



Pesticide Residues in Pineapple Juice in Abidjan, Cote D'Ivoire

AKE ASSI Yolande Epouse DATTE

Laboratoire National d'Appui au Développement Agricole (LANADA), Laboratoire Central d'Hygiène Alimentaire et l'Agro-Industrie (LCHAI), 04 BP 612 Abidjan, Côte d'Ivoire
Université Félix Houphouët Boigny, Laboratoire de Biochimie et des Sciences des Aliments, UFR Biosciences, 22 BP 582 Abidjan, Côte d'Ivoire

GNONSORO Urbain Paul (Corresponding Author)

Laboratoire National d'Appui au Développement Agricole (LANADA), Laboratoire Central d'Agrochimie et d'Ecotoxicologie (LCAE), 04 BP 612 Abidjan, Côte d'Ivoire
Email: urbainpaulgnonsoro@gmail.com

KOUAKOU Konan Jean-Marie

Laboratoire National d'Appui au Développement Agricole (LANADA), Laboratoire Central d'Agrochimie et d'Ecotoxicologie (LCAE), 04 BP 612 Abidjan, Côte d'Ivoire

KPAN KPAN Kouakou Gains

Laboratoire National d'Appui au Développement Agricole (LANADA), Laboratoire Central d'Agrochimie et d'Ecotoxicologie (LCAE), 04 BP 612 Abidjan, Côte d'Ivoire

BIÉGO Godi Henri

Université Félix Houphouët Boigny, Laboratoire de Biochimie et des Sciences des Aliments, UFR Biosciences, 22 BP 582 Abidjan, Côte d'Ivoire

GNINGNINRI Hoglan Anne-Marie Lisette

Université Félix Houphouët Boigny, UFR Sciences Pharmaceutiques et Biologiques, 22 BP 582 Abidjan, Côte d'Ivoire

Article History

Received: July 5, 2020

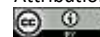
Revised: July 28, 2020

Accepted: August 3, 2020

Published: August 8, 2020

Copyright © 2020 ARPG
& Author

This work is licensed under
the Creative Commons
Attribution International



CC
BY: Creative Commons
Attribution License 4.0

Abstract

The determination of pesticides in food products is an essential issue to guarantee food safety and minimize health risks of consumers. In this study, 30 pineapple juice samples were collected randomly from 30 seller through the city of Abidjan (Côte d'Ivoire) and analyzed for the determination of pesticide residues. The aim of the work was to quantify 30 commonly used pesticides (Metolachlor, Chlorpropham, Parathion-methyl, Chlorfenvinphos, Vinclozolin, Parathion-ethyl, Fenuron, Aldicarb, Metoxuron, Monuron, Methabenzthiazuron, Chlortoluron, Monolinuron, Isoproturon, Diuron, Metobromuron, Metazachlor, Buturon, Linuron, Prometryn, Terbutryn, Desisopropylatrazine, Desethylatrazine, Simazine, Cyanazine, Atrazine, Propazine, Terbutylazine, Metamitron, Crimidine and Metolachlor) in real samples of pineapple juice. The method used for the determination of these analytes in the complex matrices was high-performance liquid chromatography with UV/Visible detector. Results obtained indicate that 30% of the investigated pineapple juices samples are free of pesticides residues or have a level below Limit Of Detection (<LOD), while 70% (21 samples) of the samples analyzed exceeds the Maximum Residue Levels (MRLs) set by the European Commission for Simazine, Metolachlor, Linuron and Aldicarb. So, two-thirds of the samples analyzed are unfit for consumption by the population. So, it is necessary to create an appropriate monitoring programs to ensure minimal residue levels in the pineapple fruit and juice produced in Cote d'Ivoire for export or local consumption.

Keywords: Pineapple juice; Pesticide residues; Liquid chromatography; Cote d'Ivoire.

1. Introduction

Fruits and vegetables are vital to human health as they are known for boosting the immune system. Many studies in the world have identified phytochemicals, minerals, and others in fruits and vegetables to be very essential in human development. Health professionals as well as nutritionists keep encouraging people to live on fruits and vegetables to avoid killer diseases such as cancer and cardiovascular diseases [1, 2]. More and more the eating habits of populations in our tropics are turning towards the consumption of fruit for pulp or juice. However, the quality of the juice is very much linked to that of the fruit from which it comes, which are constantly attacked by pests in orchards, during transport, storage or at the places of production of the juice. So, the use of chemical pesticides in fruit crops is necessary to control pest that could decrease field production, as well as to improve the fruit quality which reaches the consumer. Also, pesticides can be applied in fruits for post-harvest protection. So pesticide residues may be transferred from fruit into juice, being a significant route to human exposure. Hence, nowadays there is an increasing demand for developing sensitive and selective methods for the determination of multi-class pesticides in fruit juice at trace levels [3]. In fact, pesticide residues analysis plays an important role in food quality for food health risk assessment [4]. Pesticides are widely used in Cote d'Ivoire for agricultural practices because of its high effectivity and relatively low price. Due to pesticides toxicity, several countries, the European Union and the

Codex Alimentarius have established maximum residue levels (MRLs) in water, ground and food for a large number of pesticides. There are several studies regarding development and validation of analytical methodologies for pesticide residues analysis in juices [5]. Currently, routine methods for the determination of pesticide residues in environment and food typically require several sample preparations such as extraction, clean-up, and concentration before instrumental analysis. Liquid-liquid extraction (LLE) and solid-phase extraction (SPE) are the most useful sample preparation methods for the clean-up procedure [6, 7].

Cote d'Ivoire mainly produces pineapple for export to several identified attractive markets located in Europe. The variety produced in Cote d'Ivoire is essentially the Cayenne smooth (cultivated in Cote d'Ivoire). Ivorian production fell by 76% between 2001 and 2011, reaching 60,000 tons, of which around 40,700 tons were exported, that is 68% of its production. However, Cote d'Ivoire remains the leading exporter of the sub-Saharan region of pineapples and the third most productive country in the world with a production of 54.5 tons per hectare, something that would be due to a massive use of pesticides. Locally, the pineapples sold are those that were discarded during sorting at the packaging station. Only 20% of Ivorian pineapple production and sometimes less is sold on the local market, which has experienced a drastic decline reaching an estimated consumption of 1 kg per person per year. Pineapple is consumed on the local Ivorian market in the form of syrup slices, frozen broken chips, dried pineapple, concentrated juice and pure juice [8]. The pure juice is produced in Cote d'Ivoire in an industrial way and by hand by small traders provided with cart to the large arteries of the cities, such as Abidjan. Pineapple juice is usually commercialized by street sellers who extract the juice from the pineapple by manual pressing or by using mills. Although the use of pesticides provides unquestionable benefits in providing a plentiful, low-cost supply of high-quality fruits and vegetables, their incorrect application may leave harmful residues, which involve possible health risk [9]. The aim of this study was to assess the level of pesticide residues contamination in pineapple juice produced by hand, using liquid chromatography (LC) coupled with UV detector.

2. Materiel and Methods

2.1. Sampling

A total of 30 pineapple juice samples were collected randomly from 30 sellers through the city of Abidjan, Cote d'Ivoire. During sample collection, the pineapple juice traders were interviewed about the origin of the fruit and the methods used of producing the juice they use. Each sample of 1 liter of pineapple juice is collected in a glass bottle closed tightly and hermetically, labeled with a unique sample identity and put in a refrigerated cooler. Then the samples were transported quickly to the Laboratoire Central d'Agrochimie et d'Ecotoxicologie (LCAE), a unit of Laboratoire National d'Appui au Developpement Agricole (LANADA), Abidjan (Côte d'Ivoire). At the laboratory, samples were kept cool at 4°C until analyzes, which were carried out within 3 days after sampling.

2.2. Chemicals

All solvents used in this work for extraction were of analytical grade, while those for injection in the HPLC were of HPLC grade. Pesticide mix analytical standards were purchased from Dr Ehrenstorfer GmbH (Augsburg, Germany): Metolachlor, Chlorpropham, Parathion-methyl, Chlorfenvinphos, Vinclozolin, Parathion-ethyl, Fenuron, Aldicarb, Metoxuron, Monuron, Methabenzthiazuron, Chlortoluron, Monolinuron, Isoproturon, Diuron, Metobromuron, Metazachlor, Buturon, Linuron, Prometryn, Terbutryn, Desisopropylatrazine, Desethylatrazine, Simazine, Cyanazine, Atrazine, Propazine, Terbutylazine, Metamitron, Crimidine and Metolachlor. Dichloromethane, ethyl acetate, acetone, and acetonitrile were purchased from PROLABO, France. Methanol and hexane were purchased from SCHARLAU, France, while SPE cartridge were purchased from MAERCK, Germany. Water HPLC grade was purchased from Honeywell International Inc. (Morristown NJ, USA).

2.3. Sample Extraction and Analysis

The method of pesticides extraction from pineapple juice samples derived from that used by Topuz, *et al.* [10]. In that method, each pineapple juice sample was firstly homogenized in a conventional blender and 15 ml of methanol was added to 25 g of pineapple juice sample and mixed for 10 min in a 50 ml volumetric flask. The mixture was taken to 50 ml with water. Ten milliliter aliquot of this solution was further diluted to 50 ml water in a second volumetric flask. SPE cartridges were conditioned with 5 ml of methanol and 5 ml of water. The sample was passed through the cartridges using vacuum extraction manifold system at a rate of ca. 8–10 ml/min. After washing with 2.5 ml of water, the sorbent bed was dried under vacuum for 10 min. The analytes were eluted with 3 ml of dichloromethane into a vial for HPLC analysis [10].

In our study, the analysis were carry out by the determination of around thirty (30) pesticides, routinely researched in agriculture products, using a SHIMADZU brand HPLC, model LC-20AT equipped with a DGU-20A5 degasser, a brand UV/Visible detector SHIMADZU, model SPD-20A and an injector model SIL-20A. The device allows ultra-violet detection at variable wavelengths and it allows gradients of solvents to be obtained with a pump. Also, with software (LC-solution), it controls the entire system and ensures data acquisition. The separation was carried out on an analytical column of the VP-ODS type, of 154 mm of length and 4.6 mm internal diameter with a guard pre-column of 10 x 4.6 mm. The mobile phase used consists of a mixture of acetonitrile (A) and ultrapure water (E) (acetonitrile / water (20/80)) with a flow rate of 1 mL / min and the temperature of the column is 40°C. The injections are carried out automatically with a volume of 20 µL. Pesticides were determined by a UV/visible detector with a programmable wavelength.

3. Results

Table 1 presents the Limit of Detection (LOD), Limit of Quantification (LOQ) and Maximum Residue Levels (MRLs) of pesticide residue in pineapple juice. LOD ranged from 0.003 mg/L (Metolachlor) to 0.1 mg/L (Crimidine and Metamitron).

A survey on residues of the thirty selected pesticides in commercially available pineapple juices was performed. The results are presented in **tables 2**. The study showed that 9, i.e. 30% of the investigated pineapple juices samples are free of pesticides residues or have a level below LOD (<LOD). Of all samples analysed, 23.33% contained one pesticide residue above LOQ (>LOQ), 23.33% contained two pesticides residues above LOQ and 13.33% contained three pesticide residues above LOQ (**Table 2**). In total, 16 pesticides were found above LOQ (>LOQ) in pineapple juice samples: Chlorpropham, Parathion-methyl, Vinclozolin, Parathion-ethyl, Fenuron, Metoxuron, Monuron, Methabenzthiazuron, Chlortoluron, Metazachlor, Aldicarb, Linuron, Desisopropylatrazine, Simazine, Cyanazine and Metolachlor. **Table 3** shows pesticides number and frequency of appearance below LOD and above LOD. Between all pesticides found above LOQ (>LOQ), Simazine was the most frequent pesticide, as it was detected above LOQ in 15 pineapple juice samples on 30 samples analyzed, that is approximately 50,00% follow-up by Metolachlor with a level of 20.00% (**Table 3**). Only 2 pesticides were not detected in any pineapple juice samples: Isoproturon and Atrazine while 12 pesticides were detected below LOQ (Chlorfenvinphos, Monolinuron, Diuron, Metobromuron, Buturon, Prometryn, Terbutryn, Desethylatrazine, Propazine, Terbutylazine, Metamitron and Crimidine). Metolachlor and Simazine had the highest concentrations in some samples. Metolachlor was found in a concentration range of <LOD – 0.145 mg/L and Simazine in a range of <LOD – 0.690 mg/L.

In many countries, monitoring of pesticide residues in fruit and vegetables is one of the most important procedures in order to reduce potential hazards on human health. MRLs have been set to establish the highest content of pesticide residue in many agricultural commodities and especially are trading standards, which permits their proper use, adequate control and guarantee consumer safety [11]. However, there are no Codex MRLs established for fruit juice or tomato juice. The only ones fixed for processed edible fruits apply to dried fruits (grapes, raisins, figs, dates and fruits in general) and to animal feed (apple marc, dry citrus pulp and raisin marc), residues from fruit pressing to obtain the juice. In cases where no processing data was available, it is likely that only the MRL for unprocessed fruit has been proposed [12]. So, In front of the absence of Maximum Residue Levels in our country, the MRLs established by the European Commission [13] for pineapple fruit have been used for this study. Maximum Residue Levels (MRLs) for pineapple set by the European Union (EU) consider all tested pesticides, except for Metoxuron, Chlortoluron, Metobromuron, Buturon, Prometryn, Terbutryn, Desisopropylatrazine, Desethylatrazine, Cyanazine, Propazine and Crimidine. They range from 0.01 mg/kg to 0.05 mg/kg for Parathion-ethyl, Atrazine, Terbutylazine and Metolachlor [13]. According to the **table 1** for all 30 pesticides analysed, the LOD presented are lower or equal to the respective Maximum Residue Levels (MRLs) established by the European Commission. In all samples analyzed, 70% (21 samples) had residues of pesticides above the MRLs, whereas 30% had a residue below the MRL set by the European Commission for pineapple fruit [13]. **Table 3** shows that Simazine exceeded most frequently the corresponding MRL (50%), followed by Metolachlor (20%), Linuron (16.67%), Aldicarb (13.33%), Chlorpropham (6.67%) and Vinclozolin, Parathion-ethyl and Methabenzthiazuron (3.33% each).

4. Discussion

There are only few data on the literature regarding the presence of pesticide residues studied in this paper in pineapple juice. Results of LOD obtained in the present study are higher for simazine and atrazine, similar for Parathion-methyl and weaker for Chlorfenvinphos than those reported by *Das, et al.* [14], who analysed 86 multiclass pesticides in pineapple juice using gas chromatography tandem mass spectrometry. LOD obtained were 0.01 mg/L for atrazine, Parathion-methyl, and Simazine and were 0.05 mg/L for Chlorfenvinphos. Moreover, in comparison with results obtained in pineapple fruit in Ghana by *Donkor, et al.* [15], where LOD of Parathion-ethyl and Chlorfenvinphos detected were respectively 0.003 and 0.010 mg/L, our results are similar for Chlorfenvinphos and higher for Parathion-ethyl. The fact that some results of LOD obtained in our study are similar or weaker for some pesticides than those reported in literature means that the method used here in pineapple juice samples revealed its suitability for routine multi-residue analysis of organophosphorus, weedkillers derived from urea and nitrogenized heterocycle, carbamates, triazines, triazinone, rodenticide and organochlorine for monitoring purposes. This method could be suitable for the analysis of pesticides in pineapple juice, in laboratories not equipped with MS instrumentation.

Romero-Gonzalez, et al. [3], analysed 90 pesticides in fruit juices (peach, orange, pineapple, apple and multifruit), obtained from local supermarkets in Almeria (Spain), by ultra-performance liquid chromatography coupled to tandem mass spectrometry (UPLC–MS/MS). They have not found residues of Desisopropylatrazine, Metamitron, Desethylatrazine, Metoxuron, Aldicarb, Simazine, Chlorotoluron, Metobromuron, Atrazine, Metazachlor, Isoproturon, Diuron, Propazine, Linuron, Terbutylazine, Prometryn and Metolachlor in their study, in any samples. This result is similar to ours for some pesticides, in this meaning that atrazine was not detected in any pineapple juice samples and level of Diuron, Prometryn, Desethylatrazine and Terbutylazine were detected below LOQ. While, Desisopropylatrazine, Metamitron, Metoxuron, Aldicarb, Simazine, Chlorotoluron, Metobromuron, Metazachlor, Isoproturon, Propazine, Linuron, Metolachlor were quantified in ours samples with a higher levels when compared as reported in **Table 2**.

Also, the fact that 70% (21 samples) of the samples analyzed exceeds the MRLs set by the European Commission for pineapple fruit for certain pesticides such as Simazine, Metolachlor, Linuron and Aldicarb [13] indicates that more than two-thirds of the samples analyzed are unfit for consumption by the population. These results indicate the prevalence of Simazine content above the EU MRLs in 50% of analyzed samples followed by Metolachlor (20%), Linuron (16.67%), and Aldicarb (13.33%). Higher values of Simazine, Metolachlor, Linuron and Aldicarb found in many samples analyzed may be due to the liposolubility properties of some pesticides, they could be retained in the fruit peel, resulting in a longer half-life [16] and which appear in the fruit juices. This result is characteristic of the harmful effects that the consumption of these juices can have on the health of consumers. In fact, the consumers are likely to be contaminated by diseases caused by the pesticides, because they ingest large quantities of fruit juices although the pesticides concentrations in fruit juice are generally lower than those observed in the whole fruit [17]. Such result could be explained by the worth use of pesticides in pineapple plantations by farmers and the bad practices of pineapple juice production carried out by the traders visited.

In some studies, authors mentioned that the presence of pesticide residues in fruit-based could be attributed to the use of fruit peels in the flavor extract used as ingredient in the soft drink [16, 17], but in our case the pineapple juice traders do not add fruit peels or any other additive ingredients or substances. So, the presence of pesticides in pineapple juice may not come from additive substance brought by traders. Moreover, level of some pesticides obtained in this study, which are above EU MRLs, Shows that it is necessary to create an appropriate monitoring programs to ensure minimal residue levels in the pineapple fruit and juice produced in Cote d'Ivoire for export or local consumption. Also, since organophosphate pesticides are involved in the decline of insect pollinator populations and alterations on motor functions of bees [18], it is necessary to implement strict regulations for the use of organophosphorus pesticides, the subject of our study, in agricultural areas dedicated to the cultivation of pineapples. These results are important due to the basis provided to establish strategies to satisfy the international standards regarding food safety and to improve the local economy of the pineapple sector through the national and international trade. So, it is necessary to strengthen this study by the incorporation of other not evaluated pesticides such as glyphosate, a herbicide with broad spectrum of action, widely used in many country in the world, because it is cheap and effective [17].

Table-1. Limit of Detection (LOD), Limit of Quantification (LOQ) and maximum residue levels (MRLs) of pesticide residues in pineapple juice

Pesticides		LOD* (mg/L)	LOQ* (mg/L)	MRL (mg/kg) [12]
Family	Required pesticides			
Organo-phosphorus	Chlorpropham	0.004	0.01	0.01
	Parathion-methyl			0.01
	Chlorfenvinphos			0.01
	Vinclozolin			0.01
	Parathion-ethyl			0.05
Weedkillers derived from urea and nitrogenized Heterocycle	Fenuron	0.006	0.018	0.01
	Metoxuron			-
	Monuron			0.01
	Methabenzthiazuron			0.01
	Chlortoluron			-
	Monolinuron			0.01
	Isoproturon			0.01
	Diuron			0.01
	Metobromuron			-
	Metazachlor			0.02
	Buturon			-
	Linuron			0.01
	Carbamates			Aldicarb
Triazines	Prometryn	0.008	0.025	-
	Terbutryn			-
	Desisopropylatrazine			-
	Desethylatrazine			-
	Simazine			0.01
	Cyanazine			-
	Atrazine			0.05
	Propazine			-
	Terbutylazine			0.05
Triazinone	Metamitron	0.1	0.35	0.1
Rondonticide	Crimidine	0.1	0.35	-
Organo-chlorine	Metolachlore	0.003	0.009	0.05

*: values found in our study

Table-2. Concentrations of pesticide residues in the pineapple juice samples (µg/L)

Family	Pesticides	J ₁	J ₂	J ₃	J ₄	J ₅	J ₆	J ₇	J ₈	J ₉	J ₁₀	J ₁₁	J ₁₂	J ₁₃	J ₁₄	J ₁₅
Organo-phosphorus	Chlorpropham	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Parathion-methyl	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Chlorfenvinphos	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Vinclazolin	-	-	-	-	-	-	-	-	-	<LOQ	0.016	-	-	-	-
	Parathion-ethyl	-	-	-	-	-	-	-	-	-	-	0.017	-	-	-	-
Weedkillers derived from urea and nitrogenized Heterocycle	Fenuron	-	-	-	<LOQ	-	-	-	-	-	-	<LOQ	-	-	-	<LOQ
	Metoxuron	<LOQ	<LOQ	-	0.02	<LOQ	-	-	-	-	-	<LOQ	-	-	-	-
	Monuron	-	-	-	-	-	-	-	<LOQ	-	-	<LOQ	-	-	-	-
	Methabenzthiazuron	-	-	-	-	-	-	-	-	-	-	0.018	-	-	-	-
	Chlortholuron	-	-	-	-	-	-	-	-	-	-	0.043	-	-	-	-
	Monolinuron	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Isoproturon	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Diuron	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Metobromuron	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Metazachlor	-	-	-	-	-	-	-	-	-	-	0.033	-	-	-	-
	Buturon	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
Linuron	0.059	<LOQ	<LOQ	0.052	-	-	0.039	0.022	-	0.018	<LOQ	-	-	-	-	
Carbamates	Aldicarb	-	<LOQ	-	<LOQ	-	-	-	0.045	<LOQ	<LOQ	<LOQ	0.051	-	-	-
Triazines	Prometryn	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Terbutryn	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Desisopropylatrazine	-	-	-	-	-	-	-	-	-	-	0.038	-	-	-	-
	Desethylatrazine	-	<LOQ	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Simazine	-	<LOQ	-	-	-	-	-	-	-	-	0.690	-	-	-	0.346
	Cyanazine	<LOQ	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-
	Atrazine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Propazine	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-	
Terbutylazine	-	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-	
Triazinone	Metamitron	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-	
Rodenticide	Crimidine	-	<LOQ	-	-	-	-	-	-	-	<LOQ	-	-	-	-	
Organo-chlorine	Metolachlor	-	<LOQ	<LOQ	-	-	-	-	-	-	-	<LOQ	-	-	-	0.145
Total concentration (µg/L)		0.059	0.000	0.000	0.072	0.000	0.000	0.039	0.067	0.000	0.018	0.855	0.051	0.000	0.000	0.491
Family	Pesticides	J ₁₆	J ₁₇	J ₁₈	J ₁₉	J ₂₀	J ₂₁	J ₂₂	J ₂₃	J ₂₄	J ₂₅	J ₂₆	J ₂₇	J ₂₈	J ₂₉	J ₃₀
Organo-phosphorus	Chlorpropham	-	<LOQ	-	-	-	0.014	-	-	-	-	-	0.011	<LOQ	<LOQ	<LOQ
	Parathion-methyl	-	-	-	-	-	-	0.070	-	0.029	-	0.026	-	-	-	-
	Chlorfenvinphos	-	-	-	-	-	-	-	<LOQ	-	-	-	-	-	-	-
	Vinclazolin	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Parathion-ethyl	<LOQ	<LOQ	-	-	-	-	-	-	-	-	-	-	-	-	-
Weedkillers derived from urea and nitrogenized Heterocycle	Fenuron	<LOQ	0.021	-	-	<LOQ	-	-	-	-	-	-	-	-	-	-
	Metoxuron	-	-	<LOQ	-	-	-	-	-	-	-	-	-	-	-	-
	Monuron	0.039	-	-	<LOQ	-	-	-	-	-	-	-	-	-	-	-
	Methabenzthiazuron	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Chlortholuron	0.025	<LOQ	-	-	-	-	<LOQ	-	-	-	-	-	-	-	-
	Monolinuron	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Isoproturon	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Diuron	-	-	-	-	-	-	<LOQ	-	-	-	-	-	-	-	-
	Metobromuron	-	-	-	-	-	-	-	-	-	<LOQ	-	-	-	-	-
	Metazachlor	<LOQ	<LOQ	<LOQ	-	-	-	<LOQ	-	-	-	-	-	-	-	-
	Buturon	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Linuron	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Carbamates	Aldicarb	0.067	-	-	0.030	-	-	-	-	-	-	-	-	-	-	-
Triazines	Prometryn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Terbutryn	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Desisopropylatrazine	<LOQ	<LOQ	-	-	-	-	-	-	-	<LOQ	<LOQ	<LOQ	-	-	-
	Desethylatrazine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Simazine	0.170	0.196	-	0.128	0.150	0.26	0.156	-	0.098	0.233	0.08	0.302	0.156	0.341	0.111
	Cyanazine	-	-	-	-	<LOQ	-	0.025	-	-	-	<LOQ	-	<LOQ	-	-
	Atrazine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
Propazine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Terbutylazine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Triazinone	Metamitron	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Rodenticide	Crimidine	-	-	-	-	-	-	-	-	-	-	-	-	-	-	
Organo-chlorine	Metolachlor	-	0.083	<LOQ	-	0.068	0.106	-	-	-	-	0.065	-	0.063	-	-
Total concentration (µg/L)		0.301	0.300	0.000	0.158	0.218	0.380	0.251	0.000	0.127	0.233	0.171	0.313	0.219	0.341	0.111

- : Not Detected; <LOQ: Below the Limit of Quantification

Table-3. Pesticides number and frequency of appearance below LOQ and above LOQ in pineapple juice

Pesticides		Number of appearance <LOQ	Frequency of appearance <LOQ (%)	Number of appearance >LOQ	Frequency of appearance >LOQ (%)
Family	Required pesticides				
Organo-phosphorus	Chlorpropham	5	16.67	2	6.67
	Parathion-methyl	1	3.33	3	10.00
	Chlorfenvinphos	2	6.67	0	0.00
	Vinclozolin	1	3.33	1	3.33
	Parathion-ethyl	2	6.67	1	3.33
Weedkillers derived from urea and nitrogenized Heterocycle	Fenuron	5	16.67	1	3.33
	Metoxuron	5	16.67	1	3.33
	Monuron	3	10.00	1	3.33
	Methabenzthiazuron	0	0.00	1	3.33
	Chlortoluron	2	6.67	2	6.67
	Monolinuron	1	3.33	0	0.00
	Isoproturon	0	0.00	0	0.00
	Diuron	2	6.67	0	0.00
	Metobromuron	2	6.67	0	0.00
	Metazachlor	4	13.33	1	3.33
	Buturon	1	3.33	0	0.00
	Linuron	3	10.00	5	16.67
Carbamates	Aldicarb	5	16.67	4	13.33
Triazines	Prometryn	1	3.33	0	0.00
	Terbutryn	1	3.33	0	0.00
	Desisopropylatrazine	5	16.67	1	3.33
	Desethylatrazine	2	6.67	0	0.00
	Simazine	1	3.33	15	50.00
	Cyanazine	5	16.67	1	3.33
	Atrazine	0	0.00	0	0.00
	Propazine	1	3.33	0	0.00
Terbuthylazine	1	3.33	0	0.00	
Triazinone	Metamitron	1	3.33	0	0.00
Rodenticide	Crimidine	2	6.67	0	0.00
Organo-chlorine	Metolachlor	4	13.33	6	20.00

5. Conclusion

The method used in this paper for quantitative analysis of thirty (30) pesticide residues in 30 pineapple juice samples collected randomly from traders through the city of Abidjan (Cote d'Ivoire) provides data reliable on the level of pesticides contamination of the pineapple juice manufactured in an artisanal way and sold on the crossroads. The results indicate that 30% of the investigated pineapple juices samples are free of pesticides residues or have a level below LOD (<LOD), while 70% (21 samples) of the samples analyzed exceeds the MRLs set by the European Commission for pineapple fruit for certain pesticides such as Simazine, Metolachlor, Linuron and Aldicarb. So, two-thirds of the samples analyzed are unfit for consumption by the population. Hence, it is necessary to (1) create an appropriate monitoring programs to ensure minimal residue levels in the pineapple fruit and juice produced in Cote d'Ivoire for export or local consumption, (2) investigate other pesticides, such as glyphosate, a herbicide with broad spectrum of action, that were not included in this study, and (3) implement strict regulations for the use of pesticides by farmers.

Conflict of Interests

The authors declare that no competing interests exist.

Acknowledgments

The authors thank the Direction of LANADA (Laboratoire National d'Appui au Developpement Agricole) and all the agents of LCAE (Laboratoire Central d'Agrochimie et d'Ecotoxicologie) for their technical assistance and their expertise.

References

- [1] Claeys, W. L., Schmit, J. F., Bragard, C., Maghuin-Rogister, G., Pussemier, L., and Schiffers, B., 2011. "Exposure of several Belgian consumer groups to pesticide residues through fresh fruit and vegetable consumption." *Food Control*, vol. 22, pp. 508-516.
- [2] Hjorth, K., Johansen, K., Holen, B., Andersson, A., Christensen, H. B., and Siivinen, K., 2011. "Pesticide residues in fruits and vegetables from South America. A Nordic project." *Food Control*, vol. 22, pp. 1701-1706.

- [3] Romero-Gonzalez, R., Garrido Frenich, A., and Martinez Vidal, J. L., 2008. "Multiresidue method for fast determination of pesticides in fruit juices by ultra-performance liquid chromatography coupled to tandem mass spectrometry." *Talanta*, vol. 76, pp. 211-225.
- [4] Community Directive 93/58 EEC, 1993. *Off. J. Eur. Commun., L 211/6*. Brussels: European Community.
- [5] Furlani, R. P. Z., Marcilio, K. M., Moralez Leme, F., and Tfouni, S. A. V., 2011. "Analysis of pesticide residues in sugarcane juice using QuEChERS sample preparation and gas chromatography with electron capture detection." *Food Chemistry*, vol. 126, pp. 1283-1287.
- [6] Hernandez, F., Sancho, J. V., Pozo, O., Lara, A., and Pitarch, E., 2001. "Rapid direct determination of pesticides and metabolites in environmental water samples at sub- $\mu\text{g/l}$ level by on-line solid-phase extraction liquid chromatography-electrospray tandem mass spectrometry." *J. Chromatogr. A.*, vol. 939, pp. 1-11.
- [7] Ahmed, F. E., 2001. "Analyses of pesticides and their metabolites in foods and drinks." *Trends Anal. Chem.*, vol. 20, pp. 649-661.
- [8] Programme d'Appui au Commerce et à l'Intégration Régionale PACIR, 2013. "Évaluation du potentiel à l'exportation des fruits tropicaux, Centre du commerce international (ITC)". Fiche Export Fruits tropicaux : Cote d'Ivoire Genève, Document technique No. du document EC-10-174.E : ITC, ., p. 159
- [9] Torres, C. M., Pico, Y., and Manes, J., 1996. "Determination of pesticide residues in fruit and vegetables." *Journal of Chromatography A.*, vol. 754, pp. 301-331.
- [10] Topuz, S., Özhan, G., and Alpertunga, B., 2003. "Simultaneous determination of various pesticides in fruit juices by HPLC-DAD." *Food Control*, vol. 16, pp. 87-92.
- [11] European Food Safety Authority, 2013. "Pesticide residue in food and feed: Codex pesticides residues in food online database. [cited 2013 june 2]. Available from: European commission 2005. Regulation (ec) no 396/2005 of the European parliament and of the council of 23 february 2005 on maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending council directive 91/414/eec." *Off. J. Eur. Union.*, vol. 70, pp. 1-16.
- [12] Commission Du Codex Alimentarius, 2003. "Limites maximales de résidus pour les produits transformés ou prêts à la consommation destinés à l'alimentation humaine et animale, programme mixte FAO/OMS sur les normes alimentaires comité du codex sur les résidus de pesticides." In *Trente-cinquième session, Rotterdam (Pays-Bas), 13 mars – 5 avril 2003. CX/PR 03/17 Janvier 2003*.
- [13] Regulation (EC) No 396/2005 of The European Parliament and of The Council, 2005. "Maximum residue levels of pesticides in or on food and feed of plant and animal origin and amending Council Directive 91/414/EEC." *Off. J. Eur. Union.*, vol. 70, pp. 1-16.
- [14] Das, S., Kundu, A., Bhattacharyya, A., Singha, D., Saha, S., Bhattacharyya, A., and Roy, S., 2018. "Development of a multiresidue method for determination of 86 multiclass pesticides in pineapple juice using gas chromatography tandem mass spectrometry." *Journal of Crop and Weed*, vol. 14, pp. 174-182.
- [15] Donkor, A., Osei-Fosu, P., Nyarko, S., Kingsford-Adaboh, R., B., D., and Asante, I., 2015. "Validation of QuEChERS method for the determination of 36 pesticide residues in fruits and vegetables from Ghana, using gas chromatography with electron capture and pulsed flame photometric detectors." *Journal of Environmental Science and Health, Part B*, vol. 50, pp. 560-570.
- [16] Garcia, J. F., Gilbert-Lo, B., Ferna, A. M. R., Garcı, J. F., and Molina-Dı, A., 2008. "Determination of pesticide residues in fruit-based soft drinks determination of pesticide residues in fruit-based soft drinks." *Anal. Chem.*, vol. 80, pp. 8966-8974.
- [17] Suárez-Jacobo, A., Manuel, V., Alcantar-Rosales, AlonsoSegura, D., Heras-Ramírez, M., Elizarragaz-De La Rosa, D., Lugo-Melchor, O., and Gaspar-Ramirez, O., 2017. "Pesticide residues in orange fruit from citrus orchards in nuevo leon state, Mexico." *Food Additives and Contaminants: Part B*, vol. 10, pp. 192-199.
- [18] Williamson, S. M., Moffat, C., Gomersall, M. A. E., Saranzewa, N., Connolly, C. N., and Wright, G. A., 2013. "Exposure to acetylcholinesterase inhibitors alters the physiology and motor function of honeybees." *Front Physiol*, vol. 4, pp. 1-10.