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Assessment of Pesticide Residues in Tomatoes and Watermelons (Fruits) from Markets in Dar es Salaam, Tanzania

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ABSTRACT: This study investigated the levels of pesticide residues in selected fruits from major markets in Dar es Salaam city. Samples of tomatoes and watermelons were analysed for eighteen organochlorine, organophosphorus and pyrethroid 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 95.8% of the samples. The compounds detected included chlorpyrifos, α-endosulfan, β-endosulfan and cypermethrin and their highest concentrations were 3810 ± 50, 370 ± 20, 120 ± 6 and 50 ± 4 ng/g, respectively. Others were *p,p'*-DDD, *o,p'*-DDD, *p,p'*-DDE and α-HCH with highest concentrations varying from 1 ± 0.5 to 20 ± 1.2 ng/g. There were no significant variations in concentrations of the pesticide residues between the fruits and among the sampling sites, indicating similarities in contamination patterns. The concentrations of the contaminants were above the maximum residue limits (MRLs) in 41.7% to 50% of the tomatoes and watermelons indicating risks and concerns for public health. The Tanzanian agrochemicals and food regulatory agencies (e.g. TPRI, TFDA and TBS) and the government in general should ensure strict applications of laws that regulate pesticides in the country and develop effective educational programmes for farmers to apply good agricultural practices such as reducing the use of pesticides, applying appropriate pesticides and doses, and restrict the spray before harvesting. The consumers should thoroughly wash or process the fruits to reduce the levels. © JASEM

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Pesticides are usually used in production of fruits (e.g. tomatoes and watermelons) because of their susceptibility to pests and diseases. Pesticides find their ways into the organisms through food, water and air. However, exposure to pesticide residues through the food is assumed to be five orders of magnitude higher than other exposure routes, such as air and water (Bempah et al., 2011). Fruits are normally eaten either fresh or semi-processed, which suggests that they may contain higher levels of pesticide residues compared to other food types of plant origins which are processed or cooked. Fruits containing residues of pesticides above the maximum residue limits may pose health hazards to the consumers (Sohair et al., 2013).

The amounts of pesticides used in Tanzania have been increasing annually. However, most farmers lack awareness regarding proper use of pesticides (Ngowi et al., 2007). Consequently, cases of indiscriminate use of pesticides and non-adherence to good agricultural practices are very common. For example, some farmers spray the fields in the afternoon and pick the fruits early in the next morning for selling in the local markets. These observations suggest that the fruits sold in the markets may have serious pesticides contamination. To the best of our knowledge, no study had been undertaken to assess pesticide residues in fruits in markets in Tanzania. The aim of this study was to investigate the levels and status of pesticide residues in selected favourite fruits (tomatoes and watermelons).

MATERIALS AND METHODS

Sampling: Fresh tomato (*Lycopersicon esculenta*) and watermelon (*Citrullus lanatus*) samples were collected from four major markets in Dar es Salaam city located at Mwananyamala, Temeke, Kariakoo and Buguruni. These markets are known for their massive sales of fruits that come from different areas of the country where pesticides are widely used. The samples were collected in January to February 2014, separately wrapped in aluminium foil, transported to the laboratory and kept in a refrigerator until extraction, which was conducted within 24 hours after sampling.

Sample extraction and clean-up: The sample was minced using a stainless steel knife and homogenized. The homogenized sample (20 g) was extracted with acetone (30 mL) by sonication in ultrasonic bath for 30 min and then with dichloromethane: cyclohexane (1:1, 30 mL) sonicated for 20 min. The extract was filtered through glass wool, dried with anhydrous sodium sulphate, rinsed

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with dichloromethane: cyclohexane (1:1, 5 mL) and concentrated in a rotary evaporator at 40 ℃ to 2 mL. Clean-up of extracts was conducted using activated florisil (3 g) packed in a glass column (10 mm i.d. x 32 cm) and anhydrous sodium sulphate (5-10 cm) added on top. After rinsing the column with cyclohexane (5 mL), the extract (2 mL) was eluted with cyclohexane (20 mL) and cyclohexane: acetone (9:1, 10 mL), concentrated in a rotary evaporator and made up to 2 mL in cyclohexane: acetone (9:1).

Analytical quality assurance: All the chemicals (solvents, reagents and pesticides standards) were of analytical grade and high purity (above 95%). The glassware and tools were thoroughly cleaned with detergent and water and rinsed with distilled water and acetone. The calibration standards were stored in a freezer. Matrix and procedural blanks were analysed in every batch. Recovery (accuracy) tests involved spiking the standards into the matrix blank samples (n = 8). The blank and recovery samples were processed and analysed using the same procedures as for the samples. Detection limits of the analytes were based on signals that were 3 times higher than the noise level (EC, 2015). No significant levels of contaminants were detected in the blank samples. The percentage recoveries of the analytes ranged from 72.4% to 112% with relative standard deviations of <15%; they were suitable (EC, 2015). The detection limits ranged from 0.1 to 0.6 ng/g.

Analysis, identification, quantification and statistical analysis: The analyses were performed at Chemistry Department, University of Dar es Salaam using a GC-MS equipped with an autosampler, capillary column (Rtx-5MS of 30 m x 0.25 mm id x 0.25 µm film) and MSD. The temperature programme was: 90 ℃ held for 2 min, then increased at 5 ℃/min to 260 ℃ and held for 5 min. Splitless injection of 1 µL was carried out at 250 ℃ injector temperature with a purge flow of 3 mL/min. The carrier gas was helium, with flow rate of 2.17 mL/min and the pressure was 150 kPa. The interface temperature was 300 ℃. The mass spectrometer ionization mode was electron impact (EI) with ion source temperature of 230 ℃ and in full scan mode in the range of 45-500 *m/z*. Standards were analysed at the beginning on each day of analysis. The compounds analysed were 14 organochlorines (aldrin, dieldrin, α-endosulfan, β-endosulfan, *p,p'*-DDT, *o,p'*-DDT, *p,p'*-DDD, *o,p'*-DDD, *o,p'*-DDE, *p,p'*-DDE, α-HCH, β-HCH, γ-HCH and δ-HCH), 3 organophosphorus pesticides (chlorpyrifos, fenitrothion and pirimiphos methyl) and 1 pyrethroid (cypermethrin). The compounds were identified by comparing their retention times and mass spectra in samples to those of standards and by using the NIST 11 mass spectral library. Quantification was done using peak heights and the calibration standards with concentrations of 0.5-2 µg/mL. The mass fragment with the highest intensity was used for quantification. Statistical analysis of the data to test for significance of variations was performed using ANOVA (Analysis of Variance) and *t*-test (Motulsky, 1998).

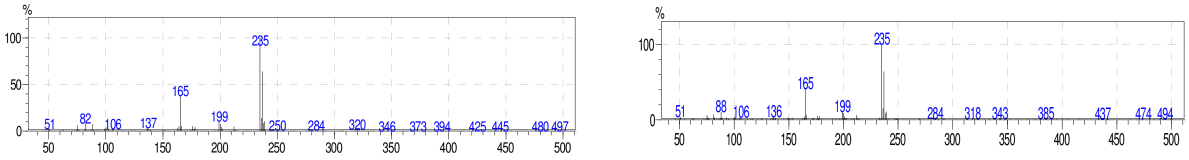
RESULTS AND DISCUSSION

The retention times of the analytes detected in the samples were the same as those of standards (within a difference of ± 0.005 min in some cases) and their mass spectra had very high match factors. Typical mass spectra of some analytes are presented in Figure 1.

The tomato samples were found to contain *p,p'*-DDD, α-endosulfan, β-endosulfan, chlorpyrifos and cypermethrin and their detection frequencies were 91.7%, 50%, 50%, 41.7%, and 33.3%, respectively. Their concentrations are presented in Table 1. The concentrations of *p,p'*-DDD were generally low, with maximum of 11 ± 9 ng/g. The findings of *p,p'*-DDD indicate its formation due to anaerobic degradation of *p,p'*-DDT in the fruits or the environment. The concentrations of α-endosulfan and β-endosulfan were up to 330 ± 20 ng/g and 120 ± 6 ng/g, respectively and they did not exceed the MRL of 500 ng/g (FAO/WHO, 2013). The concentrations of α-endosulfan were higher than of β-endosulfan, which indicated input of fresh technical endosulfan (ATSDR, 2013).

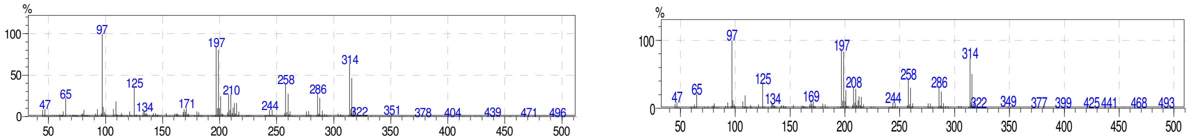
The concentrations of endosulfans are comparable to those found by Sheikh et al. (2013) in tomato samples from Sindh market in Pakistan, which ranged from nd to 680 ng/g. A study in some fields in Tanzania found higher concentrations of endosulfan of up to 4150 ng/g in tomato samples (Meela, 2009). Another study in fields in Tanzania found *p,p'*-DDT, dieldrin, β-endosulfan, α-HCH and γ-HCH in tomatoes at concentrations up to 0.62 ng/g (Mtashobya, 2010), which were lower than the concentrations found in this study.

Chlorpyrifos represented the highest concentrations in tomato samples, with concentrations up to 2340 ± 60 ng/g, which were 1.1 to 4.68 times greater than the MRL of 500 ng/g (FAO/WHO, 2013). These findings indicate potential risks and concerns for public health. Cypermethrin levels in tomato samples were up to 30 ± 0.6 ng/g and were below the MRL of 200 ng/g. The levels of chlorpyrifos were greater than the levels found in tomatoes grown in Khyber Pakistan, which ranged from 310 to 1500 ng/g, while the cypermethrin levels were lower than the levels found in Pakistan, which ranged from 60 to 1110 ng/g (Barkat et al., 2012). The field studies in Tanzania did not analyse or detect chlorpyrifos and cypermethrin in tomato samples.



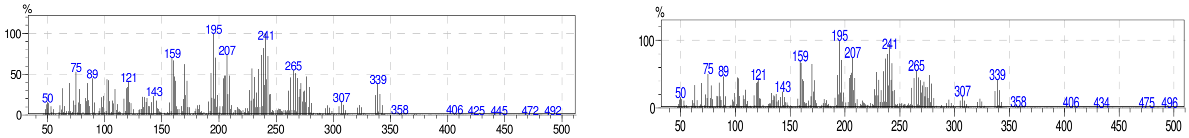
m/z, *p,p'*-DDD standard

m/z, *p,p'*-DDD in tomato sample (Temeke)



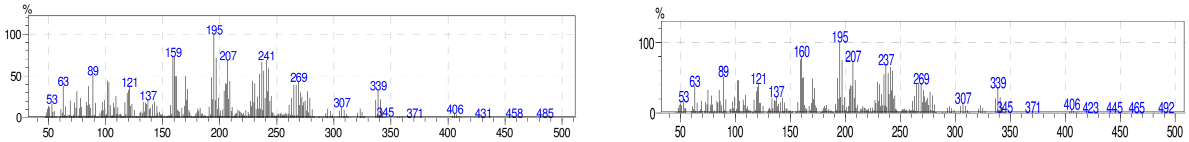
m/z, chlorpyrifos standard

m/z, chlorpyrifos in tomato sample (Buguruni)



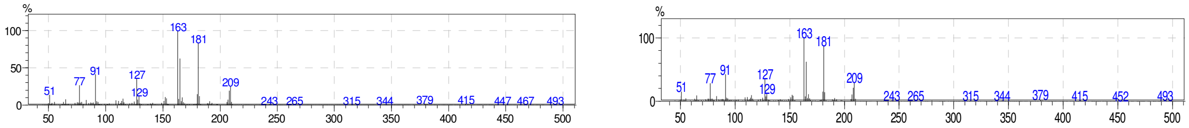
m/z, α-endosulfan standard

m/z, α-endosulfan in tomato sample (Buguruni)



m/z, β-endosulfan standard

m/z, β-endosulfan in watermelon sample (Kariakoo)



m/z, cypermethrin standard

m/z, cypermethrin in watermelon sample (Buguruni)

Fig 1: GC-MS full scan mass spectra of selected analytes in standards and samples

Table 1: Concentrations of pesticide residues in tomato samples (ng/g)

Site	Sample	*p,p'*-DDD	α-endosulfan	β-endosulfan	Chlorpyrifos	Cypermethrin
Kariakoo	FT1	11 ± 9.0	nd	nd	nd	nd
	FT2	3.0 ± 0.2	nd	nd	nd	nd
	FT3	1.0 ± 0.1	nd	nd	nd	nd
Buguruni	FT4	7.0 ± 0.4	240 ± 12	90 ± 4.0	1950 ± 50	nd
	FT5	7.0 ± 0.6	260 ± 13	90 ± 5.0	2140 ± 54	nd
	FT6	1.0 ± 0.02	nd	nd	nd	nd
Mwananyamala	FT7	5.0 ± 0.4	190 ± 10	60 ± 3.0	530 ± 20	10 ± 0.2
	FT8	3.0 ± 0.2	nd	nd	nd	30 ± 0.6
	FT9	nd	110 ± 6	40 ± 2.0	nd	nd
Temeke	FT10	1.0 ± 0.1	310 ± 20	104 ± 5.0	1860 ± 50	10 ± 0.2
	FT11	1.0 ± 0.01	nd	nd	nd	nd
	FT12	1.0 ± 0.2	330 ± 20	120 ± 6.0	2340 ± 60	20 ± 0.4

Concentrations expressed as mean ± standard deviation of duplicates; nd = not detected

Eight pesticide residues were detected in watermelon samples. Their concentrations are presented in Table 2. The compound *p,p'*-DDD was the most frequently detected (detected in 66.7% of the samples) but in low concentrations of up to 20 ± 1.2 ng/g. The concentrations of *p,p'*-DDD were greater than those of *p,p'*-DDE, indicating anaerobic degradation of DDT was favoured (ATSDR, 2002). The concentrations of DDT residues in all watermelon samples were below the MRL of 200 ng/g

(FAO/WHO, 2013). The detection of α-HCH in watermelons from only one site with concentrations of 4 ± 0.4 ng/g indicated contamination from environmental sources. The α-HCH concentrations were below the MRL of 10 ng/g. The compounds α-endosulfan and β-endosulfan were detected in 16.7% of the watermelons, with concentrations up to 370 ± 20 ng/g and 120 ± 5 ng/g, respectively, which were below the MRL. Their proportions represented fresh technical endosulfan. Chlorpyrifos was detected in 50% of the watermelon samples and the maximum concentration of chlorpyrifos was 3810 ± 50 ng/g. The concentrations of chlorpyrifos in 41.7% of the samples were 1.79 to 3.81 times greater than the MRL of 1000 ng/g (FAO/WHO, 2013). Cypermethrin was detected in 33.3% of the watermelons with concentrations up to 50 ± 4 ng/g, which were below the MRL of 300 ng/g (FAO/WHO, 2013). The levels of chlorpyrifos were much greater than the levels found by Bempah et al. (2012) in watermelon samples from Accra markets in Ghana (3 ± 2 ng/g).

Table 2: Concentrations of pesticide residues in watermelon samples (ng/g)

Site	Sample	α-HCH	*p,p'*-DDD	*o,p'*-DDD	*p,p'*-DDE	α-endosulfan	β-endosulfan	Chlorpyrifos	Cypermethrin
Kariakoo	FW1	4.0 ± 0.4	4.0 ± 0.2	nd	nd	nd	nd	nd	nd
	FW2	nd	1.0 ± 0.1	nd	nd	nd	nd	nd	nd
	FW3	nd	10 ± 0.6	1.0 ± 0.5	2.0 ± 0.7	370 ± 20	120 ± 5.0	1880 ± 60	nd
Buguruni	FW4	nd	nd	nd	nd	nd	nd	nd	nd
	FW5	nd	20 ± 1.2	nd	nd	nd	nd	nd	nd
	FW6	nd	nd	nd	nd	nd	nd	2210 ± 70	17 ± 2.0
Mwananyamala	FW7	nd	1.0 ± 0.1	nd	nd	nd	nd	3.0 ± 0.1	20 ± 2.0
	FW8	nd	nd	nd	nd	220 ± 10	80 ± 3.0	1790 ± 50	nd
	FW9	nd	1.0 ± 0.3	nd	nd	nd	nd	3810 ± 50	50 ± 4.0
Temeke	FW10	nd	14 ± 1.0	1.0 ± 0.4	nd	nd	nd	nd	nd
	FW11	nd	1.0 ± 0.4	nd	nd	nd	nd	nd	nd
	FW12	nd	nd	nd	nd	nd	nd	1910 ± 60	17 ± 1.0

Concentrations expressed as mean ± standard deviation; nd = not detected;

Generally, 95.8% of the samples contained pesticide residues. The detection frequencies of *p,p'*-DDD and endosulfans were higher in tomatoes than watermelons. Chlorpyrifos had higher detection frequency in watermelons than in tomatoes. The occurrence of cypermethrin did not vary between tomatoes and watermelons, while *o,p'*-DDD, *p,p'*-DDE and α-HCH were detected in watermelons only. There were no significant differences in mean concentrations of the pesticide residues between tomatoes and watermelons (t = 0.4238–1.367, 22 degrees of freedom, p = 0.1855–0.6758), indicating similar applications or similar contamination patterns. No significant variations were found in the concentrations of pesticide residues among the sampling sites (tomatoes F (3, 59) = 1.715, p = 0.1743 and watermelons F (3, 95) = 0.4958, p = 0.6861). This indicated that the fruits from all the markets had similar sources.

Conclusion: The concentrations of some of the pesticide residues in samples were generally high with endosulfans and chlorpyrifos representing the highest levels and which indicated input of fresh technical products. The composition of the DDT residues indicated anaerobic degradation was favoured. The contamination patterns in both types of the fruits were similar. About 46% of the samples contained pesticide residues above the maximum residue limits, indicating health risks to the consumers. Effective controls and processing are required.

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