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Plant and Food Biochemistry

Research and Evaluation of Organochlorine Pesticides in the Precooked Fonio Sold in the Food Stores of Bamako

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Abstract

Original Research Article

This study was part of a basic assessment of the level of contamination of precooked fonio by pesticide residues in Bamako. Thus, 36 samples of precooked fonio were collected. The active ingredients of five organochlorine pesticides (op' DDT, pp' DDT, Endosulfans α and β and Dieldrin), categorized as persistent and obsolete organic pollutants in Mali, have been investigated and quantified by gas chromatography. The results showed high rates of pesticide residues contamination in the tested precooked fonio samples into twenty nine of 36 samples (75%). About 59% of the samples have contained two or more pesticides while 30% three or more pesticides. The Endosulfan β was the most detected pesticides (15 times) in our samples followed by the pp' DDT (13 times). The total pesticides residues per samples of the five pesticide sactive ingredients have varied from 0.037 to 1.874 mg/kg. In other side, the total residues per individual pesticide varied from 3.377 mg/kg for op' DDT to 0.984 mg/kg for Dieldrin. According to the Codex Alimentarius norms, the most of the tested precooked fonio are unsafety for consumption. These data showed that these organochlorine pesticides are present in our foodstuffs despite their prohibition.

Keywords: Precooked fonio, pesticides, contamination, Bamako.

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INTRODUCTION

The fonio (Digitaria exilis Stapf), a traditional cereal from West Africa, is considered as the most ancient indigenous cereal. The Dogons of Mali, an ancient people, consider its seed as "the germ of the world" (Cruz et al., 2012). Today, this traditional cereal is valorized in the form of precooked fonio packaged in small plastic bags of 500 g and 1 kg and sold in different food stores throughout Bamako city (Ferré et al., 2018). This has aroused a keen interest from consumers especially during feats and ceremonies. This infatuation is due to its culinary properties: simplicity, fastness and delicious. Due to the fathered growing demand by this product, many women integrated the fonio processing sector into precooked fonio at Bamako (Sylla, 2005 ; Ferré et al., 2018). This quest for opportunities has also been accompanied by a sharp increase in fonio production across the country, from 22000 tons in 2005 (Sylla, 2005) to 40553 tons in 2021 (Agence Ecofin, 2021). The recovered increasing would be resulted of

agronomic characteristics of the species which can be cultivated on poor soils and in areas with low pluviometry (Kanlindogbe *et al.*, 2020). Likewise, the species possess a good resistance to drought conditions compared to other local basic cereals. In addition, fonio contributes to food security especially during the lean periods in the rural areas, thanks to the earliness of its harvest compared to other cereals (Sylla, 2005).

Today, thanks to numerous development projects, the sector of transformation of fonio into precooked fonio is mainly made up of women artisans, very small enterprises (TPE) and also a growing number of small and medium sized enterprises (PME) (Ferré *et al.*, 2018). While these projects have made it possible to clean up and improve the production of precooked fonio through semi-industrial or even industrial equipment, the development of cereal production of fonio, which had remained traditional till now (Kanlindogbe *et al.*, 2020), has now been accompanied by several constraints, the most important of which are the abusive and

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inappropriate use of chemical fertilizers and pesticides (Cruz et al., 2012). Although fonio is resistant to pests (Vall et al., 2011), it is very vulnerable to attacks by fungi, termites, caterpillars and other sucking insects (Kanlindogbe et al., 2020). However, the uncontrolled use of pesticides in the production and conservation of fonio constitutes a real potential source of chemical contamination of foodstuffs (OMS, 2020). Although some pesticides considered dangerous are no longer authorized or are subject to restricted use (UNEP, 2020), they remain widely used in developing countries (FAO and WHO, 2016; ACEDD and IPEN, 2021). In Mali, a study carried out in 2009 has identified 1100 tons of obsolete pesticides in the country (PASP, 2009). Similarly, Maïga et al. (2018) found quite worrying levels of organochlorine pesticides in fresh cow's milk collected in the large dairy basins in southern Mali. These pesticides are ubiquitous in the environment and are responsible for many cases of direct poisoning, contaminated food, and developmental disorders in growing children (FAO and OMS, 2021). The exposure to pesticides and their degradation products is suspected to increase the incidence of certain pathologies such as cardiovascular diseases and cancers (FAO and WHO, 2016). According to the WHO, pesticides and their by-products are also able to affect the male and female fertility process (OMS, 2020). The yearly number of poisoning cases linked to the pesticides in Mali, were estimated to 329 with 30 to 210 deaths and 1150 to 1980 of chronic poisoning (Thiam and Sagna, 2009).

According to the report of the project for the elimination and prevention of obsolete pesticides in Mali (PEPPO), about 200 people die each year from poisoning and several thousand contract illnesses due to the intensive use of obsolete pesticides (PEPPO, 2016). Furthermore, although this program has eliminated 532 tons of expired pesticides and toxic waste in Mali between 2014 and 2018, there is no regular control relative to pesticide testing in precooked fonio.

The liberalization of agricultural production market and transformation of fonio into precooked fonio in addition to these constraints could compromise the quality of this product and thus endanger the health of consumers. This is why this work aimed to evaluate the quality of precooked fonio sold in Bamako's food stores through an evaluation of the levels of five organochlorine pesticides (op' DDT, pp' DDT, Endosulfans α and β and Dieldrin) which are persistent organic pollutants.

MATERIAL AND METHODS MATERIAL

The samples used were consisted of precooked fonio sold in the food stores of Bamako.

Choice of pesticides

The searched and quantified pesticides were Dieldrin, Endosulfans (α and β) and DDT (pp' and op')

due to their persistence and their high frequency in food and environment. These pesticides are considered hazardous, so their use and production are prohibited or tightly restricted by Stockholm convention about the persistent organic pollutants (UNEP, 2020).

METHODS Sampling

The sampling was performed according to the recommended methods of sampling for the determination of pesticide residues of Codex Alimentarus (CAC, 1999). The precooked fonio samples were bought from the food stores of Bamako's six Communes. In each Commune, the two stores which are the main supply points of the populations were chosen. Three different samples of 500 g for each were purchased per store. The samples were labeled and placed under refrigerator plates to be quickly transported to the laboratory where they are kept in the refrigerator before analysis.

Extraction of pesticide residues

The samples were processed and analyzed according to the standard NF 12393-2: 1999 (UNEP/WHO/FAO, 1999) validated and updated by the Central Veterinary Laboratory (LCV) as determination method of pesticide residues using gas chromatography. Fifty grams (50 g) of samples were dissolved in a acetonitrile-water mixture (2: 1; v/v). After stirring (1h), the mixture was filtered. Then, 10 mL of NaCl and 50 mL of hexane were added to this filtrate. The new mixture was placed under magnetic stirring. The two phases (aqueous and hexanic) were separated and the aqueous phase was rinsed with 100 mL of hexane. Lastly the hexanic phases were recovered, concentrated using an evaporator and kept cold for analysis.

Quantification of pesticide residues

The levels of pesticides residues were performed using the gas chromatograph (Agilent 7890A) equipped with an electron capture detector and a Chemstation software. A solution constituted of 5% diphenyl and 95% dimethyl polysiloxane was used as stationary phase. The detector was programmed at temperature of 300°C and 1 μ L of extract solution was injected in splitless mode.

An analytical standard solution for each pesticide (Ehrenstorfer GmbH-Germany) was used to establish the calibration curve. The concentrations of pesticides residues deducted from the peak area and the calibration curve were expressed in mg/kg of samples.

RESULTS

A total of thirty-six (36) of precooked fonio samples were collected and analyzed in this study. The Figure 1 presents the results of pesticide analysis in the samples.



Figure 1: Pesticide analysis in the samples

These data revealed the high rate of pesticide residues contamination in the precooked fonio samples with 27 out of 36 samples (75%) against only 25% without contamination.

La Figure 2 gives the number of pesticides found in the 27 contaminated samples.



Figure 2: Samples repartition according to the number of pesticide found

Among the 27 contaminated samples, most of them (11) presented 1 pesticide followed by 8 samples with 2 pesticides. Moreover no sample has contained all the five pesticides.

The Figure 3 shows the detection frequencies for each searched pesticide molecule and their appreciations according to the Acceptable Daily Intakes (ADI).





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These data of Figure 3 showed that the Endosulfan B was the most detected (15 times) followed by the pp' DDT (13 times) and the Endosulfan A and op' DDT (11 times of each). All the samples in which the DDT (pp and op) has been found were over the safety standards i.e. unsafety. Likewise the 9 of 15 (either 60%) and sixth of 11 (about 55%) of samples contaminated by the Endosulfans respectively α and β were unacceptable.

The concentrations of each pesticide active ingredient are summarized in the Table 1 below. This Table 1 has revealed that the highest values were recovered with the DDT pesticides; from 0.055 to 0.964 mg/kg for op' and from 0.035 to 0.987 mg/kg for pp'. As for the Endosulfans, they varied from 0.011 to 1.120 mg/kg for α and from 0.017 to 0.940 mg/kg for β . Hence, all samples in which the pp' DDT have been detected, showed levels upper than the ADI (0.02 mg/kg). The total pesticides residues per samples of the five pesticides active ingredients have varied from 0.037 to 1.874 mg/kg. In other side, the total residues per individual pesticide varied from 3.377 mg/kg for op' DDT to 0.984 mg/kg for Dieldrin.

Sample codes	Dieldrin	Endosulfana	Endosulfan β	op' DDT	pp' DDT	Total residues per samples
F001	-	-	-	-	-	-
F002	0.080	-	-	0.102	0.987	1.169
F003	-	-	-	-	-	-
F004	-	0.341	0.720	0.058	0.059	1.178
F005	-	-	0.413	-	-	0.413
F006	-	-	-	-	-	-
F007	-	-	-	0.362	-	0.362
F008	-	-	-	0.132	0.175	0.307
F009	-	1.120	0.213	0.541	-	1.874
F010	-	-	0.940	-	-	0.940
F011	-	0.215	-	-	0.321	0.536
F012	-	-	-	-	-	-
F013	-	-	-	0.274	-	0.274
F014	-	0.028	0.017	-	0.092	0.137
F015	-	-	-	0.122	-	0.122
F016	-	0.031	0.063	-	-	0.094
F017	-	-	-	-	-	-
F018	-	-	-	-	0.056	0.056
F019	-	-	0.054	0.964	-	1.018
F020	-	0.011	0.062	-	0.035	0.108
F021	-	0.042	0.054	-	-	0.096
F022	-	-	-	-	-	-
F023	-	0.051	-	-	-	0.051
F024	-		0.037	0.303	-	0.340
F025	-	-	-	-	0.083	0.083
F026	0.883	0.168	0.078	0.303	-	1.432
F027	0.012	-	-	-	0.038	0.050
F028	-	-	-	-	-	-
F029	-		0.037	-	-	0.037
F030	-	-	-	0.083	-	0.083
F031	-	0.068	0.029	-	0.093	0.190
F032	-	-	0.044	-	-	0.044
F033	-	-	-	-	-	-
F034	0.009	0.048	-	0.055	0.064	0.176
F035	-	-	-	-	-	-
F036		-	0.055	0.078	-	0.133
Total per pesticides	0.984	2.123	2.816	3.377	2.003	11.303
ADI*	0.03	0.05	0.05	0.02	0.02	

 Table 1: Contents of pesticide active ingredients (mg/Kg of fonio)

*ADI : Acceptable daily intakes (source: FAO & WHO (2012))

F001, F002... F036: Codes of analyzed samples.

DISCUSSION

In this work, thirty (36) samples of precooked fonio were collected through the six communes of Bamako. Five pesticides (Dieldrin, pp' DDT, op' DDT, Endosulfan α and Endosulfan β) considered hazardous and persistent organic pollutants were investigated and quantified in these samples. The results showed high rates of pesticide residues contamination in the tested precooked fonio samples with 27 out of 36 samples (75%). Among the 27 contaminated samples, about 59% contained at least two pesticides; 30% of them contained three or more pesticides and about 41% have been found with a single

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pesticide. These results are closed to those of Maïga *et al.*, (2018) who found 78% of pesticides in the cow's milk collected in different zones in Mali. Likewise, other work carried out in Sub-Saharan Africa, revealed the presence of 39 pesticides in foodstuffs, commonly consumed in Benin, Cameroon, Mali and Nigeria (Ingenbleek *et al.*, 2019). They detected one pesticide or more in 45.8% of samples. Strikingly, the contamination levels were more worrying in Mali than other countries (Ingenbleek *et al.*, 2019). In the same sense, a study revealed that the 8 of 24 of street foodstuffs (including the precooked fonio) sold in Bamako were unsafety due to their high levels of pesticides (Sako *et al.*, 2014).

The results of the detection frequencies showed that the Endosulfan β was the most frequent (15 times) in our samples followed by the pp' DDT (13 times) and the Endosulfan α and op' DDT (11 times of each). The same pesticides were found in the samples of cow's milk (Maïga *et al.*, 2018) and in the drinking water in Mali (Bagayogo, 2021). Despite the ban on its use by CILSS member countries (PAN/IPEN, 2008), the Endosulfan continues to cause many damages. A study conducted at Koutiala in Mali detected Endosulfan in 85% of the wells with levels of 25.28 µg/L for isomer α and 13.74 µg/L for isomer β . In Togo, more than 500 cases of intoxication related to its use were recorded each year (Thiam and Sagna, 2009).

Regarding to the Acceptable Daily Intakes (ADI) according to the norms of Codex Alimentarius (FAO and WHO, 2012), the most of the tested precooked fonio are unsafety for consumption. As all the precooked fonio in which the DDT (pp' and op') has been found were unsafety for consumption. Likewise the 9 of 15 (either 60%) and 6 of 11 (about 55%) of samples contaminated by the Endosulfans respectively α and β were unacceptable. The total pesticides residues per samples of the five pesticides active ingredients have varied from 0.037 to 1.874 mg/kg. In other side, the total residues per individual pesticide varied from 3.377 mg/kg for op' DDT to 0.984 mg/kg for Dieldrin. Similar levels were recovered in the samples of milk consumed in Mali: from 0.15 to 0.80 mg/L for DDT, from 0.02 to 0.50 mg/L for Dieldrin, from 0.02 to 0.65 mg/L for Endosulfans α and β (Maïga *et al.*, 2018). These content variations from one sample of precooked fonio to another could be due to the provenance and production zones. In 2018, Maïga et al., showed that the milk from the high production zone of cotton were more contaminated than those from the low production zone; because of the abusive use of pesticides by cotton producers. In Senegal, a survey leaded in the agricultural zone of Niayes had revealed a bad management about pesticide used by the farmers. The authors had recovered disturbing levels of pesticides contamination especially the Endosulfan (0.006 - 0.170 mg/kg) in the agricultural products and foodstuffs sold in the market (Ngom et al., 2012). On the contrary, Assogba-Komlan et al., (2007) had found the Endosulfan concentrations (0,07 μ g/g of

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vegetables), in accordance with the standards from the vegetables samples consumed in Benin. But other pesticides like DDT and Dieldrin were unsafe in these tested vegetables. Some studies mentioned many cases of fatal poisoning due to the pesticides from different health centers in Mali (Diallo *et al.*, 2014) especially in children under 15 old of age (Diallo *et al.*, 2016).

These data showed that the pesticide residues are really present in our market and foodstuffs despite their prohibition by Malian authorities who consider them as extremely unsafe. This is why, recent investigations showed that these prohibited pesticides would still be in fraudulent circulation and use (ACEDD and IPEN, 2021). The recovered contaminations in the samples of fonio precooked could therefore emanate to an abusive and inappropriate use of phytosanitary products in agricultural, in cereal preservation and storage.

CONCLUSION

The results of this work revealed the presence of certain organochloride pesticides in the precooked fonio sold in food stores in Bamako. The individual and total pesticides residues of most of the tested samples were upper than the standards fixed by Codex Alimentarius. The presence of these pesticides, known as toxic, is a real threat for the consumption of this product highly coveted by the urban populations of Bamako. Moreover, it would be necessary to undertake in-depth investigations from the production chain to the consumption in order to locate the source of contamination. Lastly, these data constitute one more alert to challenge the National Committee for Pesticide Management in Mali for a better pesticide management.

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