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DETERMINATION OF LEVELS OF ORGANOPHOSPHORUS PESTICIDE RESIDUES IN KALES, TOMATOES AND FRENCH BEANS FROM MERU COUNTY, KENYA BY GC-MS

[1*]Marete M. G, [2]Lalah J. O, [3]Mputhia J. & [4]Wekesa V. W

[1]PhD Candidate, the Technical University of Kenya

[2]Department of Geoscience and the Environment, the Technical University of Kenya

[3]Department of Chemical Science and Technology, the Technical University of Kenya

[4]Department of Technical and Applied Biology, the Technical University of Kenya

***E-mail of the Corresponding Author: gabriel_muthee@yahoo.com**

ABSTRACT

Purpose of the Study: The aim of this study was to investigate the levels of pesticides and metabolites in kales, tomatoes and French beans from Imenti North, Imenti South and Buuri Sub County in Meru County, Kenya.

Statement of the Problem: Pesticides are known to be the most important tool for the production of adequate food supply for an increasing world population and for the control of vector-borne diseases. However, pesticides have some toxicological and environmental consequences, which include toxic residues in food substances and adverse effects on non-target organisms. The gross and improper use of synthetic pesticides is a matter of much concern. Pesticides have been associated with a wide variety of human health hazards, ranging from acute impacts such as headache, vomiting and diarrhoea to chronic impacts like cancer, reproductive harm and endocrine disruption. Many people die from pesticides poisoning and other people suffer from various health effects.

Research Methodology: Samples of fresh kales, tomatoes and French beans from the farm were analyzed for pesticide residues. Extraction was performed using acetone followed by dichloromethane: cyclohexane mixture and the extracts were cleaned up using Florisil. The

compounds were determined by gas chromatography-mass spectrometry (GC-MS). Pesticides and metabolites were detected in 72.2% of the samples.

Study Results: The detected pesticide residues and their highest mean concentrations were Azoxystrobin,15.93±1.48µg/Kg, diazinon 0.15±0.0048µg/Kg, Cabendazim 48.65±3.5848µg/Kg, imidacloprid290.76±26.3448µg/Kg,acetamiprid2.49±0.0648µg/Kg,metalaxyl 105.18±6.3248µg/Kg and chlorpyrifos 3.83±0.0048µg/Kg. Generally, there were no significant variations in concentrations of pesticide residues among samples and sampling sites, which indicated similarities in contamination patterns. The concentrations of contaminants were below the maximum residue limits (MRLs) in all of the samples.

Conclusion: The co-occurrence of pesticide residues in samples was due to various reasons including mixing of pesticides by farmers during application as farmers use more than one pesticide at one time due to resistance of pests.

Key Words: *Organophosphorus, Pesticide, Residues, Kales, Tomatoes, French Beans*

1.1 INTRODUCTION

Pesticides are widely used in vegetables to control pests and diseases during farming, transportation, and storage. Pesticides are known to be the most important tool for the production of adequate food supply for an increasing world population and for the control of vector-borne diseases [1]. However, pesticides have some toxicological and environmental consequences, which include toxic residues in food substances and adverse effects on non-target organisms. The gross and improper use of synthetic pesticides is a matter of much concern. Pesticides have been associated with a wide variety of human health hazards, ranging from acute impacts such as headache, vomiting, and diarrhoea to chronic impacts like cancer, reproductive harm, and endocrine disruption. Many people die from pesticides poisoning and other people suffer from various health effects [2, 3].

Vegetables are among the most frequently consumed food types in Kenya and the world at large. As vegetables are eaten either fresh or semi processed and due to improper agricultural practices of some farmers such as not observing the withholding periods after spraying, it could be expected that they contain high pesticide residues. Meru County is one of the Kenya's agricultural hubs and is well known for their massive sales of vegetables that come from

different areas of the county where pesticides are widely used. Thus, assessment of pesticides in samples from these farms could reflect the contamination status in the area and other areas. Literature surveys indicated that no study had been conducted on pesticide residues in vegetables in Meru County. Therefore, the above observations prompted the inception of this study.

2.0 MATERIALS AND METHODS

2.1. Study Area and Sampling.

The study was conducted in Meru County. Meru County is found in the eastern region of Kenya, approximately 225 kilometers northeast of Nairobi. Meru County has a total area of 6,936 km2 (Chiramba *et al.*, 2011) and lies within latitude 0.0515° N and longitude 37.6456° E with an altitude of 5300 feet above the sea level. It has a population of 1,601,629 people (KNBS, 2013) and is among the fastest developing towns in Kenya (Jolicoeur, 2000). The growth is associated with rising vegetable and flower farming business in the areas surrounding the lake. Tourism and its related activities in the area together with relocations from rural to urban areas because of decreasing farming incomes from the conventional cash crops have also been contributing factors towards this growth (Jolicoeur, 2000). Meru County has total of nine sub counties namely Igembe north, Igembe central, Igembe south, Tigania east, Tigania west, Buuri, Imenti central, Imenti south and Imenti north.

The selected vegetables collected were kales, tomatoes and French beans. Sampling was conducted by applying standard guidelines [4]. A total of 90 samples (200–500 g of each sample) were sampled from the farms, separately wrapped in aluminum foil, and placed into polythene bags. In the laboratory, the samples were stored in a freezer.

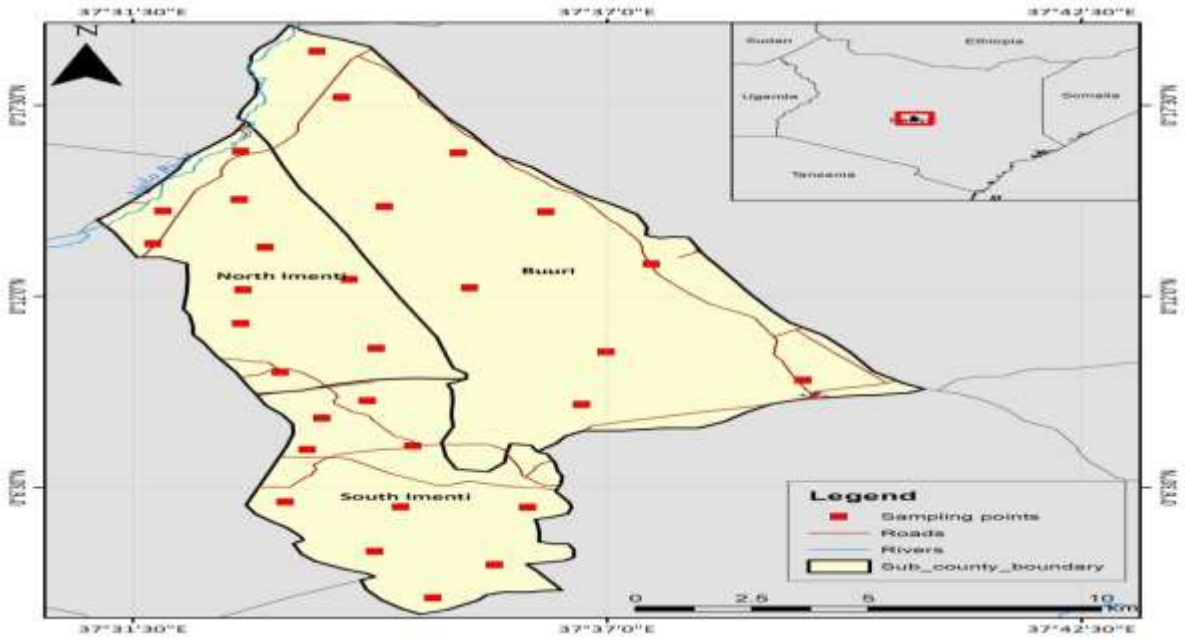

Figure 1: Map Showing Sampling Sites

2.2. SAMPLE PREPARATION AND PROCESSING.

Sample preparation and extraction were conducted within 24 hours after sampling. Each sample was homogenized by using motor and pestle. The homogenized sample (20 g) was extracted with acetone (20mL) and then with a mixture of dichloromethane: cyclohexane (1: 1, 20mL) by sonication in ultrasonic bath for 30min. The mixture was filtered through glass wool containing anhydrous sodiumsulfate for drying. The sodium sulfate was then washed with dichloromethane: cyclohexane (1: 1, 5mL).The extract was concentrated in rotary evaporator operated at 40∘C and made up to 2mL in cyclohexane [4].

The clean-up procedure for extracts was conducted according to ˚Akerblom (1995) with some modifications. A chromatographic tube of 10mm i.d. × 32 cm was plugged with glass wool, packed with activated Florisil (3 g), and topped up with sodium sulfate (5–10 cm). The column was rinsed with cyclohexane (5 mL), and then the extract (2 mL) was passed through the column and eluted sequentially with cyclohexane (20 mL) and cyclohexane: acetone (9: 1, 10 mL). The collected portions were combined and concentrated in rotary evaporator to 2mL in cyclohexane: acetone (9: 1).

2.3. QUANTIFICATION AND ANALYSIS OF THE SAMPLES.

Vegetable extracts were analyzed for selected pesticides using gas chromatography–mass spectrometry (GC–MS) on a 6890N GC instrument (Agilent, USA) equipped with a thermo scientific trace GOLD GC column (TG 5SILMS 30m X 0.25mm X 0.25 µm) coupled to an Agilent 5973 MS (USA). The mass spectrometer (MS) was operated in EI + mode in the resolution of >5000. Injection was split less with volume of 1µL to 280^{o}C, with helium as carrier gas at 1 ml min-1. The injection temperature program applied was as follows: 90˚C (3 min), 90 ºC to 200 ˚C (at 30 ˚C/ min and hold time of 15 min), 200 ˚C to 275 ˚C (at 30 ˚C/min and hold time of 5 min). Chemstation software was used in data processing.

2.4. ANALYTICAL QUALITY ASSURANCE.

All solvents and reagents were of analytical grade and above 99% purity (purchased from Thermo Fisher Scientific, UK). The glassware was cleaned with water and detergent and then with distilled water and rinsed with acetone. Other tools were also thoroughly cleaned before and after use. Sodium sulfate was heated at 130∘C for 2 hours in order to remove moisture, and Florisil was preheated at 130∘C overnight and partially deactivated with 5% distilled water. Pesticides standard solutions were of high purity (above 95%, obtained from Dr. Ehrenstorfer, Augusburg, Germany).Working standard solutions were prepared at concentrations ranging from 0.5 to 2 μg/mL and were stored in a freezer. Blank and recovery tests were done to check the performance of the procedures and instruments.

All sample types were analysed concurrently with matrix blanks; 6 blanks were analysed. A known volume of a mixture of pesticide standards solution was spiked into blank samples for recovery tests. Each spiked sample was homogenized, extracted, cleaned up, concentrated, and analyzed just like the ordinary samples. Six recovery tests were done for the matrix blank samples. The detection limits of the analytes were established based on the lowest injected amounts in samples that resulted in peak heights three times higher than the baseline noise level. Every signal below this limit was treated as not detectable. No pesticides were detected in blank samples. The percentage recoveries for the analysed pesticides ranged from 71.2 to 110%. The recoveries were within the accepted range of 70–120% [5]. The detection limits of the analytes in samples ranged from1.0×10^{-4} to 7.0×10^{-4} mg/kg.

2.5. STATISTICAL ANALYSIS.

Statistical analysis of the data was performed by using GraphPad Instat software [6]. The data were subjected to Kruskal-Wallis test (Nonparametric ANOVA) to test for significance of variations followed by post-test (Dunn's multiple comparisons test).

3.0 RESULTS AND DISCUSSION

3.1. Pesticide Residues in Tomato Samples

Among the analysed pesticide residues, the following residues were detected in tomatoes: *Cabendazim, imidacloprid, acetamiprid, Azoxystrobin*, metalaxyl and chlorpyrifos. Other pesticide residues analysed is diazinon was below the detection limits. Table 1 presents the concentrations of detected pesticides and metabolites in tomato samples.

Table 1: Mean concentrations (±SD) of pesticide residues in tomato samples (µg/kg).

Site	Sample	Carbendazim	Imidacloprid	Acetamiprid	Azoxystrobin	Metalaxyl	Diazinon	Chlorpyrifos
	C1	11.81±2.71	196.47±19.63	0.29±0.01	BDL	2.27±0.01	BDL	BDL
Buuri	C2	48.65±3.58	290.76±26.34	0.11±0.00	0.1±0.00	105.18±6.32	BDL	BDL
	C3	0.24±0.00	0.24±0.00	BDL	0.33±0.00	6.58±0.69	BDL	0.14±0.00
	C4	0.37±0.00	0.88±0.00	BDL	0.95±0.00	4.68±0.54	BDL	BDL
	C5	6.58±0.35	33.57±1.82	BDL	0.96±0.00	1.59±0.07	BDL	BDL
	C6	0.93±0.00	1.44±0.00	BDL	0.15±0.08	BDL	BDL	BDL
	C7	0.33±0.00	0.58±0.00	BDL	0.54±0.00	2.1±0.18	BDL	0.13±
Imenti North	C8	1.03±0.08	0.12±0.00	BDL	BDL	BDL	BDL	BDL
	C9	0.58±0.00	1.25±0.05	BDL	BDL	BDL	BDL	BDL
	C10	1.52±0.00	1.52±0.06	BDL	0.25±0.00	BDL	BDL	0.17±0.00
	C11	1.43±0.00	8.56±0.97	BDL	3.73±0.87	BDL	BDL	BDL
	C12	3.04±0.06	0.51±0.00	BDL	BDL	BDL	BDL	BDL
	C13	6.17±0.52	1.09±0.07	BDL	1.87±0.00	BDL	BDL	BDL
	C14	0.65±0.00	2.24±0.00	BDL	2.12±0.09	BDL	BDL	BDL
Imenti South	C15	1.1±0.00	2.87±0.04	BDL	15.93±1.48	1.05±0.01	BDL	BDL
	C16	0.56±0.00	0.1±0.00	BDL	BDL	BDL	BDL	BDL
	C17	6.4±0.63	0.56±0.00	BDL	1.26±0.63	BDL	BDL	BDL
	C18	0.98±0.00	2.7±0.08	BDL	2.9±0.00	BDL	BDL	BDL
	C19	12.97±1.64	0.11±0.00	BDL	BDL	BDL	BDL	BDL
	C20	1.65±0.87	9.24±1.42	BDL	0.69±0.00	BDL	BDL	BDL
	C21	0.79±0.00	0.56±0.00	BDL	BDL	BDL	BDL	BDL
	C22	BDL	BDL	BDL	BDL	BDL	BDL	0.12±0.00

3.2. PESTICIDE RESIDUES IN FRENCH BEANS SAMPLES

Among the analysed pesticide residues, the following residues were detected in French beans: *Cabendazim, imidacloprid, acetamiprid, Azoxystrobin*, metalaxyl diazinonand chlorpyrifos. Table 2 presents the concentrations of detected pesticides and metabolites in French beans samples.

Table 2: Mean concentrations (±SD) of pesticide residues in French Beans samples (µg/kg).

Site	Sample	Carbendazim	Imidacloprid	Acetamiprid	Azoxystrobin	Metalaxyl	Diazinon	Chlorpyrifos
	C1	0.21±0.00	BDL	0.18±0.01	BDL	BDL	0.14±0.00	BDL
Buuri	C2	0.22±0.00	BDL	0.23±0.00	BDL	BDL	0.12±0.00	0.46±0.00
	C3	0.23±0.00	BDL	0.23±0.00	BDL	BDL	BDL	BDL
	C4	0.23±0.00	BDL	0.2±0.00	0.19±0.00	BDL	BDL	0.34±0.00
	C5	16.00±0.52	BDL	0.12±0.00	1.84±0.08	0.11±0.00	BDL	BDL
	C6	0.92±0.00	BDL	BDL	BDL	BDL	BDL	BDL
	C7	0.31±0.00	BDL	0.1±0.00	0.2±0.00	BDL	BDL	BDL
Imenti North	C8	0.31±0.00	BDL	BDL	0.11±0.00	BDL	0.1±0.00	BDL
	C9	0.29±0.00	BDL	0.13±0.00	0.16±0.00	BDL	0.15±0.00	BDL
	C10	10.11±0.96	21.18±0.96	1.51±0.06	2.49±0.07	BDL	BDL	3.83±0.00
	C11	0.24±0.00	BDL	0.13±0.00	BDL	0.11±0.00	BDL	BDL
	C12	0.32±0.00	BDL	BDL	0.11±0.00	BDL	0.11±0.00	BDL
	C13	0.5±0.00	BDL	2.81±0.05	6.96±0.85	0.13±0.00	0.11±0.01	0.11±0.00
	C14	1.27±0.01	0.85±0.00	2.49±0.06	1.22±0.06	BDL	BDL	0.18±0.00
Imenti South	C15	2.16±0.08	4.3±0.05	0.16±0.00	1.35±0.02	BDL	BDL	0.85±0.00
	C16	1.11±0.00	10.12±1.07	1.56±0.05	3.68±0.01	BDL	BDL	0.22±0.00
	C17	0.3±0.00	10.12±0.36	0.14±0.00	BDL	BDL	BDL	BDL
	C18	0.38±0.00	BDL	BDL	0.1±0.00	BDL	BDL	BDL
	C19	0.33±0.00	BDL	0.2±0.00	0.19±0.00	BDL	0.11±0.00	0.13±0.00
	C20	0.3±0.00	BDL	0.16±0.00	0.21±0.00	BDL	BDL	0.12±0.00
	C21	0.93±0.01	BDL	0.16±0.00	25.76±1.68	BDL	0.15±0.00	0.62±0.00
	C22	0.45±0.00	BDL	0.23±0.00	0.13±0.00	BDL	BDL	BDL

3.3. PESTICIDE RESIDUES IN KALE SAMPLES

Among the analysed pesticide residues, the following residues were detected in kales: a*zoxystrobin*, and diazinon. Others are *Cabendazim, imidacloprid, acetamiprid*, metalaxyl

diazinonand chlorpyrifos that were below detection limit. Table 3 presents the concentrations of detected pesticides and metabolites in kales samples.

Table 3: Mean concentrations (±SD) of pesticide residues in kales samples (µg/kg).

Site	Sample	Carbendazim	Imidacloprid	Acetamiprid	Azoxystrobin	Metalaxyl	Diazinon	Chlorpyrifos
	C1	BDL	BDL	BDL	0.29±0.00	BDL	BDL	BDL
Buuri	C2	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C3	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C4	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C5	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C6	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C7	BDL	BDL	BDL	BDL	BDL	0.13±0.00	BDL
Imenti North	C8	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C9	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C10	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C11	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C12	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C13	BDL	BDL	BDL	BDL	BDL	0.14±0.01	BDL
	C14	BDL	BDL	BDL	BDL	BDL	BDL	BDL
Imenti South	C15	BDL	BDL	BDL	BDL	BDL	0.14±0.00	BDL
	C16	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C17	BDL	BDL	BDL	BDL	BDL	0.12±0.00	BDL
	C18	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C19	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C20	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C21	BDL	BDL	BDL	BDL	BDL	BDL	BDL
	C22	BDL	BDL	BDL	BDL	BDL	BDL	BDL

3.4. MRL COMPLIANCE

All the concentrations of Azoxystrobin, diazinon, Cabendazim, imidacloprid, acetamiprid, metalaxyl diazinon and chlorpyrifos residues in tomatoes, French beans and kales were below their MRL by FAO and WHO [15].

4.0 CONCLUSIONS

Seven pesticide residues were detected, which were Azoxystrobin, diazinon, Cabendazim, imidacloprid, acetamiprid, metalaxyl diazinon and chlorpyrifos. The cooccurrence of pesticide residues in samples was due to various reasons including mixing of pesticides by farmers during application as farmers use more than one pesticide at one time due to resistance of pests. Other reasons could be due to contamination through water, soil, and air. There were no significant variations of the concentrations of pesticide residues among the vegetables suggesting similar contamination sources or patterns. The levels of pesticide residues were below the MRLs set by FAO showing that the vegetables from Meru County are good for consumption. Therefore, it is recommended that effective monitoring of pesticide residues in food items is required.

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