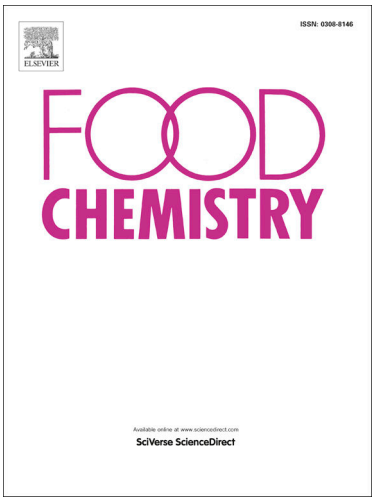
Journal Pre-proofs



Pesticide residues in vegetables produced in rural south-western uganda

Hannington Ngabirano, Grace Birungi

PII: S0308-8146(21)01978-6
DOI: https://doi.org/10.1016/j.foodchem.2021.130972
Reference: FOCH 130972

To appear in: *Food Chemistry*

Received Date: 11 April 2021
Revised Date: 27 July 2021
Accepted Date: 26 August 2021

Please cite this article as: Ngabirano, H., Birungi, G., Pesticide residues in vegetables produced in rural south-western uganda, *Food Chemistry* (2021), doi: https://doi.org/10.1016/j.foodchem.2021.130972

PESTICIDE RESIDUES IN VEGETABLES PRODUCED IN RURAL SOUTH-WESTERN UGANDA

Hannington Ngabirano[1, 2*] and Grace Birungi[2]

1. Department of Chemistry, Faculty of Science, Kabale University, P.O. Box 317, Southern Division, Kabale, Uganda.
2. Department of Chemistry, Faculty of Science, Mbarara University of Science and Technology, Mbarara-Kabale Road, P.O Box 1410, Mbarara, Uganda

Emails: hngabirano@kab.ac.ug

gbirungi@must.ac.ug

*Corresponding author

Abstract

This study investigated seven pesticides in vegetables produced in rural South-western Uganda to determine their suitability for human consumption. Pesticide residue concentrations (ppm) were determined using QuEChERS method, LC–MS/MS, GC-MS/MS and UV-Vis. Cypermethrin, dimethoate, metalaxyl, profenofos, malathion, dichlorvos and mancozeb concentrations detected in sprayed samples ranged between 0.00403 to 0.05350, 0.17478 to 62.60874, 0.12890 to 3.55681, 0.00107 to 0.59722, 0.03144 to 0.63328, 0.00240 to 0.34102 and 0.00001 to 0.00244, respectively. The residues exceeded MRLs in sprayed samples (59.52 %), unsprayed samples (18 %) and market samples (8 %). The quality index of the market vegetables was found to be optimal (14.29 %), good (75 %), adequate (3.57 %) and inadequate (14.29 %). Pesticide residues may lower food quality and pose risk to human health. Therefore, regulation and monitoring pesticide residues in vegetables produced in south-western Uganda in order to avoid harmful effects on human health would be paramount.

Keywords: Pesticide residues, QuEChERS method, Kabale District, Uganda

1.0 Introduction

Pesticides are substances including fungicides, insecticides, herbicides, rodenticides, wood preservatives to mention but a few that farmers and public health workers use in agriculture and public health programmes, respectively; to manage pests and vectors (Freedman, 1995; Nicolopoulou-Stamati *et al.,* 2016; Al-Ahmadi, 2019). However, among all agricultural crops, vegetables are more susceptible to pest infestations and as such their production attracts high pesticide use (Dinham 2003). Therefore, pesticides have become major inputs in vegetable production.

In order to overcome challenge of pests, farmers may apply high pesticide concentrations, acutely toxic pesticide types, unregistered and banned pesticides in vegetables. However, there may be limited or no training of farmers on pesticide use. While benefits associated with pesticide use are evident, there may be unregulated or indiscriminate pesticide use in vegetable production that can harm human health upon consumption of their residues in the vegetables, lower quality of the vegetables, and pollute the environment (Dinham, 2003, Ngabirano and Birungi, 2020).

Pesticide residues are either intact pesticide molecules or their derivatives that may contain measurable amounts of active ingredients and related metabolites or degradation products found in food, agricultural or other commodities as well as in environmental media like soil, air and water that result from pesticide use (EFSA, 2019). Some pesticide residues may have ability to persist or undergo bioaccumulation (Dasika *et al.,* 2012; Langenbach, 2013). Potential sources of pesticide residues may include a number of processes such as pesticide formulation, manufacture, packaging, storage, distribution, retailing, application and disposal of pesticides and their containers (FAO & WHO, 2016). Although some pesticide residues may be inert towards pests, they may be active or more toxic on non-target organisms (Bolognesi, 2003); hence, their presence in food and the environment may be deleterious.

Several studies have indicated that pesticides can affect human health causing headaches, nausea; chronic diseases like cancer and disruption of the development of vital systems including endocrine, reproductive and immune systems (Mostafalou and Abdollahi, 2013; Nicolopoulou-Stamati *et al.,* 2016; Sabarwal *et al.,* 2018). Therefore, pesticides used in agriculture need to be regulated since they can have adverse effects on fetal growth, childhood and adulthood (Kamai *et al.,* 2019) in addition to other effects caused to the crop yields, non-target organisms and the environment.

Pesticide use in vegetable production may result in presence of pesticide residues after harvest (Keikotlhaile & Spanoghe, 2014). Some pesticide residues in the vegetables may exceed MRLs. According to U.S Food and Drug Administration, (2012) majority of the fruit and vegetable samples contained pesticide residues that exceeded MRLs than any other foods; hence, pesticide use in vegetable production requires vigilance. Also, Syed *et al.,* (2014) indicated that more than 50 % of the fruit and vegetable samples collected from Pakistan had pesticide residues exceeding MRLs. Studies conducted in China and Bangladesh by Chen *et al.,* (2011) and Chowdhury *et al.,* (2013), respectively, revealed that pesticide residues detected in about 50 % of the samples exceeded MRLs. Scarcity of

data on pesticide residues in vegetables and their effects on vegetable quality in Uganda motivated this study.

The study was designed to determine residues of the common pesticides used in vegetable production in Kabale District, Uganda. The vegetables and pesticides studied were selected following the findings revealed by Ngabirano and Birungi, (2020) in a study that investigated pesticide use in vegetable production in rural Uganda. Their findings showed that cabbage, cauliflower, tomato and beetroot were the commonly grown vegetables while cypermethrin, dimethoate, metalaxyl, profenofos, malathion, dichlorvos and mancozeb the common pesticides used in the vegetables. However, some pesticide residues may remain active in the harvested vegetables either as intact molecules or breakdown products that are more stable and toxic to human health and the environment. The pesticide residues in the vegetables were determined by use of LC-MS/MS, GC-MS/MS and UV-Vis analytical instruments.

2.0 Materials and Methods

2.1 Study Area Description

Kabale District lies in the South West of the Republic of Uganda. It borders with districts of Rubanda to the West, Rukiga to the North and East and the Republic of Rwanda to the South. Kabale district is 402 km from the capital city Kampala, lying between 29^{o} 45' and 30^{o} 15' East longitude and 1^{o} 00' and 1^{o} 29' South of latitude (Langan and Farmer, 2014). Kabale District is comprised of Kabale Municipality which is divided into Kabale Northern Division, Kabale Central Division and Kabale Southern Division plus two counties of Ndorwa East and Ndorwa West.

It is a highland district that covers 593.7 km^2 and the topography is mainly a green array of interlocking and heavily cultivated hills with spectacular valleys. The altitude of the district ranges between 1,200 m and 3,000 m above sea level (Ministry of Trade, Industry and Cooperatives, 2016) that makes it cooler than the rest of the country with mean temperature of about 18 ^{o}C (64 ^{o}F) during the day and 10 ^{o}C (50 ^{o}F) at night. The relative humidity is between 90 % and 100 % in the morning and decreases to about 42 % and 75 % in the afternoon, all the year around. The land is heavily fragmented and each household owns six to seven plots of land on average located on several hills (Langan and Farmer, 2014).

Kabale district has an estimated population of 212, 506. Out of these, 49, 667 (23 %) stay in the municipality and the remaining 162,839 (77 %) stay in the rural area. The people are pre-dominantly from Bakiga tribe and a few Batwa (pigmies), Banyarwanda and Bahororo tribal clans. The district is

densely populated with projected population density approximated to be 358 people per km^2 (Uganda Bureau of Statistics, 2014).

2.2 Chemicals and reagents

Standard stock solutions (1000 mg L^{-1}) of malathion, metalaxyl, profenofos, mancozeb, cypermethrin, dichlorvos and dimethoate with certified purity ranging from 97 % to 99 %, acetonitrile for HPLC (Sigma-Aldrich, purity > 99.9%), de-ionised water (Milli-Q reagent water, < 10 MQ cm-1 resistivity, Merck, Millipore), toluene (Merck), ammonia solution, sodium chloride (99.9 % purity), acetic acid, triphenylphosphate (TPP), sodium acetate dibasic sesquihydrate, nitrogen, anhydrous magnesium sulphate (99.5 % purity), primary and secondary amines - Bondesil-PSA (PSA particle size 40 µm), and doubly distilled water were purchased from Westford Laboratory Supply Limited in Kampala, Uganda. All the organic solvents used were high performance liquid chromatography (HPLC) grade. Each pesticide stock standard solution (10 mg L^{-1}) was prepared and used for preparation of calibration standards which were subsequently diluted with acetonitrile on the day of calibration. Also, carbon disulphide (CS_2), absolute ethanol, stannous chloride ($SnCl_2$), lead acetate, and hydrochloric acid (HCl), Vile's reagent (copper (II) acetate monohydrate) and triethanolamine used in the determination of mancozeb residues were purchased from Westford Laboratory Supply Limited in Kampala.

2.3 Sample collection

The vegetables were grown in March and harvested in June, 2018 in Kabale District, Uganda. The weather conditions were characterised by a lot of rain from the month of March to late April, 2018. Sprayed and unsprayed vegetable samples were grown in gardens using square foot gardening method by placing one vegetable seedling per square foot (McGinnis, 2014). Each of the four sprayed vegetable types was grown in seven gardens in a distance of 6 metres apart in order to spray all the seven pesticides on every vegetable type (which gave a total number of 28 sprayed gardens). Each of the seven gardens was then sprayed with a solution of one of the seven pesticides (cypermethrin, dimethoate, metalaxyl, profenofos, malathion, dichlorvos or mancozeb). The vegetables were sprayed using a knapsack sprayer (Bomba Magoba (16 L) of pressure (1 - 4 bars) (Famunera Ltd, 2016-2020). Four similar gardens of the four vegetable types (cabbage, cauliflower, tomato and beetroot) were grown in a distance of 20 metres away from the sprayed vegetables without spraying in order to act as control.

Recommended quantities of the pesticides were diluted and sprayed at intervals according to the guidelines provided on pesticide containers or bags as follows: Dimethoate (30-40 mL/20L of water after 14-21 days depending season), profenofos (20 mL/L after 14 days), metalaxyl (3 spoonfuls in 15 L or 4 spoonfuls in 20 L of water after 10-14 days depending on season), malathion (50 mL in 20 L of water after 14 -21 days depending on season), cypermethrin (25-30 mL/20 L after 3-7 days depending on vegetable type), dichlorvos (100 mL/100 L after 3-7 days) and mancozeb (4 spoonful per 15 L or 5 spoonful per 20 L after 7 days). The vegetable samples (cabbage, cauliflower and beetroot) were collected for analysis of pesticide residues one month after pesticide application while tomatoes were harvested two weeks after spraying.

The vegetable samples including sprayed (28) and unsprayed or control (4) were collected from gardens while market samples (4) were collected from Kabale central market in June, 2018. The sprayed and unsprayed vegetable samples were uprooted with leaves, stems and roots while edible portions of the vegetables that are usually presented in the market were randomly bought from different stalls to ensure that the samples were representative enough. The samples were taken to the laboratory (Uganda Government Chemist Laboratory – Wandegeya Kampala) for pesticide residue analysis. The samples (1–2 kg each) were labeled, placed in sterile polythene bags, in an ice box, to avoid contamination and deterioration and transported to the laboratory for processing. After reaching the laboratory, representative portions (200 to 250 g) of the samples were chopped into small pieces using a high-speed blender with a stainless steel jar (waring, USA) at room temperature. The homogenised vegetable samples were placed in plastic bags and stored at −20 °C.

2.4 Sample Preparation

QuEChERS AOAC Official Method 2007.01 was followed during extraction and clean-up of the vegetable samples (Anastassiades *et al.*, 2003) as explained below.

2.4.1 Extraction and Clean-up using QuEChERS Method

In both GC-MS/MS and LC-MS/MS analysis, a homogenised vegetable sample (10 g) was placed in a 50 mL centrifuge tube followed by addition of acetonitrile (10 mL) and triphenylphosphate (TPP) as internal standard (50 µL, 150 µg.mL^{-1}). The mixture was vortexed for one minute and then a mixture of magnesium sulphate (4 g) and sodium chloride (1 g) was added followed by addition of sodium acetate dibasic sesquihydrate (0.5 g). The sample was then centrifuged to give a supernatant which was then removed for clean-up. A supernatant (5 mL) of the sample was transferred into another

centrifuge tube (50 mL) containing magnesium sulphate (750 mg) and primary secondary amine PSA (100 g) (for removing organic and fatty acids, sugars and anthocyanin pigments) and the resulting mixture vortexed for 30 seconds. To allow better extraction of pesticides, 100 g of PSA was used. According to Rizzetti *et al.,* (2016) 1 mL of the supernatant requires 50 g of PSA, 2 mL of the supernatant used study required 100 g of PSA. The mixture was then centrifuged for 5 minutes at 3500 rpm to give a supernatant.

For GC-MS/MS analysis, aliquots of the supernatant (4 mL) were transferred into 15 mL centrifuge tubes and centrifuged again. After agitation and centrifugation, aliquots of the supernatant (1.5 mL) were transferred to glass tubes (2 mL). The extracts were concentrated under a stream of nitrogen gas to 1 mL (to remove excess solvent) and reconstituted to 1.5 mL with toluene (0.5 mL) before injection into the GC-MS/MS (Anastassiades *et al.,* 2003).

For LC-MS/MS analysis, 4 mL extract aliquots were transferred into 15 mL tubes and each tube was vortexed for 1 min and then centrifuged at 4000 rpm for 5 min at 4 ˚C. Aliquots of the supernatant (1.5 mL) were transferred to glass tubes (2 mL) and concentrated under streams of nitrogen gas and reconstituted to 1.5 mL with acetonitrile. The extracts were then filtered through a syringe with a 0.22 µm nylon membrane filter and transferred into an autosampler vial for analysis by LC-MS/MS (Anastassiades *et al.,* 2003).

2.4.2 Extraction and Clean-up of the Vegetable Samples for Mancozeb Analysis

Mancozeb residues in the vegetable samples were determined using UV-Vis spectrophotometer. Extraction and clean-up of the samples were performed as described by Devi *et al.,* (2015). A homogenised vegetable sample (25 g) was placed in a three-necked round-bottom flask. The flask was then refluxed on a heating mantle for 30 min at 85 - 95 °C with 1.5 % $SnCl_2$ solution in 5 M HCl while maintaining a positive pressure inside the flask. The liberated carbon disulphide was adsorbed in 25 mL of Vile's (colour) reagent after passing through 30 % lead acetate to remove hydrogen sulphide. The carbon disulphide was diluted suitably in the colour reagent and absorbance measured at 435 nm against blank (Devi *et al.,* 2015).

2.5 Determination of Pesticide residues

2.5.1 Determination of Cypermethrin by GC-MS/MS

Cypermethrin was analysed by GC–MS/MS (model 7890A) and auto injector (model 7683B) coupled with a 7000A triple quadrupole (QQQ) mass spectrometer (Agilent Technologies, USA). GC separations were done using an HP-5 ms Ultra Inert capillary column (325 °C, 30 mm x 250 µm x 0.25 µm; J &W Scientifc, USA). It was preceded by a guard column (2 m x 250 µm x 0 µm; J & W Scientifc) and followed by a de-activated-current-limiting column (retention gap, 450 °C, 0.65 m×150 µm×0 µm; J & W Scientific).

Helium (purity ≥ 99.999%) was used as the carrier gas and the column head pressure was held at 0.20 MPa. The programme was as follows: 90 °C held for 0 min, ramped to 280 °C at 15 °C/min and maintained for 10 min, followed by back flushing at 300 °C and 0.41 MPa for 5 min. The GC injection port temperature was 250 °C and the transfer-line temperature was 280 °C. The injection volume was 1 µL in splitless mode.

The ionisation voltage was 70 eV in electron ionisation (EI) mode. The ion source, MS1 and MS2 quadruple temperatures were 230 ºC, 150 ºC, and 150 °C, respectively. Helium (purity ≥99.999%) and nitrogen (purity ≥ 99.999%) were used as the quench gas (2.25 $mL.min^{-1}$ flow rate) and the collision gas (1.5 $mL.min^{-1}$ flow rate), respectively. Cypermethrin residues were confirmed by comparing their molecular masses with the quantifier and qualifier ions shown in the MS/MS spectra (*see* table 2) (Stenerson, 2012).

2.5.2 Determination of metalaxyl, malathion, profenofos, dichlorvos and dimethoate by LC-MS/MS

Pesticides including metalaxyl, malathion, profenofos, dichlorvos and dimethoate were analysed by using an Agilent LC 1200 HPLC system (Santa Clara, CA, USA) that consisted of a 4000 QTRAP mass spectrometer coupled with a turbo ion-spray ionisation source (AB SCIEX, Foster City, CA, USA). Separation by LC-MS/MS was carried out at 40 °C with a Zorbax Eclipse Plus C18 column (2.1 × 100 mm, 3.5 µm) supplied by Agilent technologies. Mobile phase A (5.0 mM ammonium acetate and 0.1 vol. % formic acid in water) and mobile phase B (5.0 mM ammonium acetate and 0.1 vol. % formic acid in methanol) at a flow rate of 0.4 $mL.min^{-1}$ and the injection volume of 2.0 µL were used to perform the separation. A linear gradient of 60 % A, 0–8 min; 40 % A, 8–1.5 min; 30 % A, 1.5–2.5 min; 20 % A, 2.5–9 min; 0 % A, 9 to 12 min and 95 % A, 12–15 min was used. A positive ESI mode was used to analyse masses in a scheduled multiple reaction monitoring (MRM) mode by

using curtain gas (30 psi), ion-source gas 1 (50 psi), ion-source gas 2 (55 psi), source temperature (400 ◦C) and ion-spray voltage set at 5500 V.

The cypermethrin, metalaxyl, malathion, profenofos, dichlorvos and dimethoate residues were confirmed by comparing their molecular masses with the quantifier and qualifier ions obtained in the MS/MS spectra (*see* table 2) as explained by Stenerson (2012).

2.5.3 Determination of Mancozeb Residues Using UV-Vis Spectrophotometer

Mancozeb residues present in the vegetable samples were determined by using a Shimadzu UV-visible double beam spectrophotometer (model UV-1800, Japan) with a fixed 1 nm bandwidth and 1 cm quartz cell. The concentration of mancozeb was calculated using Beer-Lambert's law applying the equation $-\log_{10}(I_{transmitted}/I_{incident}) = \varepsilon cl$ where $I_{transmitted}$ is the transmitted light, $I_{incident}$ is the incident light, c is the concentration of mancozeb present in the vegetable samples, ε is the absorption coefficient and l is the length of the cuvette.

Finally, mancozeb residues in the vegetable samples were calculated by equating Beer Lambert's law equation to regression line equations obtained during calibration followed by substitution of the peak area values obtained from the analysis as shown below. For example, $A = \varepsilon cl$ (where A is absorbance, c is concentration and l length of sample cell) was compared with $y = mx + b$ (where y is equal to absorbance, m is equal to εl, x is concentration and b is a constant.

2.6 Analytical Method validation

All working solutions used to determine calibration curves, recovery percentages and limits of detection were prepared by dilution of pesticide standards using the formula $M_1V_1 = M_2V_2$ to give $V_1 = M_2V_2/M_1$ where M_1 = concentration of the stock solution of mancozeb, V_1 = volume of the stock solution of mancozeb, M_2 = concentration of the standard solution and V_2 = volume of the standard solution (*see* table 1). Different standard pesticide concentrations were used in method validation in order to cater for the different analyte detection efficiencies and hence quantification problems associated with matrix effects, sample concentration and other conditions like instrument sensitivity and reagent purity as explained by Saadati *et al.,* (2013). According to Hajšlová & Zrostlíková, (2003) matrix can interfere with ionization, identification and quantification in ESI interfaces in GC- and LC-MS/MS resulting in several undesirable consequences such as obscuring (masking) the peak of the analyte causing false negative result, false identification of the impurity as analyte that is in reality

absent leading to false positive result, increasing detector signal leading to overestimation of the result and reducing detector signal causing underestimation of the result.

Table 1: Standard Solutions Used in Calibration and Calculation of Percentage Recovery

Pesticide	Calibration	Percentage Recovery
Malathion	0.050, 0.500, 5.000, 10.000, 15.000 and 20.000 ppb	0.050, 0.100, 5.000, 10.000, 25.000, 100.000 ppb
Profenofos	0.050, 0.500, 5.000, 10.000, 15.000, 20.000 and 25.000 ppb	0.050, 2.000, 5.000, 10.000, 25.000, 50.000, 100.000 ppb
Dichlorvos	0.050, 0.500, 5.000, 10.000, 15.000, 20.000 and 25.000 ppb	0.050, 2.000, 5.000, 15.000, 25.000, 50.000, 100.000 ppb
Metalaxyl	0.050, 0.500, 5.000, 10.000, 20.000 and 25.000 ppb	0.050, 1.000, 5.000, 15.000, 25.000, 100.000 ppb
Dimethoate	0.500, 5.000, 50.000, 100.000, 150.000, 200.000 and 250.000 ppb	0.050, 2.000, 5.000, 10.000, 25.000, 50.000, 100.000 ppb
Cypermethrin	0.050, 0.500, 5.000, 10.000, 15.000, 20.000 and 25.000 ppb	0.050, 1.000, 5.000, 10.000, 25.000, 50.000, 100.000 ppb
Mancozeb	0.100, 1.000, 10.000, 15.000, 20.000, 25.000 and 30.000 ppb	0.050, 0.500, 1.000, 2.000, 5.000, 8.000, 10.000 ppb

Calibration curves for the pesticide of interest were generated in accordance with the European Commission guidelines (Valverde, 2015). Matrix-matched calibration standards were prepared for GC-MS/MS, LC-MS/MS and UV-Vis analysis, respectively. Calibration was done by analysing standard solutions shown in table 1 using GC-MS/MS for cypermethrin and LC-MS/MS for malathion, profenofos, dichlorvos, metalaxyl and dimethoate. The linear regression equations from the calibration curves were used to determine pesticide residue concentrations basing on the mean peak area values s of each pesticide analysed in the study. The calibration curve for mancozeb was constructed by plotting standard concentrations (*see* table 1) versus absorbance.

Accuracy was evaluated by spiking blank vegetable samples with known amounts of pesticide standards followed by extraction from the matrix for each pesticide using the equation below (Kim *et al*., 2013; Alam *et al*., 2015; Moosavi and Ghassabian, 2018). Therefore, accuracies were calculated using the formula below.

Recovery (%) = Amount recovered/Amount spiked x 100 ……. (1)

Percent recovery was determined using blank samples and standard pesticide solutions. A blank sample of each vegetable type was split into two portions and a known amount of a pesticide standard solution was added to one of the portions. This was done for the four vegetable types with the seven pesticides considered in the study. The recovered pesticide concentrations were determined for both the spiked, c_1, and unspiked, c_2, portions. The percent recovery (R) of each pesticide standard solution was calculated from the difference between the results obtained before and after spiking as a fraction of the added pesticide amount multiplied by 100 as shown in the equation below.

$$R (\%) = C_1 – C_2/C_3 \times 100 \quad \ldots\ldots (2)$$

where C_1 = measured concentration in fortified sample, C_2 = measured concentration in unfortified sample and C_3 = concentration of fortification (Zazzi *et al.*, 2005; NATA, 2012).

Mancozeb residues were analysed colorimetrically using carbon disulphide (CS_2) evolution method as described by Keppel (1971). The carbon disulphide evolved was absorbed in Vile's reagent. The intensity of the resulting colour complex was measured spectrophotometrically at 435 nm and the absorbance compared by means of a standard curve.

A stock standard carbon disulphide (CS_2) solution containing 5.04 mg mL^{-1} was prepared with 0.1 mL of CS_2 in 25 mL of absolute ethanol and working standard solutions were prepared by making suitable dilutions of stock solution in absolute ethanol and the solution was allowed to stand for 15 min. The $HCl/SnCl_2$ mixture was prepared by dissolving 5 mL of a 40 % (mv^{-1}) $SnCl_2.2H_2O$ solution in 30 mL of HCl and diluting with water to 200 mL. Vile’s solution (colour) reagent was prepared by dissolving cupric acetate - monohydrate (0.05 g) in distilled water (25 mL) in a 1000 mL volumetric flask. Thereafter, ethanol-95 % (v/v) (800 mL) was added followed by diethylamine (1 mL) and triethanolamine (20 mL). The volume was then made up to 1000 mL with absolute ethanol (Burchfield, 1965; FSSAI, 2016).

Standard solutions of mancozeb were used to calibrate the UV-Vis spectrophotometer and the percentage recovery was determined by spiking unsprayed vegetable samples with mancozeb at the concentrations shown in table 1 along with the control. The absorbances of standard mancozeb concentrations were determined using a UV–Vis spectrophotometer (UV-1800, Japan) as CS_2 at a wavelength of 435 nm and a standard curve was prepared by plotting the absorbances in the graph against corresponding mancozeb concentrations.

Inter-day precision was evaluated in terms of relative standard deviation (RSD %) at concentrations of 0.050, 5.000, 10.000, 20.000 and 25.000 ppb for malathion, profenofos, dichlorvos, metalaxyl and cypermethrin; 0.500, 100.000, 200.000, and 250.000 ppb for dimethoate and 0.100, 1.000, 10.000, 20.000, 25.000 ppb for mancozeb on different days. Limits of detection and quantification were calculated using the formulae LOD = 3.3 x δ/m and LOQ = 10 x δ/m, respectively, where δ is the standard deviation and m the slope of the calibration curve.

2.7 Determination of Quality index for Pesticide Residues

Furthermore, the study evaluated the quality of the market vegetable samples in terms of quality index for each pesticide residue (IqR). The IqR is calculated as the sum of the ratios between the residue concentrations and the corresponding MRLs as shown in the equation given below (Arienzo *et al.*, 2013; Mac Loughlin *et al.*, 2018; Ramadan *et al.*, 2020).

$$IqR = \sum_{i=1}^{n} (Concentration_i / MRL_i) \quad \ldots\ldots (3)$$

where IqR represents quality index for each pesticide residue detected in a given food commodity, $concentration_i$ represents concentrations of detected pesticide residue(s) ranging from n = 1 to n = *i* and MRL_i represents allowable limits of detected pesticide residue(s) ranging from n = 1 to n = *i*.

3.0 Results and Discussion

3.1 Confirmation of the Pesticide Residues

The pesticide residues (cypermethrin, metalaxyl, dichlorvos, profenofos, malathion and dimethoate confirmation were confirmed by monitoring two separate transitions per pesticide (quantifier and qualifier ions) produced in the MS/MS (*see* table 2).

Table 2: Molecular masses of pesticides, precursor, quantifier and qualifier ions

Pesticides	Molar masses of pesticides	Molecular mass of precursor ions in $^{+}$ESI	Molecular masses of quantifier ions m/z	MRM transition of product ions (Qualifiers) m/z
Dichlorvos $C_4H_7Cl_2O_4P$	220	221	221 → 109	221 → 127
Metalaxyl $C_{15}H_{21}NO_4$	279	280.2	280.2 → 220.1	280.2 → 160.1
Profenofos $C_{11}H_{15}BrClO_3PS$	373.6	374.9	374.9 → 304.9	374.9 → 347
Malathion $C_{10}H_{19}O_6PS_2$	330	331	331 → 127	331 → 99
Dimethoate $C_5H_{12}NO_3PS_2$	229	230	230 → 199	230 → 171
Cypermethrin $C_{22}H_{19}Cl_2NO_3$	415.07	416.3	181 → 152	181 → 127

The peak areas of the quantifier ions were used for quantification of the pesticide residues. The ratios of the qualifier peak areas to quantifier peak areas were monitored and were approximately the same

for all samples with regard to the residues of each pesticide; hence, the quantifier ions were reliable for the measurement of the pesticide residues present in the vegetable samples.

3.2 Analytical method validation

The calibration curves were constructed over the concentration range between 0.050 – 250.000 ppb for all pesticides and r^2 ranged between 0.9987 – 0.9994 for all pesticides considered in the study. Percentage recoveries calculated at concentrations from 0.050 – 100.000 ppb ranged between 83.8 % to 109.8 % with relative standard deviation (RSD) values ranging between 0.014 - 38.164% for the concentration range between 0.05 - 100 ppb. According to VICH topic GL49, (2015) the calculated percentage recoveries were within the allowed accuracy variation range of ±13.0 % for the analyte concentrations ranging from 0.05 ppb to 250 ppb (*see* Table 3, Part A). The detection and quantification limits of the pesticide residues in vegetable samples ranged between 0.006 – 0.489 ppb and 0.018 – 1.045 ppb, respectively. Generally, the values of standard deviations of the LOD, LOQ, correlation coefficient (r^2), equation of regression line and slope obtained showed suitability of the method for the study (*see* Table 3, Part A). The values of inter-day precision expressed in terms of relative standard deviations (RSD %) were below 13.323 % except outlier of 47.063 % that was ignored. The inter-day precision results were in agreement with the findings of VICH topic GL49 (2015) which revealed that the coefficient of variation decreases as the concentration of the analyte increases (*see* Table 3, Part B).

Table 3: Results of Method Validation Parameters

Part A: Method Validation Parameters

Pesticides	Spiked (ppb)	Found (ppb)	Percent recovery	RSD %	LOD (ppb)	LOQ (ppb)	Range	Linearity (R^2 and linear regression equations)	RSD % for Inter-day precision
Malathion	0.050	0.045	90.600	8.333	0.010	0.031	0.050-20.000	R^2=0.9957	4.949
	0.100	0.098	98.000	0.592	0.010	0.031			0.231
	5.000	4.945	98.900	0.100	0.016	0.047		y=324.64x -108.37	0.075
	10.000	9.980	99.800	0.021	0.006	0.018			0.000
	25.000	24.985	99.940	0.043	0.021	0.064			0.000
	100.000	108.900	108.900	0.018	0.016	0.047			
Profenofos	0.050	0.043	85.370	22.048	0.032	0.098	0.050-25.000	R^2=0.9987	9.091
	2.000	1.790	89.500	2.218	0.043	0.130			0.306
	5.000	4.920	98.400	0.260	0.044	0.134			0.052
	10.000	9.950	99.500	0.111	0.037	0.113		y=269.4x - 43.314	0.013
	25.000	24.900	99.600	0.050	0.025	0.077			0.000
	50.000	49.920	99.840	0.075	0.051	0.155			
	100.000	100.200	100.200	0.045	0.037	0.111			
Dichlorvos	0.050	0.047	93.240	12.251	0.221	0.668	0.050-25.000	R^2=0.9994	3.007
	2.000	1.924	96.200	4.872	0.171	0.519			1.129
	5.000	4.980	99.600	0.964	0.182	0.553			47.063
	15.000	14.940	99.600	0.525	0.178	0.54			0.044
	25.000	24.900	99.600	0.436	0.230	0.696		y= 157.39x+92.117	0.206
	50.000	49.920	99.840	0.298	0.202	0.612			
	100.000	102.700	102.700	0.263	0.221	0.668			
Dimethoate	0.050	0.042	83.800	6.928	0.122	0.371	0.500-250.000	R^2=0.9967	10.351
	2.000	1.910	95.500	1.155	0.266	0.806			0.048
	5.000	4.845	96.900	0.150	0.245	0.743			0.000
	10.000	9.665	98.650	0.105	0.324	0.982			0.018
	25.000	24.925	99.700	0.101	0.490	1.485		y=15.554x -27.638	
	50.000	49.940	99.880	0.052	0.324	0.982			
	100.000	100.020	100.020	0.014	0.122	0.371			
Metalaxyl	0.050	0.046	92.000	16.327	0.025	0.075	0.050-25.000	R^2=0.9979	4.871
	1.000	0.942	94.200	3.021	0.045	0.137			0.051
	5.000	4.935	98.700	0.144	0.025	0.074			0.125
	15.000	14.878	99.190	0.158	0.053	0.159		y=1066.9x -15.368	0.000
	25.000	24.978	99.910	0.061	0.039	0.117			0.008
	100.000	101.900	101.900	0.046	0.039	0.119			
Mancozeb	0.050	0.042	84.800	12.372	0.057	0.172	0.10030.000	R^2=0.9990	13.323
	0.500	0.443	88..600	1.493	0.057	0.172			0.000
	1.000	0.934	93.400	0.177	0.057	0.172			0.870
	2.000	1.947	97.35	0.120	0.057	0.172			0.104
	5.000	4.990	99.800	0.293	0.196	0.595		y = 0.033x-0.0015	0.001
	8.000	7.989	99.860	0.414	0.345	1.045			
	10.000	10.983	109.830	0.252	0.247	0.749			
Cypermethrin	0.050	0.048	95.000	38.164	0.146	0.442	0.050-25.000	R^2=0.9991	11.000
	1.000	0.965	96.500	1.540	0.022	0.065			0.000
	5.000	4.910	98.200	0.261	0.037	0.113			0.000
	10.000	9.873	98.730	0.057	0.019	0.057			0.009
	25.000	24.750	99.000	0.092	0.046	0.139		y = 1189.4x-137.98	0.014
	50.000	49.92	99.840	0.021	0.014	0.041			
	100.000	101.500	101.500	0.082	0.067	0.202			

Part B : Allowed Analyte concentration range and acceptable percentage recoveries for inter-day precision

Concentration range	Inter-day precision, RSD %
< 1 ppb	35 %
≥ 1 ppb < 10 ppb	30 %
≥ 10 ppb < 100 ppb	20 %
≥ 100 ppb	15 %

Source: VICH topic GL49 (2015). Guidelines for the Validation of Analytical Methods Used in Residue Depletion Studies

3.2 Pesticide Residue Concentrations in Sprayed, Unsprayed and Market Vegetable Samples

The concentrations of pesticide residues detected in the sprayed, unsprayed and market vegetable samples were presented with corresponding MRLs in table 4.

Table 4: Pesticide Residue Levels in Sprayed, Unsprayed and Market Vegetable Samples

A. Pesticide Residue Concentrations in Sprayed Vegetable Samples (ppm)								
Vegetable	**Portion**	**Cypermethrin**	**Dimethoate**	**Profenofos**	**Metalaxyl**	**Malathion**	**Dichlorvos**	**Mancozeb**
Cabbage	Leaf	0.00537	5.54343	0.19961	0.16029	0.19367	0.34102	0.00015
	Stem	0.00421	2.06127	0.08707	0.14254	0.11683	0.02971	0.00008
	Root	0.00403	0.82273	0.04815	0.13803	0.06100	0.01612	0.00001
Cauliflower	Leaf	0.00426	59.80261	0.07882	2.89840	0.13596	0.08041	0.00098
	Stem	0.00403	2.99747	0.04368	3.55681	0.16341	0.07243	0.00014
	Root	0.00463	0.17478	0.00712	1.99142	0.16613	0.06203	0.00004
Tomato	Leaf	0.03763	62.60874	0.08614	0.17149	0.45430	0.13948	0.00206
	Stem	0.04166	12.35660	0.01073	0.98660	0.36021	0.07780	0.00136
	Root	0.05350	1.32832	0.00253	0.12890	0.03961	0.13948	0.00048
Beetroot	Leaf	0.00501	12.05869	0.59722	0.50207	0.63328	0.34081	0.00271
	Stem	0.00433	6.14184	0.00494	0.15844	0.20880	0.01182	0.00153
	Root	0.00450	2.57855	0.00107	0.13328	0.03144	0.00240	0.00059
B. Pesticide Residue Concentrations in Unsprayed Vegetable Samples (ppm) – Control I Samples								
Cabbage	Leaf	0.00341	0.02496	0.00474	0.00272	0.00342	0.00176	0.00012
	Stem	0.00340	0.00940	0.00443	0.00279	0.00314	0.00041	0.00012
	Root	0.00340	0.00531	0.00131	0.00276	0.00188	0.00003	0.00012
Cauliflower	Leaf	0.00342	0.05483	0.00519	0.00472	0.04117	0.04113	0.00014
	Stem	0.00342	0.02296	0.00352	0.00262	0.00803	0.00362	0.00012
	Root	0.00344	0.05365	0.40033	0.00263	0.00630	0.00575	0.00011
Tomato	Leaf	0.00340	0.02297	0.00763	0.00266	0.00608	0.02107	0.00007
	Stem	0.00340	0.01183	0.00267	0.00261	0.00319	0.00068	0.00005
	Root	0.00340	0.00829	0.00070	0.00263	0.00136	0.00301	0.00004
Beetroot	Leaf	0.00341	0.02230	0.00228	0.00263	0.05347	0.24052	0.00017
	Stem	0.00340	0.01876	0.00304	0.00263	0.02046	0.04562	0.00001
	Root	0.00340	0.01142	0.00304	0.00262	0.00206	0.00232	0.00012
C. Pesticide Residue Concentrations in Market Vegetable Samples (ppm) - Control II samples								
Cabbage (Head)		0.00342	0.01085	0.00120	0.00265	0.00152	ND	0.00001
Cauliflower (Head)		0.00340	0.00485	0.00249	0.00262	0.00065	ND	0.00003
Tomato (Fruits)		0.00340	0.00957	0.00193	0.00263	0.00094	ND	0.00005
Beetroot (Roots)		0.00340	0.2035	0.00049	0.00391	0.00049	ND	0.00006
N.B Pesticide residues in market samples						**ND = Not detected**		
D. Maximum Residue Levels (ppm)								
Cabbage (Head)		1.0000	0.01000	0.01000	0.06000	0.02000	0.01000	0.10000
Cauliflower (Head)		0.5000	0.02000	0.01000	0.20000	0.02000	0.05000	0.10000
Tomato (Fruits)		0.5000	0.01000	10.00000	0.30000	0.02000	0.01000	0.10000
Beetroot (Roots)		0.70000	0.01000	0.01000	0.02000	0.02000	0.05000	0.10000
References for the MRLs		EFSA (2011)	EU 2017/1135 (2017)	EU 2017/978 (2017)	EU 2017/1164 (2017)	EU 2015/399 (2015	EU 2016/60 (2016)	EU 2017/171 (2017)

3.2.1 Pesticide Residue Concentrations in Sprayed Vegetables

The study showed that all sprayed vegetable samples contained detectable pesticide residues that decreased in the order: dimethoate > metalaxyl > malathion > dichlorvos > cypermethrin > mancozeb. Generally, the residues exceeded MRLs in 59.52 % of the sprayed samples. Dimethoate and malathion exceeded MRLs in 100 % of the vegetable samples analysed. Dimethoate residues were generally higher than other pesticides in all sprayed vegetable samples. This observation may be attributed to the fact that systemic pesticides penetrate into the vegetables and may not be easily washed off (Wise, 2019). Metalaxyl and dichlorvos residues exceeded MRLs in 83.33 % while profenofos residues exceeded MRLs in 50 % of the sprayed vegetable samples. These observations can be attributed to the tendency of pesticides to penetrate into plant tissues and move anywhere inside the plant including storage areas (Norris, 1974) that can result in their persistence in the plant.

Cypermethrin and mancozeb residues were lower than MRLs in all vegetable samples analysed. According to Yin *et al.,* (2012) low cypermethrin concentrations found in the vegetable samples can be attributed to faster degradation perhaps due to the initial concentrations applied and other factors like temperature, light and re-distribution in the environment. Also, low pesticide residues detected in some of the vegetable samples can be attributed to intrinsic detoxification mechanisms inside the vegetable plants. According to Zhou *et al.*, (2015) intrinsic detoxification mechanisms of higher plants decrease pesticide residues in food produce.

Although pesticide residues detected in 40.48 % of the sprayed vegetable samples were below MRLs, they can undergo bioaccumulation in body tissues to harmful levels. Some pesticides can persist and/or bioaccumulate in the body especially fat-soluble pesticides (Bernardes *et al.,* 2015).

Generally, pesticide residues detected in the sprayed vegetable samples decreased from leaves through stems to roots (*see* table 4). This observation was in agreement with the findings of Akan *et al.,* (2014) obtained from a study that determined organochlorine residues in vegetable and soil samples from North Eastern Nigeria. Leaves tend to retain higher pesticide residues than stems and roots as they are at the receiving end of the pesticide spray during application. A study conducted by Bull *et al.,* (1984) revealed that pesticides can accumulate in tomato leaves shortly after application. The presence of pesticide residues in stems and roots was attributed to pesticide translocation with nutrients from the leaves. This observation was in agreement with the findings of studies conducted to investigate how radioactive pesticides move along with nutrients during translocation to the storage organs which

contained much larger pesticide residues than other parts of the plants (Norris, 1974). Furthermore, pesticide residues may be concentrated in the skin or peel of the storage organs (Finlayson and MacCarthy, 1965; Finlayson and MacCarthy, 1973; Menn, 1978; Edwards, 1975). Since vegetable leaves that can work as storage organs, they are more likely to retain high pesticide residues. Thus, vegetables such as cabbage and cauliflower may contain high pesticide residues in their leaves especially when they are sprayed towards folding stage.

Further, the different pesticide residue concentrations in the sprayed vegetable samples may be a result of different plant morphologies that can influence pesticide uptake and persistence. For instance, broad leaves influence pesticide uptake, distribution and retention in plants (Edwards, 1975). In the present study, the detected pesticide residues were higher in cabbage and cauliflower samples than in tomatoes as shown in table 4. Hence, high pesticide residues detected in cabbage and cauliflower samples can be attributed to the possession of broad leaves. This observation was in agreement with the findings reported by Ravichandra (2018) which confirmed that broad leaves retain pesticides much better.

The pesticide residues that remain on plant surfaces can disappear rapidly by various reactions and the speed at which they penetrate into plants affects their persistence (Finlayson and MacCarthy, 1965). Pesticide sprays may be absorbed into plant tissues; for example, non-ionic pesticides that dissolve in plant oils and waxes can penetrate cuticular and sub-cuticular tissues of treated plant parts, even if they are not truly systemic. However, this occurs most easily in the absorptive areas of roots although it also occurs quite readily through the leaves, stems and fruits (Edwards, 1975). Therefore, high pesticide residues can be a result of direct application of pesticides and their uptake by different vegetable aerial parts (foliage) and roots as shown in table 5.

The study showed that the pesticide residues detected in vegetables sprayed with mixed pesticides were generally higher in leaves than stems and roots in cabbages. The pesticide residues decreased from leaves via stems to the roots just like when individual pesticides were used (*see* table 5).

Table 5: Pesticide residues detected in cabbage samples sprayed with mixed pesticides

Vegetable Samples	Residue concentrations (ppm) in cabbage samples sprayed with mixed pesticides						
	Cypermethrin	Dimethoate	Metalaxyl	Profenofos	Malathion	Dichlorvos	Mancozeb
Cabbage leaves	0.00353	0.06352	0.02190	0.01234	0.00810	0.03709	0.00129
Cabbage stem	0.00347	0.05439	0.00549	0.00667	0.00417	0.01067	0.00095
Cabbage roots	0.00358	0.03971	0.00529	0.00829	0.00454	0.00963	0.00068

Generally, pesticide residues found in cabbage samples that had been treated with mixed pesticides were lower than those detected in cabbage samples sprayed with individual pesticides. The pesticide residues detected in the vegetables decreased from leaves through stems to roots (*see* tables 4 and 5). Also, lower pesticide residues were detected in roots of the vegetable samples considered in the study. These results were in agreement with the findings obtained by Edwards (1975) who confirmed the tendency of pesticides to be translocated and stored in lower portions of plants where they can be excreted in root exudates.

The lower pesticide residue concentrations detected in the vegetables sprayed with mixed pesticides can be used to explain low efficiency of the pesticides to control pests. Lower pesticide residues can be attributed to the occurrence of antagonistic interactions that may reduce the concentrations of the active ingredients. According to Kapeleka *et al.,* (2021) pesticide mixing may result in chemical reactions of the pesticide components that can change the potential of active ingredients and hence lower the effectiveness of the pesticides due to antagonistic effects. Thus, it may be disastrous to mix pesticides for use in food crops to control pest.

According to Allagui *et al.,* (2018) pesticide deposition and retention in plants can depend on pesticide formulation, pesticide properties, intrinsic plant factors, application techniques, equipment efficiency spray properties, sprayer parameters and environmental factors. All pesticides used in the study dissolved easily in water to form spray solutions of different concentrations of the active ingredients. The spray solutions were easy to work with and spread easily on the vegetable surfaces in order to reach areas where pests can hide. Among the factors that determine pesticide formulation are solubility and intended use (Buzzetti, 2017). Pesticide chemistry (properties) can also influence pesticide - plant interaction, distribution, metabolism and persistence inside the plant; hence, the characteristics of pesticides determine their compatibility and ultimate fate in plants (Norris, 1974).

Further, the concentrations of pesticide residues detected in the vegetable samples can be attributed to the application techniques, equipment efficiency and sprayer parameters. According to Yarpuz-Bozdogan *et al.,* (2011) different pesticide application methods can influence spray deposits, spray drift and pesticide residue concentration in plants. In addition, environmental factors can also influence pesticide residue levels in plants. For instance, factors like wind, light and temperature affect plant structure and surface composition and hence influence wettability by pesticide sprays (Shi *et al.,* 2011) which results in a corresponding increase or decrease in pesticide residue concentrations in the plant.

In this study, a high pressure (1-4 bars; Bomba Magoba Knapsack Spray Pump) (Famunera Ltd, 2016-2020) was used to spray pesticides in the vegetables. High pressure may increase pesticide spray delivery rate and reduce spray droplet size which can result in excess spray drift and uneven coverage. Conversely, low pressures can reduce pesticide spray delivery rate in addition to failure to form a full width spray pattern (Hofman, 2018). Therefore, factors such as sprayer parameters, pesticide formulation, application techniques and environmental factors among others can influence pesticide residue levels in the vegetables.

Environmental factors such as wet conditions can favour severe pest infestations and cause high pesticide application (Rosenzweig *et al.,* 2001). However, pesticides may be washed away by rainfall or evaporate by wind and sun (Keikotlhaile and Spanoghe, 2011). Therefore, the source of the pesticide residues detected in unsprayed vegetables may be spray wash off from the sprayed vegetables, leaching and re-distribution among neighbouring gardens. Climatic conditions such as temperature and high carbon dioxide concentrations can influence photosynthetic activity, plant growth and expansion which in turn influence pesticide adhesion and uptake into a plant (Reilly *et al.,* 2003; Gutierrez *et al.,* 2008). For instance, high temperatures enhance pesticide uptake into roots due to a decrease in soil organic matter and elevated evaporation rate (Miraglia *et al.,* 2009). High plant growth rate may dilute absorbed pesticides decreasing their concentrations (Zongmao and Haibin, 1997; Holland and Sinclair, 2004). Therefore, the different pesticide residue concentrations observed in the vegetables can be attributed to plant photosynthetic activity, growth and expansion and soil properties; in addition to environmental factors such as rainfall, temperature and carbon-dioxide concentrations.

Other factors that can reduce initial pesticide concentration are volatilisation and photolysis (Keikotlhaile and Spanoghe, 2011). Volatilization can reduce pesticide residues in plants in presence of solar irradiation (Celik *et al.,* 1995). Pesticides can be blown away or volatilise by wind immediately after application depending on vapour pressure of the pesticide and temperature (Kerle *et al.,* 2007). Pesticides with high vapour pressure can volatilise faster into the air while those with low vapour pressure can stay longer on the plant surface. Therefore, higher the temperature, the faster the wind speed and the more the pesticides evaporate. Also, photolysis can degrade pesticides (Keikotlhaile and Spanoghe, 2011) leaving low pesticide concentrations in the plant.

3.2.2 Pesticide Residue Concentrations in Unsprayed Vegetables

The study showed that 18 % of the 84 unsprayed vegetable samples contained pesticide residues that exceeded MRLs; hence, pose a risk to human health and the environment. These results were in disagreement with the findings reported by FSSAI (2019) since 13 (21.7 %) of the 60 organic samples collected from organic outlets in India contained pesticide residues below the FSSAI MRLs. The presence of pesticide residues in unsprayed vegetable samples can be attributed to the transport of pesticides from the sprayed gardens (Strandberg *et al.,* 2019), spraying techniques, leaching and equipment parameters such as nozzle type and spraying pressure. Environmental factors such as temperature and relative humidity may affect pesticide droplet evaporation and drift potential causing the spread of pesticides to the unsprayed vegetable gardens. Since off target pesticides may not reach desirable doses to completely eliminate specific pest species, they may result in pest resistance and resurgence in the fields (Gill and Garg, 2014).

Further, pesticide residues detected in unsprayed vegetable samples might be a result of repeated use of persistent and non-biodegradable pesticides in the same or nearby fields. A study conducted by Dhananjayan *et al.,* (2019) revealed that pesticide handling in absence of regular inspection and follow-up may cause problems such as over application, under-doses and spraying without reaching pest habitats can result in unsafe pesticide residues in the fields. Also, pesticide residues taken up by plant roots from the soil may be retained in the root storage organs and persist for much longer than they would in the plants' leaves or stems (Edwards, 1975). Therefore, some pesticide residues detected in the unsprayed vegetables might have been obtained from the soils where the vegetables were grown.

Pesticides are believed to persist in plants. Persistence of pesticides in plants depends on physiological activities including growth rates, translocation, excretion and reserve stores (Edwards, 1975; Coats, 1991). Plant growth rate can influence persistence of pesticide in leaves and other plant parts because the spreading of pesticide residues in plants occurs over a much greater surface area as leaves and other organs grow. Moreover, doubling plant weight can reduce pesticide residue concentration by half, even if the rate of its breakdown does not change (Edwards, 1975). The residues may undergo translocation in the apoplast, the symplast or across the mesophyll and into the phloem and finally translocated to the assimilation stream (Jachetta *et al.,* 1986; Sicbaldi *et al.,* 1997). Further, the ease with which plants can take up pesticides depends upon cuticle wettability which in turn changes with age and differs on different leaf parts (He *et al.,* 2019). Thus, the persistence of pesticide residues may depend on the amounts of pesticides taken up by the plants which are turn influenced by several

factors such as re-distribution that occurs during growth, translocation, storage processes and plant surface wettability.

High pesticide residue levels detected in leaves of the sprayed vegetable samples can be attributed to direct application of pesticides, their uptake by the plant and environmental factors. The presence of pesticide residues in the unsprayed vegetable samples might have been a result of pesticide spray drifts, pesticide emissions, leaching and volatilisation processes that occurred in the sprayed vegetable gardens causing contamination of the unsprayed vegetables. Also, the residues in unsprayed vegetables can be attributed to repeated use of persistent and non-biodegradable pesticides in the same or nearby vegetable fields.

3.2.3 Mean Pesticide Residue Concentrations in the Market Vegetable Samples

The findings of this study showed that 86 % of the market vegetable samples contained detectable pesticide residues, of which 8 % had residues that exceeded MRLs while 14 % had residues below detectable levels (*see* table 4, C). These results were in agreement with the findings of Bempah *et al.,* 2012; FSSAI, 2019; Ali *et al.,* 2020). The lower pesticide residue levels detected in market vegetables can be attributed to pesticide loss during storage (Rasmusssen *et al.,* 2003) or the vegetables were sprayed with other pesticides different from what was analysed or the vegetables were not sprayed at all and were contaminated through contact and aerial spreading of different pesticide types in the market.

Further, pesticide residues detected in the market vegetable samples can be a result of bio-accumulation of off-target residues from sprayed vegetables or seed materials (Iyaniwura, 1991; Karthikeyan *et al.,* 2003). Bioaccumulation of off-target pesticides in plants may depend on pesticide lipophilicity. According to Langenbach, (2013) different lipophilicity pesticides can undergo bio-accumulation to different levels in different plant species or parts resulting in low or high uptake. The low pesticide residues detected in the market vegetable samples can also be due to higher pesticide degradation rates (Kocourek *et al.,* 2017). It is also known that pesticide concentrations used, the number of pesticide applications and time lag between the last applications in fields and the time of display in the market can account for the amounts of pesticide residues found in the vegetable harvests. According to the international atomic energy agency (1984) pesticide residue concentrations may depend on the number of applications and the period of time between the last applications and harvesting.

Low pesticide residues detected in the market vegetables can attributed to degradation processes such as photolysis (Keikotlhaile, and Spanoghe, 2011), microbial metabolism (Holland and Sinclair, 2004), enzymatic activities and other reactions with normal plant constituents (Ortiz-Hernaanhez *et al.*, 2013). Lastly, the low pesticide residues detected in the vegetable samples can be a result of short half-lives. According to Tiryaki and Temur, (2010) pesticide degradation heavily depends on half-life. In the present study, dimethoate showed shorter half-life of 3.29 days while cypermethrin had longer half-life of 5.4 days in the cabbage samples in analysed. Thus, low pesticide residues detected in some of the sprayed and market vegetable samples can be attributed to photolysis, microbial degradation, breakdown by enzymatic reactions and shorter half-lives.

Some pesticides can degrade easily (Copley, 2009); however, their residues may persist and re-distribute in the environment (Linde, 1994; Yin *et al.*, 2012; UK Environment Agency, 2019). Thus, the pesticide residues detected in the market vegetables may be a result of re-distribution into the market environment and subsequent contamination of food products including the vegetables. According to El-Wakeil *et al.*, (2013) most pesticides used in food crops may disperse into the environment and consequently affect human health. Pesticide residues in various market commodities can undergo dissipation and reach humans through various food types bought from the market. Pesticide dissipation in markets may be influenced by factors like storage facilities, pesticide formulation and nature of commodities sold in the market in addition to environmental factors such as wind speed and direction and temperature.

Different sources of pesticides may lead to the presence of multiple residues in market vegetables. However, the presence of multiple pesticide residues and their interactions in vegetables may affect their quality. Therefore, the low pesticide residues detected in the market vegetables did not mean that these vegetables were of the required quality since may contain multiple pesticide residues that can affect their quality; of course, not forgetting that the residues can also undergo bio-accumulation.

It is worth noting that there are modern techniques that can be used to reduce pesticide residues in some vegetables such as use of electrolysed water (Sachadyn-Krol *et al.*, 2016), ultra-sound (Liang *et al.*, 2012), pulsed light (Bhilwadikar *et al.*, 2019), ultra-violet light (Wang *et al.*, 2019), non-thermal plasma (NTP) (Phan *et al.*, 2018), irradiation (Basfar *et al.*, 2012), high hydrostatic pressure (Iizuka and Shimizu, 2014); low-intensity electric current (Cengiz *et al.*, 2018), biological techniques (Pino and Penuela, 2011) and combination treatments (Bhilwadikar *et al.*, 2019).

3.3 Quality Index of the Market Vegetables for the Pesticide Residues

The present study determined the quality index values of the market vegetables for each pesticide residue and placed the vegetable samples into categories (*see* table 6).

Table 6: Quality Index Values (IqR) and Quality Categories of the Market Vegetables

Part A: Calculated market vegetable quality index values for the pesticide residues (IqR)

Vegetables	Cypermethrin	Dimethoate	Metalaxyl	Profenofos	Malathion	Dichlorvos	Mancozeb
Cabbage	0.0034	1.0850	0.0440	0.1200	0.0760	0	0.0001
Cauliflower	0.0068	0.2425	0.0131	0.2490	0.0325	0	0.0003
Tomato	0.0068	0.9570	0.0088	0.0002	0.0047	0	0.0005
Beetroot	0.0049	20.3500	0.1955	0.0490	0.0245	0	0.0006

Part B: Quality categories of the market vegetable samples

Vegetable samples	Optimal (IqR: 0)	Good (IqR:0-0.6)	Adequate (IqR:0.6-1)	Inadequate (IqR:>1)
Cabbage	1	5		1
Cauliflower	1	6		
Tomato	1	5	1	
Beetroot	1	5		1
Total of vegetable samples	4	21	1	2

Different percentages of the market vegetable samples had different quality categories depending on their quality index values (IqR) for the pesticide residues. For example, the percentages of the market vegetables with their quality categories were 14.29 %, 75 %, 3.57 % and 14.29 % for optimal quality, good quality, adequate quality and inadequate quality, respectively (*see* table 6). These findings were in agreement with the results obtained by Ramadan *et al.*, (2020). In general, market vegetable samples had good quality; however, there is a need for efforts to work towards achieving optimal quality. Hence, determination of IqR values is a useful way of indicating the quality index for the pesticide residues in different plant products.

Conclusion

In this study pesticide residues were detected in all parts of the sprayed, unsprayed and market vegetables. All sprayed vegetable samples contained detectable pesticide residues which can risk human health and the environment. Pesticide residues detected in the sprayed vegetable samples were higher than those detected in the unsprayed vegetable samples. The pesticide residues exceeded MRLs

in 59.52 % of the sprayed samples, 18 % of the unsprayed and 8 % of the market vegetable samples. The study revealed that use of mixed pesticides may lead to antagonistic or synergistic effects that may affect pesticide efficiency and multiple pesticide residues that may affect food quality. Therefore, farmers should avoid use of mixed pesticides in food crops and look for crop specific pesticides.

Apart from the risk that pesticide residues can pose on human health upon vegetable consumption, they have a greater potential to re-distribute and accumulate in the environment resulting in adverse effects on soil micro-organisms, groundwater and surface water quality and biodiversity. Therefore, there is a strong need for proper monitoring of pesticide use in agriculture and regulation of pesticide residues in food produced in Uganda more especially vegetables that are sometimes consumed in raw forms by humans. Pesticide use regulation in vegetable production and hence other crops can be easily achieved by training farmers on appropriate pesticide use practices, empowering agricultural extension workers so that they can assist in description of pesticides for specific pests and establishment of pesticide residue detection centres at least one in every district or at regional level.

References

1. Freedman, B. (1995). Environmental Ecology (Second Edition).
2. Nicolopoulou-Stamati, P., Maipas, S., Kotampasi, C., Stamatis, P. & Hens, L. (2016). Chemical Pesticides and Human Health: The Urgent Need for a New Concept in Agriculture.
3. Al-Ahmadi, M.S. (2019). Pesticides, Anthropogenic Activities, and the Health of our Environment Safety DOI: 10.5772/intechopen.84161.
4. Dinham, B. (2003). Growing vegetables in developing countries for local urban populations and export markets: problems confronting small-scale producers.
5. Ngabirano, H. & Birungi, G. (2020). Pesticide use in vegetable production in rural Uganda - A case study of Kabale District, South - western Uganda.
6. EFSA (European Food Safety Authority), (2019). Scientific report on the 2017 European Union report on pesticide residues in food. EFSA Journal 2019;17(6):5743, 152 pp. https:// doi.org/10.2903/j.efsa.2019.5743.
7. Dasika, R., Tangirala, S., & Naishadham, P. (2012). Pesticide residue analysis of fruits and vegetables. Department of Chemistry, Osmania University, Hyderabad, India; Journal of Environmental Chemistry and Ecotoxicology, 4(2), 19-28.
8. Langenbach, T. (2013). Persistence and Bioaccumulation of Persistent Organic Pollutants (POPs).
9. Food and Agricultural Organisation of the United Nations, FAO, & World Health Organisation, WHO. (2016). International Code of Conduct on Pesticide Management and Guidelines on Highly Hazardous Pesticides.

10. Bolognesi, C. (2003). Genotoxicity of pesticides: A review of human biomonitoring studies. Mutat. Res. 543, 251–272.

11. Mostafalou, S., & Abdollahi, M. (2013). Pesticides and human chronic diseases: Evidences, mechanisms, and perspectives.

12. Sabarwal, A., Kumar, K., & Singh, R.P. (2018). Hazardous effects of chemical pesticides on human health-Cancer and other associated disorders.
13. Kamai, E.M., McElrath, T.F., & Ferguson, K.K. (2019). Fetal growth in environmental epidemiology: mechanisms, limitations, and a review of associations with biomarkers of non-persistent chemical exposures during pregnancy.
14. Keikotlhaile, B.M., & Spanoghe, P. (2014). Pesticide Residues in Fruits and Vegetables.

15. U.S Food and Drug Administration. (2012). "Pesticide monitoring program fiscal year 2012 pesticide report."

16. Syed, J.H., Alamdar, A., Mohammad, A., Ahad, K., Shabir, Z., Ahmed, H., Ali, S.M., Sani, S.G.A.S., Bokhari, H., Gallagher, K.D., Ahmad, I., & Eqani, S.A.M.A.S. (2014). Pesticide residues in fruits and vegetables from Pakistan: a review of the occurrence and associated human health risks.
17. Chen, C., Qian, Y., Chen, Q., Tao, C., Li, C., & Li, Y. (2011). Evaluation of pesticide residues in fruits and vegetables from Xiamen, China. Food Control 22: 1114-1120.
18. Chowdhury, A.Z., Fakhruddin, A.N.M, Islam, N., Moniruzzaman, M., Gan S.H, & Alam, K. (2013). Detection of the residues of nineteen pesticides in fresh vegetable samples using gas chromatography–mass spectrometry. Food Control 34: 457–465.
19. Langan, C., & Farmer, J. (2014). Profile of Kabale District, Uganda.
20. Uganda Bureau of Statistics. (2014). National Population and Housing Census 2014. Area Specific Profiles.
21. McGinnis, E. (2014). The Facts of Square Foot Gardening.
22. Famunera Ltd. (2016-2020). Bomba Magoba Knapsack Spray Pump.
23. Anastassiades, M., & Lehotay, S.J. (2003). Fast and Easy Multi-residue Method Employing Acetonitrile Extraction/Partitioning and "Dispersive Solid-Phase Extraction" for the Determination of Pesticide Residues in Produce. Anastassiades *et al.*: Journal of AOAC International Vol. 86(2).
24. Rizzetti, T.M., Kemmerich, M., Martins, M.L., Prestes, O.D., Adaime, M.B. & Zanella, R. (2016). Optimization of a QuEChERS based method by means of central composite design for pesticide multiresidue determination in orange juice by UHPLC–MS/MS. Food Chemistry, 196, pp 25-33.

25. Devi, P.A., Paramasivam, M. & Prakasam, V. (2015). Degradation pattern and risk assessment of carbendazim and mancozeb in mango fruits. Environ Monit Assess 187:4142.

26. **S**tenerson. K.K. (2012). Resolving by Mass.

27. Saadati, N., Abdullah, P., Zakaria, Z., Sany, M. Rezayi, S.B.T., & Hassonizadeh H. (2013). Limit of detection and limit of quantification development procedures for organochlorine pesticides analysis in water and sediment matrices.

28. Hajšlová, J. & Zrostlíková, J. (2003). Matrix effects in (ultra) trace analysis of pesticide residues in food and biotic matrices. Journal of chromatography A, 1000(1-2), pp 181-197.

29. Kim, J.S., Kim, Y., Han, S., Jeon, J., Hwang, M., Im, Y., Kim, J.H., Lee, S.Y., Chae, S., & Kim, M. (2013). Development and validation of an LC-MS/MS method for determination of compound K in human plasma and clinical application. 37(1): 135–141.

30. Alam, M.A., Al-Jenoobi, F.I., & Al-Mohizea, A.M. (2015). High-Throughput Ultra-Performance LC–MS-MS Method for Analysis of Diclofenac Sodium in Rabbit Plasma 53(1): 47-53.

31. Moosavi, S.M., & Ghassabian, S. (2018). Linearity of Calibration Curves for Analytical Methods: A Review of Criteria for Assessment of Method Reliability.

32. Zazzi, B.C., Creapeau, K.L., Fram, M.S. & Bergamaschi, B.A. (2005); Method of analysis at the U.S Geological Survey California water science centre, sacramento laboratory – Determination of haloacetic acid formation potential, Method Validation, and Quality- Control Practices

33. NATA (National Association of Testing Authorities), Australia. (2012). Guidelines for the validation and verification of quantitative and qualitative test methods: Technical Note 17.

34. Burchfield, H.P., (1965). Guide to the Analysis of Pesticide Residues, Volume 2.
35. FSSAI, (2019); Food Safety and Standards Authority of India (Ministry of Health and Family Welfare) (Regulatory Compliance Division) FSSAI – File No 7(5). (2019). Pesticides residues/RCD/FSSAI; FDA Bhavan, Kotla Road, New Dew Dhelhi-110 002.
36. Arienzo, M., Cataldo, D., & Ferrara, L. (2013). Pesticide residues in fresh-cut vegetables from integrated pest management by ultra-high performance liquid chromatography coupled to tandem mass spectrometry. 31:108–115. doi: 10.1016/j.foodcont.2012.09.021.

37. Mac Loughlin, T.M., Peluso, L., Etchegoyen, A., Alonso, L.L., Castro, C., Percudani, C., & Marino, J.G. (2018). Pesticide residues in fruits and vegetables of the argentine domestic market: Occurrence and quality. 93:129–138. doi: 10.1016/j.foodcont.2018.05.041.

38. Ramadan, M.F.A., Abdel-Hamid, M.M.A., Altorgoman, M.M.F., AlGaramah, H.A., Alawi, M.A., Shati, A.A., Shweeta H.A., & Awwad, N.S. (2020). Evaluation of Pesticide Residues in Vegetables from the Asir Region, Saudi Arabia.

39. VICH topic GL49. (2015). Studies to evaluate the metabolism and residues kinetics of veterinary drugs in human food-producing animals: validation of analytical methods used in residue depletion studies.

40. Commission Regulation, (EU), 2015/399. (2015). Amending Annexes II, III and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for 1,4-dimethylnaphthalene, benfuracarb, carbofuran, carbosulfan, ethephon, fenamidone, fenvalerate, fenhexamid, furathiocarb, imazapyr, malathion, picoxystrobin, spirotetramat, tepraloxydim and trifloxystrobin in or on certain products.
41. Commission Regulation, (EU), 2016/60. (2016). Amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for chlorpyrifos in or on certain products.
42. Commission Regulation, (EU), 2017/1135. (2017). Amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for dimethoate and omethoate in or on certain products.
43. Commission Regulation, (EU), 2017/1164). (2017). Amending Annexes II and III to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for acrinathrin, metalaxyl and thiabendazole in or on certain products.
44. Commission Regulation, (EU), 2017/171. (2017). Amending Annexes II, III and IV to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for aminopyralid, azoxystrobin, cyantraniliprole, cyflufenamid, cyproconazole, diethofencarb, dithiocarbamates, fluazifop-P, fluopyram, haloxyfop, isofetamid, metalaxyl, prohexadione, propaquizafop, pyrimethanil, Trichoderma atroviride strain SC1 and zoxamide in or on certain products.
45. Commission Regulation, (EU), 2017/978. (2017). Amending Annexes II, III and V to Regulation (EC) No 396/2005 of the European Parliament and of the Council as regards maximum residue levels for fluopyram; hexachlorocyclohexane (HCH), alpha-isomer; hexachlorocyclohexane (HCH), beta-isomer; hexachlorocyclohexane (HCH), sum of isomers, except the gamma isomer; lindane (hexachlorocyclohexane (HCH), gamma-isomer); nicotine and profenofos in or on certain products.

46. Wise, J. (2019). Rainfast characteristics of insecticides on fruit; Accessed on 06 November, 2020.

47. Norris, L.A. (1974). Behavior of pesticides in plants.
48. Yin, L.B., Zhao, L.Z., Liu, Y., Zhang D.Y., Zhang, S.B., & Xiao, K. (2012). Isolation and Characterisation of Cypermethrin Degrading Bacteria Screened from Contaminated Soil.
49. Zhou, Y., Xia, X., Yu, G., Wang, J., Wu, J., Wang, M., Yang, Y., Shi, K., Yu, Y., Chen, Z., Gan, J., & Yu, J. (2015). Brassinosteroids play a critical role in the regulation of pesticide metabolism in crop plants.
50. Bernardes, M.F.F., Pazin, M., Pereira, L.C. and Dorta, D.J. (2015). Impact of Pesticides on Environmental and Human Health.
51. Akan, J.C., Jafiya, L., Chellube, Z.M., Mohammed, Z., & Abdulrahman, F.I. (2014). Determination of Some Organochlorine Pesticide Residues in Vegetable and Soil Samples from Alau Dam and Gongulong Agricultural Sites, Borno State, North Eastern Nigeria.
52. Bull, D.L., Ivie, G.W., MacConnell, J.G., Gruber, V.F., Ku, C.C., Arison, B.H., Stevenson, J.M., & VandenHeuve, W.J.A. (1984). J. Agric Food Chem 32:94-102. Fate of avermectins BIa in soil and Plants.
53. Finlayson, D.G., & MacCarthy, H.R. (1965). The movement and persistence of insecticides in plant tissue vol. 9, pp 114-152.
54. Finlayson, D.G., & MacCarthy, H.R. (1973). Pesticide residues in plants.
55. Menn, J.J. (1978). Comparative aspects of pesticide metabolism in plants and animals 27: pp. 113–124.
56. Edwards, C.A. (1975). Factors that affect the persistence of pesticides in plants and soils.
57. Ravichandra, N.G (2018). Agrochemicals in Plant Disease Management.
58. Kapeleka, J.A., Sauli, E., Sadik, O., & Ndakidemi, P.A. (2021). Changing Patterns and Drivers of Increased Pesticides Use in Smallholder Vegetable Production Systems in Tanzania.
59. Allagui, A., Bahrouni, H., & M'Sadak, Y. (2018). Deposition of Pesticide to the Soil and Plant Retention during Crop Spraying: The Art State.
60. Buzzetti, K. (2017). Role of the formulation in the efficacy and dissipation of agricultural insecticides.
61. Yarpuz-Bozdogan, N., Atakan, E., Bozdogan, A.M., Yilmaz, H., Daglioglu, N., Erdem, T., & Kafkas, E. (2011). Effect of different pesticide application methods on spray deposits, residues and biological efficacy on strawberries. Vol. 6(4), pp. 660-670.

62. Shi, H., Wang, H. and Li, Y. (2011). Wettability on plant leaf surfaces and its ecological significance.
63. Hofman, V. (2018). Spray Equipment and Calibration.
64. Rosenzweig, C., Iglesias, A., Yang, X., Epstein, P.R., & Chivian, E. (2001). Climate change and extreme weather events; implications for food production, plant diseases, and pests. Global Change and Human Health, 2(2), 90–104.
65. Keikotlhaile, B.M. and Spanoghe, P. (2011). Pesticide Residues in Fruits and Vegetables.
66. Reilly, J., Tubiello, F., McCarl, B., Abler, D., Darwin, R., Fuglie, K., Hollinger, S., Izaurralde, C., Jagtap, S., Jones, J., Mearns, L., Ojima, D., Paul, E., Paustian, K., Riha, S., Rosenberg, N., & Rosenzweig, C. (2003). US agriculture and climate change: New results. Climatic Change, 57(1–2), 43–67.
67. Gutierrez, A.P., Ponti, L., d'Oultremont, T., & Ellis, C. (2008). Climate change effects on poikilotherm tritrophic interactions. Climatic Change, 87(1), 167–192.
68. Miraglia, M., Marvin, H.J.P., Kleter, G.A., Battilani, P., Brera, C., Coni, E., Cubadda, F., Croci, L., De Santis, B., Dekkers, S., Filippi, L., Hutjes, R.W.A., Noordam, M.Y., Pisante, M., Piva, G., Prandini, A., Toti, L., van den Born, G.J., & Vespermann, A. (2009). Climate change and food safety: An emerging issue with special focus on Europe. Food and Chemical Toxicology, 47(5), 1009–1021.
69. Zongmao, C., & Haibin, W. (1997). Degradation of pesticides on plant surfaces and its prediction - A case study on tea plant. Environmental Monitoring and Assessment, 44(1–3), 303–313.
70. Holland, J., & Sinclair, P. (2004). Environmental fate of pesticides and the consequences for residues in food and drinking water, in: Pesticide Residues in Food and Drinking Water: Human Exposure and Risks, Hamilton D. & Crossley S. (Ed.), 27 – 62, John Willey &Sons LTD, 0-471-48991-3, West Sussex, England.
71. Celik, S., Kunc, S., & Asan, T. (1995). Degradation of some pesticides in the field and effect of processing. Analyst, 120, 1739 – 1743.
72. Kerle, E.A., Jenkins, J.J, & Vogue, P.A. (2007). Understanding pesticide persistence and mobility for groundwater and surface water protection. Oregon State Univ Extension Service, EM8561-E.
73. Strandberg, B., Boutin, C., Carpenter, D., Mathiassen, S.K., Damgaard, C.F., Sørensen, P.B., Bruus, M., Dupont, Y.L., Bossi, R., Andersen, D.K., Baatrup-Pedersen, A., & Larsen, S.E. (2019). Pesticide effects on non-target terrestrial plants at individual, population and ecosystem level.
74. Gill, H.K., & Garg, H. (2014). Pesticides: Environmental Impacts and Management Strategies.
75. Dhananjayan, V., Jayakumar, S., & Ravichandran, B. (2019). Conventional methods of pesticide application in agricultural field and fate of the pesticides in the environment and human health.

76. Coats, J.R. (1991). Pesticide Degradation Mechanisms and Environmental Activation.

77. Jachetta, J.J., Appleby, A.P., & Boersma, L. (1986). Apoplastic and Symplastic Pathways of Atrazine and Glyphosate Transport in Shoots of Seedling Sunflower.
78. Sicbaldi, F., Sacchi, G.A., Trevisan, M., & Re, A.A.M.D. (1997). Root uptake and xylem translocation of pesticides from different chemical classes.
79. He, Y., Xiao, S., Wu, J., & Fang, H. (2019). Influence of Multiple Factors on the Wettability and Surface Free Energy of Leaf Surface.

80. Bempah, C.K., Asomaning, J., & Boateng J. (2012). Market basket survey for some pesticides residues in fruits and vegetables from Ghana.
81. Ali, S.E.A, Aziz, M.E.A. and Mohamed, S.E. (2020). Determination of Pesticides Residues in Eggplant and Tomatoes from Central Marked in Khartoum State Using QuEChERS Method and Gas Liquid Chromatography-Mass Spectrometry.
82. Rasmusssen, R.R., Poulsen, M.E., & Hansenn, H.C.B. (2003). Distribution of multiple pesticide residues in apple segments after home processing.

83. Iyaniwura, T. T. (1991). Non-target and environmental hazards of pesticides, vol. 9(3):161-76.

84. Karthikeyan, R., Davis, L.C., Erickson, L.E., Al-Khatib, K., Kulakow, P.A., Barnes, P.L., Hutchinson, S.L. & Nurzhanova, A.A. (2003); Studies on responses of non-target plants to pesticides: A review.

85. Kocourek, F., Stará, J., Holý, K., Horská, T., Kocourek, V., & Kováčová, J. (2017). Evaluation of pesticide residue dynamics in Chinese cabbage, head cabbage and cauliflower: 34(6).

86. International Atomic Energy Agency, (IAEA). (1984). Radiotracer studies of bound pesticide residues in soil, plants and food, îAEA-TECDOC-306.
87. Ortiz-Hernaanhez, L., Sanchez-Salinas, E., Dantan-Gonzalez, E. & Castrejon-Godinez, M.L. (2013). Pesticide biodegradation: Mechanisms, genetics and strategies to enhance the process.

88. Tiryaki, O., & Temur, C. (2010). The Fate of Pesticide in the Environment.
89. Copley, S.D. (2009). Evolution of Efficient Pathways for Degradation of Anthropogenic Chemicals.
90. Linde, C.D. (1994). Physico-Chemical Properties and Environmental Fate of Pesticides, State of California.
91. UK Environment Agency. (2019). Cypermethrin: Sources, pathways and environmental data.

92. El-Wakeil, N., Shalaby, S., Abdou, G., & Sallam, A. (2013). Pesticide-Residue Relationship and Its Adverse Effects on Occupational Workers; DOI: 10.5772/54338.

93. Sachadyn-Krol, M., Materska, M., Chilczuk, B., Karas´, M., Jakubczyk, A., Perucka, I., & Jackowska, I. (2016).Ozone-induced changes in the content of bioactive compounds and enzyme activity during storage of pepper fruits. Food Chemistry, 211, 59–67.

94. Liang, Y., Wang, W., Shen, Y., Liu, Y., & Liu, X.J. (2012). Effects of home preparation on organophosphorus pesticide residues in raw cucumber. Food Chemistry, 133(3), 636–640.

95. Bhilwadikar, T., Pounraj, S., Manivannan, S., Rastogi, N.K. & Negi, P.S. (2019). Decontamination of Microorganisms and Pesticides from Fresh Fruits and Vegetables: A Comprehensive Review from Common Household Processes to Modern Techniques; doi: 10.1111/1541-4337.12453, Vol.18.

96. Wang, X., Ji, R., & Chen, R. (2019). Research on thiamethoxam detection and ultraviolet degradation modeling based on fluorescence analysis. Optik, 176, 476–481.

97. Phan, K.T.K., Phan, H.T., Boonyawan, D., Intipunya, P., Brennan, C.S., Regenstein, J. M., & Phimolsiripol, Y. (2018). Non-thermal plasma for elimination of pesticide residues in mango. Innovative Food Science & Emerging Technologies, 48, 164–171.

98. Basfar, A.A., Mohamed, K.A., & Al-Saqer, O.A. (2012). De-contamination of pesticide residues in food by ionizing radiation. Radiation Physics and Chemistry, 81(4), 473–478.

99. Iizuka, T., & Shimizu, A. (2014). Removal of pesticide residue from Brussels sprouts by hydrostatic pressure. Innovative Food Science & Emerging Technologies, 22, 70–75.

100. Cengiz, M.F., Baslar, M., Basancelebi, O., & Kılıclı, M. (2018). Reduction of pesticide residues from tomatoes by low intensity electrical current and ultrasound applications. Food Chemistry, 267, 60–66.

101. Pino, N., & Penuela, G. (2011). Simultaneous degradation of the pesticides methyl parathion and chlorpyrifos by an isolated bacterial consortium from a contaminated site. International Bio-deterioration & Biodegradation, 65(6), 827–831.

Highlights (for Review)

The English in this manuscript may be edited where necessary without change of meaning.

The samples used in the study were sprayed (with individual and mixed pesticides), unsprayed (control) and market of vegetable samples (cabbage, cauliflower, tomato and beetroot).

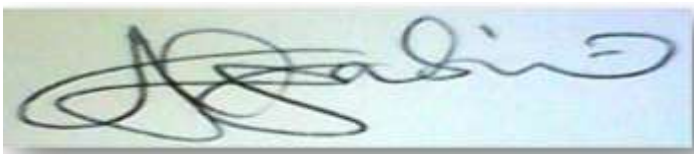
Standard methods were used in the extraction of pesticide residues (cypermethrin, malathion, dichlorvos, profenofos, dimethoate, mancozeb and metalaxyl) from the vegetable samples (cabbage, cauliflower, tomato and beetroot).

LC-MS/MS, GC-MS/MS and UV-Vis analytical equipment were used in the analysis of pesticide residues in sprayed, unsprayed and market vegetable samples.

The detected pesticide residue levels in all vegetable samples (sprayed, unsprayed and market) were compared with the allowed MRLs.

The study also involved the determination quality index of the market vegetables for the pesticide residues detected therein in order to determine the suitability of the market vegetables for human consumption.

Thank you.



Hannington Ngabirano