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Effectiveness of Common Household Washing of Tomatoes on the Removal of Pesticide Residues

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Abstract

The effectiveness of common household washing processes of tomatoes on the removal of pesticide residues was investigated in Iringa, Tanzania. Analyses of cleaned-up extracts were carried out using gas chromatography-mass spectrometry (GC-MS). Nine pesticide residues were detected in unwashed and washed samples. The compounds detected were chlorothalonil, pirimiphos-methyl, chlorpyrifos, profenofos, endosulfan sulphate, endosulfan ether, lambda cyhalothrin, cypermethrin and metalaxyl. The concentrations of chlorothalonil, pirimiphos-methyl, chlorpyrifos, profenofos, cypermethrin and lambda cyhalothrin in some unwashed and washed samples exceeded the maximum residue limits (MRLs). Washing reduced the concentrations of chlorothalonil and endosulfan sulphate in tomatoes by 22.2–98.0% (mean = 70%) and 33.3–55.6% (mean = 44.4%), respectively. The effectiveness of washing processes on the removal of pirimiphos methyl, chlorpyrifos and profenofos residues in tomatoes had mean values of 78.1%, 73.2% and 47.4%, respectively. The mean reduction of cypermethrin residues due to washing process was 70.2%, whereas that for lambda cyhalothrin was 56.7%. The effectiveness of washing process on the removal of metalaxyl residues had a mean of 44.9%. The results have shown that household washing removes large amounts of pesticide residues from contaminated crop produce, although large proportions of some compounds remain and can pose health risks to the consumers.

Keywords: pesticide; organophosphorus; pyrethroid; organochlorine; tomato; household washing.

Introduction

Tomatoes are highly cultivated and widely consumed vegetables by people in many countries. Tomatoes are among the most popular fresh-market vegetables. They contain antioxidants, such as ascorbic acid, vitamin E, carotenoids (such as lutein and lycopene), flavonoids, and phenolic acids, which are of great benefits to human health (Schiavon et al. 2013). Tomato is a nutrient-dense super food that offers benefits to a range of bodily systems. Its nutritional contents support skin health, weight loss, heart health, healthful blood pressure, cancer prevention, diabetes prevention, reduction of constipation and protection of the eyes (Ware 2017).

On the other hand, tomatoes are susceptible to pests; they are attacked by a variety of pests, including insects such as fruit borers, and hence pesticides are required in the different stages of cultivation to control pests and diseases that may cause reduction of yields (Gambacorta et al. 2005, Menezes et al. 2006). Farmers use various pesticides, and the common ones are organophosphates and pyrethroids. The pesticides are widely used in tomato production to reduce food loss and thus increase food productivity. However, the presence of pesticide residues in tomatoes may

be harmful to human health. Due to lack of sufficient knowledge, many farmers in developing countries usually apply pesticides in higher dosage than the recommended dosage, and they usually do not observe the safety intervals while harvesting the tomatoes. These are among the causes for high accumulation of pesticide residues in tomatoes which can increase the risks of human exposure to pesticides and can have negative health effects on the consumers (Keikotlhaile et al. 2010, Kariathi et al. 2016).

Processing of crop products before consumption can reduce pesticide residues from the products. The proportions of reduction of pesticides achieved during processing vary depending on the methods used, physicochemical properties of pesticides, and the nature of commodities. Generally, processing methods (e.g. washing, peeling, and blanching) can effectively remove pesticide residues from agricultural products. Investigations on the effects of food processing have revealed that processing generally reduces the levels of pesticide residues in fruits and vegetables (Abou-Arab 1999, Krol et al. 2000, Soliman 2001, Chavarri et al. 2005, Guardia-Rubio et al. 2007, Liang et al. 2012, Bonnechère et al. 2012). However, in some cases, processing actually increases the levels; for example, some processing methods such as drying can increase pesticide residue levels due to concentration effects (Cabras and Angioni 2000, Noh et al. 2012). Other processing methods such as baking, boiling, canning, and juicing, can reduce or increase the levels of pesticide residues (Keikotlhaile et al. 2010).

Many studies have reported pesticide residues in tomatoes. Although the household processing of vegetables such as boiling, frying, roasting and blanching lead to significant reduction of pesticide residues (Chavarri et al. 2004, Chavarri et al. 2005, Radwan et al. 2005), tomatoes are most often consumed without cooking such as in wraps, salads, cold soups, sandwiches and sauces. Thus, it is important to estimate the reduction of residues using the simple washing procedures (Vemuri et al. 2014). Some studies on effects of household processing on pesticide residues in tomatoes have been conducted in several countries (Vemuri et al. 2014, Kwon et al. 2015, Andrade et al. 2015), but there are variations in the methods used and the compounds studied. No previous study had been conducted on this subject in Tanzania. Therefore, the aim of this study was to evaluate the levels of organochlorine, organophosphorus, pyrethroids and xylylalanine pesticide residues in tomatoes by gas chromatography-mass spectrometry (GC-MS) method after washing with water, and laboratory preparations of the samples.

Materials and Methods

Sampling

Tomato samples used in this study were collected from small farms in Iringa Region, Tanzania. Samples of tomatoes were collected randomly from 5 different farms at each sampling site in Kilolo District and Iringa Rural District. The study areas included Mgama, Lulanzi, Ilula and Mazombe. The samples were enveloped in aluminium foil, then placed in polyethylene bags and kept into an ice box for transportation to the laboratory.

Glassware, equipment, solvents and reagents

All glassware used in this study was thoroughly cleaned with tap water using detergents and rinsed with distilled water and then using acetone. This was followed by drying in an oven prior to use. Teflon-lined screw caps were cleaned just as above, except these were soaked in acetone overnight instead of drying in an oven. Purity of all the solvents was checked before use. Solid reagent, anhydrous sodium sulphate was heated at 130 °C for three hours before use to free it from moisture. It was then allowed to cool to room temperature in a desiccator and stored in a stoppered flask. Florisil 60-100 mesh preheated at 300 °C overnight was allowed to cool in a desiccator and stored in a tightly stoppered flask in a desiccator. The solvents and reagents used in this study were of analytical grade with above 99% purity (Thermofisher Scientific, UK).

Reference standards

Certified reference standards of high purity of above 99% (Sigma Aldrich, Germany) were used for identification and quantification of the analytes. The following reference standards were used in this study: chlorothalonil, α-endosulfan, β-endosulfan, endosulfan sulphate, cypermethrin, permethrin, lambda cyhalothrin, profenofos, chlorpyrifos, pirimiphos methyl and metalaxyl. The standards were decided based on information obtained during the preliminary surveys regarding the common pesticides used in the study areas. Working standard solutions were prepared by diluting the stock solutions in cyclohexane and stored in a freezer. The concentrations of working standard solutions ranged from 0.284 to 4.545 µg/mL.

Sample preparations and extraction

The samples were divided into two groups. Each sample in one group was washed with water following the same method commonly used in the study areas. Sub-samples of washed and unwashed fresh tomatoes (about 100 g each) were separately chopped using a clean stainless steel knife and homogenized by grinding using clean mortar and pestle, and replicate aliquots were taken for analysis. Homogenized samples of tomatoes were extracted using the same procedures. For each sample, 20 g were weighed, mixed with dichloromethane (50 mL) in a glass bottle and tightly stoppered with a screw cap. The bottles were placed in an ultrasonic bath for 30 minutes. The supernatant was carefully transferred into an E-flask, the residue was rinsed with 10 mL dichloromethane and the supernatant was combined with the other extract in the E-flask. Anhydrous sodium sulphate (20 g) was added into the E-flask containing the sample in order to absorb any moisture present. The contents in the E-flask were swirled and left for 10 minutes and swirled again until the sodium sulphate floated freely. The extract was filtered through a plug of glass wool into the evaporating flask for concentration. The extract was evaporated under vacuum to about 2 mL using a rotary evaporator at 40 ºC ready for clean-up.

Sample clean-up

The clean-up was performed according to the procedures by Mahugija et al. (2017) using florisil (3.0 g) packed in a glass chromatographic column (10 mm i.d. × 32 cm) topped up with 5–10 cm sodium sulphate. The column was rinsed with 5 mL of cyclohexane, and then the extract (2 mL) was added and eluted with 20 mL of cyclohexane and 10 mL of cyclohexane/acetone mixture (9:1). The eluates were concentrated to 2 mL on a rotary evaporator ready for GC-MS analysis.

Blanks, recovery tests and method detection limits

Samples of tomatoes not treated with pesticides were used for blank experiments. These samples were collected from untreated garden in a greenhouse. Each sample was prepared, extracted and cleaned concurrently and using the same procedures as for test samples. Recovery tests were conducted using known volumes of the mixtures of pesticides standard solutions that were spiked to 20 g of each blank sample. Thereafter, the samples were extracted and analysed using the same procedures as the ordinary samples to determine the recovery (Kocourek 2012). The recoveries between 70 and 120% are normally acceptable. Any values out of this range are recommended to correct the results to recovery (SANCO 2013, EC 2017), otherwise the sample-set results are thrown out. The method detection limit for each pesticide or metabolite identified was determined using the concentration of analyte which induced signals three times higher than the background noise level (Kocourek 2012).

Analysis, identification and quantification

The analyses were performed at the University of Dar es Salaam using a Shimadzu gas chromatograph coupled to a mass spectrometer (GC-MS QP2010 Ultra). The column used was Rtx-5MS (30 m × 0.25 µm). The temperature programme was 90 °C held for 2 mins then increased at 5 °C/min to 260 °C

and held for 5 mins. Splitless injection mode of 1 mL was carried out at 250 °C with a purge flow of 3 mL/min. The carrier gas used was helium with a flow rate of 2.17 mL/min and the internal pressure was 150 kPa. The interface temperature was 300 °C. The mass spectrometer ionization mode was electron impact (EI) set at 0.2 volts with ion source temperature of 230 °C and in full scan mode in the range of 45-500 *m/z*. The analytes were identified by comparing the retention times and mass spectra to those of reference standards run in parallel and at the same conditions with the samples. The analytes were also identified using the NIST 11 mass spectral library (US National Institute of Standards and Technology). Quantification of analytes was done using peak heights. The mass fragment with the highest intensity of the molecular ion was used for quantification.

For quantitative analysis of the analytes, the calibration curves were established from the measured peak heights of each standard. The calibration curves were constructed by running series of standard solutions of each pesticide standard prepared from 9.091 µg/mL stock solutions into serial dilutions of 0.284, 0.568, 1.136, 2.273 and 4.545 µg/mL. The best fit lines of peak heights against their respective concentrations were drawn through the data points. Each compound showed good linearity with correlation coefficients (R^2) in the range of 0.969–0.9812. The concentrations of the compounds in sample extracts were determined using the equations of the calibration curves. The concentration of each pesticide residue in the samples was obtained by multiplying the concentration obtained from the calibration curve with the final volume of the extract per mass of the sample extracted.

Statistical analysis

Statistical analysis was performed using GraphPad Instat software (GraphPad Software, Inc., San Diego US) and Maxstat Lite Version 3.60 Build L 24032015 software. The mean concentrations of the pesticide residues for the unwashed and washed tomato samples were compared by using paired samples *t*-test.

Results and Discussion

Pesticide residues in tomato samples

A total of nine pesticides out of eleven pesticide residues analysed were detected in unwashed and washed tomato samples, out of which three were organochlorine pesticide residues, three were organophosphorus pesticides, two were pyrethroids and one was xylylalanine pesticide (metalaxyl).

Organochlorine pesticide residues

Concentrations of organochlorine pesticide residues in unwashed tomatoes

Organochlorine pesticide residues and metabolites detected in unwashed tomato samples included chlorothalonil, endosulfan sulphate and endosulfan ether. Their concentrations are presented in Table 1, except for endosulfan ether which was identified using the mass spectral library but it was not quantified due to absence of its reference standard. The detection of metabolites of endosulfan isomers, i.e., endosulfan sulphate and endosulfan ether, suggested that the contamination was due to old application of endosulfan or environmental contamination (ATSDR 2015). The compounds α- endosulfan and β-endosulfan were not detected in all the samples. Among the organochlorine pesticides detected in unwashed tomato samples, chlorothalonil was the most frequent pesticide (100%) with the highest concentration of 6.15 mg/kg and the lowest concentrations of 0.17 mg/kg. High concentrations of chlorothalonil were found in tomatoes indicating fresh use. This may be attributed to its high and frequent application as a means of controlling fungal diseases which are the most damaging pests in the areas. The concentrations of endosulfan sulphate were up to 0.33 mg/kg with detection frequency of 20%. The detection of endosulfan sulphate and endosulfan ether implied that oxidation and hydrolysis of endosulfan isomers residues were the dominant degradation pathways (ATSDR 2015, Deng et al. 2016).

Table 1: Concentrations of organochlorine pesticide residues in tomato samples (mg/kg)

Site	Sample	Category	Chlorothalonil	α-endosulfan	β-endosulfan	Endosulfan sulphate
Mgama	M1U	Unwashed	5.11	Bdl	Bdl	Bdl
	M1W	Washed	2.82	Bdl	Bdl	Bdl
	M2U	Unwashed	2.05	Bdl	Bdl	0.03
	M2W	Washed	0.64	Bdl	Bdl	0.02
	M3U	Unwashed	5.67	Bdl	Bdl	Bdl
	M3W	Washed	4.41	Bdl	Bdl	Bdl
	M4U	Unwashed	0.33	Bdl	Bdl	Bdl
	M4W	Washed	0.01	Bdl	Bdl	Bdl
	M5U	Unwashed	5.89	Bdl	Bdl	Bdl
	M5W	Washed	3.86	Bdl	Bdl	Bdl
Lulanzi	L1U	Unwashed	6.15	Bdl	Bdl	Bdl
	L1W	Washed	1.18	Bdl	Bdl	Bdl
	L2U	Unwashed	1.01	Bdl	Bdl	Bdl
	L2W	Washed	0.33	Bdl	Bdl	Bdl
	L3U	Unwashed	2.65	Bdl	Bdl	0.09
	L3W	Washed	0.10	Bdl	Bdl	0.04
	L4U	Unwashed	2.74	Bdl	Bdl	Bdl
	L4W	Washed	0.62	Bdl	Bdl	Bdl
	L5U	Unwashed	2.94	Bdl	Bdl	0.18
	L5W	Washed	0.62	Bdl	Bdl	0.08
Ilula	I1U	Unwashed	1.76	Bdl	Bdl	Bdl
	I1W	Washed	0.57	Bdl	Bdl	Bdl
	I2U	Unwashed	1.84	Bdl	Bdl	0.33
	I2W	Washed	1.11	Bdl	Bdl	0.22
	I3U	Unwashed	0.51	Bdl	Bdl	Bdl
	I3W	Washed	0.35	Bdl	Bdl	Bdl
	I4U	Unwashed	1.10	Bdl	Bdl	Bdl
	I4W	Washed	0.08	Bdl	Bdl	Bdl
	I5U	Unwashed	1.79	Bdl	Bdl	Bdl
	I5W	Washed	0.49	Bdl	Bdl	Bdl
Mazombe	MZ1U	Unwashed	6.15	Bdl	Bdl	Bdl
	MZ1W	Washed	2.66	Bdl	Bdl	Bdl
	MZ2U	Unwashed	0.34	Bdl	Bdl	Bdl
	MZ2W	Washed	0.01	Bdl	Bdl	Bdl
	MZ3U	Unwashed	0.50	Bdl	Bdl	Bdl
	MZ3W	Washed	0.01	Bdl	Bdl	Bdl
	MZ4U	Unwashed	0.69	Bdl	Bdl	Bdl
	MZ4W	Washed	0.14	Bdl	Bdl	Bdl
	MZ5U	Unwashed	0.17	Bdl	Bdl	Bdl
	MZ5W	Washed	0.01	Bdl	Bdl	Bdl
Detection frequency		Unwashed	100	0	0	20
(%)		Washed	100	0	0	20

Bdl: Below detection limit (not detected).

These findings revealed reduced or no use of endosulfan as compared to other studies conducted earlier in different fields in Tanzania. For example, a study in tomatoes from four major markets in Dar es Salaam found higher concentrations of α- and β-endosulfan of up to 0.33 ± 20 mg/kg and 0.12 ± 6 mg/kg, respectively (Mahugija et al. 2017). Another study conducted in tomato samples from Kilolo District observed maximum concentrations of 0.00283 mg/kg for α-endosulfan and 0.00041 mg/kg for β-endosulfan (Mtashobya and Nyambo 2014). As well, previous studies in some fields in Tanzania found higher concentrations of endosulfan in tomato samples of up to 0.0006 mg/kg (Mtashobya 2010) and 4.15 mg/kg (Meela 2009). On the other hand, the field studies in Tanzania did not analyse chlorothalonil residues in tomato samples. The observations from this work agree with the findings of the work carried out by Salghi et al. (2012) in terms of compliance to MRL of 5 mg/kg set by FAO/WHO. However, the mean concentrations obtained in this study were higher than those obtained by Salghi et al. (2012) who reported 0.001 to 0.25 mg/kg residue levels for chlorothalonil.

Concentrations of organochlorine pesticide residues in washed tomatoes

The organochlorine pesticide residues detected in washed tomato samples included chlorothalonil, endosulfan ether and endosulfan sulphate (Table 1). Their frequencies of detection were 100% for chlorothalonil and 20% for endosulfan sulphate. The concentrations of chlorothalonil ranged from 0.01 to 4.41 mg/kg. The concentrations of endosulfan sulphate detected in samples were up to 0.22 mg/kg. All the concentrations of chlorothalonil in washed tomatoes did not exceed the FAO/WHO MRL of 5 mg/kg. Also the concentrations of endosulfan sulphate in washed tomatoes were all below the MRL of 0.5 mg/kg. Other organochlorine pesticide residues analysed were α-endosulfan and β-endosulfan and were not detected in all the washed samples.

The reduction of chlorothalonil and endosulfan sulphate pesticide residues due to washing of tomatoes varied between 22.2% and 98.0% (mean = 70%) and 33.3% to 55.6% (mean = 44.4%), respectively. The results indicated the increased reductions for chlorothalonil than for endosulfan sulphate. The reason behind may be because chlorothalonil has high solubility in water (0.6-1.2 mg/l) and lower octanol-water partition coefficient (log K_{ow} = 2.94) (IPCS 1996) than endosulfan sulphate which has 0.22 mg/L water solubility and log K_{ow} = 3.66 (ATSDR 2015). Holland et al. (1994) supported the idea that pesticides with high water solubility are readily removed by washing whilst Kong et al. (2012) supported the idea that pesticides with low octanol-water partition coefficient are easily washed out. The results concur to those obtained by Kwon et al. (2015) who reported up to 92% removal of chlorothalonil residues by hand washing in tap water. Another study conducted by Uysal-Pala and Bilisli (2006) reported 30.62% reduction of endosulfan sulphate residue levels on tomatoes by washing.

Organophosphorus pesticide residues

Concentrations of organophosphorus pesticide residues in unwashed tomatoes

Pirimiphos methyl, chlorpyrifos and profenofos residues were detected in unwashed tomato samples (Table 2). Pirimiphos methyl was detected in 85% of all samples. The highest concentration of pirimiphos methyl was 1.53 mg/kg. Another organophosphorus pesticide residue detected was chlorpyrifos with the detection frequency of 90% of all samples. The highest concentration of chlorpyrifos was 9.22 mg/kg. Profenofos was detected in 90% of the samples with the maximum concentration of 18.49 mg/kg.

Table 2: Concentrations of organophosphorus pesticide residues in unwashed and washed tomato samples (mg/kg)

Site	Sample	Category	Pirimiphos methyl	Chlorpyrifos	Profenofos
Mgama	M1U	Unwashed	Bdl	0.01	9.36
	M1W	Washed	Bdl	Bdl	8.21
	M2U	Unwashed	Bdl	7.77	12.36
	M2W	Washed	Bdl	7.06	4.59
	M3U	Unwashed	0.06	8.11	14.53
	M3W	Washed	Bdl	1.47	10.38
	M4U	Unwashed	0.02	6.38	6.96
	M4W	Washed	Bdl	3.08	4.40
	M5U	Unwashed	0.25	0.01	14.74
	M5W	Washed	0.03	Bdl	7.33
Lulanzi	L1U	Unwashed	0.42	8.75	13.09
	L1W	Washed	Bdl	3.08	7.87
	L2U	Unwashed	0.26	8.38	15.95
	L2W	Washed	0.06	1.03	8.43
	L3U	Unwashed	0.05	2.58	15.29
	L3W	Washed	0.05	0.09	7.58
	L4U	Unwashed	1.53	Bdl	2.13
	L4W	Washed	0.15	Bdl	0.22
	L5U	Unwashed	0.07	9.22	12.02
	L5W	Washed	0.02	0.90	1.50
Ilula	I1U	Unwashed	0.31	7.85	15.66
	I1W	Washed	0.08	2.60	14.71
	I2U	Unwashed	0.54	8.89	18.42
	I2W	Washed	0.28	4.83	0.64
	I3U	Unwashed	0.30	8.86	Bdl
	I3W	Washed	0.14	2.65	Bdl
	I4U	Unwashed	0.60	0.43	18.49
	I4W	Washed	0.36	0.07	9.46
	I5U	Unwashed	0.47	3.02	16.14
	I5W	Washed	0.23	0.90	4.09
Mazombe	MZ1U	Unwashed	0.02	8.42	13.35
	MZ1W	Washed	Bdl	4.83	8.43
	MZ2U	Unwashed	Bdl	8.37	Bdl
	MZ2W	Washed	Bdl	3.51	Bdl
	MZ3U	Unwashed	0.06	0.23	11.44
	MZ3W	Washed	0.02	Bdl	7.34
	MZ4U	Unwashed	0.01	0.50	10.67
	MZ4W	Washed	Bdl	0.01	8.86
	MZ5U	Unwashed	0.09	Bdl	15.47
	MZ5W	Washed	0.01	Bdl	10.57
Detection frequency		Unwashed	85	90	90
(%)		Washed	60	75	90

Although, the mean concentrations of pirimiphos methyl for each sampling site did not exceed the MRL of 0.5 mg/kg set by FAO/WHO, one sample was 1.2 times greater than the MRL. The concentrations of chlorpyrifos in 65% of the samples were 5.16 to 18.44 times greater than the MRL of 0.5 mg/kg. On the other hand, profenofos presented concentrations in 90% of the samples that were 1.1 to 9.25 times greater than the MRL of 2 mg/kg for tomatoes (FAO/WHO 2013). The high concentrations of chlorpyrifos and profenofos residues found in this study could be caused by application of inappropriate dosage of pesticides by the farmers, non-adherence to safe waiting period and mixing of pesticides (Busindi 2012). These observations thus, indicate potential risks of pesticides exposures and concerns for public health to the tomato consumers. These findings are similar to those observed in a study conducted on tomatoes from Meru District (Kariathi et al. 2016) and Dar es Salaam markets (Mahugija et al. 2017) where chlorpyrifos was detected in high concentrations of up to 15.056 and 4.68 times greater than the MRL, respectively. The levels of profenofos obtained in this study were comparable to the levels found in tomatoes grown in West Sumatra, Indonesia which were 8.03 mg/kg (Alen et al. 2016). No previous study had reported on the levels of profenofos residues in raw tomatoes in Tanzania.

Concentrations of organophosphorus pesticide residues in washed tomatoes

The types and concentrations of organophosphorus pesticide residues detected in washed tomato samples are presented in Table 2. The detection frequencies of pirimiphos methyl, chlorpyrifos and profenofos were 60%, 75% and 90%, respectively. The concentrations of pirimiphos methyl and chlorpyrifos were up to 0.36 and 7.06 mg/kg, respectively. As for unwashed samples, profenofos was the most frequent compound with highest concentration of 14.714 mg/kg. The concentrations of profenofos in most samples were far above the MRL of 2 mg/kg (FAO/WHO 2013). The concentrations of profenofos in 75% were 2.05 to 7.4 times greater than the MRL. This situation presents potential risks to consumers especially when freshly consumed.

The results from this study revealed that the organophosphorus pesticide residues were predominant in tomatoes, and that most pesticide residues reside on the outer surfaces of the crops. The effectiveness of washing processes on the removal of pirimiphos methyl, chlorpyrifos and profenofos pesticide residues in tomatoes ranged 40-100% (mean 78.1%), 9.1-100% (mean 73.2%) and 6.1-96.5% (mean 47.4%), respectively. These findings are comparable to those reported by Alen et al. (2016) who showed removal of 56% of profenofos and 76.93% of chlorpyrifos residues in tomatoes due to washing. Another study conducted by Abou-Arab (1999) showed as well that washing by tap water, sodium chloride and acetic acid removed 22.7%, 86.0% and 82.4% of profenofos residues and 16.2%, 93.7% and 91.4% of pirimiphos methyl residues on tomatoes, respectively. Assessment of the obtained results indicates the important role of washing on the removal of surface pesticide residues before using tomatoes. Despite the high percentage reductions, the levels of pesticide residues may still be above the MRLs as observed in the present study. This partly depends on the severity of the contamination and treatments.

Pyrethroids and xylylalanine pesticide residues

Concentrations of pyrethroids and metalaxyl pesticide residues in unwashed tomatoes

The pyrethroids residues analysed in this study included lambda cyhalothrin, permethrin and cypermethrin (Table 3). While 70% and 50% of the samples were found contaminated with lambda cyhalothrin and cypermethrin, respectively, permethrin was not detected in any of the samples. The concentrations of cypermethrin in 20% of the samples exceeded the FAO/WHO MRL of 0.5 mg/kg by 3.1 to 17.48 times. This situation signifies the risks to consumers associated with these pesticides such as development of various cancers,

neurological, genotoxic effects and even death as reported by toxicological and epidemiological studies (ATSDR 2003). The results of this study are similar to those of a previous investigation carried out in Bangladesh in which cypermethrin along with other pesticides exceeded the MRL in 7% of the tomato samples (Chowdhury et al. 2013).

Lambda cyhalothrin was another pyrethroid residue found in the tomato samples, with the highest concentration of 0.9 mg/kg. Among the contaminated samples, 100% were found contaminated with lambda cyhalothrin with the concentrations exceeding the FAO/WHO MRL of 0.05 mg/kg by 1.6 to 18 times. The findings revealed that lambda cyhalothrin was used in all the studied sites and may be the farmers used much more than the prescribed dose as observed in other areas (Ngowi et al. 2007, Mdegela et al. 2013). The situation could have been caused by frequent applications of this compound and not observing the waiting periods before harvesting as observed by Busindi (2012). A similar study carried out on analysis of some pesticide residues in tomatoes collected from different market places in Kumas and Cape coast regions in Ghana, showed that the levels exceeded the MRL in three out of four samples (Essumang et al. 2008). The highest concentration of lambda cyhalothrin reported was 1.45 mg/kg which was 29% times greater than the MRL. This implies that there is a need of regular monitoring of these pesticides in foods to prevent health risks associated with their exposure.

Metalaxyl pesticide residues were also detected in unwashed tomato samples as shown in Table 3. It was found that 95% of the samples were contaminated with metalaxyl residues at concentrations up to 0.65 mg/kg. The concentration of metalaxyl in only one sample exceeded the FAO/WHO MRL of 0.5 mg/kg. Comparing the results obtained in this work with those found in tomato samples from a study carried by Lozowicka et al. (2015) who found the concentrations of metalaxyl in a range of 0.05-0.15 mg/kg, it was observed that the metalaxyl residues in tomatoes from Iringa presented higher levels. On the other hand, Iringa tomato samples are less contaminated with metalaxyl as compared to the results obtained in the study conducted in Meru District where the concentration of ridomil (a mixture of mancozeb and metalaxyl) were 2854.729 mg/kg far above the MRL (Kariathi et al. 2016).

Concentrations of pyrethroids and xylylalanine pesticide residues in washed tomatoes

The concentrations of pyrethroids and xylylalanine (metalaxyl) pesticide residues detected in washed tomato samples are presented in Table 3. Among the three pyrethroids analysed, only cypermethrin and lambda cyhalothrin were detected in washed tomatoes. The detection frequency of cypermethrin was 35% and the concentrations varied up to 3.26 mg/kg. The concentrations of cypermethrin in 20% of the samples exceeded the MRL of 0.5 mg/kg (FAO/WHO 2013) by 1.5 to 6.52 times. The detection frequency of lambda cyhalothrin was 50% with maximum concentration of 0.32 mg/kg. The concentrations of lambda cyhalothrin in 45% of the samples were 1.2 to 6.4 times greater than the FAO/WHO MRL of 0.05 mg/kg. Reduction of cypermethrin pesticide residues due to washing process ranged between 36.99% and 100% (mean 70.2%), whereas for lambda cyhalothrin, the reduction ranged between 0% and 100% (mean 56.7%). The high reduction of these compounds residues could be because they have non-systemic characteristics which make them amenable to simple washing processes. Their differences in percentage reduction may be explained through the analysis of relationships between their physicochemical properties such as water solubility and octanol-water partition coefficients (Holland et al. 1994), which are 0.004 and 5.5 for cypermethrin and 0.005 and 6.9 for lambda cyhalothrin, respectively.

Table 3: Levels of pyrethroids and xylylalanine pesticide residues in tomato samples (mg/kg)

Site	Sample	Category	Permethrin	Cypermethrin	λ-cyhalothrin	Metalaxyl
Mgama	M1U	Unwashed	Bdl	Bdl	0.32	0.12
	M1W	Washed	Bdl	Bdl	0.25	0.10
	M2U	Unwashed	Bdl	Bdl	0.29	0.26
	M2W	Washed	Bdl	Bdl	0.17	0.14
	M3U	Unwashed	Bdl	Bdl	0.21	0.16
	M3W	Washed	Bdl	Bdl	0.07	0.10
	M4U	Unwashed	Bdl	2.92	0.14	0.04
	M4W	Washed	Bdl	1.84	0.05	0.04
	M5U	Unwashed	Bdl	8.74	0.28	0.23
	M5W	Washed	Bdl	3.26	Bdl	0.18
Lulanzi	L1U	Unwashed	Bdl	0.13	0.08	0.65
	L1W	Washed	Bdl	0.06	0.08	0.63
	L2U	Unwashed	Bdl	0.04	Bdl	0.14
	L2W	Washed	Bdl	Bdl	Bdl	0.03
	L3U	Unwashed	Bdl	Bdl	Bdl	0.27
	L3W	Washed	Bdl	Bdl	Bdl	0.23
	L4U	Unwashed	Bdl	0.32	Bdl	0.23
	L4W	Washed	Bdl	0.09	Bdl	0.06
	L5U	Unwashed	Bdl	3.22	0.16	0.24
	L5W	Washed	Bdl	1.84	0.14	0.09
Ilula	I1U	Unwashed	Bdl	Bdl	Bdl	0.23
	I1W	Washed	Bdl	Bdl	Bdl	0.05
	I2U	Unwashed	Bdl	Bdl	0.25	0.11
	I2W	Washed	Bdl	Bdl	0.15	0.09
	I3U	Unwashed	Bdl	0.10	Bdl	0.04
	I3W	Washed	Bdl	Bdl	Bdl	0.01
	I4U	Unwashed	Bdl	0.48	Bdl	0.16
	I4W	Washed	Bdl	0.09	Bdl	0.12
	I5U	Unwashed	Bdl	Bdl	0.13	0.21
	I5W	Washed	Bdl	Bdl	0.10	0.10
Mazombe	MZ1U	Unwashed	Bdl	Bdl	0.90	0.07
	MZ1W	Washed	Bdl	Bdl	0.32	0.03
	MZ2U	Unwashed	Bdl	Bdl	0.10	0.02
	MZ2W	Washed	Bdl	Bdl	Bdl	Bdl
	MZ3U	Unwashed	Bdl	Bdl	0.15	0.07
	MZ3W	Washed	Bdl	Bdl	0.06	0.06
	MZ4U	Unwashed	Bdl	1.55	0.19	0.09
	MZ4W	Washed	Bdl	0.74	Bdl	0.02
	MZ5U	Unwashed	Bdl	0.09	0.10	Bdl
	MZ5W	Washed	Bdl	Bdl	Bdl	Bdl
Detection frequency		Unwashed	0	50	70	95
(%)		Washed	0	35	50	90

Bdl = Below detection limit.

The results obtained indicated that the amounts of pesticides removed due to washing do not correlate with the water solubility. The levels of lambda cyhalothrin, which is more soluble than cypermethrin in water, were reduced the least, and this observation is in accordance to the results obtained by Krol et al. (2000). The findings from this study are also comparable with those an earlier study that showed residues of six pesticides on olives decreased after washing with no correlation to water solubility of the pesticides (Cabras et al. 1997). In that study, dimethoate which is the pesticide with the highest water solubility decreased by 15% while the remaining five pesticides decreased between 29% and 39% (Cabras et al. 1997). The more reduction of cypermethrin residues than lambda cyhalothrin residues could be due to its lower octanol-water partition coefficient. This observation is supported by a number of researches that have reported that pesticides with lower octanol-water partition coefficients are more readily removed by washing because pesticides with high octanol-water partition coefficients are quickly absorbed and strongly retained by waxes on the tomato skin, and thus, not easily removed by washing (Kong et al. 2012, Zhao et al. 2014). On the other hand, metalaxyl was the only xylylalanine pesticide residue analysed in this study. Metalaxyl was detected in 55% of all the samples. The concentrations of metalaxyl were up to 0.63 mg/kg. Residues of metalaxyl were the most frequently encountered in samples from almost all the sites, indicating that the pesticide was frequently used or it was mixed with other types of pesticides. The concentration of metalaxyl in one washed tomato sample exceeded the MRL of 0.5 mg/kg (FAO/WHO 2013). The effectiveness of washing process on the removal of metalaxyl residues ranged between 0% and 100% (mean 44.9%). Despite the lower octanol-water partition coefficient and higher solubility in water, the mean losses of metalaxyl after washing process (44.9%) were lower than that of the pyrethroids cypermethrin (70.2%) and lambda cyhalothrin (56.7%). Such a decreased reduction may be possible due to the systemic mode of action of metalaxyl that makes it penetrate to the cuticle of the fruit, thus making it not amenable to simple washing. It is also possible that because the skin surface of tomatoes is waxy, some of the residues may have been adsorbed, thus it would not allow solubilisation with water. These findings are consistent to the findings previously obtained by Cabras et al. (1997), Kong et al. (2012), Lozowicka et al. (2015) and Lozowicka et al. (2016). Generally, they reported that the rinsability of pesticides are not always correlated with their physicochemical properties such as water solubility and octanol-water coefficients, but different modes of action may influence changes in the levels of pesticide residues.

Comparison of the levels of pesticide residues between unwashed and washed tomatoes

The results showed that there were variations in the concentrations of pesticide residues between the unwashed and washed samples. Generally the concentrations of the pesticide residues in unwashed samples were considerably higher than those detected in washed samples. Statistical analysis using the unpaired samples *t*-test showed that there were significant differences in the mean concentrations of chlorothalonil (t = 2.601 at 38 degrees of freedom (*df*) and p = 0.0132), chlorpyrifos (t = 3.091 at 38 *df* and p = 0.0037), profenofos (t = 3.597 at 38 *df* and p = 0.0009) and pirimiphos methyl (t = 2.168 at 38 *df* and p = 0.0365) between unwashed and washed tomato samples. These results indicate the significant reductions of the named pesticide residues due to washing. Unlikely, although the mean concentrations of endosulfan sulphate were higher in unwashed tomato samples than in washed samples, statistically there were no significant differences between the two sample types (t = 0.6190 at 38 *df* and p = 0.5396) indicating that washing process did not significantly reduce the contaminant.

Statistical analysis using unpaired *t*-test showed that there were no significant

differences in the mean concentrations of cypermethrin (t = 0.9549 at 38 *df* and p = 0.3456) and lambda cyhalothrin (t = 1.909 at 38 *df* and p = 0.0638) between unwashed and washed tomato samples. This indicated the inefficiency of washing process on the removal of synthetic pyrethroids residues on tomatoes due to strong interactions of cypermethrin and lambda cyhalothrin molecules with the waxy layer of the tomatoes skin as affirmed by Holland et al. (1994). On the other hand, there were no significant differences in the mean concentrations of metalaxyl between unwashed and washed tomato samples (t = 1.424 at 38 *df* and p = 0.1627) indicating that metalaxyl residue levels were not significantly reduced by washing. This is partly due to the systemic mode of action of metalaxyl which makes it penetrate into the inner parts of tomato fruits, hence not readily available for removal by simple washing. These results indicated that, although all the pesticide residues detected in the unwashed samples still persisted in the washed samples, but most of the contaminants were reduced (Figure 1). The findings revealed the important role of washing procedure on the removal of pesticide residues before using tomatoes. This is be due to the fact that most of the pesticides, particularly non-systemic ones, have a tendency to reside on the surface of vegetables, and therefore, they can simply be removed by mechanical washing (Krol et al. 2000). These observations concur with numerous studies that have examined the effects of washing agricultural produce on the removal of pesticide residues as a preliminary step in household and industrial crop processing (Holland et al. 1994, Abou-Arab 1999, Krol et al. 2000, Chavarri et al. 2005, Uysal-Pala and Bilisli 2006, Rani et al. 2013, Kwon et al. 2015, Reiler et al. 2015). They reported that washing operations may entirely or significantly remove pesticide residues contained in harvested crop. However, the effectiveness of washing in removing pesticide residues depends on the physical and chemical properties of the pesticide, age of the residue, location of the residue, the temperature of the washing water and type of wash (Holland et al. 1994, Abou-Arab 1999).

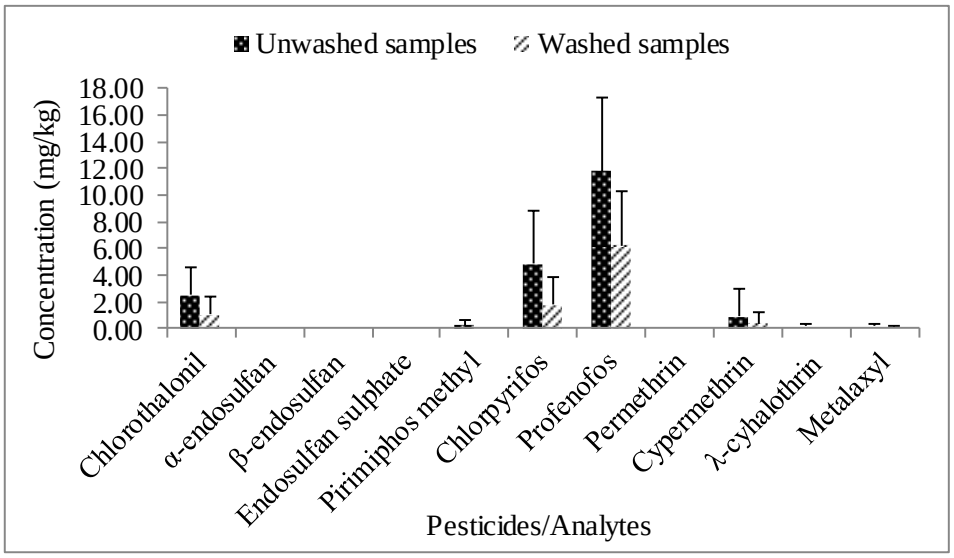

Figure 1: Overall distributions of pesticide residues in unwashed and washed tomato samples. Data are expressed as mean values and error bars indicate standard deviations.

Conclusions

In the present study, all the washed tomato samples showed significantly reduced amounts to no pesticide residues. The mean losses (reductions) of the detected residues due to washing were 70% for chlorothalonil, 44.4% for endosulfan sulphate, 78.1% for pirimiphos methyl, 73.2% for chlorpyrifos, 47.4% for profenofos, 70.2% for cypermethrin, 56.7% for lambda cyhalothrin and 44.9% for metalaxyl. From the results obtained in this study, it can be concluded that washing play an important role in the reduction of pesticide residues from contaminated crop produce. However, the metabolites formed may be more toxic than the parent compounds and the levels of the residues may be higher than the MRLs and hence pose health risks to the consumers.

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