDD, DDE, lindane and heptachlor (Mavura and Wangila, 2004) [15].

5 Conclusion

Agriculture and fishing are the activities most practiced by the population of Sô-Ava and strongly contribute to the pollution of Lake Nokoué. The present study made it possible to list the pesticides sold in the study area, to identify and describe the health problems related to the use of pesticides by the producers with the associated risk factors. A total of 13 different formulations of pesticides were identified from farmers. This extreme diversity of the products marketed contrasts with the modesty of the means implemented to minimize the health and environmental consequences of their use. Less than 30% of pesticides used around Lake Nokoué are approved by the Sahelian Pesticides Committee (CSP). A wide range of unapproved pesticides representing 73.68% is also used in the study environment. Laboratory analyzes determined the presence of active ingredients whose levels greatly exceed those of the WHO. It is therefore urgent to take adequate measures to limit the use of pesticides in the vicinity of this ecosystem, in order to guarantee the quality of its fishery resources.

Compliance with ethical standards

Acknowledgments

We thank all those who contributed to the writing of this manuscript. We particularly thank the fishermen and the authorities of the municipality of Sô-Ava.

Disclosure of conflict of interest

The writing of this manuscript is without conflict of interest. Each of the authors contributed to the success of this manuscript.

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