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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

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Abstract

In this study, controlled applications of captan and procymidone were carried out on tomatoes grown in two different greenhouses at different times. The first group of samples were collected immediately after the application and the second group were collected 14 days later. Additionally, control samples were collected before application. The effects of washing, peeling and predetermined storage period, at 4 °C for 7 and 14 days, on the reduction of residue levels in the plant tissues were investigated in the two groups. A gas chromatographic method using acetone, dichloromethane and petroleum ether as extraction solvents, was used to analyse residual captan and procymidone in tomatoes, with obtained recoveries higher than 83%. Captan and procymidone were determined by gas chromatography-electron capture detection (GC-ECD), using a 5% phenylmethylpolysiloxane-coated fused-silica capillary column.

Results showed that waiting for the recommended pre-harvest intervals, indicated on the prospectuses of both pesticides, lowered the residue levels to within acceptable limits. Culinary applications, such as washing and peeling and refrigeration storage, were also effective in reducing the residue levels.

Keywords: Pesticide residues; Tomatoes; Culinary applications; PHI; Captan; Procymidone

1. Introduction

Pesticides are chemical substances that are widely used against plant pests and diseases. The use of pesticides in commercial agriculture has led to an increase in farm productivity (Krol, Arsenault, Pylypiw, & Mattina, 2000). Pesticides are essential in modern agricultural practices but, due to their biocidal activity and potential risk to the consumer, the control of pesticide residues in foods is a growing source of concern for the general population (Torres, Picó, & Mañes, 1996). Governments and international organizations are regulating the use of pesticides, setting the acceptable MRLs in foods. When these compounds are applied according to good agricultural practices, MRLs are not exceeded, but their incorrect application may leave harmful residues, which involve possible health risk and environmental pollution.

A substantial body of laboratory and epidemiological evidence suggests that certain pesticides are associated with carcinogenesis, immunotoxicity, neurotoxicity, behavioral impairment, reproductive dysfunction, endocrine disruption, developmental disabilities, skin conditions and respiratory diseases, such as asthma (Solomon, Ogunseitan, &

Abbreviations: PHI, pre-harvest interval; MRL, maximum residue level; LD_{50}, lethal dose 50; AOAC, association of official analytical chemists; ADI, acceptable daily intake; ECD, electron capture detection; FAO, Food and Agricultural Organization.

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Kirsch, 2000). The presence of their residues in fruits and vegetables can be a significant route to human exposure (European Community, 1990).

Especially in developing countries, residue problems are gaining increasing importance, due to the lack of government inspections and awareness of the producer and consumer about this matter. As a consequence, food consumers are face to face with food products which have high residue levels.

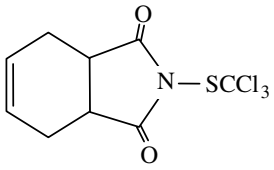
Residual pesticides on food materials decrease by various culinary applications or with time, depending on the type and properties of the pesticides. Several investigators have found that levels of captan and procymidone residues were reduced by the pre-harvest intervals and/or culinary application, such as washing, peeling, storage (Lentza-Rizos & Balokas, 2001; Ritcey, McEwen, Frank, & Braun, 1983; Teixeira, Aguiar, Afonso, Alves, & Bastos, 2004; Teixeira, Aguiar, Afonso, Alves, & Bastos, 2002; Yoshikawa, Kaihara, & Nakanishi, 1998).

Captan is a non-systemic phthalimide fungicide used to control diseases of many fruit, ornamental and vegetable crops (Extoxnet, 1996). The rat oral LD_{50} for captan ranges from 8400 to 15,000 mg/kg and the mouse LD_{50} is 7000 mg/kg (Chemical Information Systems, 1988).

There is strong evidence that captan causes cancer in female mice and in male rats at high doses. In addition, captan is chemically similar to two other pesticides, Folpet and Captafol that have been shown to produce cancer in test animals. Tumors are associated with the gastrointestinal tract and, to a lesser degree, with the kidneys (US Department of Agriculture, 1984; US National Library of Medicine, 1995). The US EPA has classified captan as B2, a probable human carcinogen (Reregistration Eligibility Decision, 1999).

Tumors appeared in the test animals at doses of about 300 mg/kg/day (US Department of Agriculture, 1984; US National Library of Medicine, 1995). Bernard and Gordon (2000) have also indicated that captan and Folpet share a common mechanism in the formation of duodenal tumors in mice. JMPR estimated the ADI of captan for humans to be 0–0.1 mg/kg bw (JMPR, 1984). The chemical structure of captan is represented in Fig. 1.

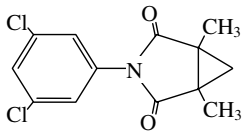
Procymidone is a dicarboximide fungicide with moderate systemic activity (FAO, 2001). The rat and mice oral



Captan

N-(trichloromethylthio)cyclohex-4-ene-1,2-dicarboximide (UIPAC)
3a,4,7,7a-tetrahydro-2-[(trichloromethyl)thio]-1H-isoindole-1,3(2H)-dione (CAS)

Fig. 1. Structure and chemical name of captan.



Procymidone

N-(3,5-dichlorophenyl)-1,2-dimethylcyclopropane-1,2-dicarboximide (UIPAC)
3-(3,5-dichlorophenyl)-1,5-dimethyl-3-azabicyclo (3,1,0) hexane-2,4-dione (CAS)

Fig. 2. Structure and chemical name of procymidone.

LD_{50} for procymidone is >5000 mg/kg bw. The effects on reproduction and the induction of testicular tumors in a long term rat study can be explained by the effects of procymidone on the endocrine system. The ADI was set at 0–0.1 mg/kg bw (FAO, 2001). Chemical structure of procymidone is represented in Fig. 2.

Effects of washing, peeling and storage for different periods applied with the aim of reduction of captan and procymidone, widely used in greenhouses in Antalya, Turkey, residue quantities in tomato samples, were investigated in this study. These effects were evaluated in tomatoes collected after two pre-harvest time intervals following the pesticide application. The first group of tomatoes was collected 4 h after the pesticide application and the second group was collected after the duration of 14 days, which was the longer one of the pre-harvest time intervals recommended by the pesticide manufacturers.

2. Material and methods

2.1. Chemicals

The dichloromethane, acetone and petroleum ether (for the analysis of pesticide residues) used in the study were purchased from Merck (Darmstadt, Germany). Pesticide analytical standards were purchased with purity certification (10 ng/μl in cyclohexane) from Dr. Ehrenstorfer (Augsburg, Germany). Anhydrous sodium sulphate and sodium chloride for residue analysis were obtained from Merck (Darmstadt, Germany). The commercial captan (captan'H, 50% WP) and procymidone (Sumisclex®, 50% WP) which were applied onto the tomato plants which were procured from Hektaş (Kocaeli, Turkey) and Sumitomo Co. Inc. (Osaka, Japan), respectively.

2.2. Apparatus

Experiments were carried out by using a HP 5890 Series 2 Plus GC System (Hewlett Packard, USA) equipped with a ^{63}Ni ECD system. Chromatographic separation was achieved by using a DB-5 30 m × 0.25 mm I.D., 0.25 μm film thickness analytical column from J&W Scientific (Folsom, CA, USA). Nitrogen (99.999% purity) was used as carrier gas. All data were collected on HP Chemstation software.

2.3. Instrumental conditions

The injector and detector temperatures were kept at 250 and 300 °C throughout the analysis. The column temperature was raised from 70 °C (hold 2 min) to 150 °C at 25 °C/min, then to 200 °C at 3 °C/min, and finally to 280 °C (hold 10 min) at 8 °C/min. Total time for the GC analysis was 43.95 min. A split/splitless injector, operating in the splitless mode, was used. The carrier was nitrogen at 14.1 psi column head pressure. The flow of carrier gas was applied as 30 ml/min. The injection volume was 1 μl. GC analysis conditions are shown in Table 1.

2.4. Preparation of commercial pesticides and application in greenhouse

Commercial captan and procymidone were diluted in water and mixed. In this way, a sufficient quantity of suspension was obtained for application on the field area. An aqueous suspension containing both commercial pesticides (each 50% WP) was prepared by mixing 200 g of each in 100 l. The prepared suspension was applied uniformly onto the tomato plant, using a sprayer. The amount to be delivered per plant was calculated, based on the amount of pesticide that is generally recommended per acre and the number of tomato plants that would be grown in this area. Approximately, 1 l of suspension was sprayed over 10 tomato plants.

2.5. Sample collection and storage

Tomato samples used in the analyses were grown in two different commercial greenhouses in Antalya. The absence of residual pesticides on samples was confirmed by residue analysis prior to the application of commercial pesticides.

Mature tomato samples were collected after application of commercial pesticides suspension according to Section 2.4. Samples were grown and prepared as shown in Fig. 3.

Table 1
GC analysis conditions

GC	HP 5890 Series2 Plus
Detector	ECD
Colon	Capiler Colon, DB5
Injection bloc temperature	250 °C
Detector temperature	300 °C
Oven temperature	Temperature programme 70 °C 2 min 25 °C/min increase 150 °C 3 °C/min increase 200 °C 8 °C/min increase 280 °C 280 °C 10 min
Carrier gas	Nitrogen
Carrier gas flow	30 ml/min, constant pressure
Make-up	Nitrogen
Injection volume	1 μl

The collected samples were transferred to the laboratory and analysed immediately. Samples which required a washing procedure were washed for 15 s by rubbing under running tap water. Samples that required a peeling procedure were peeled with a knife which was previously submersed in acetone for a short time. Samples to be stored were kept at +4 °C in the refrigerator in polyethylene bags.

The recommended pre-harvest intervals were 7 days for captan and 14 days for procymidone, as suggested in the prospectuses supplied by the manufacturers of each pesticide. Therefore, tomato samples in the second group were collected 14 days after the pesticide application.

2.6. Analytical procedure

2.6.1. 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.

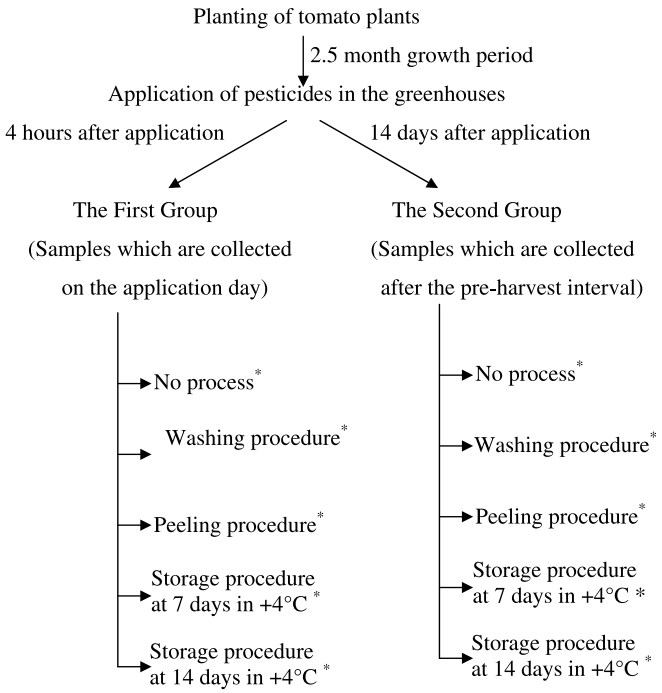
Working solutions were obtained by appropriate dilutions with acetone and stored in a refrigerator (4 °C) (2 months of maximum storage time). No degradation was observed for the compounds in the mentioned storage times. Various standards of pesticides (0.05–2 μg/ml) were prepared and injected into the GC system under the conditions stated in Fig. 3 and the retention times and areas were recorded. A calibration curve was prepared for these concentrations (Figs. 4 and 5). In this method, detection limits of 0.01 ng/ml for both captan and procymidone were determined.

2.6.2. Recovery studies

The method was optimized by recovery studies before the determination of kinds and quantities of pesticides on collected samples. Recovery studies were carried out by spiking fresh samples which did not contain any pesticides, with 1 ml of 1 ppm pesticide standard in solution in acetone. This standard solution was added to chopped tomato sample in the blender jar before homogenization. The same extraction procedures and GC conditions as applied for sample analyses were used for recovery studies. In this way, recoveries were obtained as 83% for captan and 86% for procymidone, with coefficients of variation 5.6% and 1.4%, respectively ($n = 3$).

2.6.3. Extraction procedures

An AOAC (1986) method was used in this study. According to this method a non-fatty test portion was blended with acetone, filtered and pesticides were transferred from aqueous filtrate to organic phase by shaking with petroleum ether and CH_2Cl_2. After drying, the organic phase was concentrated in the presence of petroleum ether, and then acetone, to remove CH_2Cl_2. An aliquot of concentrated organic phase was injected into the GC systems for determination of pesticide residues.



*Analysis (Tomato samples obtained from each treatment were analysed separately).

Fig. 3. Scheme for the analysis of pesticide residues in tomatoes subjected to different treatments.

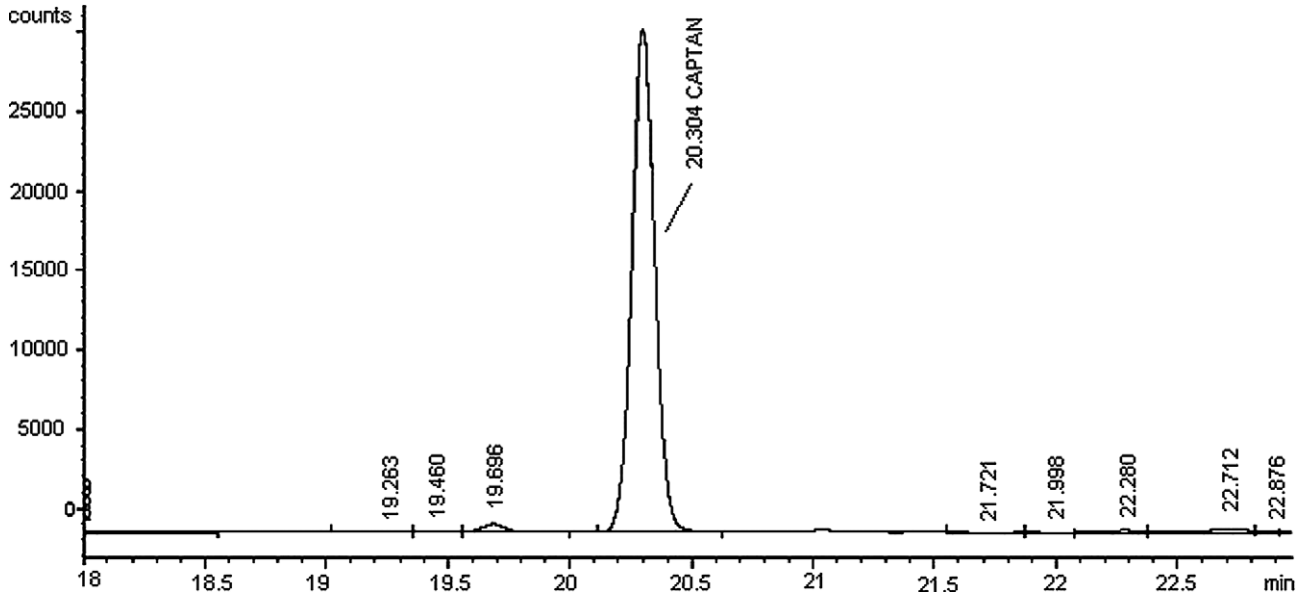


Fig. 4. Gas chromatogram of captan standard (concentration 1 μl/ml).

About 2 kg of vegetable samples were chopped to approximately 1 cm^3 and mixed inside a deep bowl. A test proportion of 100 g was weighed and transferred into a Waring blender jar with 200 ml acetone, and blended for 2 min at high speed. The homogenate was filtered using a vacuum system through a 12 cm Buchner funnel fitted with filter paper. Extracts were collected in 250 ml volumetric flasks. The amount of extract was recorded and 80 ml of extract were transferred into a 1 l separatory funnel. To form a secondary phase, 100 ml of petroleum ether and 100 ml of dichloromethane were added. The separatory funnel was shaken vigorously for 1 min and separation of the two phases was observed. The lower aqueous layer was transferred to a second 1 l separatory funnel. The upper organic layer, in the first separatory funnel, was passed through anhydrous sodium sulphate placed over a

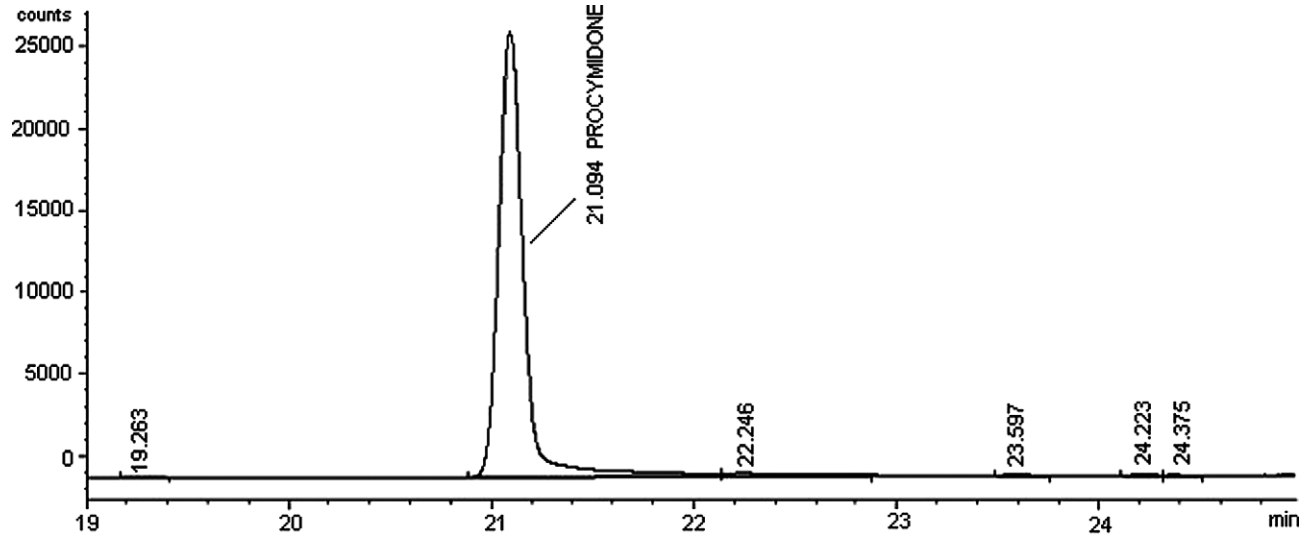


Fig. 5. Gas chromatogram of procymidone standard (concentration 1 μl/ml).

filter paper fitted funnel into a 500 ml rotary evaporator flask. Into the second 1 l separatory funnel, 7 g NaCl were added and the funnel was shaken vigorously for 30 s until most of the NaCl was dissolved. Hundred milliliters of dichloromethane were added shaken 1 min and the separations of the two phases were observed. The lower organic phase was dried by passing through the same sodium sulphate. Hundred milliliters of dichloromethane were added to the extract aqueous phase, which was dried as above. Sodium sulphate was rinsed with ca. 50 ml dichloromethane. All extracts were collected in a rotary evaporator flask.

The extract was concentrated using a rotary evaporator (45 °C). When the liquid level in the rotary evaporator flask was ca. 2 ml, 100 ml petroleum ether were added and the mixture reconcentrated to ca. 2 ml. The concentration step was repeated with another addition of 50 ml petroleum ether. After the addition of 20 ml of acetone, the mixture was reconcentrated to ca. 2 ml. Care was taken to avoid absolute dryness during the concentration steps. The contents of the flask were then completed to a volume of 7 ml with acetone.

2.6.4. Calculation of equivalent test portion weight

Equivalent test portion weights in the final solution were calculated as follows:

$$\frac{\text{mg test portion equivalent}}{\mu\text{l final extract}} = \left(\frac{80}{200 + W - 10}\right) \times \left(\frac{1}{\text{ml final volume}}\right) 100$$

where 200 = ml acetone blended with 100 g test portion; W = amount (ml) H_2O present in test portion; 10 = adjustment for water–acetone volume contraction.

2.6.5. Statistical evaluation

All residue analyses were replicated in two different greenhouses. Each replicate sample was analysed for residues in duplicate analyses. All analyses were performed on duplicate samples and the results were statistically analysed by ANOVA ($P < 0.01$). Significant means were subjected to analysis by Duncan's multiple range test ($P < 0.05$). All statistical analyses were performed using the Statistical Analysis System (SAS Institute, Cary, NC, USA).

3. Result and discussion

3.1. Results of the captan application

The results of captan residue analyses are presented in Table 2. These results were subjected to ANOVA and Duncan's multiple range test and significantly different means are presented in Table 3.

According to results of variance analysis, significant reductions in residue levels for captan were obtained through both the pre-harvest time and processes which were done aiming at decreasing pesticide residues ($P < 0.01$). Significant interaction of these two parameters were observed on the reduction of residues ($P < 0.01$).

According to results of Duncan's multiple range comparisons shown in Table 3, when compared to the samples which were collected 4 h after the pesticide application, captan residues were significantly ($P < 0.05$) reduced in samples which were collected 14 days following the pesticide application.

In addition, processes, such as washing, peeling and storage which were applied for reducing the level of residues, resulted in a significant ($P < 0.05$) decrease in captan residues. These results agree with Yoshikawa et al. (1998) who reported that captan residues were reduced by the peeling procedure.

No statistical differences were observed between effects of peeling and washing processes on the reduction of residue levels. Thus, the effects of these processes were similar.

Table 2
Analytical parameters of analyzed captan in tomato samples expressed as mg/kg

Processes	1st Greenhouse		2nd Greenhouse	
	First group[a]	Second group[b]	First group[a]	Second group[b]
No process	1.60 ± 0.10	0.43 ± 0.01	0.97 ± 0.03	0.31 ± 0.02
Washed	0.15 ± 0.00	0.07 ± 0.00	0.09 ± 0.00	0.05 ± 0.01
Peeled	0.08 ± 0.00	0.03 ± 0.01	0.07 ± 0.00	0.03 ± 0.00
Stored at 7 days in 4 °C	0.77 ± 0.12	0.24 ± 0.03	0.37 ± 0.02	0.15 ± 0.01
Stored at 14 days in 4 °C	0.55 ± 0.04	0.19 ± 0.02	0.34 ± 0.00	0.12 ± 0.02

Values are given as means ± standard error.
[a] Mean residue contents in samples which were collected 4 h after the pesticide application.
[b] Mean residue contents in samples which were collected 14 days after the pesticide application.

Table 3
Results of Duncan's multiple range test for means of captan residues in tomato samples

Pre-harvest time	Mean residues (ppm)	Processes	Mean residues (ppm)
4 h	0.50 ± 0.11[aA]	No process	0.83 ± 0.19[a]
14 days	0.16 ± 0.03[b]	Washed	0.09 ± 0.01[c]
		Peeled	0.05 ± 0.01[c]
		Stored at 7 days in 4 °C	0.38 ± 0.09[b]
		Stored at 14 days in 4 °C	0.30 ± 0.06[b]

[A] Results are expressed as means ± standard error. Within each application, values with different superscripts are significantly different ($p < 0.05$).

In addition, the results show that captan residues of samples stored in +4 °C at 7 and 14 days were not statistically different ($P < 0.05$).

Fig. 6 shows percentages of detected average residues, after different processing applications, on the tomato samples. Percentage average residues determined after collection of tomato fruit after the pesticide application, and following different pre-harvest intervals, are shown in Fig. 7. Also process and time effects are presented together in Fig. 8.

The initial captan residue level was decreased 89% by washing procedure, 93% by peeling procedure, 54% by storage procedure at +4 °C for 7 days and 64% by storage

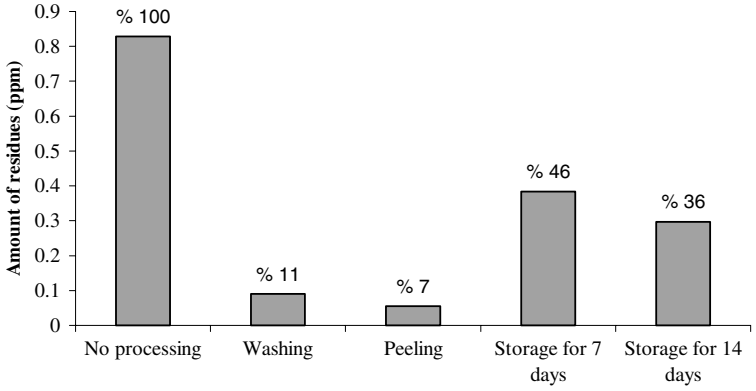


Fig. 6. Percentages of detected average residues after different processes in tomato samples to which commercial captan was applied.

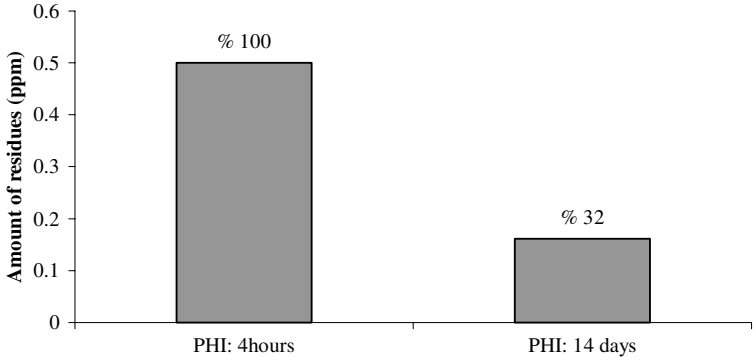


Fig. 7. Percentages of detected average captan residues after the pesticide application on samples collected following different pre-harvest intervals (PHI).

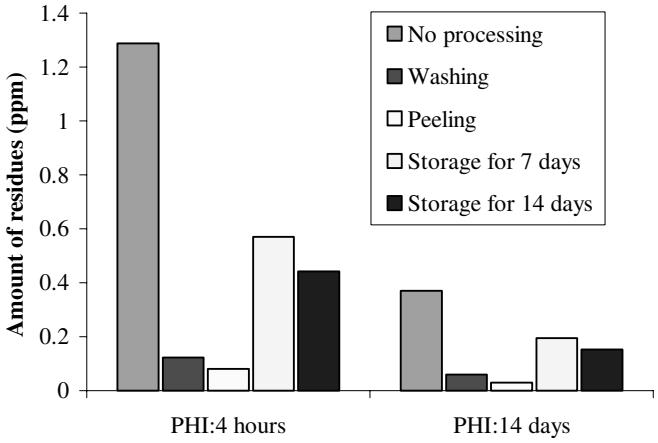


Fig. 8. Variation of detected average captan residues after different processes in tomato samples which were collected 4 h and 14 days after the pesticide application.

procedure at +4 °C for 14 days. On the other hand, a 14 day pre-harvest interval resulted in a 68% reduction of captan residue levels in tomato samples in which no process was applied (Figs. 6 and 7).

3.2. Results of the procymidone application

The results of procymidone residue analyses are presented in Table 4. These results were subjected to ANOVA and Duncan's multiple range test and significantly different means are presented in Table 5.

According to results of variance analysis, significant reductions in residue levels for procymidone were obtained through both the adherence to the pre-harvest time and the application of processes which were aimed at decreasing pesticide residues ($P < 0.01$).

The results also agree with Lentza-Rizos and Balokas (2001) and Teixeira et al. (2002) who reported that procymidone residues were reduced by a washing procedure. However, in this study, no significant interactions of pre-harvest time and culinary applications were observed on reducing the residue contents ($P < 0.05$).

According to the results of Duncan's multiple range test shown in Table 5, no statistical differences were observed between effects of peeling and washing processes on the

Table 5
Results of Duncan's multiple range test for means of procymidone residues in tomato samples

Pre-harvest time	Mean residues (ppm)	Processes	Mean residues (ppm)
4 h	0.74 ± 0.14^{aA}	No process	0.86 ± 0.26^{a}
14 days	0.29 ± 0.02^{b}	Washed	0.28 ± 0.04^{cd}
		Peeled	0.20 ± 0.03^{d}
		Stored at 7 days in 4 °C	0.70 ± 0.21^{ab}
		Stored at 14 days in 4 °C	0.53 ± 0.14^{bc}

[A] Values in a column followed by different letters are significantly ($P < 0.05$) different (Duncan's multiple range test). Values are means ± standard error.

reduction of procymidone residue levels. In addition, when compared to the samples which were collected 4 h after the pesticide application, procymidone residues were significantly reduced in samples which were collected 14 days following the pesticide application ($P < 0.05$).

In addition, tomato samples which were not subjected to any process had the highest levels of residues. No significant reduction was observed in tomato samples which were stored for 7 days in 4 °C. Thus, it can be presumed that procymidone maintains its stability at low temperatures ($P < 0.05$).

Fig. 9. shows percentages of detected average residues after different processing applications on the tomato samples. Percentage average residues determined after collection of tomato fruit after the pesticide application and following different PHI are shown in Fig. 10. Also process and time effects are presented together in Fig. 11.

The initial procymidone residue level was decreased 68% by washing procedure, 77% by peeling procedure, 19% by storage procedure for 7 days at +4 °C and 38% by storage procedure for 14 days at +4 °C. On the other hand, a 14 day PHI resulted in a 62% reduction of procymidone residue levels in tomato samples to which no process was applied (Figs. 9 and 10).

Procymidone is known to have moderate systemic activity whereas captan is a non-systemic pesticide. This is thought to be the most important reason why procymidone residues are higher than captan residues, depending on various culinary applications and following different PHI. It is

Table 4
Analytical parameters of analysed procymidone in tomato samples expressed as mg/kg

Processes	1st Greenhouse		2nd Greenhouse	
	First group[a]	Second group[b]	First group[a]	Second group[b]
No process	0.57 ± 0.04	0.37 ± 0.01	2.02 ± 0.15	0.49 ± 0.01
Washed	0.20 ± 0.00	0.19 ± 0.00	0.47 ± 0.05	0.26 ± 0.02
Peeled	0.14 ± 0.01	0.10 ± 0.00	0.33 ± 0.01	0.22 ± 0.01
Stored at 7 days in 4 °C	0.44 ± 0.00	0.29 ± 0.03	1.66 ± 0.00	0.39 ± 0.01
Stored at 14 days in 4 °C	0.41 ± 0.00	0.24 ± 0.01	1.18 ± 0.07	0.30 ± 0.01

Values are given as means ± standard error.
[a] Mean residue contents in samples which were collected 4 h after the pesticide application.
[b] Mean residue contents in samples which were collected 14 days after the pesticide application.

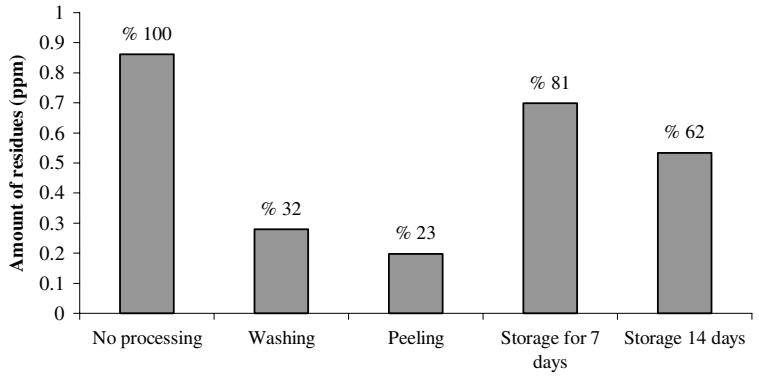


Fig. 9. Percentages of detected average residues after different processes in tomato samples to which commercial procymidone was applied.

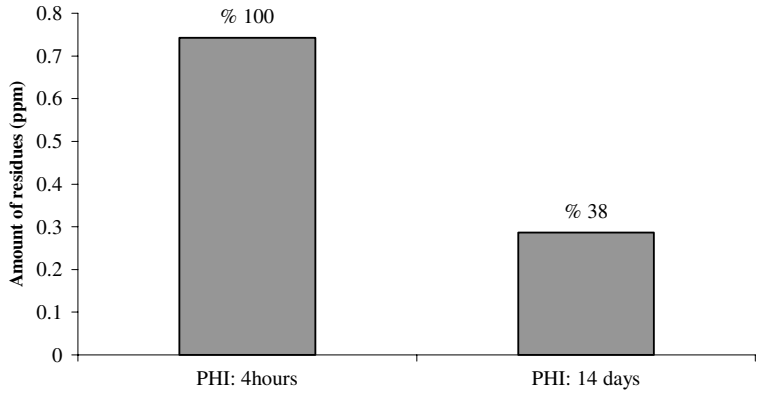


Fig. 10. Percentages of detected average procymidone residues after the pesticide application on samples collected following different PHI.

presumed that some procymidone which penetrated into the plant tissue could not be removed effectively by washing and peeling.

It can be observed from Fig. 10 that, that the recommended PHI (14 days) following application of pesticides has an obviously decreasing effect on procymidone residues in tomatoes. Also washing and peeling processes reduced procymidone residues. The effect that refrigerated storage at +4 °C for 7 and 14 days had on reducing procymidone residue contents were not as pronounced in samples for which a pre-harvest interval was used. This can be attributed to lower rates of physiological elimination reactions under refrigerated storage for samples where a PHI was used.

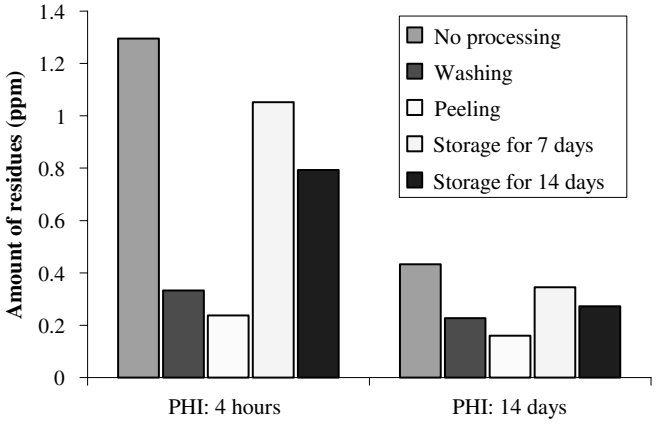


Fig. 11. Variation of detected average procymidone residues after different processes in tomato samples which were collected after 4 h and 14 days from pesticide application.

4. Conclusions

The MRL's for the two pesticides are 3 and 2 ppm for captan and procymidone, respectively as stated by the EU Codex (EEC, 2004), and 3 and 0.5 ppm as stated by the Turkish Food Codex (Turkish Food Codex, 2001). Captan levels were found to be below the MRLs; however, the procymidone levels were above the limits in the samples which were not processed. On the other hand, the levels of procymidone were also reduced to acceptable levels by adherence to the recommended preharvest interval and the application of cullinary procedures.

Based on the obtained data, the most effective processes for reduction of residues of captan, applied on tomato plants, were peeling and washing. Also storage at +4 °C for 7 and 14 days in the refrigerator decreased captan residues, although not as effectively as the peeling and washing procedures.

In addition, the results show that the most effective process for residue reduction of procymidone in tomatoes was

peeling. Also, washing and storage for 7 and 14 days at +4 °C decreased procymidone residues, but not as effectively as peeling.

It can be concluded that, processes, such as controlled dose setting for the use of these pesticides, controlled greenhouse treatments, harvest and storage processes, and culinary applications before consumption have a crucial role in the reduction of residual pesticides which pose a serious threat to human health and the environment.

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