

RESEARCH OF PESTICIDES IN FRUITS AND VEGETABLES GROWN IN THE DISTRICT OF ABIDJAN, IVORY COAST

Abstract

Introduction: The presence of pesticide residues in primary and derived agricultural products raises serious health problems for consumers. The aim of this study was to assess the level of pesticide residues in commonly consumed vegetables.

Method : Pesticide residues were extracted from market garden products (*Solanum lycopersicum*, *Capsicum* sp, *Cucumis sativus* and *Lactuca sativa*) by the QuEChERS method and analyzed by a gas chromatograph coupled to a mass spectrometer.

Results: These analyzes made it possible to detect 32 pesticide residues. All market garden products contained pesticide residues, 12.82% of which exceeded the maximum residue limits (MRLs). The pesticide families found were triazines (34.34%), urea derivatives (31.25%), organophosphorus residues (9.37%), organochlorines (9.37%), triazinones (9.37%) and carbamates (6.25%).

Among the market garden products, only lettuce was contaminated by residues from all families with concentrations of pesticide residues exceeding their limits of quantification at the level of 5 molecules : Chlorpropham (0.016 mg/kg), Linuron (0.02 mg/kg), Chlorfenvinphos (0.026 mg/kg) Parathion-ethyl (0.014) and Metolachlor (0.013 mg/kg) which is an organochlorine pesticide . Organochlorines are among the prohibited pesticides. Among the agrochemical specialties used, some were not approved.

Conclusion : The results indicate the presence of pesticide residues in commonly consumed vegetables and highlight the urgent need to develop comprehensive intervention measures to reduce the potential health risk to consumers.

The need for regular monitoring of pesticide residues and raising farmers' awareness of better pesticide safety practices are actions to be taken for the health of consumers.

1. INTRODUCTION

The use of synthetic pesticides is increasingly common in developing countries, particularly as part of actions to combat disease vectors and pests in order to improve crop yields. Africa uses the least amount of pesticides, mainly due to poverty [1]. However, it is one of the continents where these toxic products cause the most damage to populations and the environment, particularly in rural regions [2].

The use and management of these substances have become a very worrying multidisciplinary subject. Pesticides are therefore closely monitored by international organizations, notably the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO). Through their specialized bodies, these organizations regulate the synthesis, sale and use of pesticides and then set toxicological reference values (TRVs) for pesticide residues in foodstuffs and environmental matrices [3 - 4]. In Ivory Coast, the number of studies devoted to

pesticides is becoming increasingly high. Chronic exposure to organophosphate pesticides confirmed in Port Bouët by the significant inhibition of butyrylcholinesterase among market gardeners in the commune of Port-Bouet was revealed [5]. Unsafe practices such as fraudulent use of unregistered pesticides, non-compliance with recommended doses of pesticides, use of pesticides intended for cotton cultivation and persistent molecules have been observed [6].

The use of phytosanitary products in market gardening in Korhogo revealed that 52% of the phytosanitary products used by them are intended for cotton and other crops [7]. 93.33% of lettuce samples non-compliant with Codex Alimentarius and European Union standards were found [8].

Furthermore, the intensive use of chemical pesticides and poor phytosanitary practices are associated with environmental contamination and have numerous effects on human health. These effects are, in the short term, irritation of the skin and mucous membranes, headaches, nausea and chronically respiratory problems, reproductive disorders, endocrine diseases, cancer and death [6 - 8].

Faced with the negative effects of pesticides on human health, concerns arise among consumers of market garden products, although they are renowned for their nutritional values [9].

Analysis of pesticide residues in foods is one way to determine the level of human exposure to these chemicals and, therefore, their potential risks to human health [10]. It is in this context that this study took place, which focused on market gardening products in the Port Bouët area.

The objective of the study was to evaluate the level of exposure to phytosanitary products of consumers of market garden products grown in the commune of Port Bouët. Specifically, this involved determining the level of residues of the various pesticides present in market garden products and searching for the presence of prohibited pesticides in fruits and vegetables.

2. MATERIALS AND METHODS

2.1 Materials

2.1.1 Biological material

The biological material consisted of batches of plant products _

These were *Solanum lycopersicum*, *Capsicum sp*, *Cucumis sativus* and *Lactuca sativa* lettuce.

2.1.2 Technical equipment

This consists of a sampling sheet, a data collection sheet and laboratory equipment (grinder, mixer, precision balance, shaker, rotary evaporator, HPLC).

2.2 Method

2.2.1 Canvassing market garden production sites

This operation consisted of collecting the various packagings of agro-pharmaceutical specialities, in order to gather all the useful information. For each agrochemical product, the information sought was the commercial name of the product, the nature of the active ingredients, the dosage of the active ingredient, the usual dose, the nature

of the crop or crops for which the formulation was initially intended, the registration number, the name of the manufacturer or distributor and the pre-harvest interval.

2.2.2 Sampling

Sampling was carried out on plant material consisting of lettuces (*Lactuca sativa*), peppers (*Capsicum* sp), tomatoes (*Solanum lycopersicum*) and cucumbers (*Cucumis sativus*) harvested directly from the various production sites.

The sampling plan consisted of dividing each production site into plots of at least 10 × 10 m². On each plot, a sample of 1 kg of each market garden product was taken at random so as to be representative of the environment. A total of 39 vegetable samples were collected, including 27 lettuce samples, 6 cucumber samples, 4 chilli samples and 2 tomato samples. The samples were wrapped in aluminium foil and placed in stomachers to limit oxidation. They were labelled and stored at 4°C in a cooler during transport, then in the freezer at -18°C until they were analysed.

2-2-3 Extraction and purification of pesticide residues

The extraction and purification were carried out according to the French standard: NF EN 12393-3.

For each species, a sample of approximately 100 g was crushed with a blender (Omni-mixer ultra trax) in a clean jar. A mass of 50 g of homogeneous ground material was weighed using a precision balance (OHAUS PR series) into a bottle to which 100 mL of pure dichloromethane was added for residue analysis (HPLC grade, purity at 99.9 %); to cover the sample. This mixture was homogenised vigorously with a stirrer for 3 min. The resulting mixture was filtered through Whatmann 114 paper containing glass wool mounted on a 100 mL graduated cylinder containing 15 g of sodium chloride for synthesis (99.9% purity). A volume of approximately 80 mL of the filtrate was obtained in the test tube, then shaken vigorously by hand for 1 min. After standing at room temperature, the two phases were separated : the pellet and the supernatant. A 10 mL aliquot of the supernatant was then taken into a 100 mL flask. The extract was dried using a rotary evaporator (heidolph labo rata 4000 efficient) at a temperature of 40-70°C. The dry extract was recovered with 5 mL of pure methanol for residue analysis (99.9% purity). Using a vacuum pump, the sample was filtered again on column C 18, previously activated with 3 mL methanol and 2 mL doubly distilled water. The filtrate obtained was again passed through a disc filter and recovered in vials for HPLC quantification of the pesticides.

Pesticides were detected in fruit and vegetable extracts using an HPLC chain (SHIMADZU, Japan) consisting of a SIL-20A sampler, LC-20AT pump, TRAY tank, DGU-20A5 degasser, CTO-20A oven (40°C) and SPD-20A UV/VIS detector. Elution was carried out in isocratic mode at a flow rate of 0.5 mL/min for all pesticides. Pesticide residue concentrations were determined using the following formula [10]:

$$C = (C_i \times V_i \times S_e \times V_t) / (V_e \times S_i \times P)$$

With C_i = concentration of the standard range; V_i = injected volume of the standard range (μL); S_e = peak area of the extract (cm^2); V_t = total volume of the extract (mL); V_e = injected volume of the extract (μL); S_i = peak area of the standard range (cm^2); P = weight of the extract.

The limits of quantification of pesticides are determined from Table 1.

TABLE I: Family/molecule/limit of quantification (LOQ) breakdown

FAMILIES	MOLECULES	LQ* (mg/kg)
CARBAMATE	Aldicarb	0.009
	Chlorpropham	0.009
CHLOROACETAMIDE	Metazachlor	0.010
	Metolachlor	0.010
UREA DERIVATIVES	Buturon	0.018
	Chlortoluron	0.018
	Diuron	0.018
	Fenuron	0.018
	Isoproturon	0.018
	Linuron	0.018
	Methabenzthiazuron	0.018
	Metoxuron	0.018
	Monolinuron	0.018
	Monuron	0.018
ORGANOPHOSPHORUS	Chlorfenvinphos	0.009
	Parathion-éthyl	0.009
	Parathion-méthyl	0.009
TRIAZINE	Atrazine	0.018
	Cyanazine	0.018
	Déséthylatrazine	0.018
	Désisopropylatratzine	0.018
	Metamitron	0.018
	Métoxuron	0.018
	Prometryn	0.018
	Propazine	0.018
	Simazine	0.018
	Terbutylazine	0.018
	Terbutryn	0.018
TRIAZINONE	Hexazinone	0.025
	Metamitron	0.025
	Metribuzin	0.025

3. RESULTS AND DISCUSSION

3.1 Characteristics of the crop protection products used

Surveys of the various sellers of these plant protection products revealed 22 specialities ranging from Almaneb 80 WP to Tango 500 Ec via Diafuran 5G, Lambdax 2, 5 EC, Pyrical 480 Ec, Sefpyrifos 480 EC, Sunpyrifos 48% EC, etc. These 22 products contain 11 types of active ingredient (AI), which were found 28 times. These 22 products contain 11 types of active ingredient (AI) listed 28 times, the most abundant being Lambdacyhalothrin (3/28); Chlorpyrifos ethyl (4/28); Cypermethrin (6/28) and Profenofos (7/28). These different pesticides are used on different plants depending on their active ingredient composition. Pesticides containing Cypermethrin and Lambdacyhalothrin are used for vegetables, those containing Profenofos for cotton and Dimethoate for wood (Table II).

Our results are in line with those of Angbo and Kapoor [5-10] who, in a study of market gardeners, found that many of the agrochemical specialities used are not suitable for market gardening. In fact, these products were sold at low prices thanks to the subsidy from which cotton growing benefited. A financial reason could explain this practice.

The same economic situation could also be behind the rush by these growers to use less expensive agrochemicals that are not recommended for vegetable production. This is the case with agrochemical specialities such as SEFPYRIFOS 480 EC and SUNPYRIFOS 48% EC, which were found to be pesticides not approved by the Côte d'Ivoire government.

Table II: Characteristics of agrochemical products used by market gardeners

Trade name	Active ingredient (AI)	[AI]	RU	Registration number.
<i>Almaneb 80 WP</i>	Manebe	80%	Market garden	960347 Fo
<i>Banko Plus</i>	Chlorothalonil	550g/L	Market garden	990483 Fo
	Carbendazim	100g/L	Market garden	
<i>Calfos 720 EC</i>	Profenofos	720g/L	Cotton	07 0759 In
<i>Callidim 40 EC</i>	Dimethoate	400g /L	Wood	980417 In
<i>Cigogne 50 EC</i>	Cypermethrin	50g/L	Market garden	04 0652 In
<i>Curacron 500EC</i>	Profenofos	500g/L	Cotton	99 0466 In/Ac
<i>Cypalm 336 EC</i>	Cypermethrin	36g/L		
	Profenofos	300g/L	Cotton	99 0494 In
<i>Cypalm 50 EC</i>	Cyperméthrin	50g/L	Market garden	00 04 94 In
<i>Cypercal 50 EC</i>	Cypermethrin	50g /L	Market garden	900100 In
<i>Diafuran 5G</i>	Carbofuran	5%	Market garden	010552 In/Ne
<i>Duel 186 EC</i>	Profenofos	150 g/L		
	Cypermethrin	36g/L	Cotton	000518 In
<i>Furadan 5G</i>	Carbofuran	5g/kg	Market garden	900 091 In/Ne
<i>Kart 500 SP</i>	Cartap	500g/L	Market garden	970355 In
<i>sefpyrifos 480 EC</i>	Chlorpyrifos Ethyl	25g/L	Market garden	Pas
<i>sunpyrifos 48% EC</i>	Chlorpyrifos Ethyl	25 g/L	Market garden	Pas
<i>Lambdax 2, 5 EC</i>	Lambdacyhalothrin	25g/L	Market garden	Pas
<i>Lamdex 315 Ec</i>	Lambdacyhalothrin	15 g/L		
	Chlorpyrifos Ethyl	300g /L	Cotton	06 0708 In
<i>Lampfos 168 Ec</i>	Lambdacyhalothrin	18g/L		08 090 In
	Profenofos	150g/L	Cotton	
<i>Polytrine 186 Ec</i>	Cypermethrin	36 g/L		
	Profenofos	150 g/L	Cotton	950329-In/Ac
<i>Pyrical 480 Ec</i>	Chlorpyrifos Ethyl	Non précisé	Wood	00 0498 In
<i>Starter 350 Ec</i>	Endosulfan	350g/L	Cotton	Apv: 01 010 In/Ac
<i>Tango 500 Ec</i>	Profenofos	500g/L	Cotton	02 0575 In / Ac

[AI]: concentration of active ingredient; W.S.A.P.T: Wynca sunshine agro products & trading; F/D: Manufacturer or Distributor; S.J.A.: sefa and jane agrochemicals; AI: Active Ingredient; RU: Recommended Use; In: insecticide; Ac: acricide; Ne: nematocide.

3-2 Nature of pesticide residues in market garden produce

Analysis of market garden produce revealed the presence of pesticide residues in fruit and vegetables due to 32 molecules including Chlortoluron, Fenuron, Metoxuron, Monolinuron, Monuron, Parathion-ethyl, Parathion-methyl, Chlorfenvinphos, Linuron, Désethylatrazine, Désisopropylatrazine, propazine, Simazine, Métamitrone, Chlorprophame, Aldicarb and Métolachlor. The 32 pesticide residues found in the batches of market garden produce were divided into 6 major pesticide families: triazines were predominant with a proportion of 34.37%, urea derivatives were in second place with 31.25%, organophosphorus, triazinones and chloroacetamides were in third place, each representing 9.37%, and carbamates came last with 6.25% (Table III). Herbicides are used less frequently than fungicides. Farmers prefer herbicides to manual weeding, as they are more effective and easier to apply. The contamination of market garden produce by pesticides from different chemical families has also been reported by some authors [9-13]. Research of pesticide residues in vegetables in Benin has revealed the presence of 13 pesticides, including dichlorodiphenyltrichloroethane (DDT), endosulfan, aldrin and lindane [13]. On the other hand, the presence of 18 pesticides, the most predominant of which are dicofol, chlorpyrifos, DDT, dimethoate and cyhalothrin, in samples of cabbage, lettuce and tomatoes from the Niayes region of Senegal has been reported [12]. In Côte d'Ivoire, studies have shown that most of the pesticides found in market garden produce in the south-east region are bifenthrin, deltamethrin and cyhalothrin, all members of the pyrethroid family [12]. These results differ from ours because the pyrethroid family is not one of the families of pesticides found in our study.

On the other hand, residues of chlorothalonil, maneb, chlorpyrifos ethyl, carbendazine, cypermethrin and lambda-cyhalothrin were present in lettuces from market gardening sites in the Port-Bouët commune of Abidjan [9]. In Korhogo, families of tetrionic acids, benzamides, neonicotinoids, organophosphates, phenols and pyrethroids were found in market garden produce [15]. The quantities of pesticides found in market garden produce depend not only on the composition and quantity of plant protection products sprayed, but also on the pesticide content of the soil and the water used for irrigation. In addition, the diversity of pesticides detected in market garden produce could probably be explained by the fact that market garden crops require the use of numerous molecules to combat insects, nematodes and weeds. The work of certain authors corroborates this hypothesis [16]. This work revealed the presence of 13 active molecules belonging to 11 chemical families in the savannah region of Côte d'Ivoire.

Table III: Family/molecule/frequency distribution

FAMILY	MOLECULE	Number of batches
CARBAMATE	Aldicarb	2
	Chlorpropham	2
CHLOROACETAMIDE	Metazachlor	1
	Metolachlor	1
	Terbutryn	1
DERIVES DE L'UREE	Buturon	4
	Chlortoluron	8
	Diuron	1
	Fénuron	6
	Isoproturon	5
	Linuron	4
	Methabenzthiazuron	3
	Metoxuron	13
	Monolinuron	6
	Monuron	9
ORGANOPHOSPHORUS	Chlorfenvinphos	3
	Parathion-éthyl	5
	Parathion-méthyl	1
TRIAZINE	Desethylatrazine	14
	Atrazine	6
	Cyanazine	5
	Desisopropylatratzin	7
	Metamitron	2
	Metoxuron	1
	Prometryn	5
	Propazine	3
	Simazine	11
	Terbuthylazine	2
TRIAZINONE	Terbutryn	3
	Hexazinone	2
	Metamitron	10
	Metribuzin	1

3-3 Level of pesticide residue contamination in market garden produce

3-3-1 Lettuce

Concentrations of pesticide residues exceeding their limits of quantification were observed in 5 of the 29 molecules found in lettuce (figure 1). The molecules concerned were Chlorpropham (0.016 mg/kg), Linuron (0.02 mg/kg), Métolachlor (0.013 mg/kg), Chlorfenvinphos (0.026 mg/kg) and Parathion-ethyl (0.014), which were found in 5 samples, 1 of which alone contained 2 molecules (Chlorpropham and Métolachlor) (Figure 2).

Our results are similar to those of a study in Colombia, where 23 pesticide compounds were found in lettuce [17].

The high contamination of lettuce could also be explained by the frequency with which pesticides are applied. Given that the recommended doses are not respected, certain pests and agents responsible for crop diseases can prove resistant to agrochemicals at low doses. In their desire to eliminate these pests and diseases, market gardeners increase the frequency of application, resulting in the permanent presence of chemical molecules in or on crops.

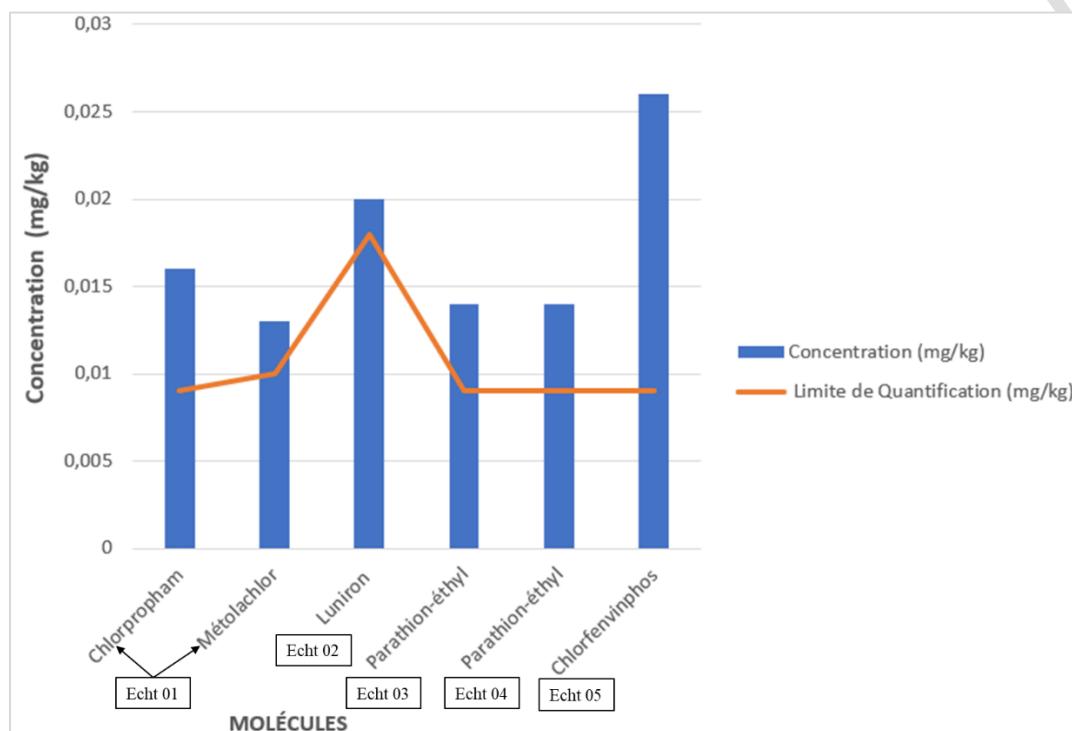


Figure 1: Study of reference values of phytosanitary products according to approved concentrations

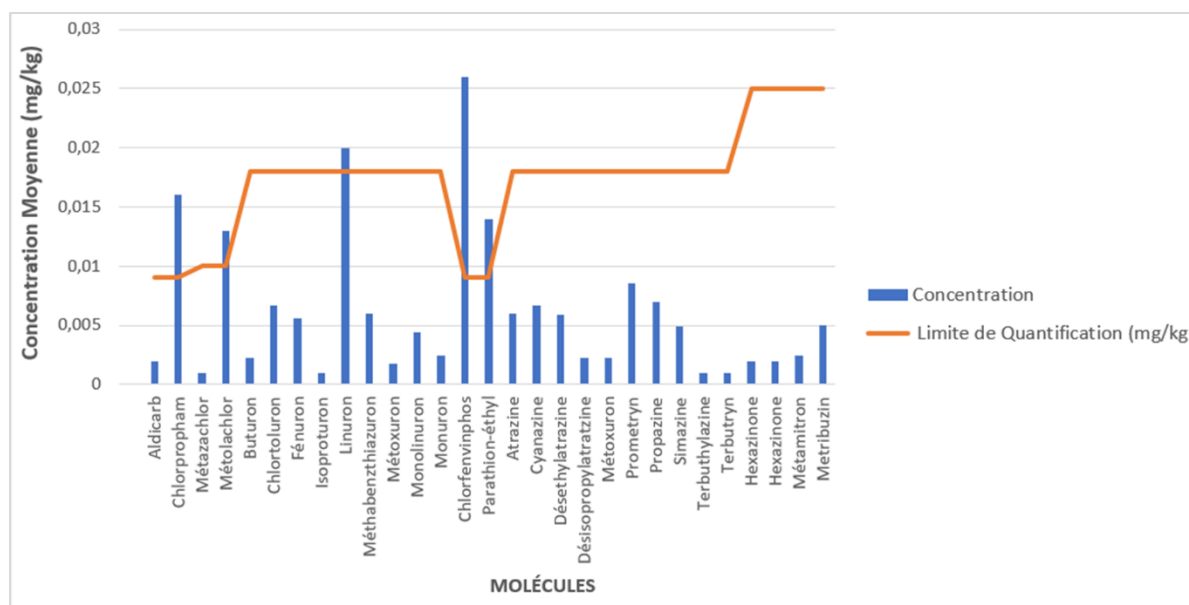


Figure 2: Variation of the the concentration of phytosanitary products according to the active ingredient tested in lettuce

3-3-2 Cucumbers, peppers and tomatoes

The various investigations revealed the presence of 32 pesticide residues overall. In cucumber, 16 residues were detected, representing 40.63% (Figure 3), as well as in the chilli pepper (Figure 4), while in the tomato, 6 residues were present, representing 18.75% (Figure 5). It should be noted, however, that the concentrations of these different molecules did not exceed their quantifiable limits in these three products (Figures 3, 4 and 5).

Maximum residual limits (MRLs) were high in tomato samples from Kenya and Botswana [18-19], while in Tanzania no pesticide residues were detected [20]. These results differ from those of this study, which found pesticide residues in 100% of tomatoes but below the MRLs.

In the case of peppers, our results are not consistent with those found in China, where no pesticide residues were detected [21].

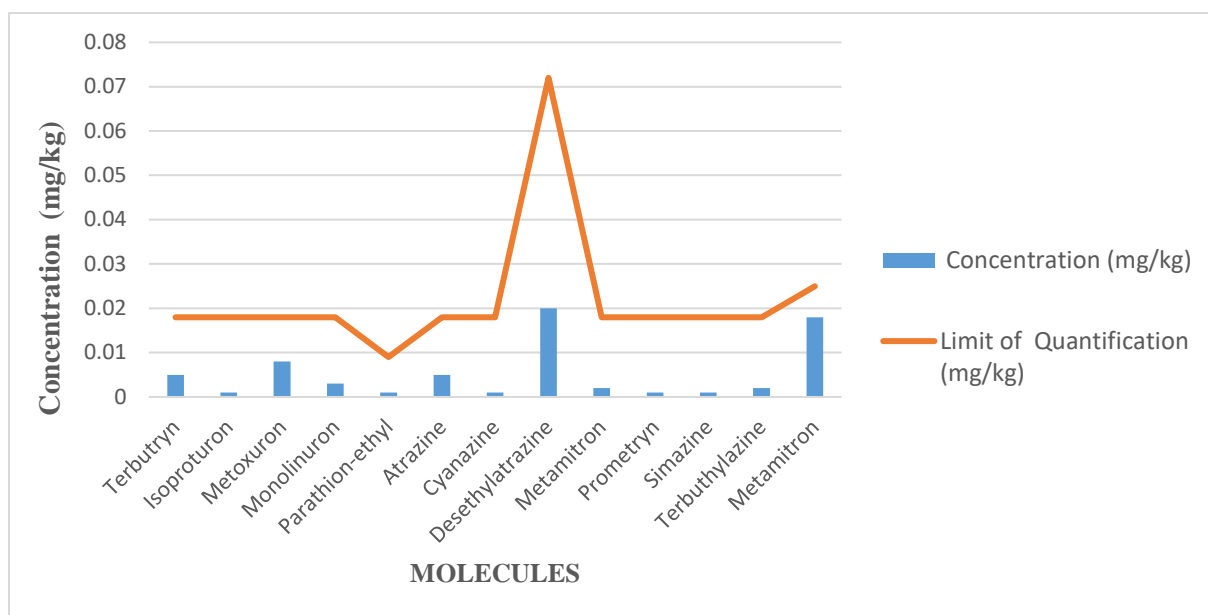


Figure 3: Variation of the concentration of plant protection products according to the active ingredient tested in cucumbers

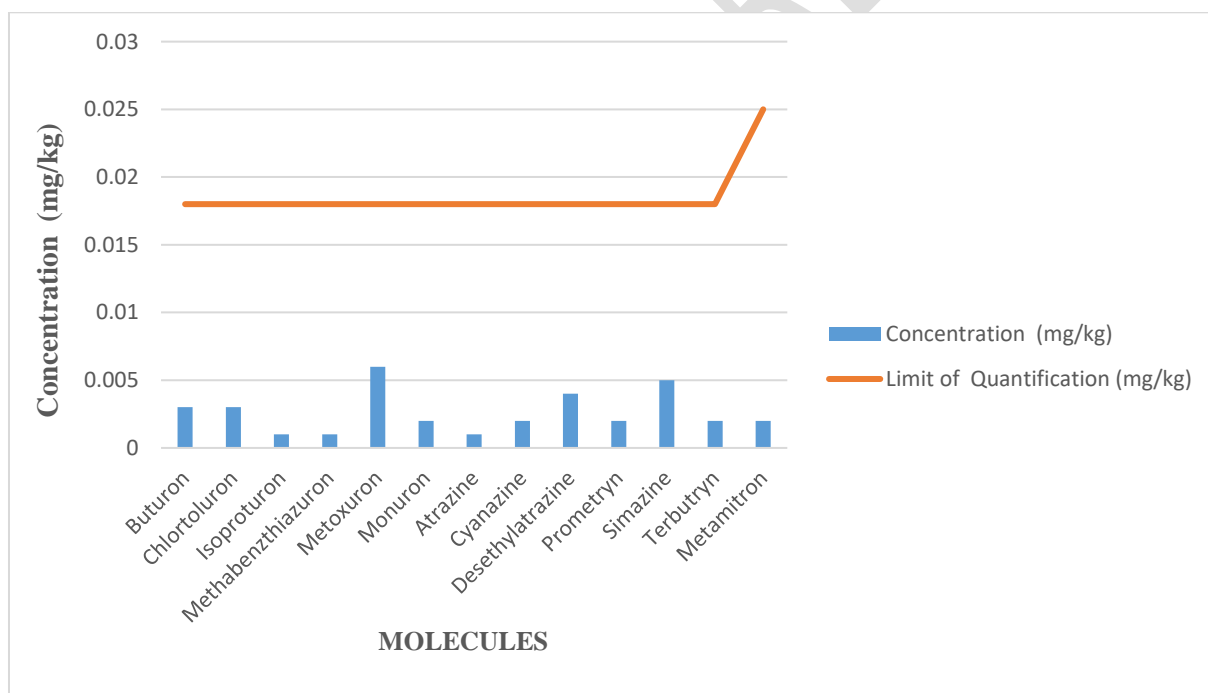


Figure 4 : Variation of the concentration of plant protection products according to the active ingredient tested in peppers

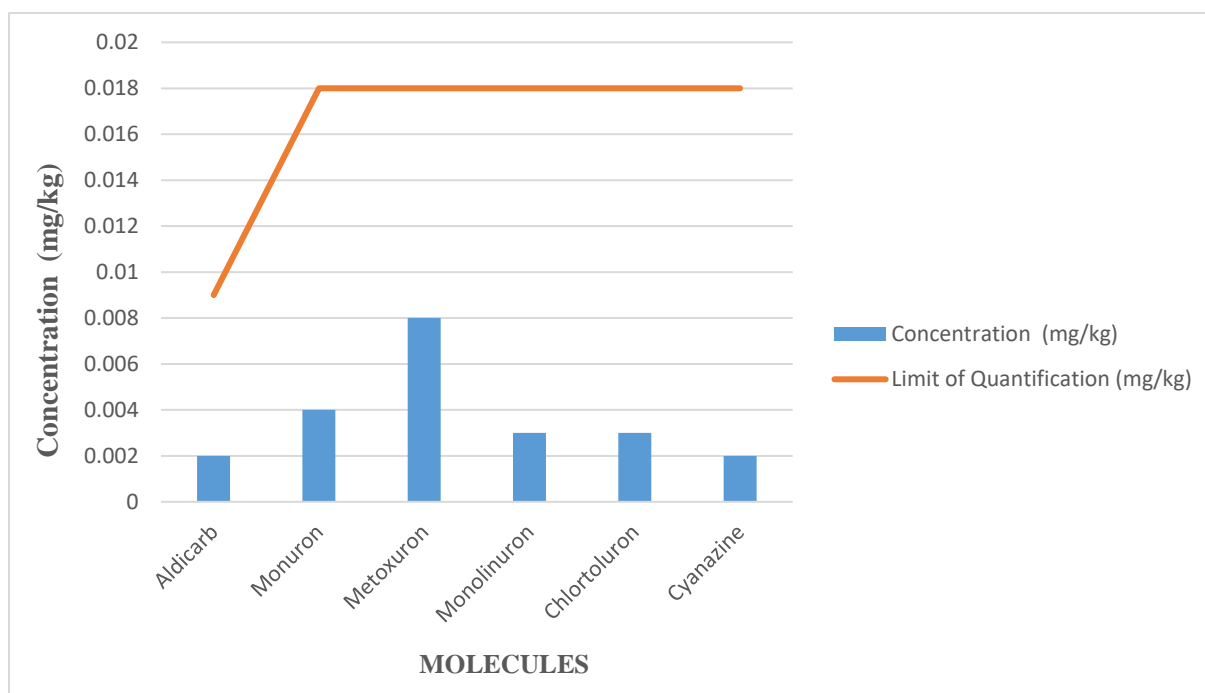


Figure 5 : Variation of the concentration of plant protection products according to the active ingredient tested in tomatoes

3-3-3. Pesticide families found in market garden produce

It was found that pesticide residues were included in 6 different families. However, our research has shown in Figure 6 that the levels of contamination by pesticide families differ from one vegetable product to another (Figure 6). Lettuce was contaminated by residues from all 6 families, with a preponderance of urea derivatives and triazine. Peppers were contaminated by urea derivatives and triazine, while tomatoes were contaminated by carbamate and urea derivatives, with a predominance of urea derivative residues. Cucumbers were poisoned by 5 families, except for carbamate residues, with a preponderance of molecules from the triazine family.

The analyses also showed that all market garden produce contained at least one pesticide residue (Figure 6). These observations are in line with the findings of a study in Italy, where 29.6% of vegetable samples were contaminated with more than one pesticide residue [22]. Among the various vegetables studied, leafy vegetables showed the highest percentage of contamination. This high proportion of contamination in leafy vegetables could be explained by the sensitivity of this type of vegetable to attack by insects and pathogens, which requires the use of different active ingredients to control these pests and direct contact of the leaves with pesticides.

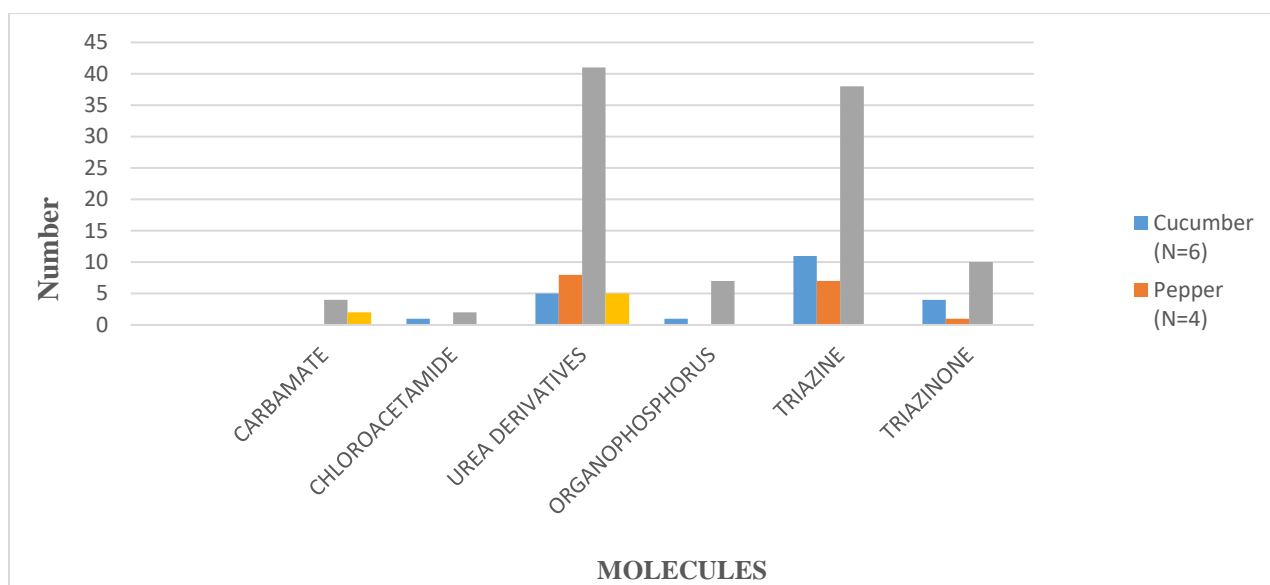


Figure 6 : Families of pesticides found in plants

A total of 39 samples were taken and analysed for pesticide residues. A considerable proportion (100%) of all the samples analysed for pesticide residues contained at least one detectable pesticide residue. Among these 39 batches of samples analysed, 34 (87.18%) had pesticide residue contamination levels below their threshold values. These batches still conformed to the expected results, making the products fit for consumption. Conversely, 5 samples (12.82%) contained pesticide residues higher than normal. This state of affairs leads to a non-conformity with our expected results (figure 7).

3-3-4. Consumption risk level for market garden produce

A total of 39 samples were taken and analysed for pesticide residues. A considerable proportion (100%) of all the samples analysed for pesticide residues contained at least one detectable pesticide residue. Among these 39 batches of samples analysed, 34 (87.18%) had pesticide residue contamination levels below their threshold values. These batches still conformed to the expected results, making the products fit for consumption. Conversely, 5 samples (12.82%) contained pesticide residues higher than normal. This results in non-compliance with our expected results (Figure 7).

Although contaminated by a range of pesticides, with the presence of 32 active ingredients for leafy vegetables, the maximum load of pesticide residues observed on market garden produce in 87.18% does not reach the maximum residue limits (MRLs) set by the Food and Agriculture Organization of the United Nations (FAO) and the World Health Organization (WHO) (EU, 2018) (Figure 7). The residue level observed below the MRLs could indicate, on the one hand, education of farmers and rational use of pesticides i.e. use in compliance with the manufacturer's recommendations (Bakırcı et al., 2014). On the other hand, this low level of pesticide residues in market garden produce could be related to the length of the period between application and sampling (Shoiful et al., 2013).

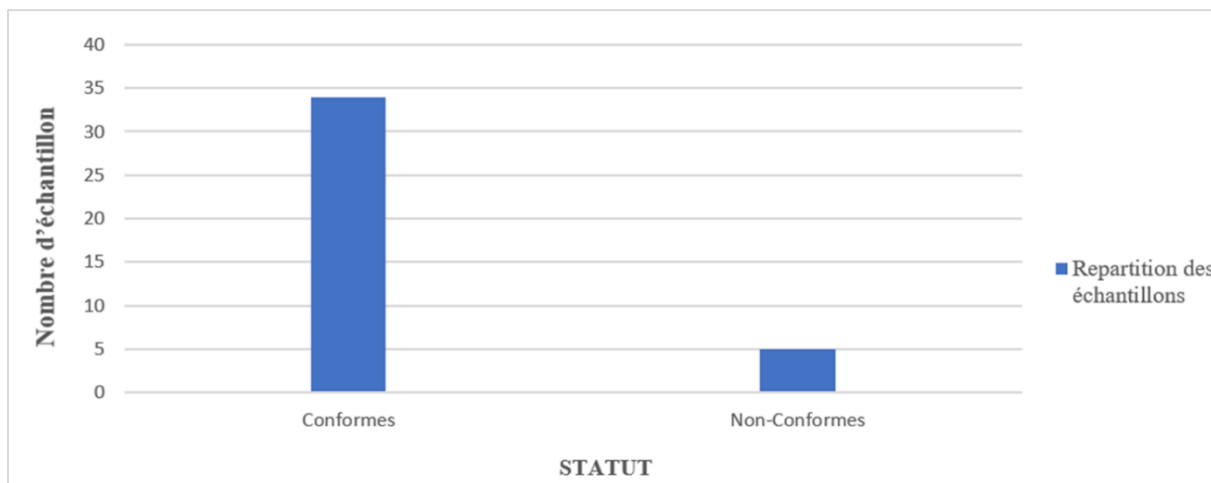


Figure 7: Histogram of batch conformity against reference values

5 CONCLUSION

The aim of our study was to assess the level of pesticide residues in commonly consumed vegetables. It therefore highlighted the nature and level of contamination of lettuce (*Lactuca sativa*), chillies (*Capsicum* sp), tomatoes (*Solanum lycopersicum*) and cucumbers (*Cucumis sativus*) by pesticide residues in the Port-bouët commune of Abidjan. Several pesticide residues have been identified in these market garden produce products. These pesticide residues belong to the triazine family, urea derivatives, organophosphates, triazinones, chloroacetamides and carbamates. 100% of the products contained pesticide residues. However, 87.18% had pesticide residue levels below their threshold values and 12.82% had pesticide residue levels above normal. The high maximum residue limits (MRLs) were found only in lettuce. It is recommended that the levels of pesticide residues in leguminous fruits in particular, and lettuce in particular, be periodically monitored, especially when eaten raw. Based on the results of this study, we believe that raising awareness among market gardeners could lead to better results.

6 LIMITATIONS OF THE STUDY

The sample size is not large. It could be increased by extending the study to the 10 communes of the city of Abidjan in order to gain a better overview of the evaluation of residues.

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