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DETERMINATIN OF PESTICIDE RESIDUES IN TOMATOES COLLECTED FROM AYDIN PROVINCE OF TURKEY

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Abstract

Aydın is mainly an agricultural city of Turkey with its tomatoes, figs, olives, cottons, grapes. These crops are economically very important and frequently damaged by diseases and pests. This leads to yield and food quality losses. The intensive usage of pesticides to protect the crops from pests and diseases causes great concerns about the pesticide residues. The aim of this study was to evaluate the residue level of pesticides in tomatoes collected from different markets in Aydın province of Turkey. Samples were taken in different time intervals and analysed by GC-MS/MS. The concentration of all analysed pesticides were between 0.04 ppm and 1.4 ppm. The concentration of Acetamiprid, Endosulfan and Chlorpyrifos were detected above the maximum residue level in November. The level of Acetamiprid, Endosulfan beta and Chlorpyrifos in tomatoes were above the MRL in December, and only chlorpyrifos was above the MRL in January. In February all the insecticides were below the limit and in March, Tetradifon was above the MRL limit. The possible sources of pesticide residues in tomatoes are not to account into preharvest intervals, uncontrolled pesticide usage at recommended dosage.

Key words*: maximum residue limit (MRL), pesticide residues, tomato.*

INTRODUCTION

Turkey is the fourth biggest tomato production in the world with a tomato production of 11.3 milyon tons (Anonymous, 2014). The annual tomato consumption in Turkey per capita is over 80 kg because of the vitamin and mineral content, nourishment habits, cheap price and suitable ecological conditions (Keskin et al., 2010). In 2014 totaly 4.8 million hectare tomato cultivation is done in the world with China being the largest producer by 50 milyon ton production followed by India (17.5 milyon ton), USA (13.2 milyon ton) and Turkey (11.3 milyon ton) respectively. Tomatoes account for 38 percent of all vegetable production in Turkey and 30 % of Turkish tomato production is processed in to products such as tomato juice, tomato puree, tomato paste, ketchup and chapped tomatoes. Tomato paste is the leading export among fruit and vegetable sector. Fresh consumption of tomatoes grown in Mediterranean region, especially in greenhouses (Nelson and Çakiroğlu, 2009).

The increase in the demand for tomatoes led to the use of more pesticide. Pesticides are using to kill pests, diseases and weed but they also results residues on food (Rehber and Turhan, 2002; Turgut et al., 2011). Pesticide residues is an important subject for human health, aquatic and soil organisms and environment (Turgut 2006; 2007). Some pesticides are persistent and can be seen in soil, water or foods. Food and Agriculture Organization of the United Nations (FAO) and World Health Organization (WHO) organized a workshop about the principles and methods of risk assessment: 'Maximum residue levels (MRLs) for pesticides and Veterinary Drugs' (FAO/WHO, 2006). MRL is the amount of residue accepted according to the consumption of food. For example, a 68 kg man would have to eat 3000 heads of lettuce every day in his life to exceed the residue level which has no effect on laboratory animals (Anonymous, 2015). Practically one MRL is set for one pesticide and one crop. It also shows farmers to use the best suited pesticide for the crop. Such as table grapes' and wine grapes' maximum residue limit for acetamiprid is 0.5 ppm while tomatoes' maximum residue limit for acetamiprid is 0.2 ppm. When the results of

the 2007 and 2010 European Union-coordinated control programs (EFSA, 2013) for tomato samples compared, the percentage of samples without detectable residues decreased from 68% in 2007 to 51% in 2010. The percentage of tomato samples exceeding the MRLs increased from 0.9% to 1.2% in 2007 and 2010 respectively (Lozowicka et al., 2015). The aim of this study was to investigate the concentrations of pesticide residues in tomatoes collected from local and chain markets and evalulate possible source of pesticide residues in tomatoes.

MATERIALS AND METHODS

Tomato fruits were collected from local and chain markets in Aydın province of Turkey. Totaly 100 tomato samples were taken between November to March, stored at -20°C and sampled as the procedure outlined in European Union Directive 91/4/4/EC.

Chemicals were purchased from different companies. Bondesil sorbents (rimary and secondary amine, PSA) were purchased from Varian. Pesticide standarts (99%) were obtained from Dr. Ehrensdorfer GmbH, Germany, Sodium chloride, $MgSO_4$, acetonitrile (high-performance liquid chromatography grade) were obtained from Merck, Germany.

QuEChERS method was used for extraction and analysis (Anastassiades et al., 2003).this method was developed the quick, easy, cheap and effective (QuEChERS) method to extract the pesticides (Anastassiades et al., 2007; Diez et al., 2006).

The tomato samples were weighed 10 g in a 50 ml fluoroethylenepropylene centrifugation tube and 10 ml acetonitrile was added then 15 sn shaken by vortex. 4 g $MgSO_4$ and 1 gram Sodium acetate was added to sample and shaken by vortex for 1 minute. The contents were centrifuged at 4000 rpm for 2 min. 2 ml was taken from the supernatant to a tube and 0.15 g $MgSO_4$ and 0.05 g PSA was added to a tube then vortex by 30 s. and centrifuged at 4000 rpm for 2 min again. The supernatant was taken to a tube again and filtered by PTFE filters. The final volume was put in vials.

The repeatability of the experiment and recoveries were evaluated with pesticide standarts. A varian gas chromatography (GC)-mass spectrometry (MS)-MS was used for analysis. The carrier gas was Helium with a constant flow at 1.2 ml min^{-1}. The temperature of oven programmed as 70°C held in 2 min, ramped to 220°C at 30°C/min, at the end ramped to 260°C at 45°C/min and held 10 min. The MS transfer line was at 280°C. The mass spectrometry was used to determine the pesticides in tomatoes.

RESULTS AND DISCUSSIONS

The most frequently found pesticides were acetamiprid (3 samples), endosulfan β (2 samples), chlorpyrifos (3 samples) and tetradifon (1 samples) (Table 1). The concentration of all detected pesticide residues found in 100 tomato samples was compared by maximum residue levels set by the European Comission (EC, 2005) (Table 1). The most pesticide residues in tomato samples were evaluated in November and January. No pesticide residues were detected on February and only 1 sample was found above maximum residue level on March.

Acetamiprid which is one of the most applied pesticide is a neonicotinoid insecticide in 4A group of IRAC (Insecticide resistance action committe). The persistence of acetamiprid in some crops such as tomatoes, tea, mustard has been mentioned by Barrakat et al. (2015), EFSA (2011), Gupta and Shanker (2008), Sanyal et al. (2008), Paramanik et al. (2006), Din et al. (2012). In November, 22 tomatoes samples were taken from local and chain markets and only 4 of them were contained pesticides and 2 of the 4 samples acetamiprid maximum residue level was above the MRL level. In December, 9 tomato samples were taken from local and chain markets and 4 of them found with pesticide residues. One of the 4 samples has 0.2 ppm acetamiprid residue which is above the maximum residue level (Table 1).

Endosulfan is a organochlorine pesticide and used globally since 1954. Although It is banned in more than 60 countries because of its persistency, its toxic and accumulation properties, some countries continue to use it. . Endosulfan has classified as a persistent

organic pollutants (POPs) and identified as a priority hazardous substances (EC, 2008). In some countries endosulfan and its metabolits were observed in human placenta and breast milk (Cerrillo et al., 2005; Shen et al., 2007; Çok et al., 2012) The commercial endosulfan consists of 70% endosulfan α and 30% endosulfan β. They have similar insecticidial activity while they have different chemical properties (Anonymous, 2010). The results showed that while endosulfan α wasn't above the maximum residue level, endosulan β was above the maximum residue level with the concentration of 0.9 ppm and 1.4 ppm in November and December respectively and no residues were found between January and March both for endosulfan α and endosulan β. According to the results residue levels were higher in winter time and the lower degradation of pesticides in winter time can explain this situation. In one study analysis of endosulfan residue levels in tomatoes of Ghana were 0.30 mg/kg and 0.43 mg/kg for endosulfan α and endosulan β respectively. In Ghana markets it can be concluded that tomatoes are safety (Essumang et al., 2008).

Chlorpyrifos is used to control Diptera, Homoptera, Coleoptera and Lepidoptera to protect the vegetable crops, maize, cotton and citrus (Aysal et al., 1999). It is an acetylcholinesterase inhibitor and found in organophosphates group (IRAC, 2016). It is moderately toxic to humans and affects the central nervous, cardiovascular and respiratory system. The maximum residue level of chlorpyrifos is 0.2 ppm. The residue levels of chlorpyrifos was obtained higher in November, December and January with the values of 0.4 ppm, 0.2 ppm and 0.3 ppm respectively.

Tetradifon is a non systemic acaricide that penetrates through the leaf tissue. It has larvicidial and ovicidial action against phtophagous mites and it can be used on many fruits, cotton and vegetables. In the experiment on November, December and February no residue value was established while on January 0.2 ppm and on March 0.5 ppm residue was detected. According to the MRL level of tetradifon (0.5 ppm), on March the residue level was found above the MRL limits. For example in Bangladesh 14 tomato samples were investigated and five of the samples were contaminated with cypermethrin residues ranging from 0.002 to 0.55 mg/kg and one sample was contaminated with chlorpyrifos (0.34 mg/kg) and none of the samples were contaminated with diazinon. According to this experiment cypermethrin wasn't found in the samples while chlorpyrifos residue values are same with Chouwdhury's experiment (Chowdhury et al., 2013).

Cypermethrin is a pyrethroid insecticide and acts as contact and stomach insecticide. It has wide scale use in vegetables, fruits, cotton, cereals etc. It was synthesized in 1974 and start to marketing in 1977. Although rapid degradation property of cypermethrin, its residues have been found in cucumber samples at the residue level between 0.03-0.2 mg/kg (Ahmed et al., 2014), in tomato samples taken from Sudan markets at the residue level between 0.08-0.6 mg/kg (Shinger et al., 2011). According to the tomato samples taken from Aydın markets cypermethrin residue levels weren't found above the maximum residue limits. The highest residue level was found 0.3 ppm on January (Table 1).

Table 1. Pesticide residues in tomatoes collected from markets in Aydın

Pesticides	November	December	January	February	March	MRL (ppm)	Above the MRL values
Acetamiprid	n.d.-0.2	n.d.-0.2	n.d.	n.d.	n.d.	0,1	3
Endosülfan α	n.d.-0.2	n.d-0.3	n.d-0.2	n.d.	n.d.	0,5	-
Endosülfan β	n.d.-0.9	n.d.-1.4	n.d.	n.d.	n.d.	0,5	2
Chlorpyrifos	n.d.-0.4	n.d.-0.2	n.d.-0.3	n.d.	n.d.-0.06	0,2	3
Tetradifon	n.d.	n.d.	n.d.-0.2	n.d.	n.d.-0.5	0,5	1
Cypermethrin	n.d.	n.d.	n.d.-0.3	n.d.	n.d.	0,5	-
Chlorpyrifos methyl	n.d.	n.d.	n.d.	n.d.	n.d.-0.04	0,2	-

ND = not detectable.

CONCLUSIONS

Results indicate that some concentrations of pesticide residues in tomatoes collected from local and chain markets in Aydın were above the maximum residue limits. According to the time intervals the concentration which were above the MRL levels were experimented between November to January. It can be concluded that because of the low degradation of pesticides in winter these pesticides can be more persistent. However, the prohibited pesticides were detected in tomatoes collected

from Aydın such as endosulfan α, β and tetradifon so there is need for urgent action to control the use of some prohibited pesticides.
On the other hand, the residue levels of these pesticides on tomatoes can pose a serious toxicity to the consumers. To minimize the health risks and to reduce the toxicity to the environment we need to give importance to the pesticide monitoring system and pesticide regulations.

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