PESTICIDE RESIDUES IN IRISH POTATOES FROM MANGU, PLATEAU STATE

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Ogah E*., [1]Dodo J.D., [1]Awode A.U., [2]Longbap B.V., [2]Egah G.O., [2]Yerima E.A., [1]Agaba A.A., [1]Ebereonwu P.U
[2]Department of Chemistry University of Jos, Jos, Plateau State, Nigeria
[1]Department of Chemical Sciences, Federal University Wukari, Wukari-Taraba State
Corresponding Author's Email: Uhinyohe@gmail.com

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Abstract: This study aimed to assess the levels of organochlorine pesticide (OCPs) and organophosphate (OPPs) residues in irish potato in Mangu local government of Plateau state. Liquid-liquid extraction (LLE) method was used for extraction of pesticides from irish potatoes from Mangu town, Ampang and Bwai and subjected to gas chromatography coupled to an electron capture detector (GC-ECD) for the detection and quantification of the pesticides. From the result of this research, concentrations of DDT detected in Ampang and Bwai were 4.3650 mg/kg and 4.0443 mg/kg respectively; DDVP found in Ampang and Bwai were 0.0542 mg/kg and 0.0791 mg/kg respectively; endosulfan detected in Mangu town was 0.2439 mg/kg while carbofuran and heptachlor detected in Mangu town were 1.5902 mg/kg and 0.1362 mg/kg respectively and were found to be above the maximum residue limits (MRLs) set by WHO/FAO for Irish potato hence, the need for continuous monitoring. While the concentration of dichlorvos confirmed in Mangu town and Ampang were 0.0089mg/kg and 0.0004 mg/kg respectively; g-chlordane detected in Ampang was 0.0033 mg/kg while at Bwai it was 0.1970 mg/kg; lindane found in Mangu town was 0.0385 mg/kg; Aldrin detected in Ampang was 0.0564 mg/kg. From the result shown, the concentrations of these pesticides are below the maximum residue limits (MRLs) set by WHO/FAO. As a result of this, consumption of irish potatoes from Mangu town, Ampang, and Bwai do not constitute health hazard. On the other hand, the concentration of g-chlordane, DDT, DDVP, aldrin in Mangu town; lindane, HCB, endosulfan, profenfos, carbofuran in Ampang and lindane, HCB, endosulfan, profenfos, carbofuran, and heptachlor in Bwai were below the limit of detection.

Keywords: Organochlorine, organophosphate, irish potato, hazard, maximum residue limit, concentration

Introduction

Pesticide residue is any substance in human foods or animal feeds resulting from the use of a pesticide and includes any specified derivative such as degradation and conversion products and impurities that are considered of toxicological significance (FAO/WHO, 1986). For a long past, pests have plagued man, causing diseases, loss of animals and crops. The discovery of chemical compounds that could be used to eliminate or control these pests was received with exuberance. In those early days pesticides commonly used were inorganic compounds such as arsenicals and fluorides or natural plant products such as rotenone and pyrethrum extract (Matsumura, 1975). The organochlorine pesticides particularly DDT, came into the market during the Second World War to combat vector borne diseases such as malaria; bubonic plague and typhoid. The pesticides proved even more important in the protection of crops and crop products in order to feed the ever-increasing human population, without the use of pesticides it is estimated that up to 50% of our agricultural food supply would be lost (Tschirley, 1979). The initial use of organochlorine pesticides proved effective and popular because of long residual effect, low cost and low toxicity until 1960s when some studies showed their persistence in the ecosystem due to their long residual effect and resultant damage to the environment much more than it eased pest menace. Since the introduction of DDT in 1941 a number of halogenated organic compounds were synthesized and used as pesticides. These compounds generally referred to as organochlorines (OC) or chlorinated hydrocarbons include cyclodiene compounds, hexachlorocyclohexanes (HCH), toxaphene and others. These compounds have been of great concern. The investigations of adverse effects of pesticide residues started in the early 1960s, resulting in strict restriction on the use of bio accumulative organochlorine pesticides in some countries and others banning their use altogether (McEwen and Stephenson, 1979); (EPA 1985).

Potato is a root vegetable, a starchy tuber of the plant *Solanum tuberosum,* and the plant itself, a perennial in the family *Solanaceae,* native to the Americas. Potato was originally believed to have been domesticated by indigenous people of the Americas independently in multiple locations, but later after genetic testing of the wide variety of cultivars and wild species, it was believed that potato originated in the area of present-day southern Peru and extreme northwestern Bolivia. Potatoes were introduced to Europe from the Americas in the second half of the 16th century by the Spanish.

As of 2014, potatoes were the world's fourth largest food crop after maize (corn), wheat, and rice. Currently, Nigeria is the eighth largest producer of Irish potatoes in Africa. In Nigeria, there are some states where there are high yields of Irish potatoes, namely; Plateau, Kano, Katsina, and Kaduna. This is due to the favorable climatic conditions in these places. Potato production was introduced into Jos, Plateau State Nigeria in the1940's by the colonial government.

Jos Plateau's elevation ranges from 1,100m – 1,400m above sea level and is the second highest highland in Nigeria after the Mambilla Plateau (1,800m). The highest temperatures of about 30^{o}C are recorded in the months of March to May each year while the lowest temperatures of about 20^{o}C are between December and January. Potato requires an optimum temperature of 15^{o}C for tuber formation. Mangu, Plateau state meets this condition in both the rainy and dry seasons. In the dry season, potato is planted in late October or early November to take advantage of the low December and January temperatures for tuberization. Generally, potato is planted between the last week of April and end of May each year (Okonkwo *et al*., 1995).

A raw potato contains 79% water, 17% carbohydrates (88% is starch), 2% protein, and contains negligible fat. In an amount measuring 100 grams, raw potato provides 322 kilojoules (77 kilocalories) of energy. It has no fat, sodium or cholesterol. With its low level of calories, it is a healthy food. It contains majority of potassium, iron, fibre, vitamin B6, and vitamin C.

Potato is rarely eaten raw because raw potato starch is poorly digested by humans.

In Nigeria, the yield per year is about 843,000 tones; however, the potato consumption in the country is over 1 million tones. With this, there is clear shortage in the production of potato. In order to meet this huge demand pesticides are applied to reduce pest infestation, improve quality, increase yield, and extend the storage life of crops (Fernandez-Alba and Garcia-Reyes 2008). However, the results of using heavy application of pesticides on the potato have resulted in pesticides residues above their respective maximum Residue Limits (MRLs) which may pose health hazards to consumer (Agnihotri, 1999; Kalara, 2003; Taneja, 2005; Mukherjee and Gopal, 2003). The MRLs, reduces the number of residues that can be legally present in foods. Unfortunately, not all farmers follow the legal practice and due to the tremendous number of pesticides and crops in production, a number of analytical methods were designed to determine multiple pesticide residues. Thus, analysis of pesticide residue in foods, especially vegetable, becomes an essential requirement for consumers, producers, and food quality control authorities (Ashutosh *et al*., 2011).

The objectives of this study are: to assess the concentration of pesticides residues in irish potatoes in Mangu and to compare concentration in this work with regulatory limits.

Materials and Methods

Sampling Area

Mangu (Mongu) Local Government Area is located in Central part of Plateau state, Nigeria. Its headquarters is located in the town of Mangu. It lies at 9°26'N9°08'E/9.433° N9.133°E. It has a total area of 1,653km and a population of 294,931 at 2006 census (NPC, 2006). Their occupation is mostly farming and local tin mining. The Local Government Area is bordered to the North/West by Pankshin, North/East by Barkin Ladi and South/West by Quaanpan.

Sample Collection and Preparation.

Tubers of Irish potato were collected from three locations in Mangu LGA; Mangu town (A), Ampang (B) and Bwai (C). The samples were grouped into three and labeled according to the sample area. After sampling, the tubers were peeled, chopped into smaller pieces and sun-dried for three days. The sun-dried samples were pounded using pestle and mortar into powdery and sieved with a sieve of mesh (400nm).

Sample Extraction and Analysis.

Liquid-liquid extraction (LLE) procedure was adopted from US EPA Method 3510C (US EPA, 1996). A known amount (1g) of each of the grinded and sieved sample was weighed into a washed glass beaker. To each sample, 5 mL of distilled water was added and homogenized in the beaker. The homogenate was transferred into separating funnel, additional 5 mL of distilled water and 10 mL of dichloromethane (CH_2Cl_2) were added. The mixture was then shaken thoroughly and allowed to settle and separate for 40 minutes. The lower layer liquid (aqueous phase) was run through the funnel leaving dichloromethane (DCM) and pesticide residues (organic phase) which was collected in a different container. The organic phase was concentrated by rotary evaporation and the water molecules were dried with sodium sulphate (Na_2SO_4). The extract was reconstituted with 5 mL of DCM and the reconstituted extract was taken for organochlorine and organophosphate pesticide residues analysis using a gas chromatography (GC-ECD) (Wang, 2002). This procedure was repeated for the two samples.

Agilent 5890 Gas Chromatograph (GC) equipped with Electron capture detector (GC-ECD) was used for detection and quantification of pesticides. The column condition as used in the analysis of the samples to determine the different pesticide groups is shown in Table (2). The detection and confirmation of presence of residues in potato tuber samples depended on the use of chromatography columns of different polarities. For OP pesticide residues, the column was programmed from an initial oven temperature of 150°C and later raised at 4°C/min to 300°C, and then held for 10 min, the flow rate of hydrogen was 75 mL/min, while the flow rate of air was 100 mL/min, and flow rate of nitrogen was 11.7 mL/min. The Total run time: 35 min. For OC pesticide residues, the GC instrument was adjusted as follows, with an injector temperature of 225°C, flow rate of hydrogen was 75 mL/min, flow rate of air was 100 mL/min, and flow rate of nitrogen was 3 mL/min. The total run time: 43 min. The splitless mode was used for the sample injection. Sample volumes of 2 µL were injected.

Table 1: Conditions Used for the Pesticide Analysis

Carrier gas	Helium
Carrier gas pressure	16 psi
Injector temperature	225°C
Initial temperature	150°C, hold 2 minutes
Temperature program	150°C to 300°C at 4°C/min
Final temperature	300°C at 10°C/min

Results and Discussion

The result of the determination of organochlorine pesticide (OCPs) and organophosphate (OPs) are as presented in table 2. Figure 1, 2 and 3 presents the graphical concentration of OCPs and OPPs at Mangu, Amper and Bwai respectively

Table 2: A Table Showing the Concentration of Pesticide Residues in Irish Potatoes at the Various Sample Locations

Pesticide Residue	Concentration (ppm)			FAO/CODEX Maximum residue limit (mg/kg)
	Sample A	Sample B	Sample C	
Isopropylamine	0.2660	0.3665	0.3004	
Glyphosphate	0.9141	0.7472	0.0001	
P'P'-DDD	0.0267	0.0793	0.0791	
Dichlorvos	0.0089	0.0004	0.0004	0.02
t-nonachlor	0.0154	0.0454	0.0151	
g-chlordane	<LOD	0.0033	0.1970	0.05
DDT	<LOD	4.3650	4.0443	1
DDVP	<LOD	0.0542	0.0791	0.02
Lindane	0.0385	<LOD	<LOD	0.05
HCB	0.0058	<LOD	<LOD	
Endosulfan	0.2439	<LOD	<LOD	0.05
Profenofos	0.8412	<LOD	<LOD	
Carbofuran	1.5902	<LOD	<LOD	0.02
Heptachlor	0.1362	<LOD	<LOD	0.05
Aldrin	<LOD	0.0564	<LOD	0.1

<LOD — Limit of detection

Sample A=Mangu Town, Sample B=Ampang, Sample C=Bwai

Table 3: A Table Showing the Retention Times of Pesticide Residues in Irish Potatoes at the Study Locations

Pesticides residues	Retention time (mins)
Isopropylamine	1.126
Lindane	3.376
HCB	7.853
Endosulfan	9.793
Glyphosphate	13.016
P 'p' – DDD	19.050
Profenofos	19.606
Carbofuran	22.793
Dichlorvos	26.116
Heptachlor	36.016
t-nonachlor	42.233

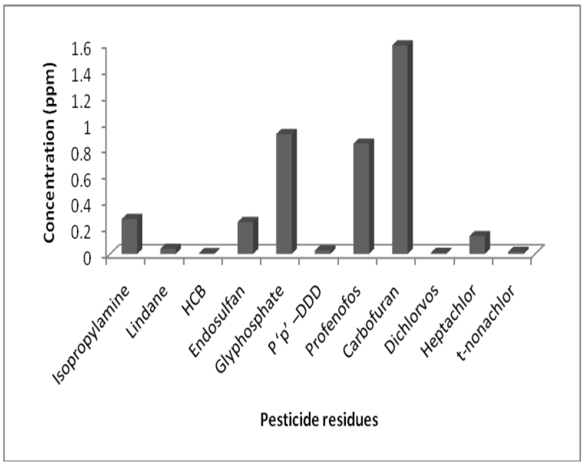

Figure 1: Concentration of Pesticide residues in Irish Potato at Mangu Town

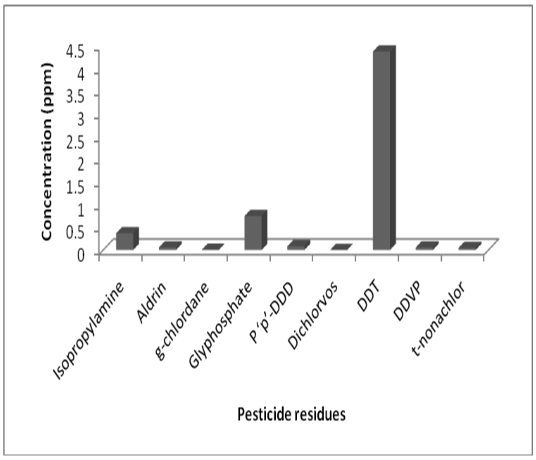

Figure 2: Concentration of Pesticide residues in Irish Potato at Ampang

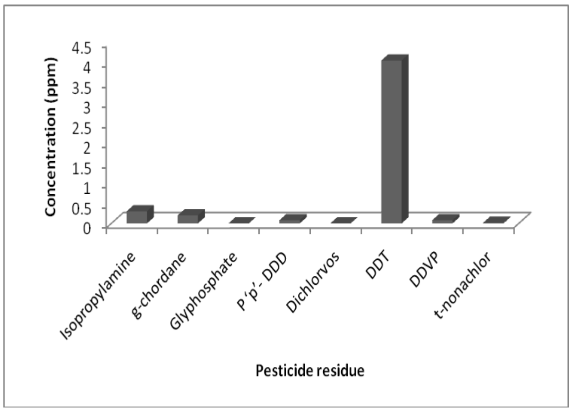

Figure 3: Concentration of Pesticide residues in Irish Potato at Bwai

Discussion

Dichloro-diphenyl-trichloroethane (DDT) is one of the best-known synthetic pesticides, it was discovered in sample B (4.3650 mg/kg), and in sample C (4.0443 mg/kg) respectively. The major metabolites and breakdown products of DDT in the environment are dichlorodiphenyldichloroethylene (DDE), which is produced by the dehydrohalogenation of DDT, and dichlorodiphenyldichloroethane (DDD). DDT was the OCP whose level was detected in the highest concentration in all the Irish potato samples and as compared with the regulatory limit, these levels are above the 1.0000mg/kg maximum residue limit (MRLs) for DDT stated by FAO/WHO (2013). Dioxins, produced when organic matter is burned in the presence of chlorine, and other insecticides, like DDT, are persistent organic pollutants which pose significant hazards when released into the environment. It is a well-known fact that DDT, which was widely used to control insects in the mid-20th century, also accumulates in food chains, and causes reproductive problems (Geisz *et al.*, 2008).

Carbofuran is another pesticide residue that was detected with the concentration of 1.5902 mg/kg and is higher than the maximum limit of 0.0200 mg/kg. It is used to control insects in a wide variety of field crops, including potatoes, corn and soybeans. It is a systemic insecticide, which means that the plant absorbs it through the roots, and from there the plant distributes it throughout its organs. Carbofuran is highly toxic after acute oral administration. Carbofuran is an endocrine disruptor and a probable reproduction/development intoxicant. At low-level exposures, carbofuran may cause transient alterations in the concentration of hormones. These alterations may consequently lead to serious reproductive problems following repeated exposure. The main systemic effect of carbofuran poisoning in short- and long-term toxicity studies in humans appears to be cholinesterase inhibition, therefore, it is considered a neurotoxic pesticide. A recent study reports that carbofuran is a structural mimic of the neurohormone melatonin and could directly bind to MT2 melatoninreceptor (Popovska-Gorevski *et al*., 2017). Disruption of melatonin is linked to elevated risk of developing diabetes.

Aldrin recorded in sample A (0.0564 mg/kg) is an organochlorine insecticide that was widely used until the 1990s, when it was banned in most countries. Aldrin and related "cyclodiene" pesticides (a term for pesticides derived from Hexachlorocyclopentadiene) became notorious as persistent organic pollutants. Aldrin, being marketed as Aldrin dust and Aldrex 40EC, is an emulsifiable concentrate. As dust, Aldrin is used as soil insecticide for potato beetles, termites and crickets. Potato seeds set for planting are rolled completely in Aldrin dust just before planting. Aldrin rapidly breaks down to Dieldrin in food and other materials in the environment (ATSDR, 2002). The predominance of Aldrin in potato from Ampang (sample C) suggests non-observance of the waiting period or abuse of the insecticide because, Dieldrin (a metabolite of Aldrin) was expected to be found as residues. There were reported cases of workers who developed anemia after multiple Dieldrin exposures during application. However, the main adverse effect of Aldrin and Dieldrin is in relation to the central nervous system.

Heptachlor is another organochlorine pesticide present in one of the samples (Sample A) with the concentration of 0.1362 mg/kg which was above the maximum residue limit of 0.0500 mg/kg. Due to its high stable structure, heptachlor can persist in the environment for decades. In Nigeria, Heptachlor is among the insecticides that have been banned and is supposed to have been phased out of agrochemical stores. It is, however, suspected that it is still being sold under different names or labels or added as one of the active ingredients to other insecticides currently in use by Nigerian farmers. The US EPA has limited the sale of heptachlor products to specific application entailing the control in underground transformers. The amount that can be present in different foods is carefully regulated (Pogăcean *et al*., 2014). The US FDA allowed limit on food crops of 0.05 mg/kg (ATSDR, 2007).

Endosulfan was present in only sample A with the concentration of 0.2439 mg/kg as against the maximum limit of 0.05 mg/kg. It is another organochlorine pesticide which was detected and very toxic and responsible for many fatal poisoning incidents around the world (WHO, 2005). Endosulfan which is marketed under various trade names such as Thionex 35EC, Endocel 35EC, is a broad-spectrum insecticide. Endosulfan is acutely neurotoxic to both insects and mammals, including humans. The US EPA (2002) classified it in the first Category as “Highly Acutely Toxic”, while the World Health Organization classifies it in the second Class II “Moderately Hazardous”. (WHO, 2005). It can act as an endocrine disruptor, causing reproductive and developmental damage in both animals and humans.

Profenfos, an organophosphorus insecticide, was confirmed in only sample A (0.8412 mg/kg). Profenfos can be used on a variety of crops including cotton and vegetables such as, potato, soybean, maize, and sugar beet. Profenfos can cause cholinesterase inhibition in humans; that is, it can overstimulate the nervous system causing nausea, dizziness, confusion, and at very high exposures (e.g., accidents or major spills), respiratory paralysis and death.

Lindane with the concentration of 0.0385 mg/kg in sample A was found in amounts lower than the MRLs of 0.0500 mg/kg for irish potato. Although lindane is the only isomer with pesticidal properties, they are known to be persistent, bioaccumulative, toxic, and mobile in the environment including the environmentally significant alpha- and beta-HCH isomers. (ATSDR, 2005).

2,2-dichlorovinyl dimethyl phosphate (DDVP) which was detected in sample B (0.0542 mg/kg), and in sample C (0.0791 mg/kg) is an organophosphate insecticide with contact, respiratory and stomach action (Ecobion, 1996). Like other organophosphate insecticides, it is neurotoxic in action, and acts on the nervous system by inhibiting the enzyme acetyl cholinesterase (AchE) (Zhao *et al*., 2015).

The presence of glyphosphate was detected in samples A (0.9141 mg/kg), B (0.7472 mg/kg), and C (0.0001 mg/kg) respectively. Glyphosphate is the active ingredient in herbicide formulations containing it. Skin exposure to ready-to-use concentrated glyphosphate formulations can cause irritation, and photo contact dermatitis has been occasionally reported. These effects are probably due to the preservative benzisothiazolin-3-one. Severe skin burns are very rare. Inhalation is a minor route of exposure, but spray mist may cause oral or nasal discomfort, an unpleasant taste in the mouth, or tingling and irritation in the throat. Eye exposure may lead to mild conjunctivitis. Superficial corneal injury is possible if irrigation is delayed or inadequate. Death has been reported after deliberate overdose.

The concentrations of trans-nonachlor351 recorded in the three samples A, B, C were 0.0154 mg/kg, 0.0454 mg/kg, and 0.0151 mg/kg respectively but g-chlordane was detected in just two samples, B (0.0033 mg/kg) and C (0.1970 mg/kg) which is higher than the maximum limit of 0.0500 mg/kg. Trans-nonachlor is the most bioaccumulative major constituent of the insecticide chlordane, a cyclodiene that is used extensively in home and agricultural applications. Like DDT, chlordane compounds are very persistent in the environment, resistant to metabolism, have a strong affinity for lipid, and bio magnify in aquatic food webs.

Dichlorvos, sometimes called DDVP, is the common name of dimethyl 2,2-dichlorovinyl phosphate which was detected in all the three samples; (0.0089 mg/kg), (0.0004 mg/kg), (0.0004 mg/kg) in sample A, B, and C respectively is an organophosphate widely used as an insecticide to control household pests, in public health, and protecting stored products from insects. In all of the three samples, it was found to be below the maximum limit of 0.0200 mg/kg.

Isopropylamine with the concentration of; sample A (0.2660 mg/kg), sample B (0.3665 mg/kg), and C (0.3004 mg/kg) respectively is an amine. It is a hygroscopic colourless liquid with ammonia-like odor. Isopropylamine is a building block for the preparation of many herbicides and pesticides including atrazine, bentazon, glyphosate, imazapyr, ametryne, desmetryn, prometryn, pramitol, dipropetryn, propazine, fenamiphos, and iprodione.

HCB with the concentration of 0.0058 mg/kg detected in sample A is a fungicide that has been banned globally under the Stockholm Convention on persistent organic pollutants (UNEP, 2004). Hexachlorobenzene is a known animal carcinogen causing increased incidences of liver, kidney (renal tubular tumors) and thyroid cancers (IARC, 2001).

The concentration of p,p'-Dichlorodiphenyl dichloroethane (DDD)351 in Mangu Town, Ampang and Bwai were (0.0267 mg/kg, 0.0793 mg/kg, and 0.0791 mg/kg) respectively. P'P'-DDD is an organochlorine insecticide that is slightly irritating to the skin. DDD is a metabolite of DDT. DDD is colorless and crystalline; it is closely related chemically and is similar in properties to DDT, but it is considered to be less toxic to animals than DDT.

From the study, out of the 15 pesticide residues detected in all the three samples, g-chlordane, DDT, DDVP and aldrin were below the limit of detection in Mangu Town (Sample A). Lindane, HCB, Endosulfan, Profenfos, Carbofuran, and Heptachlor were below the limit of detection in Ampang (Sample B) and Bwai (Sample C) has fewer pesticide residues detected, Lindane, HCB, Endosulfan, Profenfos, Carbofuran, Heptachlor and Aldrin were not detected in sample C.

A similar study reported that, the residue of pesticides in Irish potato tuber samples in Egypt agrees with this study (Abd El Rahman, 2005; Mansour *et al*., 2009; Wang *et al*., 2008; Quinetro *et al*., 2008)

Conclusion

It is obvious that pesticides contamination is on the increase in the country as a result of their usage for different activities and despite this considerable increased pesticide use over the past decades, not much research has been done to determine their amount, fate and the toxicity or hazard of the pesticide and the likelihood of exposure via foodstuffs in Nigeria. It is obvious from the results that some organochlorine and organophosphate pesticide residues, specifically DDT, Endosulfan, Carbofuran, and Heptachlor found to be higher than the recommended MRLs may pose threat to human health and should give cause for concerns considering that potatoes are widely consumed in Nigeria. Also, the potato might not be safe for human consumption all the time as the continued exposure to sub-lethal quantities of the pesticides for a prolonged period of time may result in chronic illness in humans of which the symptoms are not immediately apparent but manifest later. Hence, there is the need for the relevant agency to educate the farmers and consumers of this crop on the implications of high concentrations of these organohalogens present in potato that were reported to be above the MRL values in food items and the safe methods of pesticide applications to ward off pests.

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