

International Journal of Food Properties

ISSN: 1094-2912 (Print) 1532-2386 (Online) Journal homepage: https://www.tandfonline.com/loi/ljfp20

Reduction of methomyl and acetamiprid residues from tomatoes after various household washing solutions

M. Angela Rasolonjatovo, Mustafa Cemek, M. Fatih Cengiz, Deniz Ortaç, H. Büşra Konuk, Elif Karaman, A. Tuba Kocaman & Sadık Göneş

To cite this article: M. Angela Rasolonjatovo, Mustafa Cemek, M. Fatih Cengiz, Deniz Ortaç, H. Büşra Konuk, Elif Karaman, A. Tuba Kocaman & Sadık Göneş (2017) Reduction of methomyl and acetamiprid residues from tomatoes after various household washing solutions, International Journal of Food Properties, 20:11, 2748-2759, DOI: 10.1080/10942912.2016.1250099

To link to this article: https://doi.org/10.1080/10942912.2016.1250099

© 2017 Taylor & Francis Group, LLC

Published online: 10 Jul 2017.

Submit your article to this journal

Article views: 1818

View related articles

View Crossmark data

Citing articles: 12 View citing articles

Full Terms & Conditions of access and use can be found at
https://www.tandfonline.com/action/journalInformation?journalCode=ljfp20

INTERNATIONAL JOURNAL OF FOOD PROPERTIES
2017, VOL. 20, NO. 11, 2748–2759
https://doi.org/10.1080/10942912.2016.1250099

Taylor & Francis
Taylor & Francis Group

Check for updates

Reduction of methomyl and acetamiprid residues from tomatoes after various household washing solutions

M. Angela Rasolonjatovo[a], Mustafa Cemek[a], M. Fatih Cengiz[b], Deniz Ortaç[a], H. Büşra Konuk[a,c], Elif Karaman[a], A. Tuba Kocaman[a], and Sadık Göneş[a]

[a]Faculty of Chem. and Met. Eng., Department of Bioengineering, Biochemistry Division, Yıldız Technical University, Istanbul, Turkey; [b]Food Safety and Agricultural Research Center, Akdeniz University, Antalya, Turkey; [c]Faculty of Engineering, Department of Bioengineering, Gebze Technical University, Kocaeli, Turkey

ABSTRACT

The removal of pesticide residues is essential in order to control and reduce the harmful effects of pesticides commonly used in agriculture. The aim of this study was to investigate the effectiveness of 18 different household washing solutions for the reduction of methomyl and acetamiprid residues from tomatoes. These basic household solutions were used to prepare washing solution to remove pesticides. During this study, tomatoes were divided into two groups: in the first group, tomatoes were treated with the pesticides and the second group was washed with household solutions (distilled water, acetic acid, sodium chloride, ethanol, sodium bicarbonate, hydrogen peroxide, sodium hypochlorite, and liquid soap, lemon juice, mineral water, zam-zam water, whey, milk, and their combinations) after treating with pesticides. The pesticides residues in all samples were extracted by the QuEChERS technique, analyzed by LC-MS/MS. The results showed significant reduction in residues of all washed groups compared with the control ($p < 0.01$). Acetic acid, sodium chloride+sodium bicarbonate, zam-zam water, acetic acid+sodium chloride, sodium hypochlorite, milk, acetic acid+sodium chloride+sodium bicarbonate, liquid whey, liquid soap, lemon juice, ethanol, and sodium bicarbonate were found to remove more than 50% of both pesticide residues. The effectiveness of washing solutions was different for every type of pesticide. In the same way, blend of washing solutions has shown a synergetic effect on the removal of pesticides and was more effective compared to one solution. This research has raised the potential use of household solutions easily found at home that could be used to remove pesticide residues.

ARTICLE HISTORY
Received 3 August 2016
Accepted 15 October 2016

KEYWORDS
Pesticide residue; Methomyl; Acetamiprid; Tomatoes; Washing; Household

Introduction

In recent years, the importance of agricultural productivity has been increasing due to the growing world population and limited agricultural fields. Therefore, obtaining qualified and large quantities of foods and improving their shelf life are becoming more important. On the other hand, the favorable effects of fresh fruits and vegetables on human health are associated with various classes of compounds, and the composition of fresh tomato can vary according to cultivation conditions.[1,2,3]

Pesticides are chemical materials comprising compounds having different structures and properties, and commonly used in various forms to fight against or control plant enemies (pests) and diseases.[4] Although the pesticides exhibit beneficial features in agriculture, they also have toxic, immunotoxic, mutagenic, and carcinogenic effects on organisms. Acute and chronic poisoning caused by the ingestion of foods containing pesticide residues result in severe diseases such as respiratory, dermatological,

CONTACT Mustafa Cemek mcemek@yahoo.com Faculty of Chem. and Met. Eng., Department of Bioengineering, Biochemistry Division, Yıldız Technical University, Istanbul, Turkey.

© 2017 Taylor & Francis Group, LLC

neurological, and cancer.[5] Especially, food consumed raw such as fruits and vegetables such as tomato possess a high risk.

The overuse of pesticide intake causes contamination of products with these chemicals and triggers serious threats to human health and to the environment. To limit its usage, acceptable maximum dose levels of pesticides (Maximum Residue Limits, MRLs) were determined by national and international organizations.[6,7] In our previous *in vivo* studies we have investigated the effects of organophosphate insecticides on rats. We have observed that the hematological and biochemical parameters, oxidant–antioxidant systems, many organs and tissues such as brain, heart, jejunum, kidney, liver, lung, muscle, and pancreas were negatively affected by the toxicity of organophosphate compounds.[4,8,9,10,11,12,13]

Methomyl and acetamiprid are important pesticide-active ingredients commonly used in the growing process of fruit and vegetables. Methomyl, S-methyl N-(methylcarbamoyloxy)-thioacetimidate, belongs to the carbamate group and it is highly soluble in water (5.8 g/L).[14] Methomyl is a highly toxic insecticide, and a genotoxic agent, which leads to DNA damage and apoptosis.[15,16] Carbamate insecticides deactivate acetylcholinesterase similar to organophosphorus.[5] Methomyl is classified in Toxicity Category I (highly toxic) according to acute mammalian toxicity (LD_{50} = 34 mg/kg body weight male rats).[17] Acetamiprid, N-[(6-chloropyridin-3-yl)methyl]-N'-cyano-N-methylethanimidamide, is included in the neonicotinoids group and the insecticidal action is due to the activation of nicotinic acetylcholine receptors. The solubility of acetamiprid in distilled water at 25°C is reported as 2.95 g/L.[18] It has been used instead of organophosphorus showing severe effects by deactivating acetylcholinesterase irreversibly due to the relatively low chronic toxicity to mammals.[19,20] However, it has been shown that acute acetamipridi has a poisoning effect on humans.[21,22] Acetamiprid is classified in Toxicology Class II (moderately toxic) for acute oral toxicity by EPA (LD_{50} = 217 mg/kg body weight male rats).[23]

Methomyl can be used to control a wide range of insects, particularly Lepidoptera, Hemiptera, Homoptera, Diptera, and Coleoptera and spider mites. Acetamiprid is an effective agent against aphids, white-flies, some insect families, and other pests. Both pesticides mentioned above have been widely used in tomato crops.[15,19] Tomato (*Lycopersicon esculentum* Mill.) is one of the most popular and widely grown vegetables in the world. Turkey is ranked as fourth in tomato production in the world.[23] Due to the exposure of tomatoes to the pests and diseases during growth, pesticide usage has become inevitable during cultivation. Therefore, residues of pesticides, which pose serious threats to human health, should be removed from tomatoes by using appropriate removal methods.

Washing is the most commonly used method to remove pesticide residues from various vegetables.[1] However, only rinsing with tap water cannot provide efficient removal of residues. Based on the literature related to the usage of pesticides, many researchers have studied the effectiveness of the different washing solutions in the removal of pesticide residues from various foods.[6,7,24,25,26,27,28,29,30] Although residues were partially removed by various culinary applications, easy and complete removal of the residues is not possible yet.

Using chemical solvents as washing solutions to remove pesticide residues causes the exposure of foods to the toxic chemicals for the second time after pesticides. Therefore, different non-toxic washing solutions have been attempted effectively.[1,31] Besides, the difficulty to access these chemical solutions represented a limiting factor to apply these removal methods in daily life. On the other hand, many non-toxic solutions easily available at home may represent the same washing potential as these chemicals. This shows the importance of this study: the purpose of this study is to develop easily applicable and effective household washing treatments for removing the pesticide residues, in order to improve food safety and consumers health.

In the present study, to eliminate the residue of pesticides we have focused on determining the effectiveness of simple and non-toxic chemicals, which have different biochemical properties such as pH, dissolution capability, and polarity (distilled water, acetic acid, sodium chloride, ethanol, sodium bicarbonate, hydrogen peroxide, sodium hypochlorite, and liquid soap), some liquids that can be found easily in household (lemon juice, mineral water, zam-zam water, whey, and milk), and mixtures of these solutions in various proportions.

Materials and methods

Materials

Tomato samples were obtained from the same local market in Istanbul, Turkey, in August 2015. All tomatoes were of the same type and size (120 ± 10g). In order to assess the effects of household processing, the collected samples were divided into two different groups (n = 4). The first group consisted of tomatoes treated by pesticides (methomyl and acetamiprid), without washing solutions, which was called the control group. The second group was exposed to pesticides and then these samples were treated with household washing solutions to investigate their effects on removing pesticide residues. Control samples were tested to compare the effect of the washing for each solution.

Two most commonly used pesticides were selected, which have different characteristics and are frequently used in the cultivation of tomatoes. Commercial methomyl (Ekomyl, 90%, SP) and acetamiprid (Acetamiprid, 50%, WG) for preparation of the dipping solution were provided from EKO-TEK, Istanbul, Turkey. Pesticide analytical standards for LC/MSMS analysis were purchased with purity certification (10 ng/L in cyclohexane) from Dr Ehren Storfer (Augsburg, Germany).

Quechers kits (quick, easy, cheap, effective, rugged, and safe) were used for the extraction of pesticide residues from tomatoes, which were purchased from Restek (Bellefonte, USA). Methanol, ammonium formate, and acetonitrile were used for chromatographic analysis. Acetic acid, sodium chloride, ethanol, sodium bicarbonate, hydrogen peroxide, and sodium hypochlorite were used for the washing process. All chemicals were purchased from Sigma-Aldrich (Munich, Germany). The water (18.2 MΩ cm at 25°C) was produced by an ultrapure purification system (Millipore, USA).

Dipping solution experiments

Stock solutions of commercial methomyl and acetamiprid were diluted using 5 L of distilled water as specified in the prospectuses of pesticides, and then mixed. All dipping solution experiments were operated in 10-L containers with 5 L of dipping solution to allow for complete submersion of the tomatoes. About 500 g of tomatoes was placed in the container. The experimentation was performed under ambient temperature (ca. 20°C). The dipping solutions' temperature and pH were 20 ± 2°C and 7 ± 0.2 (distilled water), respectively. The samples were dipped into the solutions for 60 min. The contaminated tomatoes were air-dried on a blotting paper. The control samples were also analyzed prior to each experiment. After each experiment, residues on the samples were analyzed and the reduction percentages of residues were calculated compared to the control group.

Application of household washing solutions

A total of 18 non-toxic solutions with different biochemical properties were selected to investigate the effect of different washing solutions on pesticide residues. Simple chemicals that are easily found at home were used. The chemicals are listed in Table 1. Tomato samples were soaked in a deep bowl filled with 500 mL of any of the solutions for 10 min; the treated tomatoes were air-dried at room conditions for 30 min, then extracted by the Quechers kit, and then analyzed by LC-MS/MS.

To investigate the effect of temperature, distilled water was used at 25°C and 40°C. Throughout the study, distilled water was obtained from a Milli-Q system. The concentration of hydrogen peroxide was 3%. The concentration of soap was 1%, because soaps have high surfactant property. The optimum dose of all other simple chemicals was determined as 5%. Besides, all combinations were prepared from the solutions, and their final concentration was 5% such as acetic acid (5%), sodium chloride (5%), sodium bicarbonate (5%), and lemon juice (5%). These washing solutions were prepared using distilled water. The total volume of all washing solutions was 500 mL. The mineral water, zam-zam water, whey, and milk (500 mL) were used directly as washing solutions. The same washing procedure was accomplished by different solutions in order to evaluate their effectiveness on the removal of methomyl and

Table 1. Washing solutions in study groups.

Group	Washing solutions	Groups	Washing solutions
1	Distilled water (25°C)	**10**	Acetic acid (5%) + Sodium chloride (5%)
2	Distilled water (40°C)	**11**	Sodium chloride (5%) + Sodium bicarbonate (5%)
3	Acetic acid ($C_2H_4O_2$) (5%)	**12**	Lemon juice (5%) + Sodium chloride (5%)
4	Sodium chloride (NaCl) (5%)	**13**	Acetic acid (5%) + Sodium chloride (5%) + Sodium bicarbonate (5%)
5	Ethanol (C_2H_6O) (5%)	**14**	Lemon juice (5%)
6	Sodium bicarbonate ($NaHCO_3$) (5%)	**15**	Mineral water
7	Hydrogen peroxide (H_2O_2) (3%)	**16**	Zam-zam water
8	Sodium hypochlorite (NaClO) (5%)	**17**	Whey
9	Liquid soap (1%)	**18**	Milk

acetamiprid residues from tomatoes. After each experiment, residues on the samples were analyzed and the reduction percentages of residues were calculated compared to the control group.

Analytical procedure

Preparation for analysis

All glassware, filter papers, and auxiliary equipment (such as knife) were cleaned and rinsed with extra-pure acetone prior to the residue analyses and recovery studies. In this way interference caused by materials, which contaminate the analyte from the apparatus, was avoided.[7] Various standards of pesticides were diluted with acetone and prepared at different concentrations of each pesticide standard. Then, the diluted pesticides were injected into the LC-MS/MS system under the conditions stated in Table 2. In this way, the calibration curves were prepared for these concentrations.

Extraction and clean-up

The samples were extracted by the QuEChERS AOAC extraction method. The QuEChERS method uses a single-step buffered acetonitrile extraction and salting out liquid–liquid partitioning from the water in the sample with magnesium sulfate ($MgSO_4$). Dispersive-solid-phase extraction clean-up was carried out to remove organic acids, excess water, and other components with a combination of primary secondary amine sorbent and $MgSO_4$.Then the extracts were analyzed by LC-MS/MS to identify and determine a wide range of pesticide residues.

According to this method, tomatoes were blended for 2–3 min at high speed and 15 g homogenate was transferred to a 50 mL centrifuge tube; 15 mL 1% of acetonitrile in acetic acid was added and the tube was shaken vigorously for 1 min. 'Restek' extraction kit was added to the tube and then it was shaken vigorously for 1 min. The sample was centrifuged at 4000 rpm for 10 min. Around 8 mL of the liquid-

Table 2. LC-MS/MS analysis condition.

LC-MS/MS	LCMS-8030 Triple Quadrupole Series
Column	Inertsil ODS-4 2.1 mm x 50mm, 3µm
Ionization techniques	ESI
Column oven temperature	limit 40 °C, max 85 °C
Polarity	+
Injection volume	10 µL
Injection rate	0.5 mL/min
Starting Mobile Phase B	5.0%
Nebulizing Gas Flow	2 L/min (Nitrogen)
Drying gas	12 L/min (Nitrogen)
Desolvation Line Temperature	250°C
Ion source voltage	4500 V
Injection block temperature	250°C
Heat block temperature	400°C
Pressure limit (pump A, pump B)	Max 3000 Bar, Min 0 Bar
Pump mode	Binary gradient
LC Stop time	8 min

Table 3. Gradient Conditions.

Time	Concentration
0 min	Pump B: 5.0%
3 min	Pump B: 95.0%
5 min	Pump B: 95.0%
5.1 min	Pump B: 5.0%
8 min	Control post

phase layer was transferred into a 15-mL Restek clean-up tube, which contains a clean-up kit. The tube was shaken vigorously for 1 min. It was centrifuged at 4000 rpm for 10 min. The upper organic layer was transferred to the vials. In this way, the extracts were preserved at +4°C until further analysis.

Instrumental analysis

LC-MS/MS analysis conditions are shown in Table 2 and gradient conditions are shown in Table 3. All data were collected on Lab Solutions software, which offers a unified platform for LCMS-8030. An aliquot of concentrated organic phase was injected into the LC-MS/MS systems for determination of pesticide residues. These pesticide residues on tomatoes were qualitatively determined by retention time and quantitatively determined by the peak-area external standards.[32]

Method validation

The validation of the analytical method was performed following recovery analysis, linearity, and analytical curves. The method was optimized by recovery studies before the determination of pesticides in samples. The same extraction procedure and LC–MS/MS conditions as applied for sample analysis were used for the recovery studies. Two different pesticide concentrations (0.1 mg/kg and 0.05 mg/kg) were selected for recovery analysis.

Recovery studies were carried out by spiking fresh samples that did not contain any pesticides with 1 mL of 1.5 mg/L pesticide standard in solution in acetonitrile. In addition, the same procedure was applied for 0.5 mL of 1.5 mg/L pesticide standard. These standard solutions were added to chopped tomato sample in the blender jar before homogenization. The same extraction procedures and LC-MS/MS conditions were used for recovery studies.

Statistical analysis

Statistical analysis of the control group and the 18 experimental groups for two pesticides was performed using a one-way analysis of variance (ANOVA) and Tukey's post-test. A value of $p < 0.05$ was considered statistically significant. All values were expressed as mean standard deviation (SD). Statistical tests were performed using SPSS version 12.0 PL for Windows. All treatments were replicated four times. Values are shown as means ± SD.

Results

Methodological findings

The method was validated for linearity and recovery before the determination of methomyl and acetamiprid levels on the tomato samples (n = 4) (Fig. 1). These methodological parameters were optimized using blank tomato samples, where no treating has been implemented. The method demonstrated acceptable performance for the analysis of methomyl and acetamiprid residues in the tested tomato samples. In this study, recoveries were 91% for methomyl and 90.2% for acetamiprid (4.853 ± 0.45 and 0.512 ± 0.05, respectively). It was obtained as the average for each pesticide. Moreover, a good linear relationship with high correlation coefficient values ($r^2 > 0.99$) was obtained under the chromatographic conditions. These results from the analytical studies were compatible with the experimental data existing in the literature.[27]

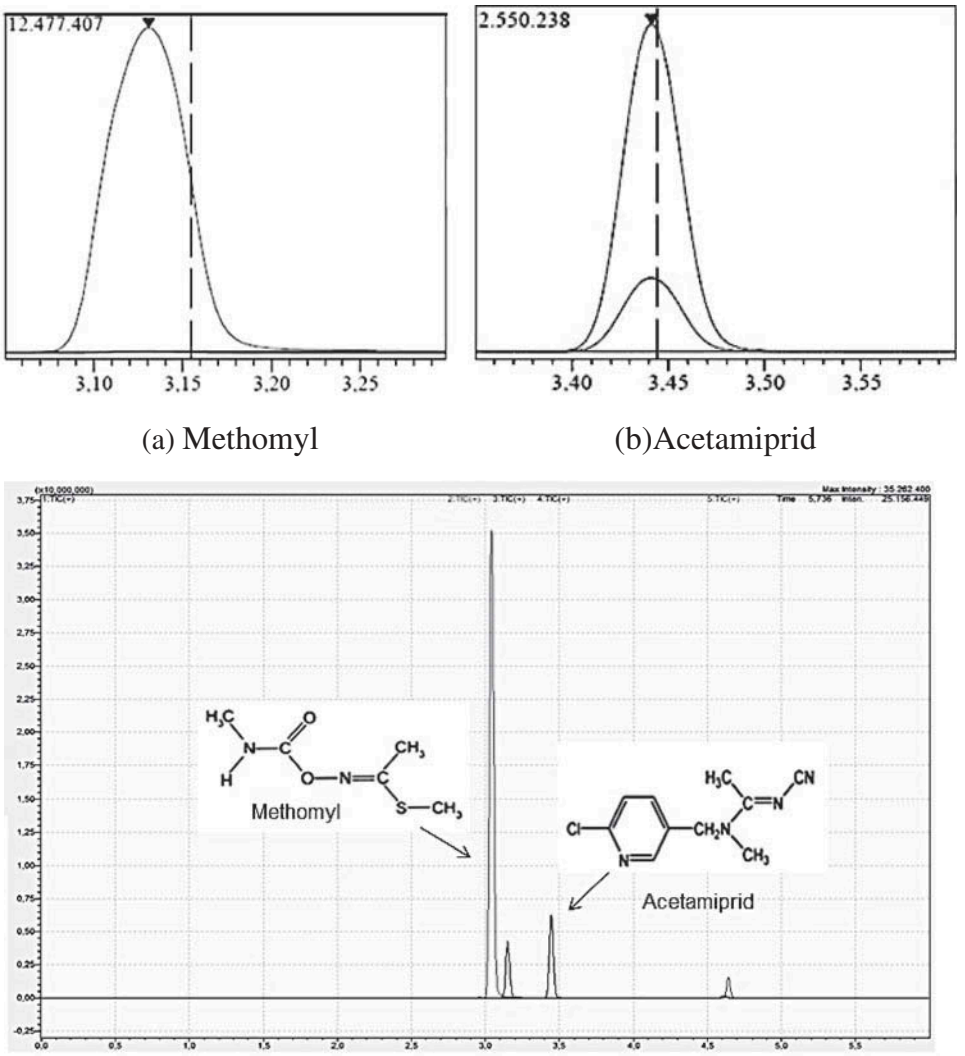


Figure 1. Total ion chromatogram of pesticide standards for methomyl (a) and acetamiprid (b).

Washing solutions treatments

The results of washing methomyl and acetamiprid residues on tomato samples by 18 different household solutions are shown in Table 4. According to the result of variance analysis, statistically significant reductions in residue levels for both pesticides were obtained in all washing groups.

Methomyl application

The results of methomyl treating and statistical analyses are presented in Table 4. According to the results of different washing groups, statistically significant reduction of methomyl residue levels was determined in all washing groups compared to the control group. After the methomyl application, pesticide residues were decreased in group 1 and group 2 compared to the control group ($p < 0.01$). In addition, the level of residues in groups 3–18 was significantly lower than in the control group ($p < 0.001$). Residue levels were diminished in group 6 and group 9 washing process than in group 1 ($p < 0.05$). Furthermore, in groups 3, 5, 14, 16, 18, and groups 8, 10, 13, and 17, the methomyl residue levels were significantly lower than the

Table 4. Pesticide residues in tomato samples in each group.

Groups	Washing solutions	Methomyl (mg/kg)	Acetamiprid (mg/kg)
Control	(No washing)	4.776 ± 0.805	0.503 ± 0.137
1	dH_2O (25°C)	3.389 ± 0.568 [a]	0.304 ± 0.019 [a]
2	dH_2O (40°C)	3.160 ± 0.438 [a]	0.294 ± 0.009 [a]
3	$C_2H_4O_2$ (5%)	2.000 ± 0.131[b,d,f]	0.143 ± 0.035 [b,d]
4	NaCl (5%)	2.428 ± 0.280 [b]	0.265 ± 0.050 [b]
5	C_2H_6O (5%)	1.944 ± 0.798[b,d]	0.184 ± 0.085 [b]
6	$NaHCO_3$ (5%)	2.184 ± 0.585[b,c]	0.158 ±0.043[b,c]
7	H_2O_2 (3%)	2.421 ± 0.827 [b]	0.192 ± 0.086 [b]
8	NaClO (5%)	1.547 ± 0.447[b,e,g]	0.096 ± 0.033[b,e,g,i]
9	Liquid soap (1%)	2.184 ± 0.302[b,c]	0.177 ± 0.057 [b]
10	$C_2H_4O_2$+ NaCl (5%)	1.634 ± 0.159[b,e,g]	0.029 ± 0.009 [b,e,h,j,k,l,m]
11	NaCl + $NaHCO_3$ (5%)	2.316 ± 0.272 [b]	0.058 ± 0.021[b,e,g,i]
12	Lemon juice + NaCl (5%)	2.651 ± 0.184[b,u]	0.089 ± 0.018 [b,e,g,i]
13	$C_2H_4O_2$+ NaCl + $NaHCO_3$ (5%)	1.616 ± 0.269[b,e,g]	0.068 ± 0.012[b,e,g,i]
14	Lemon juice (5%)	2.041 ± 0.195[b,d]	0.166 ± 0.043 [b,c]
15	Mineral water	2.653 ± 0.341[b,u]	0.159 ± 0.041[b,c]
16	Zam-zam water	1.755 ± 0.139[b,d,g]	0.232 ± 0.072[b,n,o,p,r]
17	Whey	1.333 ± 0.289[b,e,h.]	0.093 ±0.021 [b,e,g,i,s]
18	Milk	1.767 ± 0.524[b,d,g]	0.065 ± 0.046 [b,e,g,i,t]

[a]: $p<0.01$ with respect to control; [b]: $p<0.001$ with respect to control; [c]: $p<0.05$ with respect to group 1; [d]: $p<0.01$ with respect to group 1; [e]: $p<0.001$ with respect to group 1; [f]: $p<0.05$ with respect to group 2; [g]: $p<0.01$ with respect to group 2; [h]: $p<0.001$ with respect to group 2; [i]: $p<0.01$ with respect to group 4; [j]: $p<0.001$ with respect to group 4; [k]: $p<0.05$ with respect to group 5; [l]: $p<0.01$ with respect to group 7; [m]: $p<0.05$ with respect to group 9; [n]: $p<0.001$ with respect to group 10; [o]: $p<0.01$ with respect to group 11; [p]: $p<0.05$ with respect to group 12; [r]: $p<0.01$ with respect to group 13; [s]: $p<0.05$ with respect to group 16; [t]: $p<0.01$ with respect to group 16; [u]: $p<0.05$ with respect to group 17.

group 1 washing procedure ($p < 0.01$ and $p < 0.001$, respectively). Group 3 process, which was applied for reducing the level of residues, resulted in a significant decrease in methomyl residues when compared with the group 2 process ($p < 0.05$). The residue levels after the application of group 17 processes were statistically significantly lower than the group 2 process ($p < 0.001$). Additionally, methomyl residues were statistically decreased in groups 8, 10, 13, 16, and 18 than in group 2 ($p < 0.01$). Washing with groups 12 and 15 decreased the residue levels than in group 17 ($p < 0.05$).

The percentage of methomyl residues in tomato samples after the washing processes is presented in Fig. 2. As seen in Fig. 2, the amount of residues in all washing processes reduced compared to the control group. To determine the reduction percentage of methomyl residues, each treated sample was compared with the non-treated sample, which was defined as the control group.

Acetamiprid application

The results of acetamiprid residues and statistical analyses are presented in Table 4. According to the results of different washing groups, statistically significant reduction of acetamiprid residue levels was seen in all the washing groups compared with the control group in tomato samples. After the acetamiprid application, the amount of pesticide decreased more in groups 1 and 2 than in the control group ($p < 0.01$). Besides, the residue levels in groups 3–18 were significantly lower compared to the control group ($p < 0.001$). The amount of acetamiprid residues in groups 6, 14, 15, and 3 decreased compared to group 1 ($p < 0.05$ and $p < 0.01$, respectively). Likewise, residues were markedly lower in groups 8, 10–13, 17, and 18 than in group 1 washing process ($p < 0.001$). Residue levels were statistically significantly decreased in groups 8, 11, 12, 13, 17, and 18 washing process than in group 2 ($p < 0.01$). The residue level treated with group 10 was decreased compared to group 2 ($p < 0.001$). By comparing group 4 and group 10, acetamiprid residues treated with the group 10 process were lower than in group 4 ($p < 0.001$). Moreover, the residue levels were decreased in groups 8, 11, 12, 13, 17, and 18 washing processes when compared to group 4 ($p < 0.01$). After the acetamiprid application, pesticide residue was decreased

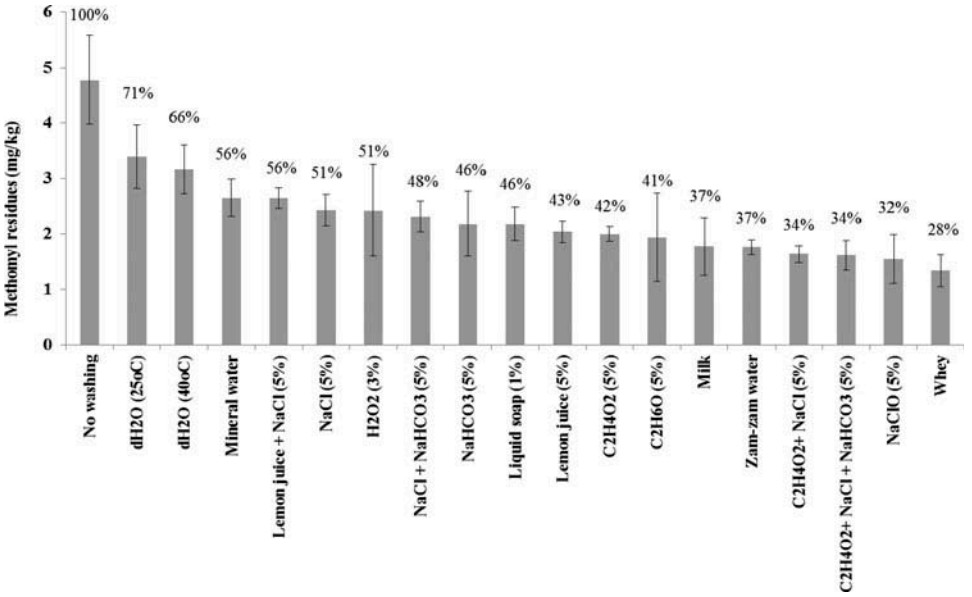


Figure 2. Percentage of detected average methomyl residues after 18 different washing processes in tomato samples.

in group 10 than in group 5 ($p < 0.05$). Similarly, pesticide residue was lower in group 10 than in group 7 ($p < 0.01$) and also the residue level was lower in group 10 than in group 9 ($p < 0.05$). Group 16 resulted in a significant increase in acetamiprid residue when compared to the group 10 process ($p < 0.001$). Likewise, the group 16 process, which was applied for reducing the level of residue, resulted in a significant decrease than in the group 11 process. Furthermore, pesticide residues in groups 12 and 13 were lower than in group 16 ($p < 0.05$ and $p < 0.01$, respectively). Acetamiprid residue in group 16 was higher than in group 17 and group 18 ($p < 0.05$ and $p < 0.01$, respectively).

The percentage of acetamiprid residues in tomato samples after washing processes is presented in Fig. 3. According to Fig. 3, acetamiprid residues in all washing solutions were reduced compared to the control group. To determine the reduction percentage of acetamiprid residues, each sample treated with washing solution was compared to the untreated sample, which was described as the control group.

Discussion

Nowadays, pesticide removal techniques to reduce residues from food commodities have a great importance on human health. Our work focused on washing methods by using different household chemical solutions with different biochemical properties to remove methomyl and acetamiprid residues on tomatoes. We compared their efficiencies with pure water solution at 25°C. While the reduction of acetamiprid residues was 0% for pure water at 25°C, the residues were found to be reduced by 13% by washing with sodium chloride (5%); 24% by washing with zam-zam water; 37% by washing with hydrogen peroxide (3%); 39% by washing with ethanol (5%); 42% by washing with liquid soap (1%); 45% by washing with lemon juice (5%); 48% by washing with mineral water; 48% by washing with sodium bicarbonate (5%); 53% by washing with acetic acid (5%); 68% by washing with sodium hypochlorite (5%); 69% by washing with whey and lemon juice + sodium chloride; 77% by washing with acetic acid + sodium chloride + sodium bicarbonate; 78% by washing with milk; 81% by washing with sodium chloride + sodium bicarbonate; and 90% by washing with acetic acid + sodium chloride. Similarly, methomyl residues were relatively decreased compared to pure water at 25°C. The amount of residues diminished 18% by washing with lemon juice + sodium chloride and mineral water; 25% by

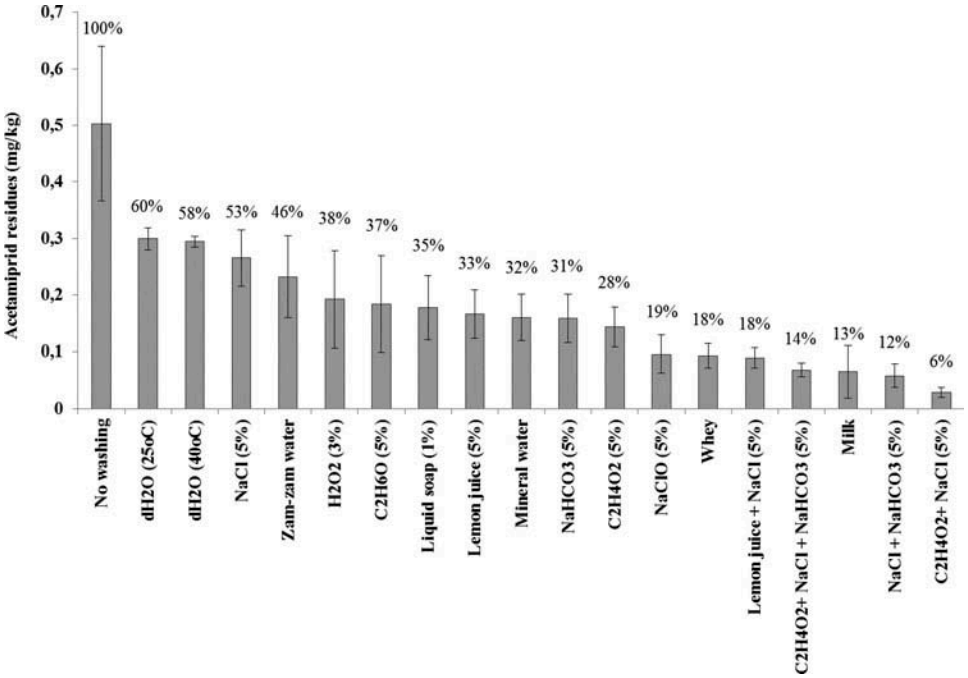


Figure 3. Percentage of detected average acetamiprid residues after 18 different washing processes in tomato samples.

hydrogen peroxide (3%); 29% by washing with sodium chloride + sodium bicarbonate; 33% by washing with sodium bicarbonate (5%) and liquid soap (1%); 37% by washing with lemon juice (5%); 38% by washing with acetic acid (5%); 40% by washing with ethanol (5%); 46% by washing with zam-zam water and milk; 50% by washing with acetic acid + sodium chloride and acetic acid + sodium chloride + sodium bicarbonate; 52% by washing with sodium hypochlorite (5%); and 59% by washing with whey.

The results showed that the washing solutions, which used to decrease pesticide residue, have removal potentials. This is due to the chemical properties of these solutions: acidity, alkalinity, presence of electrolytes, positively or negatively charged ions, and surfactant. These properties interfere with the binding process of pesticides on the cuticle of tomatoes, which ease the removal of pesticides during washing. However, some of these solutions such as whey, sodium hypochlorite, mixed solutions of sodium chloride + sodium bicarbonate, and acetic acid + sodium chloride have the highest removal potential for methomyl and acetamiprid residues on tomatoes. This shows the synergic effect of chemical properties of solutions when used in blend. It has been noticed also that acetamiprid was more sensitive to different washing solutions compared to methomyl. This indicates more attention since methomyl represents higher toxicity to humans compared with acetamiprid. In our study, tomato samples were selected as the research material. Several pesticides such as methomyl and acetamiprid are applied during the growth period of tomato crop. However, these pesticides not only protect plants but also have important risks for human health. This research has evidenced also the danger of carbamate pesticides like methomyl, which is highly toxic and very difficult to remove but is not yet banned in many countries.

Several researchers have found that some washing solutions have a significant effect on the reduction of pesticide residues. Krol et al.[33] reported the effect of simple household technique of rinsing with tap water to reduce pesticide residues on product. An experiment, which was conducted to find out the effect of processing on acetamiprid, in eggplant fruits via washing with water, residue reduction was minimal after washing. In our study, we have found similar results for methomyl and acetamiprid. Not only washing with water but also various preparations with usual chemical solutions available in household can eliminate the residues.[34] Satpathy et al.[29] studied different household solutions (water, 0.9% NaCl,

0.1% $NaHCO_3$, 0.1% acetic acid, 0.001% $KMnO_4$, 0.1% ascorbic acid, 0.1% malic acid, 0.1% oxalic acid) to remove pesticides from different vegetables including tomatoes. The authors reported that 0.001% $KMnO_4$ washing solution was found to be the most effective in reducing pesticide residues, which was due to its high effect on pesticide degradation. They also confirmed that acidic solutions are more effective than water for removal. Klinhoml[34] worked on the removal of methomyl using various household chemicals (NaCl, $NaHCO_3$, and $C_2H_4O_2$) and determined that these household chemicals were more effective than water. In our study, acetic acid, sodium chloride + sodium bicarbonate, zam-zam, acetic acid + sodium chloride, sodium hypochlorite, milk, acetic acid + sodium chloride + sodium bicarbonate, whey, liquid soap, lemon juice, ethanol, and sodium bicarbonate have permitted the removal of more than 50% of both methomyl and acetamiprid residues.

The study of Zhang Yu Shan[35] to remove pesticide by washing with a mixture of sodium bicarbonate, salt, and tap water showed that mixed sodium bicarbonate and salt were more efficient. When sodium bicarbonate is dissolved in water, it forms carbonic acid, which is responsible for the removal of pesticide by oxidation. The present study showed that sodium bicarbonate has removal efficiencies more than 50% for methomyl and acetamiprid residues. In addition, salt solution is a strong electrolyte, which has a charge that can interact with the pesticides and create an attractive force to ensure their removal. The removal rates of methomyl and acetamiprid by salt solution were found to be 49% and 47%, respectively. It may be explained that the studied pesticides have higher solubility in salt medium and they can access the salt solution more easily when the tomato samples are soaked in the solution. Similarly, in our study acetic acid + sodium chloride showed a greater potential for the removal of acetamiprid. This effect can depend on its components of acid and salt. Whey also showed a greater removal potential for methomyl due to its component of lactic acid and salt.

Milk can dissolve environmental contaminants such as pesticides because most of the pesticides are lipophilic or hydrophilic and milk has these special properties to have lipophilic and hydrophilic phases. Milk also contains many minerals that may interact with pesticides molecules and helps during the removal process.[36] In addition, the results obtained with milk are also removal of 87% acetamiprid and 63% methomyl. Mineral water showed 68% removal potential for acetamiprid than pure water. This effect is due to the carbonic acid content. However, mineral water did not show high removal potential for methomyl. In the same way, the removal potential of lemon juice is also superior to 50% for methomyl and acetamiprid due to its main components: citric acid. Zam-zam water has less salty and sulfur contents, but has higher sodium content. In our study, zam-zam water showed higher removal potential for methomyl than acetamiprid. This effect may be caused by the sodium content of zam-zam. Radwan et al.[37] found that soap solution (1%) washing eliminated the initial residues from eggplant fruit by about 50%. Our study has the same result with soap for methomyl, but it showed a higher removal potential affect for acetamiprid. The removal of pesticides from tomatoes depends on the type and nature of the washing solution and pesticides. The concentration of the solution also affects the removal of pesticides.[38] In addition, we showed that some mixed solutions were more efficient than simple solutions and acidic solutions were also better than others for acetamiprid. When these chemical elements are combined, they interact with each other by synergy and their removal potential can be higher than their removal potential individually.

Conclusion

In our study, we have used various chemical solutions that are easily accessible at home to remove methomyl and acetamiprid pesticides from tomatoes. With selected solutions, residues of acetamiprid were removed better than methomyl residues. It is due to the fact that methomyl is a systemic pesticide that migrates inside the cuticula of the tomatoes and its chemical structure is more subject to creating different bounds with the inner media compounds of tomatoes. Due to that the removal of methomyl by washing methods is more difficult than acetamiprid, which is more sensitive with acidic solutions. We conclude that reducing the pesticide residue depends on not only the behavior and physiochemical properties of the pesticides but also the active content of household and chemical washing solutions.

Household washing solutions that can be easily found at home may be used to remove effectively pesticide residues.

Acknowledgement

We thank ANTTEKNIK for assistance.

Declaration of interest

The authors declare no conflict of interest.

Funding

This study was supported by grants from the Yıldız Technical University research fund (2015-07-04-YL02).

References

1. Kin, C.M.; Huat, T.G. Headspace Solid-Phase Micro Extraction For The Evaluation of Pesticide Residue Contents in Cucumber and Strawberry After Washing Treatment. Food Chemistry **2010**, *123*, 760–764.
2. Liaudanskas, M.; Viškelis, P.; Kviklys, D.; Raudonis, R.; Janulis, V. A Comparative Study of Phenolic Content in Apple Fruits. International Journal of Food Properties **2015**, *18*(5), 945–953.
3. Wanlapa, S.; Wachirasiri, K.; Sithisam-ang, D.; Suwannatup, T. Potential of Selected Tropical Fruit Peels as Dietary Fiber in Functional Foods. International Journal of Food Properties **2015**, *18*(6), 1306–1316.
4. Büyükokuroğlu, M.E.; Cemek, M.; Tosun, M.; Yürümez, Y.; Baş, O.; Yavuz, Y. Dantrolene may Prevent Organophosphate-Induced Oxidative Stress and Muscle Injury. Pesticide Biochemistry and Physiology **2008**, *92*, 156–163.
5. Solomon, G.; Ogunseitan, O.A.; Kirsch, J. Pesticides and Human Health: A Resource for Health Care Professionals. Physicians for Social Responsibility and Californians for Pesticide Reform **2000**, 5–59.
6. Cengiz, M.F.; Certel, M.; Göçmen, H. Residue Contents of DDVP (Dichlorvos) and Diazinon Applied on Cucumbers Grown in Greenhouses and Their Reduction by Duration of A Pre-Harvest Interval and Post-Harvest Culinary Applications. Food Chemistry **2006**, *98*(1), 127–135.
7. Cengiz, M.F.; Certel, M.; Karakaş, B.; Göçmen, H. Residue Contents of Captan and Procymidone Applied on Tomatoes Grown in Greenhouses and Their Reduction by Duration of a Pre-Harvest Interval and Post-Harvest Culinary Applications. Food Chemistry **2007**, *100*(4), 1611–1619.
8. Cemek, M.; Büyükokuroğlu, M.E.; Büyükben, A.; Aymelek, F.; Özcan L. Effects of Vitamin E and Selenium on Tissue Bio-Element Status in Organophosphate Toxicity in Rats. Pesticide Biochemistry and Physiology **2010**, *98*, 9–18.
9. Cemek, M.; Büyükokuroğlu, M.E.; Yürümez, Y.; Yavuz, Y.; Aslan, A.; Buyukben, A.; Aymelak, F. Tissue Trace and Major Element Levels in Organophosphate Insecticide Fenthion (Lebaycid®) Toxicity in Rats: Prophylactic and Therapeutic Effect of Exogenous Melatonin. Ecotoxicology and Environmental Safety **2010**, *73*, 206–212.
10. Cemek, M.; Büyükben, A.; Büyükokuroğlu, M.E.; Aymelek, F.; Tür L. Protective Roles of Vitamin E (A-Tocopherol), Selenium and Vitamin E Plus Selenium in Organophosphate Toxicity In Vivo: A Comparative Study. Pesticide Biochemistry and Physiology **2010**, *96*, 113–118.
11. Büyükokuroğlu M.E.; Cemek, M.; Yürümez, Y.; Yavuz, Y.; Aslan A. Antoxidative Role of Melatonin in Organophosphate Toxicity in Rats. Cell Biology and Toxicology **2008**, *24*, 151–158.
12. Bulut, S.; Erdoğmuş, S.F.; Konuk, M.; Cemek, M. The Organochlorine Pesticide Residues in the Drinking Waters of Afyonkarahisar, Turkey. Ekoloji **2010**, *19*(74), 24–31.
13. Yürümez, Y.; Cemek, M.; Yavuz, Y.; BirdaneY. O.; Büyükokuroğlu M.E. Beneficial Effect of N-Acetylcysteine Againts Organophosphate Toxicity in Mice, Biological & Pharmaceutical Bulletin **2007**, *30*, 490–494.
14. USEPA. Methomyl Reregistration Eligibility Decision (RED). *Prevention, Pesticides AndToxic Substances* (7508C) *EPA 738-R-98-021*, **1998**, 78.
15. Pereira, J.L.; Goncalves, F. Effects of Food Availability on the Acute and Chronic Toxicity of The Insecticide Methomyl to Daphnia Spp. Science of the Total Environment **2007**, *386*, 9–20.
16. Guanggang, X.; Diqiu, Li.; Jianzhong, Y.; Jingmin, G.; Huifeng, Z.; Mingan, S.; Liming, T. Carbamate Insecticide Methomyl Confers Cytotoxicity Through DNA Damage Induction. Food and Chemical Toxicology **2013**, *53*, 352–358.

17. USEPA. Analytical Reference Standards and Supplemental Data: The Pesticides and Industrial Chemicals Repository. USEPA Environmental Monitoring Systems Laboratory, Las Vegas, NV, **1984**.
18. USEPA. Name of Chemical: Acetamirid*Pesticide Fact Sheet*, *7501C*, **2002**, 14.
19. Jin D.; Xu, Q.; Yu, L.; Mao, A.; Hu, X. A Novel Sensor for the Detection of Acetamiprid in Vegetables Based on Its Photocatalytic Degradation Compound. Food Chemistry **2016**, *194*, 959–965.
20. Romeh, A.A.; Hendawi, M.Y. Effect of Processing on Acetamiprid Residues in Eggplant Fruits, Solanummelongena L. African Journal of Agricultural Research **2013**, *8*(18), 2033–2037.
21. Lin, P.; Lin, H.; Liao, Y.; Guo, H.; Chen, K. Acute Poisoning with Neonicotinoid Insecticides: A Case Report and Literature Review. Basic & Clinical Pharmacology & Toxicology **2013**, *112*, 282–286.
22. Imamura, T.; Yanagawa, Y.; Nishikawa, K.; Matsumoto, N.; Sakamoto, T. Two Cases of Acute Poisoning With Acetamiprid in Humans. Clinical Toxicology **2010**, *48*, 851–853.
23. FAOSTAT. Food and Agriculture Organization. **2013** http://faostat3.fao.org/browse/Q/QC/E.
24. Kumari, B. Effects of Household Processing on Reduction of Pesticide Residues in Vegetables. ARPN Journal of Agricultural and Biological Science **2008**, *3*(4), 46–51.
25. Zohair, A., Behaviour of Some Organophosphorus and Organochlorine Pesticides in Potatoes During Soaking in Different Solutions. Food and Chemical Toxicology **2001**, *39*, 751–755.
26. Shiboob, M.H.; Madkour, M.H.; Zaitoun, A.A., Effect of Washing and Household Processing on Removal Performance of Some Organophosphorus Insecticides. Journal of Food, Agriculture and Environment, **2014**, *12* (2), 1255–1259.
27. Lopez- Fernandez, O.; Rial-Otero, R.; Simal-Gàndara J. Factors Governing the Removal of Mancozeb Residues From Lettuces With Washing Solutions. Food Control, **2013**, *34*, 530–538.
28. Liang, Y.; Wang, W.; Shen, Y.; Liu, Y.; Liu, X.J. Effects of Home Preparation on Organophosphorus Pesticide Residues in Raw Cucumber. Food Chemistry **2011**, *133*(3), 636–640.
29. Satpathy, G.; Tyagi, Y.K.; Gupta, R.K. Removal of Organophosphorus (OP) Pesticide Residues from Vegetables Using Washing Solutions and Boiling. Journal of Agricultural Science **2011**, *4*(2), 69–78.
30. Ghani, S.B.A.; Hanafi, A.; Nasr I.N. Nontoxic Washing Solutions for Decreasing Myclobutanil, Fenhexamid and Boscalid Residues in Sweet Pepper and Cherry Tomatoes. Australian Journal of Basic and Applied Sciences **2010**, *4*(8), 3360–3365.
31. Saadi, A.; Randhawa M.A.; Akthar, S.; Mansoor-Ul-Hassan; Asqhar, A.; Sohaib, M; Jahangir, M.A. Assessment of Different Washing Treatments to Mitigate Imidacloprid and Acetamiprid Residues in Spinach. Journal of the Science of Food and Agriculture **2016**, *96*(11), 3749–3754.
32. Zhang Z.Y.; Liu X.J.; Hong X.Y. Effects of Home Preparation on Pesticide Residues In Cabbage. Food Control **2007**, *18*, 1484–1487.
33. Krol, W.J.; Arsenault T.L.; Pylypiw H.M.; Incorvia MattinaJr . and M.J. Reduction of Pesticide Residues on Produce by Rinsing. Journal of Agricultural and Food Chemistry **2000**, *48*, 4666–4670.
34. Klinhoml P.; Halee A.; Methawiwat S. The Effectiveness of Household Chemicals in Residue Removal of Methomyl and Carbaryl Pesticides on Chinese-Kale. Kasetsart Journal (Natural Science) **2008**, *42*, 136–143.
35. Zhang Y.S.; Li, X.P.; Liu, H.M.; Zhang, Y.K.; Zhao, F.F.; Yu, Q.; Li, H.; Chen, J.W. Study on Universal Cleaning Solution in Removing Blended Pesticide Residues in Chinese Cabbage. Journal of Environmental Chemistry and Ecotoxicology **2013**, *5*(8), 202–207.
36. Kampire, E.; Kiremire, B.T.; Nyanzi, S.A.; Kishimba, M. Organochlorine Pesticide in Fresh and Pasteurized Cow's Milk from Kampala Markets. Chemosphere **2011**, *84*(7), 923–927.
37. Radwan, M.A.; Abu-Elamayem, M.M.; Shiboob, M.H.; Abdel-Aal, A. Residual Behaviour of Profenofos on Some Field-Grown Vegetables and Its Removal Using Various Washing Solutions and Household Processing. Food and Chemical Toxicology **2005**, *43*, 553–557.
38. Abou-Arab, A.A.K. Behavior of Pesticides in Tomatoes During Commercial and Home Preparation. Food Chemistry **1998**, *65*(1999), 509–514.