

Effects of Types of Washing and Peeling in Relation to Pesticide Residues in Tomatoes

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Tomatoes are widely consumed and most often without cooking, therefore it is important to estimate the reduction of residues using simple washing procedures. An experiment was carried out to evaluate the effects of household processing such as: washing with water, washing with 10% of vinegar solution and washing with 10% of sodium bicarbonate solution on pesticide residue levels of acetamiprid, azoxystrobin, diflubenzuron, dimethoate, fipronil, imidacloprid, procymidone and thiamethoxam, in spiked tomato samples. The amount of residue remaining in the peel and pulp was also investigated. The pesticide residues were monitored using the quick, easy, cheap, effective, rugged and safe (QuEChERS) extraction and analysed by liquid chromatography tandem mass spectrometry method (LC-MS/MS) in dynamic multiple-reaction monitoring mode (DMRM). The effect of the number of washing treatments (n = 3) and control, with six replicates, differed significantly for all pesticides evaluated (n = 8), but despite washing, fipronil residues were not removed from the tomato samples. Overall, washing with water or other solutions, and peeling before consumption are shown to reduce pesticide residues in tomatoes.

Keywords: QuEChERS, washing procedure, peeling, LC-MS/MS

Introduction

Tomatoes are widely consumed in several countries and are considered a functional food, because they contain antioxidant molecules, such as ascorbic acid, vitamin E, carotenoids, flavonoids, lycopene, and phenolic acids,¹ which bring benefits to human health. On the other hand, tomatoes are susceptible to pests, and pesticides are needed in the different phases of cultivation to control pests and diseases that may cause yield reduction;^{2,3} however, the presence of pesticide residues in tomatoes may be harmful to health.

The European Union (EU) legislation lists 451 pesticides containing maximum residue limits (MRLs) for tomato.⁴ The Codex Alimentarius presents 71 pesticides with MRLs.⁵ In Brazil, 143 pesticides are registered for the tomato crop with MRLs and they are formulated in isolate or in mixture, totaling 424 commercial brands of

pesticides.⁶ Incorrect use of these pesticides may result in food contamination and consequently, cause harm to the consumers, so it is important to estimate the level of pesticide exposure in tomatoes. Knowledge of the effects of household processing on the levels of pesticide residues in vegetables is required to reduce dietary exposure.^{7,8}

Many studies have reported pesticide residues in tomatoes,^{9,10} and although the household processing of vegetables such as boiling, frying, roasting and blanching lead to a significant reduction of pesticide residues,¹¹⁻¹³ tomato is most often consumed without cooking such as in salads, in a sandwich or in cold soups. Thus, it is important to estimate the reduction of residues using simple washing procedures.

A previous study was conducted by quantifying 57 pesticides in 58 tomato samples collected from supermarkets in the city of Piracicaba, SP, Brazil, and 12 compounds were found in 35 samples.¹⁴ From those pesticides found in the samples were selected acetamiprid, azoxystrobin, imidacloprid and thiamethoxam because

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its systemic action and different solubility in water and diflubenzuron due to no systemic action. The dimethoate and procymidone are commonly used in tomato crop and fipronil was chosen because it is a very common insecticide with contact action and various forms of employment (soil, foliar, seed applications and irrigation water). Pesticides with foliar application were chosen in this study because we believe there is a similarity in absorption of pesticide spray that deposit on tomato surfaces and transfer properties through the cuticle when compared with immersion bath.

The aims of this study were to evaluate the residue levels of acetamiprid, azoxystrobin, diflubenzuron, dimethoate, fipronil, imidacloprid, procymidone and thiamethoxam in tomatoes by liquid chromatography tandem mass spectrometry (LC-MS/MS) method in dynamic multiple-reaction monitoring mode (DMRM) after some household processes (washing with water, 10% of vinegar solution and 10% of sodium bicarbonate solution, and peeling) on these residues. With this study, we hope to understand how the effects of washing and peeling procedures influence the decrease of systemic and non-systemic pesticide residues in tomatoes.

Experimental

Reagents and materials

Eight pesticides of standard grade were purchased from ChemService (West Chester, PA, USA), ranging from 98.5% to 99.5% of purity. Acetonitrile degree HPLC/Spectro was purchased from Tedia Company (Fairfield, OH, USA), formic acid 99% and glacial acetic acid from J.T. Baker (Phillipsburg, NJ, USA). The quick, easy, cheap, effective, rugged, and safe (QuEChERS) kits containing 6 g of anhydrous magnesium sulfate (MgSO_4) and 1.5 g of anhydrous sodium acetate (50 mL of volume, tube 1) and containing 150 mg of MgSO_4 and 50 mg of primary secondary amine (PSA) (2 mL of volume, tube 2) were purchased from Thermo Fisher Scientific (Waltham, MA, USA). The stock solutions were prepared by solubilizing the standards in acetonitrile at concentration of $1000 \mu\text{g mL}^{-1}$, and an intermediate mixture solution of all standards was prepared at concentration of $50 \mu\text{g mL}^{-1}$, which was kept at -18°C in a freezer before its use.

Samples preparation

Preparation of pesticide-free tomato samples

Blank tomato samples were obtained from a supplier with certification label by the Biodynamic Institute where chemicals had not been applied (blank values were not

higher than 30% of the limit of quantification, LOQ). The blank samples were analyzed to confirm the absence of pesticide residues. For the method to determine pesticide residues, see section Analytical methods.

Preparation of spiked tomatoes

Were prepared 2 L of aqueous solution of 50 g L^{-1} mixed pesticides of the following commercial formulations: Convence[®] (Iharabras S.A., SP, Brazil) containing 20% of acetamiprid as active ingredient, Amistar WG[®] (Syngenta, SP, Brazil) containing 50% of azoxystrobin, Dimax 480 SC[®] (Nufarm, CE, Brazil) containing 48% of diflubenzuron, Perfekthion 400[®] (BASF, SP, Brazil) containing 40% of dimethoate, Regent 800 WG[®] (BASF, SP, Brazil) containing 80% of fipronil, Confidor 700 WG[®] (Bayer, SP, Brazil) containing 70% of imidacloprid, Sumilex 500 WP[®] (Iharabras S.A., SP, Brazil) containing 70% of procymidone and Actara 750[®] (Syngenta, SP, Brazil) containing 75% of thiamethoxam. Blank tomato samples (1 kg) were immersed in a solution freshly prepared during 20 min. After that the tomato samples were air dried in room temperature. These spiked tomatoes were designated as control samples.

Washing experiments

The washing experiments were based on study from Abou-Arab¹⁵ (1999), Pugliese *et al.*¹⁶ (2004) and Zhang *et al.*¹⁷ (2007).

Spiked tomatoes were left to soak in different solutions of 10% vinegar, 10% sodium bicarbonate solution, and water tap for 20 min (without shaking). After immersion, the spiked tomatoes were removed of the solutions and placed in a surface with aluminum foil, to avoid transferring of pesticides and allow its penetration, then air-dried in room temperature for 25 min and, after homogenized in a blender, extracted according to section Extraction. The six replicate were analyzed.

Peel and pulp experiments

After tomatoes were spiked, the peel was removed in small pieces with a knife and ground in a blender. The same procedure was followed for the pulp assessment. The pulp was cut, taking care to avoid pulp contamination from the peel, and then ground in a blender.

Analytical methods

Extraction

Pesticide residues were extracted according to the QuEChERS method described previously by Lehotay *et al.*¹⁸ Tomato samples (15 g) were extracted with 15 mL

acetonitrile 1% of acetic acid into a 50 mL Teflon centrifuge tube. Subsequently, 6 g of anhydrous magnesium sulfate and 1.5 g of anhydrous sodium acetate were added, immediately shaken for 5 min, and then the extract was centrifuged at $2991 \times g$ for 5 min. One milliliter of the upper layer was transferred to a 2 mL Teflon centrifuge tube containing 150 mg of anhydrous magnesium sulfate and 50 mg of PSA (tube 2). The tube was shaken for 1 min followed by centrifugation for 5 min at $2991 \times g$. Following this, an aliquot of 800 μL from the supernatant was evaporated under nitrogen stream and reconstituted with 800 μL solution of acetonitrile and water (20:80, v/v) for LC analysis. Prior to injection into the LC-MS/MS system, the samples were filtered through a 0.22 μm polytetrafluorethylene (PTFE) filter (Whatman, Florham Park, NJ, USA).

LC-MS/MS analysis

For the LC analysis, an Agilent 1200 HPLC system with a binary pump was used equipped with a Zorbax C18 analytical column of 50 mm \times 2.1 mm and 1.8 μm particle size (Agilent Technologies-Wilmington, DE, USA). The mobile phases, A and B, were Milli-Q[®] (Millipore; Bedford, MA, USA) water and acetonitrile with 0.1% formic acid, respectively. The gradient program started with 20% of B with a linear gradient up to 90% B in 10 min, then constant for 3 min. After a 15 min runtime, 7 min of post-time followed using the initial 20% of B. The flow rate was constant, 0.35 mL min^{-1} during the whole process, the column temperature was fixed at 30 $^{\circ}\text{C}$ and 2 μL of sample was injected.

For the mass spectrometric analysis, an Agilent 6430 Triple-Quad LC/MS (Agilent Technologies-Wilmington, DE, USA) system was applied. The electrospray ionization (ESI) source was operated in positive ionization mode and its parameters were as follows: gas temperature: 325 $^{\circ}\text{C}$, gas flow of 11 L min^{-1} , nebulizer gas: 43 psi; capillary voltage: 3500 V. Nitrogen was served as the nebulizer and collision gas. The DMRM was used, with a delta time of 1.0 min for each analyte. The most intense transition was used as a quantifying ion and the second most intense was used as a qualifying ion, respectively, for the mass transitions.

Validation

Validation studies were carried out according to previous study.¹⁴ The eight-point-calibration curves in solvent and in tomato matrix were constructed and compared at the 0.01, 0.025, 0.05, 0.1, 0.25, 0.5, 0.75 and 1 mg kg^{-1} concentration levels ($n = 5$). The tomato matrix was prepared using blank samples that were extracted according to the sample preparation procedure. This

comparison provided information on linearity, detectivity and matrix effect (signal suppression or enhancement).

The limit of detection (LOD) and limit of quantification (LOQ) were estimated based on the injection of matrix-matched solution at concentration 0.005 mg kg^{-1} and expressed as three and ten times, respectively, the signal-to-noise (S/N) ratio in the transition DMRM of the quantifying ion.

During the recovery experiments, the main objective was to determine the accuracy of the method, comparing the real concentration of each pesticide measured by performing the complete procedure with the known pesticide concentration initially added to the blank matrix at three levels (0.01, 0.1 and 0.5 mg kg^{-1}) in five replicates. The method's precision was expressed as the relative standard deviation (RSD) for repeatability.

Statistical analysis

All statistical tests were carried out using the computer program ASSISTAT.¹⁹ The analysis of variance (ANOVA) verified the existence of the effect of one factor at a concentration of eight pesticides residue after the washing process. Once detected to be of significant effect, the comparison of the mean of residues between the washing methods was done through Tukey's test.

Results and Discussion

In order to identify the best household processing for the following pesticides: acetamiprid, azoxystrobin, diflubenzuron, dimethoate, fipronil, imidacloprid, procymidone and thiamethoxam in spiked tomato samples and quantify the remaining residue in the peel and pulp, the method QuEChERS was applied with the following conditions of LC-MS/MS and statistical data analysis.

Identification and validation of pesticides

The monitored ions for each compound are listed in Table 1. The most intense transition was used as a quantifying ion and the second most intense was used as a qualifying ion for the confirmation of the pesticides. The identification procedure for the pesticide residues used was retention time, two transitions at DMRM mode.

The concentration range (0.01 to 1.0 $\mu\text{g mL}^{-1}$) presented linearity with the analytical signal, indicated by the values of determination coefficient (r^2) greater than 0.99 for all compounds in solvent, and at the matrix, as shown in Table 2.

For the pesticides validated, diflubenzuron and procymidone presented medium matrix effect (ME)

Table 1. Chromatographic parameters for the selected compounds

Compound	Retention time / min	Quantitation DMRM ^a 1		Qualifying DMRM ^a 2		Fragmentation / V	Collision E / V	
		1	2	1	2		1	2
Acetamiprid	1.04	223.1	126	223.1	299	90	20	39
Azoxystrobin	12.07	404.1	372	404.1	344.1	100	8	24
Diflubenzuron	12.42	311	158	311	141	120	10	35
Dimethoate	0.99	230	198.9	230	124.9	60	4	20
Fipronil	13.27	437	368.2	437	314.9	130	13	25
Imidacloprid	0.92	256.1	209	256.1	175.1	90	12	16
Procymidone	12.57	284	133	284	145	95	51	45
Thiamethoxam	0.72	292	211	292	181	70	4	20

^aDynamic multiple-reaction monitoring mode (DMRM).

(Table 2), that required the preparation of the matrix calibration curve. The LOQ ranged from 0.004 to 0.07 mg kg⁻¹ (Table 3). All the pesticides investigated showed recovery values (88-114%) and RSD ($\leq 17\%$), Table 3, within the recommended range by the European Commission.²⁰

Washing experiments

Statistical analysis

The results were subjected to variance analysis by F-test, and when there was significance of the averages, Tukey's test at 1% probability was applied. The Table 4

Table 2. Calibration curve data and matrix effect

Product	Solvent			Matrix			ME ^a
	Slope	Linear coefficient	r ²	Slope	Linear coefficient	r ²	
Acetamiprid	80426.5	-779.91	0.99990	69567.08	130.03	0.99985	-13.50
Azoxystrobin	652207.5	7115.69	0.99976	535047.77	5086.54	0.99992	-17.96
Diflubenzuron	22431.9	701.49	0.99995	17307.65	165.85	0.99996	-22.84
Dimethoate	98334.6	-64.57	0.99997	79281.82	299.58	0.99999	-19.38
Fipronil	6312.6	-4.05	0.99989	5359.23	28.17	0.99886	-15.10
Imidacloprid	43410.9	-67.05	0.99995	37833.25	183.02	0.99999	-12.85
Procymidone	6992.9	113.83	0.99925	5266.21	105.97	0.99991	-24.69
Thiamethoxam	23544.2	-198.82	0.99995	19941.46	207.01	0.99979	-15.30

^aME: matrix effect.

Table 3. Limit of detection, limit of quantification, recovery mean of values of 0.01, 0.1 and 0.5 mg kg⁻¹ levels (n = 5) and relative standard deviation

Product	LOD ^a / (mg kg ⁻¹)	LOQ ^b / (mg kg ⁻¹)	Rec ^c ± RSD ^d / (mg kg ⁻¹)			Rec _m ^c ± RSD ^d / (mg kg ⁻¹)
			0.01 ^e	0.1 ^e	0.5 ^e	Global mean
Acetamiprid	0.001	0.004	108 ± 12	107 ± 6	104 ± 5	106 ± 7
Azoxystrobin	0.001	0.004	99 ± 7	111 ± 8	106 ± 6	105 ± 7
Diflubenzuron	0.003	0.01	-	109 ± 9	112 ± 7	110 ± 8
Dimethoate	0.003	0.01	101 ± 9	113 ± 5	110 ± 5	108 ± 6
Fipronil	0.02	0.07	-	88 ± 13	107 ± 10	98 ± 12
Imidacloprid	0.002	0.01	104 ± 4	109 ± 7	110 ± 6	108 ± 6
Procymidone	0.01	0.05	-	104 ± 17	102 ± 17	103 ± 17
Thiamethoxam	0.002	0.01	120 ± 9	114 ± 4	113 ± 6	116 ± 6

^aLimit of detection (LOD); ^blimit of quantification (LOQ); ^crecovery mean of values of 0.01, 0.1 and 0.5 mg kg⁻¹ levels (Rec) (n = 5); ^drelative standard deviation (RSD); ^eknown pesticide concentration initially added to the blank matrix.

contains the physical chemical properties of pesticides and the summary of the analysis of pesticide treatments by washing is presented in Table 5.

In most treatments the pesticides were eliminated by washing, Figure 1, with exception procymidone that had little effect with water washing and the fipronil residue actually increased after washing with vinegar. This behavior cannot be explained considering its physicochemical properties and/or its mode of action or can be assigned to any experimental error. Samples from vinegar solution may have acid residues. It is believed that the use of vinegar may alter the effect of the tomato matrix, as they have ionizable groups. The decrease in matrix effects led to the increase of fipronil response in samples with vinegar wash, so bigger concentrations are possible.

In comparison with MRL most of the washing treatments decreased the concentration of pesticides below the MRL of Brazil and the EU, with the exception of fipronil, which has MRL of 0.005 mg kg⁻¹ in EU and is not applied to the tomato crop in Brazil, and procymidone and diflubenzuron that, while treatments have decreased residues below the MRL Brazil (2.0/0.5 mg kg⁻¹), not have achieved EU (0.01/0.05 mg kg⁻¹).²¹

Effect of different washing processes

The most important mechanism that may lead to the possible residue alteration during household washing processes is the dissolution, which is related to the water solubility of the pesticide residue. The penetration is also a dynamic process that may control the fate of a pesticide residue during washing. Other factors may further affect the pesticide dissolution mechanism, such as the type of formulation applied, temperature and initial concentration of the pesticide residue on commodity, pesticide partition coefficient (K_{ow}), ionic strength and pH of the aqueous media.²²

In this study, the most suitable washing treatment that reduces the amount of residues of acetamiprid and procymidone was with 10% vinegar, reducing 93% and 43%, respectively. For the pesticides imidacloprid and thiamethoxam, washing with bicarbonate and vinegar were more efficient, and had not differed significantly, reducing 62% and 71%, and 72% and 78%, respectively. In another study that analyzed procymidone in samples of cucumber, washing with water reduced 24% of residues and 85% was eliminated with the removal of the peel,²³ even though this pesticide has systemic action. In a study with

Table 4. Physicochemical properties of pesticides

Pesticide	Chemical group	Mode of action	Solubility ^a / (mg L ⁻¹)	pK _{ow} ^b	MRL ^c / (mg Kg ⁻¹)	Vapor pressure (at 25 °C) / mPa
Acetamiprid ^d	neonicotinoid	systemic with translaminar activity having both contact and stomach action	2950	0.8	0.2 / 0.5	1.73 × 10 ⁻⁴
Azoxystrobin ^e	strobilurin	systemic translaminar and protectant action having additional curative and eradicator properties	6.7	2.5	3.0 / 0.5	1.10 × 10 ⁻⁷
Diflubenzuron	benzoylurea	selective, non-systemic with contact and stomach action, acts by inhibiting chitin synthesis	0.08	3.89	0.05 / 0.5	0.00012
Dimethoate	organophosphate	systemic with contact and stomach action; acetylcholinesterase (AChE) inhibitor	39800	0.704	0.02 / 1.0	0.247
Fipronil	pyrazole	broad-spectrum with contact and stomach action; GABA-gated chloride channel antagonist	3.78	3.75	0.005 / N.A. ^f	0.002
Imidacloprid ^g	neonicotinoid	systemic with contact and stomach action; acetylcholine receptor (nAChR) agonist	610	0.57	0.5 / 0.5	4.0 × 10 ⁻⁷
Procymidone	dicarboximide	systemic with protective and curative properties	2.46	3.3	0.01 / 2.0	0.023
Thiamethoxa ^h	neonicotinoid	broad spectrum, systemic with contact and stomach action; acetylcholine receptor (nAChR) agonist	4100	-0.13	0.2 / 1.0	6.60 × 10 ⁻⁶

^aSolubility in water at 20 °C; ^boctanol-water partition coefficient at pH 7 (20 °C); ^cmaximum residue limits (MRL) in European Union and Brazil, source: European Union⁴ (2015), Brazil⁶ (2015), pesticide properties database²¹ (2015); ^dformulated product with a mixture of cypermethrin in Brazil; ^eformulated product with a mixture of difenoconazole or flutriafol or tebuconazol or mancozeb or tetraconazole or fludioxonil + metalaxyl or benzovindiflupyr or cyproconazole; ^fN.A.: not allowed; ^gformulated product with a mixture of β-cyfluthrin or thiodicarb or bifenthrin or flutriazol or triadimenol; ^hformulated product with a mixture of cyproconazole or cypermethrin or fludioxonil + metalaxyl + thiabendazole or λ-cyhalothrin or cloranthraniliprole.

Table 5. Tukey's test to compare different washing processes for tomato samples (n = 6)

Pesticide	Washing	Average / (\pm SD) ^a	RSD ^b / %	Tukey ^c ($\alpha = 0.01$)
Acetamiprid	control	0.05393 \pm 0.001740	3.74	A
	water	0.02228 \pm 0.009283		B
	bicarbonate	0.01758 \pm 0.007289		C
	vinegar	0.00400 \pm 0.007584		D
Azoxystrobin	control	0.2055 \pm 0.012470	7.67	A
	water	0.05642 \pm 0.006061		C
	bicarbonate	0.1107 \pm 0.009035		B
	vinegar	0.06419 \pm 0.002652		C
Diflubenzuron	control	0.5374 \pm 0.06853	10.89	A
	water	0.1381 \pm 0.004624		C
	bicarbonate	0.3513 \pm 0.01324		B
	vinegar	0.3181 \pm 0.02243		B
Dimethoate	control	0.03360 \pm 0.01742	5.29	A
	water	0.01565 \pm 0.0006920		C
	bicarbonate	0.01282 \pm 0.0006790		D
	vinegar	0.01922 \pm 0.001267		B
Fipronil	control	0.4430 \pm 0.02587	9.13	B
	water	0.4037 \pm 0.01569		B
	bicarbonate	0.4327 \pm 0.02029		B
	vinegar	0.9406 \pm 0.05395		A
Imidacloprid	control	0.06931 \pm 0.02914	11.35	A
	water	0.02941 \pm 0.0009830		B
	bicarbonate	0.02630 \pm 0.001450		BC
	vinegar	0.02044 \pm 0.0009710		C
Procymidone	control	0.9183 \pm 0.06878	7.01	A
	water	0.9450 \pm 0.06591		A
	bicarbonate	0.7846 \pm 0.04264		B
	vinegar	0.5191 \pm 0.03453		C
Thiamethoxam	control	0.03821 \pm 0.003902	11.40	A
	water	0.01351 \pm 0.0004200		B
	bicarbonate	0.01065 \pm 0.0006890		BC
	vinegar	0.008300 \pm 0.0006010		C

^aStandard deviation (SD); ^brelative standard deviation (RSD); ^caverage with the same letter are not significantly different ($p < 0.01$).

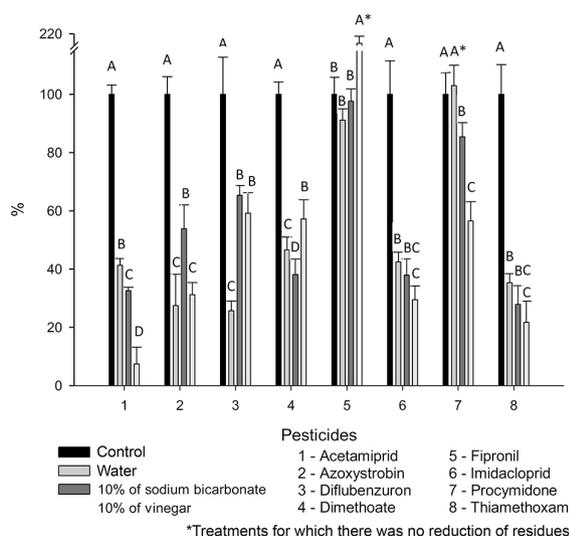


Figure 1. Percentage of pesticide residues in tomato samples after washing procedures.

peaches intended for baby food, a simple washing with water eliminated 51% of procymidone residues contained in the fruit.²⁴

For dimethoate, the best treatment in this study was washing with 10% of sodium bicarbonate solution, reducing 62% of the residue in the tomato sample.

According to a study conducted with cucumbers,⁸ washing with sodium carbonate and sodium bicarbonate solution proved to be an effective method for removing organophosphorus pesticides (trichlorfon, dimethoate, dichlorvos, fenitrothion, and chlorpyrifos). It was the same finding in this study.

In a study with field-grown pepper,¹³ washing with acetic acid provided high removal of residue of profenofos organophosphorus. In a study with naturally contaminated potato, organophosphate pesticides (pirimiphos-methyl, profenofos, and malathion) were more efficiently

eliminated by acidic solutions than in neutral and alkaline solutions.²⁵

Washing with water showed the lowest residue concentration for diflubenzuron in this study (74% of reduction), and the effect of water and vinegar did not differ significantly for azoxystrobin (73% and 69% of residue reduction, respectively).

In a study with strawberries when pesticides were applied in the field, washing with tap water reduced azoxystrobin and fenhexamid, but did not reduce pyrimethanil residues. Consequently, when the fruits were washed with commercial detergent solution (water and detergent 5:1, v/v), larger amounts of residues were removed (about 45% of azoxystrobin and pyrimethanil and 60% of fenhexamid).²⁶

Despite washing, fipronil residues were not removed from the tomato samples. In a study of washing processing of fipronil residues in green beans in Spain, the residue levels of fipronil were reduced by around 50%,²⁷ but in other similar studies, pesticide reduction rates out of this range have also been reported, including reduction rates of 0% and 100% for some pesticide/crop combinations.^{28,29}

Results obtained in our study indicate that the reduction of pesticide residues by washing the tomatoes is correlated with Kow (Figure 2) with greater intensity in the case of washing with 10% of sodium bicarbonate ($r^2 = 0.8543$), for which reduction increases as the log Kow decreases (Figure 2b). This correlation was also found in a study of green beans contaminated with acrinathrin, fipronil and kresoximmethyl,²⁷ when washed with water. This fact shows a tendency that partition coefficients between cuticle and washing treatments is correlated well with Kow of pesticides.^{16,27,30}

In general, the washing effect is more pronounced for the more soluble pesticide in water. But cleaning efficiency did not show higher correlation of 0.12 with the solubility values in water, indicating no correlation. In this study, the pesticides with higher water solubility were: dimethoate, acetamiprid and thiamethoxam that showed higher washing efficiency at acidic pH, using vinegar solution, and also the lower pKow. This indicates that the ionizable groups have more influence than solubility on the efficiency on the wash.

In a field study performed in Belgium, to quantify the effect of household processing on residues of pesticides

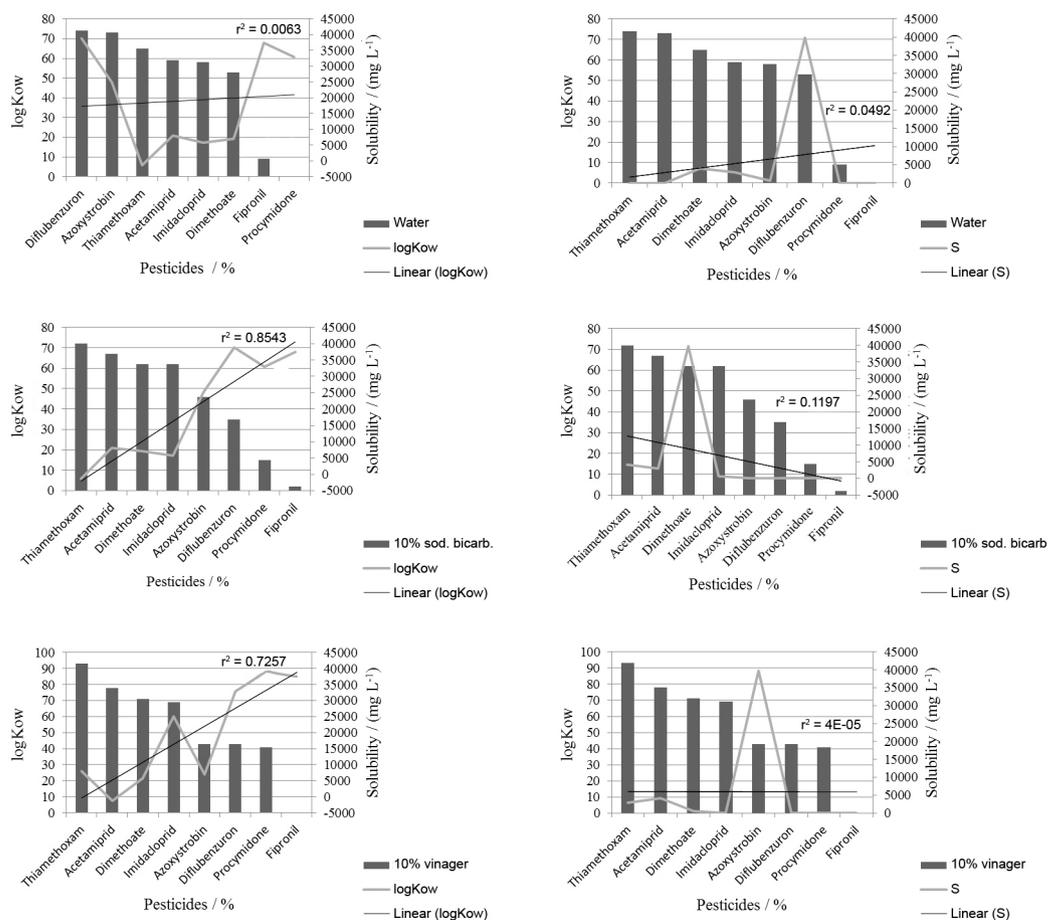


Figure 2. Pesticide reduction by washing with (a) water; (b) 10% of sodium bicarbonate; (c) 10% of vinegar; and correlation with partition coefficient (log Kow) with (d) water; (e) 10% of sodium bicarbonate; (f) 10% of vinegar and correlation with the solubility (S).

(carbendazim, maneb, acetamiprid, cyromazine, imazalil and thiamethoxam) in two varieties of melon, it was observed that the reduction of pesticides cannot be completely explained by systemic pesticide features.³¹ However, agricultural practices (such as, time of application), the solubility and mode of action of pesticides (systemic and contact action) can be used to explain the difference in the processing factors for the studied pesticides.

The data reported in the literature regarding the effect of washing of pesticide residues in fruits and vegetables are contradictory and all have shown a lack of correlation between solubility in water and pesticide reduction after washing.²⁶ Although differences manifest between types of washing (with water or soaked first before washing), different washing solutions and freezing prior to analysis are observed to reduce pesticide residues regardless of chemical class or solubility.²²

Peel and pulp

Statistical analysis

Tukey's test ($p < 0.01$) was used to evaluate the percentage of pesticide retention in the tomato peel and in the pulp (Table 6).

Table 6. Average of pesticide retention in the peel in relation to whole tomato and Tukey's test ($n = 4$)

Pesticide	Average (\pm SD ^a) / %	RSD ^b / %	Tukey ^c ($\alpha = 0.01$)
Diflubenzuron	73 \pm 1.70	3.65	a
Azoxystrobin	66 \pm 0.83		b
Procymidone	35 \pm 0.41		c
Acetamiprid	19 \pm 1.99		e
Dimethoate	21 \pm 0.95		d
Imidacloprid	17 \pm 1.30		e
Thiamethoxam ^d	–		
Fipronil	1.0 \pm 0.04		f

^aStandard deviation (SD); ^brelative standard deviation (RSD); ^caverage with the same letter are not significantly different ($p < 0.01$); ^dthe thiamethoxam presented much variability in results and was removed from the statistical analysis.

Concentration in the peel and pulp

The main factors that may affect the penetration of a pesticide residue are the characteristics of the pesticide (Kow, molar mass, systemic action and the formulation of applied pesticide) in relation to the nature of the commodity. The initial concentration of the pesticide residue and the processing temperature could also affect penetration mechanism significantly.²²

Mechanical peeling, typical for household processing and chemical peeling, applied mostly in industrial processing, are procedures that make a substantial contribution to the reduction of residue levels in the fruit flesh. Most of the residues are removed with the peel.^{24,32} The systemic action of a pesticide residue, in this case, is not always correlated with decreased reduction of pesticide residues through peeling.²² Chinese researchers observed the same effects using washing, blanching, peeling, and boiling for chlorothalonil, oxadixyl, and thiophanate-methyl.³³

In relation to concentration of pesticides in the peel, the study did not show a correlation with Kow ($r^2 = 0.0016$). The highest residue concentration was in the diflubenzuron that is not systemic and has the largest value of pKow (3.89) with lower solubility (0.08 mg L⁻¹).²¹ The pulp retained a substantial proportion of lipophilic residues,²² and fipronil showed highest concentration, it being an insecticide that is quite lipophilic, and having broad spectrum with contact and stomata action.

Diflubenzuron, azoxystrobin, and procymidone, which had higher concentrations in the tomato peel, were efficiently removed with washing procedures, as expected.

Acetamiprid did not show statistical difference with imidacloprid, since they are systemic and with high-water solubility (2950 and 610 mg L⁻¹, respectively).

The insecticide fipronil also had smaller amounts of pesticides eliminated during washing process. Thiamethoxam was removed from the statistical analysis because it showed high variability between replicates (11% \pm 9.93), and this behavior cannot be explained considering its physicochemical properties and/or its mode of action.

In the same way that washing is highly recommended to reduce residues of pesticides, peeling is also recommended as it decreases the values even for systemic pesticides.

Conclusions

Washing with 10% of sodium bicarbonate solution is efficient for reducing dimethoate organophosphorus residues. For acetamiprid and procymidone, washing with 10% vinegar solution is recommended. For the pesticides imidacloprid and thiamethoxam, washing with bicarbonate and 10% vinegar solution were more efficient, and did not differ significantly. Washing with water showed the lowest residue concentration for diflubenzuron; and washing with water and vinegar, did not differ significantly for azoxystrobin. Despite washing, fipronil residues were not removed from the tomato samples.

In relation to the concentration of pesticides in the peel of the tomatoes, diflubenzuron had the highest residue

concentration and fipronil showed the highest concentration in the pulp.

In summary, washing with water or other solutions, and peeling before consumption are recommended for the reduction of pesticide residues in tomatoes. Any one of these processes contributes substantially to reduced consumer exposure to pesticides.

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