



Monitoring and Assessment of Pesticide Residue in Tomato from Four Selected Markets in Port Harcourt

Azeez, O. M., Zakka, U., Akinyemi Y.* and Akpore, O.

*Department of Crop and Soil Science, Faculty of Agriculture, University of Port Harcourt
Choba, Port Harcourt, Rivers State*

**Department of Crop Protection, College of Agriculture, Osun State University
Osogbo, Osun State*

Abstract

Investigation of pesticide residues of tomato was carried out in Fruit garden, Rumuokoro, Mile 3 and Oil Mill markets, Port Harcourt. The pesticide residues of the fruit obtained in open markets was monitored and compared with established safety limits. The pretreated samples were Soxhlet extracted and analysed for groups of pesticide most especially Organochlorine pesticides (OCPs) content using a Gas Chromatograph coupled with an Electron Capture Detector (GC-ECD). A total of 12 OCPs and other residues were detected in most of the samples with the percentage occurrence ranging from 35%-100%, and the levels found exceeding their Maximum Residue Limits (MRLs). The Method Detection Limit (MDL) of the samples was 0.0408 mg/kg α Chlordane and 0.0723 mg/kg endosulfan sulfate; while the limit of quantitation (LOQ) of these pesticides were 0.0047mg/kg and 0.3952 mg/kg respectively. Among the pesticides determined 58.7% insecticides (14), 22.7% fungicides (5) and 17.9% Herbicide (4) were detected in the tomato samples. The mean concentration of Metoxychlor was excessively higher in samples obtained across the four markets. Also, the concentration of O'p Pp, DDT (0.18 \pm 0.20) was higher than its metabolite, (0.13 \pm 0.03) in Oil Mill and Mile 3 markets (0.14 \pm 0.02) which might portend danger for our health.

Keywords: MDL, LOQ, pesticides, residues, markets, fruits.

INTRODUCTION

Tomato (*Solanum lycopersicum*) is the second most important vegetable crop after potato (*Solanum tuberosum*). Based on the FAO world data (2004), the total acreage is approximately 2.8 million hectares with

yearly worldwide fruit production of 84.7 million metric tons. Fresh tomatoes and other processed tomato products make a significant contribution to human nutrition owing to the concentration and availability of several nutrients in these products and to their

*Correspondence email:
azeezowolabi@yahoo.com

widespread consumption. Composition tables show that ripe tomato contains 93-95% water and low levels of solid matter.

A good diet rich in vegetables has been shown to be an important factor in reducing the risk of diseases. The consumption of tomatoes may be important in prostate and pancreatic cancer prevention. These vegetables contain all four major carotenoids (alpha- and beta-carotene, lutein and lycopene) and all three high powered antioxidants (beta-carotene which has vitamin A activity in the body, vitamin E and vitamin C), may have individual benefits and display synergy as a group (that is, they interact to provide health benefits).

Pesticides are toxic substances that are designed to control pests ranging from insects, fungi, bacteria and weeds which at the same time are known to be toxic to other living species including humans (Yanez *et al.*, 2002; Toxipedia, 2015).

Pesticides due to mankind food shortage has been used to reduce Post-harvest losses in food production, Nevertheless, the use of pesticides has left the challenge of food safety and health hazard (Erhunmwunse, 2012; Carvalho, 2016). The continual usage of pesticides can lead to their accumulation on soils which can lead to pesticides overload on our soils and consequently their uptake by the plant under favorable conditions. Bertolote *et al.* (2008) reported that an estimated three million farmers in developing countries are known to have experienced acute poisoning from pesticides and 18,000 of these aforementioned farmers have been reported to die from this. Nigeria is not excluded from this as Consumer Safety Bulletin [CBS] (2008); Shaibu (2008) reported incidences of food poisoning and deaths in Cross River, Taraba and Gombe States in 2007 and 2008. Pesticide residues

on vegetables constitute a possible risk to consumers and have been a human health concern. When a chemical is used as recommended on the label of the product, any residues that occur should not exceed the maximum residue levels (MRLs). Residues detected in excess of the MRL rarely constitute a toxicological concern. A good knowledge of the pesticide concentration is necessary to properly assess human exposure. Health risk assessment of pesticide residues in contaminated vegetables is performed in developed countries (Akoto *et al.* 2013; EFSA 2013); however, these residues are minimally explored in developing countries (Vieira *et al.* 2014).

Several researchers have reported in the previous study that specific pesticides such as organochlorines, organophosphates or carbamates insecticides or herbicides have all been found to be guilty of causing parkinson's disease, cancer, sterility in males and neurological disorders. Therefore they posited that exposure to pesticides may increase risk of Parkinson's disease, cancer, sterility in males (Vergucht *et al.* (2006); Wallig *et al.* (2002)).

The broad objective of the study is to assess pesticide residue in Tomato fruit from four selected markets in Port Harcourt.

While the specifics were to:

- i. identify pesticide residue in tomato fruit
- ii. analyze and compare the residual levels with established safety limits of four different markets in Port-Harcourt.
- iii. evaluate the dietary exposure of pesticide residues in tomato.

MATERIALS AND METHODS

Sample Collection and Preparation

A total of 12 samples of tomato consisting of three each from four different markets in Port

Harcourt were randomly collected from Fruit garden (4.7988° N, 7.0009° E) Oil mill (4.8585° N, 7.0648° E), Rumuokoro (4.8664° N, 6.9991° E) and Mile 3 (4.8042° N, 6.9924° E) Markets in June, 2021. Tomato sample collections was made at these wholesale markets that are popularly patronized. The samples (300g each) were packed in black polyethylene plastic bags, labelled and transported to the laboratory. Each of the samples was cut into pieces and blended with a blending machine and then poured in a specimen bottle, with each bottle containing each of the samples. Specimen bottles were labelled and stored in a refrigerator at 4°C prior to further analysis. Samples collected were based on Codex Alimentarius Commission (CAC, 1999).

Sample Collections

Samples collected was based on Codex Alimentarius Commission (CAC, 1999) and the selection of vegetable cut across the local markets in Port Harcourt viz Rumuokoro, Mile 3, Fruit Garden and Oil Mill Markets. Thereafter, 1kg of each sample of wet fruits was randomly collected into polythene bags and replicated eight times. The research work and Laboratory analyses were carried out in the Crop Protection Laboratory, Uniport and Austino Research Laboratory, Port Harcourt, Rivers State.

Reagents, Equipment and materials

The reagents obtained from Austino Research Laboratory were Air-zone grade, Nitrogen gas-UPH grade, n-hexane and methylene chloride for pesticide residue analysis and anhydrous sodium sulphate, standard of the pesticide (internal standard) (Merck, Germany). Equipment and materials such as Autosampler vials, 150µL vial inserts, and crimp seals, Vail crimper and decrimper, 10 micro-liter autosampler, 2.5mL airtight syringe or 3mL disposable

hypodermic syringe, 30-m x 0.25-mm or 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1µm film thickness and Soxhlet extractor.

Sample Preparation

A 20-g aliquot of sample is homogenized, and a 10-g aliquot is spiked with the labeled compounds. The ground sample is mixed with anhydrous sodium sulfate, allowed to dry for 30 minutes minimum, and extracted for 18 - 24 hours using methylene chloride in a Soxhlet extractor. The extract was evaporated to dryness, and the lipid content is determined. Thus, a method or analysis blank is a laboratory prepared sample, which is known to contain no analyte. A method blank was ran for each analyte once every 20 samples or part thereof. A duplicate sample is a complete duplicate analysis of the sample, including extraction. The variation between the original and the duplicate analysis provides an estimate of the precision of the method. A duplicate sample was run for each analyte once every 20 samples or part thereof and the precision shall be expressed as a relative percentage difference (RPD %) which is between 70-130%. If outside this range, laboratory must flag this result in the final report and comment on likely reasons for this.

Extraction Procedure

Extracts for pesticide analysis may be subjected to a sequential methylene chloride-n-hexane (1:1) clean up specifically for these analytes, 40µL of the sample was injected into a gas chromatograph equipped with either a narrow- or wide-bore fused-silica capillary column and either an electron capture detector (GC/ECD) or an electrolytic conductivity detector (GC/ELCD).

Clean-up Procedures

A column of about 15cm (Length) x 1cm (Internal diameter) was packed first with glass wool and then with about 7.5g activated silica gel prepared in a slurry form in Dichloromethane (DCM). About 5g of anhydrous sodium sulphate was placed at the top of the column to absorb any water in the sample or the solvent; pre-elution was done with 15mL of DCM, without exposing the sodium sulphate layer to air, so as to prevent the drying up and cracking of the packed silica gel absorbent. The reduced extract was ran through column and allowed to sink below the sodium sulphate layer. Elution was done with 3 x 10mL portions of DCM. The eluate was collected and the accompanying solvent was evaporated to dryness under stream analytical grade nitrogen (99.99%). The dried eluate was reconstituted with 1mL 2, 2, 4-trimethylpentane (Isooctane) in readiness for instrumental analysis.

Qualitative Identification and Quantitative Evaluation

GC-MS analysis was carried out using an Agilent 6890 gas chromatograph with a 5973 MS detector equipped 30-m x 0.25-mm or 0.32-mm ID fused-silica capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1- μ m film thickness. (Agilent). The following temperature ramp was used: injector at 250 °C, oven initially at 200 °C, held for 1 min and heated to 230 °C (1.5 °C min⁻¹, then held for 10 min). The characterization and identification of pesticides, from the sample was completed in the SCAN mode with the m/z range varied from 35 to 450. The flow rate of the nitrogen as carrier gas was 1mL min⁻¹; manual injection; the injection volume was 1 μ L. The composition of the pesticides from the sample was determined using an Agilent 6820 gas chromatograph equipped with 30-m x 0.25-mm or 0.32-mm ID fused-silica

capillary column chemically bonded with SE-54 (DB-5 or equivalent), 1- μ m film thickness injection port. The initial oven temperature was 200°C, which was held for 1 min, subsequently increased to 230°C at 1.5 °C min⁻¹ and then held for 1 min. The injector was set at 250 °C, and the detector at 280 °C. Nitrogen was used as the carrier gas at a flow rate of 1 mL min⁻¹. The split ratio was 50:1, and the sample size was 1 μ L.

Quality Control Measures

Quality control measures were adopted to ensure that the analytical procedures used complied strictly with appropriate standards and specifications and also to further ensure that the results obtained were reliable, valid and of high quality included the determinations of percentage recovery and detection limit.

A laboratory control sample (LCS) is a reference sample either prepared by the laboratory or purchased from an external source, which contains a known amount of analyte. A laboratory control sample was ran for each analyte once every 20 samples or part thereof and be reported in % recovery. The percentage recovery is between 70-130% and if outside this range, laboratory must flag this result in the final report and comment on likely reasons for this.

Percent Recovery (%R) Determination

Recovery data was obtained at the three spiking levels of pesticides in the matrix each day using blank tomato samples in accordance with European Commission (EC) guidelines (EC 2009, 2013). Blank samples (2.0g) after homogenization were spiked by addition of appropriate volumes of pesticide standard mixture in hexane/acetone (9:1 v/v) solution and were left for 1h (equilibration times) and then prepared according to the procedures described in the sample

preparation section. Method accuracy and precision were evaluated by performing recovery studies. The precision was expressed as the relative standard deviation (RSD). Accuracy can be measured by analyzing the samples with known concentration and comparing the measured values with the true values.

A matrix spike (MS) and a matrix spike duplicate (MSD) is a laboratory prepared sample, which contains a known amount of analyte, which in most cases is comparable to a relevant regulatory level, and is analysed in the laboratory. The results for the matrix spike and the matrix spike duplicate are reported in percentage recovery of the spiked amount. The matrix spike and matrix spike duplicate were conducted on an actual water sample from a batch of samples. The matrix spike and matrix spike duplicate was ran for each analyte once every 20 samples or part thereof. Thus MS and MSD % recovery value was between 70-130% for the consideration of researchers or project Manager as requirements for the commencement of a research/project.

Method Detection Limit (MDL) – The lowest level at which an analyte can be detected, but not necessarily quantified. Usually this is determined by statistical analysis of the calculated concentration of multiple injections (commonly seven) at a concentration estimated to be below the practical reporting limit. A signal to baseline noise level of 2 or 3 is used as the MDL of the analyte. MDL studies must be performed annually or every time major changes affect the method, instrument or as part of new analyst training.

Determination of Limit of Detection (LOD)

The limit of quantification (LOQ) was defined as the lowest concentration of the

analyte that could be quantified with acceptable precision and accuracy. The LOQ and LOD were evaluated as the signal-to-noise ratio (S/N) of 10:1 and 3:1 for the pesticide, respectively. The limits of detection (LOD) were evaluated by the determination of concentrations that gave signals equal to the blank based on the empirical and more specific definition described by Miller and Miller (2000) using the relationship; $y_C = y_B + 3SB$.

Where, y_C = analyte signal equivalent to detection limit; y_B = blank signal; and SB = standard deviations of the blank. From the value of y_C , the analyte concentration corresponding to the detection limit was evaluated for GC-ECD determination of pesticides.

Limit of Quantitation – Statistically determined concentration level that produces quantitative measurements in the target matrix with acceptable precision. A signal to baseline noise level of 10 to 20 is used as the limit of quantitation of the analyte.

Statistical Analysis

All data were subjected to Analysis of variance (ANOVA). Significant means were separated using New Duncan multiple test (Using SPSS, Version 2.0).

RESULTS

Percentage Recovery (%R) Values in Tomato Fruit

The percentage recovery (%R) values of some of the analytes in the tomato samples in the range of 82% β BHC and 100% O'p DDE including Methoxychlor are shown in Table 1. The detection limit of method used, (MDL) which is the lowest level at which the analyte was detected though not necessary quantified of the samples ranged 0.0010-0,0408 in α Chlordane to 0.0408-0.1035

endosulfan sulfate; while the limit of quantitation (LOQ) is 0.0039-0.0055 in α Chlordane and 0.2539-0.5364 had by endosulfan sulfate (Table 1 & 2).

Table 1: Percentage recovery, Method of detection limit and limit of quantitation for insecticides

Pesticide	%Recovery RSD	MDL (mg/kg)	LOQ (mg/kg)
Organochlorine			
O'p DDT	85	0.0852	0.3209
Pp DDT	90	0.0025	0.0062
O'p DDE	100	0.0066	0.0218
Methoxychlor	100	0.0021	0.0055
Perthane	86	0.0045	0.0079
Octachlorostyrene	98	0.0297	0.1039
α BHC	87	0.0066	0.0167
β BHC	82	0.0031	0.0073
γ BHC	95	0.0038	0.0084
α Endosulfan	86	0.0049	0.0119
Endosulfan sulfate	83	0.0721	0.3952
α Chlordane	93	0.00175	0.0047
Organophosphorus			
Diazinon	83	0.0166	0.0045
Malathion	93	0.0042	0.0451

Table 2: Percent recovery, Method of detection limit and limit of quantitation for Fungicide and Herbicide

Pesticide	%Recovery RSD	MDL (mg/kg)	LOQ (mg/kg)
Fungicide			
Captan	89	0.0029	0.0055
Chlorotalonil	98	0.0037	0.0069
Hexachlorobenzene	96	0.0044	0.0083
Quintozene	89	0.0021	0.0054
Tecnazene	80	0.0054	0.0093
Herbicide			
Atrazine	95	0.0107	0.0353
Hexazinone	90	0.0126	0.0395
Simazine	98	0.0056	0.0161
Cyanazine	84	0.0072	0.0182

The mean concentration of different group of pesticides viz; Organochlorine (OC), Organophosphorus (OP), Fungicide (F) and Herbicide (H) pesticide residues in tomato samples obtained from four markets (Fruit

garden, Rumuokoro, Mile 3 and Oil Mill markets) in Port Harcourt are presented in Tables 1 & 2. Among the pesticides detected, 58.7% insecticides (12 Organochlorine & 2 Organophosphorus insecticides), 22.7%

fungicides (5) and 17.9% Herbicide (4) were detected in the tomato and cucumber samples. Table 2 showed the frequency occurrence of pesticides residue recorded were 45% for α BHC and 85% for α Endosulfan in tomato samples obtained from the fruit garden markets. The observed levels of α Chlordane were 0.02 ± 0.01 and 0.31 ± 0.01 for O'p DDE which is relatively higher than Standard Maximum Residue Limit. The percentage occurrence for Organophosphorus compound, Diazinon and Malathion were the same, 45% while their concentration range between 0.10 ± 0.05 to

0.22 ± 0.02 . However, the reverse was the case in Rumuokoro market where these residues recorded different percentage occurrence but similar mean concentration. Similarly, the concentration of residues in tomato samples from the Rumuokoro markets was least in Methoxychlor (0.02 ± 0.01) while higher concentration was recorded in Endosulfan sulfate (0.20 ± 0.90) among the insecticides detected. The frequency occurrence of these pesticides residue ranged from 35% O'p DDT% to 100% isomer ($\alpha\beta$) BHC in tomato samples obtained in Rumuokoro.

Table 3: Mean concentration of pesticide residues in tomato samples from open market

Pesticide	Fruit garden		Rumuokoro			
	Mean +SD	% Occurrence	Mean +SD	% Occurrence	MRL	% above MRL
Organochlorine						
O'p DDT	0.19±0.59	62	0.08±0.65	35	0.05	100
Pp DDT	0.19±0.59	50	0.08±0.65	70	0.05	100
O'p DDE	0.31±0.01	75	0.17±0.01	85	0.05	100
Methoxychlor	0.14±0.40	65	0.02±0.01	95	0.05	100
Perthane	0.16±0.02	65	0.19±0.01	55	0.02	100
Octachlorostyrene	0.14±0.04	55	0.14±0.02	55	0.02	100
α BHC	0.07±0.08	45	0.14±0.12	100	0.01	100
β BHC	0.07±0.08	60	0.14±0.12	100	0.01	100
γ BHC	0.07±0.08	62	0.14±0.12	65	0.01	100
α Endosulfan	0.11±0.10	85	0.11±0.10	65	0.002	100
Endosulfan sulfate	0.17±0.02	55	0.20±0.90	64	0.002	100
α Chlordane	0.02±0.01	75	0.13±0.02	65	0.01	100
Organophosphorus						
Diazinon	0.22±0.02	45	0.15±0.05	80	0.10	100
Malathion	0.10±0.05	45	0.15±0.02	55	0.10	100

n = 10 for each market

ND = Not Detected

SD = Standard Deviation

MRL = Maximum Residue Limit

Table 3 showed the percentage occurrence of the fungicide (Chlorotalonil and Tecnazene) range between 45 – 80%; while Herbicide (Atrazine and Cyanazine) recorded 55 -90%. The mean concentration of these residues were 0.47 ± 0.07 and 0.09 ± 0.07 in tomato collected in Fruit garden market, though the residue detected was higher than standard

maximum standard residue limit (0.01). In Rumuokoro market, the frequency occurrence of pesticide residue, fungicide was 55% Captan and 85% Hexachlorobenzene though similar to percentage of pesticide residue recorded in Fruit garden market but for different pesticide residue entirely. The mean

concentration of the residues (Quintozene and Captan) range from 0.24 ± 0.06 to 0.05 ± 0.02 respectively. Also, Atrazine recorded the least percentage occurrence (40%), while the highest residue percentage (95%) was recorded by Simazine and

Cyanazine in tomato samples obtained in Rumuokoro market. Here, the least pesticide residues detected recorded in herbicide was Hexazinone 0.02 ± 0.01 . However, all the pesticide residues detected samples were above their respective MRLs.

Table 4: Mean concentration of pesticide residues in tomato samples from open market

Pesticide	Fruit garden		Rumuokoro		MRL	%above MRL
	Mean +SD	% Occurrence	Mean +SD	% Occurrence		
Fungicide						
Captan	0.15 ± 0.05	60	0.24 ± 0.06	55	0.05	100
Chlorotalonil	0.13 ± 0.03	45	0.18 ± 0.01	75	0.05	100
Hexachlorobenzene	0.39 ± 0.90	85	0.11 ± 0.10	85	0.02	100
Quintozene	0.17 ± 0.02	55	0.05 ± 0.02	78	0.02	100
Tecnazene	0.25 ± 0.05	80	0.08 ± 0.02	60	0.02	100
Herbicide						
Atrazine	0.47 ± 0.07	55	0.14 ± 0.02	40	0.10	100
Hexazinone	0.36 ± 0.06	60	0.02 ± 0.01	70	0.10	100
Simazine	0.10 ± 0.05	65	0.04 ± 0.02	95	0.02	100
Cyanazine	0.09 ± 0.01	90	0.16 ± 0.02	95	0.02	100

n = 10 for each market

ND = Not Detected

SD = Standard Deviation

MRL = Maximum Residue Limit

Table 4 showed that all the isomers of DDT, Endosulfan and BHC were detected in all the samples obtained from the four markets except α BHC and β BHC which were the only compound not detected from tomato samples in Mile 3 market. The percentage of occurrence ranging from 45% to 88% in Organochlorine pesticide (α BHC and α Endosulfan), while Diazinon and Malathion recorded the least percentage occurrence (45%). This showed that the Organophosphorus compounds are not frequently used by the farmer. The mean concentration of Organochlorine compound

ranged from no detection to highest concentration recorded by Methoxychlor in tomato samples bought in Mile 3. This is excessively higher in samples obtained in Oil Mill. Also, in the samples from Oil Mill the concentration of O'pPp, DDT (0.18 ± 0.20) was higher than its metabolite, (0.13 ± 0.03). However, in Mile 3, (0.14 ± 0.02) the highest concentration. In Organophosphorus compound, Diazinon had high frequent Occurrence (85) and mean concentration (0.28 ± 0.02) in Oil Mill compared to Mile 3 that recorded the least.

Table 5: Mean concentration of pesticide residues in tomato samples from open market

Pesticide	Mile 3		Oil Mill		MRL	% above MRL
	Mean +SD	% Occurrence	Mean +SD	% Occurrence		
Organochlorine						
O'p DDT	0.10±0.32	62	0.18±0.20	35	0.05	100
Pp DDT	0.10±0.32	52	0.18±0.20	74	0.05	100
O'p DDE	0.14±0.02	80	0.13±0.03	85	0.05	100
Methoxychlor	0.70±0.01	65	0.05±0.00	55	0.05	100
Perthane	0.18±0.01	65	0.26±0.04	54	0.02	100
Octachlorostyrene	0.05±0.01	55	0.18±0.02	95	0.02	100
α BHC	0.01±0.01	45	0.20±0.08	100	0.01	100
β BHC	ND	60	0.20±0.08	100	0.01	100
γ BHC	ND	62	0.20±0.08	62	0.01	100
αEndosulfan	0.08±0.10	88	0.28±0.02	64	0.002	100
Endosulfan sulfate	0.04±0.01	58	0.17±0.02	42	0.002	100
α Chlordane	0.19±0.01	75	0.13±0.02	58	0.01	100
Organophosphorus						
Diazinon	0.01±0.00	45	0.28±0.02	85	0.10	100
Malathion	0.10±0.00	45	0.47±0.07	55	0.10	100

n = 10 for each market

SD = Standard Deviation

ND = Not Detected

MRL = Maximum Residue Limit

Quintozene recorded higher mean concentration (0.23±0.06) in both markets and with average percentage occurrence above 50%. The fungicides residues recorded the lowest mean concentration for Chlorotalonil 0.03±0.02 in Mile 3, whereas Hexachlorobenzene had

0.03±0.02 in Oil Mill market. Thus herbicide, Simazine and Cyanazine were the pesticide residue not detected in tomato samples in Oil Mill compared to Mile 3 where higher mean concentration (0.12±0.02) was recorded; Cyanazine had the least (0.04±0.02) (Table 5).

Table 6: Mean concentration of pesticide residues in tomato samples from open market

Pesticide	Mile 3		Oil Mill		MRL	%above MRL
	Mean +SD	% Occurrence	Mean +SD	% Occurrence		
Fungicide						
Captan	0.11±0.10	60	0.05±0.02	68	0.05	100
Chlorotalonil	0.03±0.02	45	0.19±0.02	75	0.05	100
Hexachlorobenzene	0.16±0.02	88	0.03±0.02	85	0.02	100
Quintozene	0.23±0.06	55	0.25±0.05	80	0.02	100
Tecnazene	0.17±0.01	80	0.14±0.02	63	0.02	100
Herbicide						
Atrazine	0.19±0.01	55	0.16±0.02	42	0.10	100
Hexazinone	0.05±0.01	60	0.02±0.01	70	0.10	100
Simazine	0.12±0.02	70	ND	62	0.02	100
Cyanazine	0.04±0.02	90	ND	90	0.02	100

n = 10 for each market

SD = Standard Deviation

ND = Not Detected

MRL = Maximum Residue Limit

DISCUSSION

This study established the presence of different group of pesticides residues in tomato samples from the selected markets in Port Harcourt, Nigeria. The level of precision was shown by the percent recovery and limit of detection. The MDL of the samples was 0.0408 mg/kg α Chlordane and 0.0723 mg/kg endosulfan sulfate; while the limit of quantitation (LOQ) of these pesticides were 0.0047mg/kg and 0.3952 mg/kg respectively.

Among the pesticides determined 58.7% insecticides, 22.7% fungicides and 17.9% Herbicide were detected in the tomato samples. Pesticide include Chlordane, Hexachlorbe, Perthane, Atrazine, Hexazinone, and Malathion, DDEetc, This quite agrees with the study of Islam *et al.* (2015) who reported that pesticide residues in tomato samples from local markets detected were Endosulfan, Mancozeb, Perthane and atrazine (about 50 ppm) in one out of three samples. In a similar study, Kaya and Tuna (2019) also investigated pesticide residues in tomato and detected thiamethoxam residues as 0.025 mg/kg. Adeniyi (2016) in his findings detected the likes of several pesticide residues of Endosulfan 2, Glyphosate, Methoxychlor, Atrazine and Malathionas pesticide residues found in tomato.

The mean concentration of Methoxychlor was excessively higher in samples obtained across the four markets. Also, the concentration of O'p Pp, DDT was higher than its metabolite in Oil Mill and Mile 3 markets which might portend danger for our health. This implicated regular use of common all purpose insecticides that still available in the markets despite outlawed by the government. This group of pesticide residues is frequently detected in food items in Southwestern, Nigeria (Sosan *et al.*,

2018). The preponderance and high concentrations of Endosulfan sulfate and isomer in all the markets monitored underscored to the fact that these compounds are still much in use despite its ban by the government. In similar research reported by Olufade *et al.*, (2014) that the presence of this insecticide in yam chips and cowpea grains in markets. Also, Reksa-Naik and Prasad (2006) stated that endosulfan residues in wheat were reported in all market samples in India. In Cameroon, Aro *et al.*, (2010) reported Lindane and Endosulfan in maize samples with mean concentrations higher than the EU-MRL for the insecticides.

The detection of high Methoxychlor, DDT and O'p Pp metabolite in Oil Mill and Mile 3 markets might be as a result of the past usage which resulted in bioaccumulation or probably arising from the cultivation of the crop on contaminated soils where application of insecticides were intense. The preponderance of Quitozene pesticide residues in all markets monitored showed that fungicides are regular used because of the decaying nature of tomato. The susceptibility of tomato to fungi and bacteria diseases cannot be underestimated. In Mile 3 and Oil Mill markets, isomer of BHC and Octachlorostyrene pesticides residue were not detected. This has proven that less quantity of organochlorine compounds are used in these markets compared with Fruit garden and Rumuokoro. This is in contrary to the report by Bakore *et al.*, (2004) that all of the wheat samples from India were contaminated with various organochlorine pesticide residues of DDTs and its metabolites and its isomers. The organophosphorus group (Diazinon and Malathion) pesticides analysed recorded the highest occurrence when compared with organochlorine compound in Oil Mill and Mile 3 markets. This could be attributed to

the ban on Lindane marketed as Gammalin 20EC which made it difficult to get in the markets.

Based on acceptable dietary intake, the pesticides residue detected in both tomato has a value less than 100% of the ADI estimates given by WHO (1 – 20Mg/kg) (WHO, 1997). Dietary estimates recorded for most of the pesticide residues are above the EU-MRL (0.05mg/kg) (European Commission 2005). The diversity of classes of pesticide residues such as organo-phosphorus (Malathion, and Diazinon) detected in this study show that the proposed method to determine residues of pesticides in various vegetables and fruits is rapid, simple, sensitive and uses smaller amount of organic solvents, reducing the risk for workers and the environment.

CONCLUSION

This study assessed the levels of pesticide residues tomato fruit from four selected markets in Port Harcourt. The results indicated that 100% of the samples were contaminated with pesticide residues, however tomato samples from open markets in Port Harcourt were contaminated with pesticide residues above the standard Maximum Residue Limits (MRLs). Therefore contamination may pose a danger to human since fruit contamination is the main route of exposure to all groups of pesticides.

RECOMMENDATIONS

Education, training and information on pesticide safety and management should be strengthened and legislation to control the indiscriminate use of pesticides should be enforced. Also, farmers should be sensitized to better pesticide safety practices and the need for continuous pesticide residue monitoring is highly recommended and more

emphasis should be laid on the practice of organic agriculture.

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