Süleyman Demirel Üniversitesi
Fen Bilimleri Enstitüsü Dergisi
Cilt 22, Sayı 3, 1121-1124, 2018

Süleyman Demirel University
Journal of Natural and Applied Sciences
Volume 22, Issue 3, 1121-1124, 2018

DOI: 10.19113/sdufenbed.468816

Determination of Pesticide Residues in Grapes From Vineyards Implemented Good Agricultural Practice in Uşak

Erdal ZENGİN*[1], İsmail KARACA[1]

[1]Isparta University of Applied Sciences, Faculty of Agricultural Sciences and Technologies, Department of Plant Protection, 32260, Isparta

(Alınış / Received: 18.01.2018, Kabul / Accepted: 02.10.2018, Online Yayınlanma / Published Online: 09.10.2018)

Keywords
Residue,
Pesticide,
Grape,
Uşak

Abstract: This study was conducted to determine pesticides residue levels in grapes samples which taken from vineyards implemented good agricultural practice in Uşak province in 2017 growing seasons. A total of 51 grape samples from three districts were collected. Liquid chromatography with mass spectrometry (LC-MS/MS) and gas chromatography with mass spectrometry (GC-MS/MS) devices were used for all analyses. In 45.1% of the samples taken weren't detected any pesticide residue. In 54.9% of grape samples found residue, none of this pesticides exceeded the maximum residue limits given in Turkish Food Codex. The most common pesticides detected in grape samples with residue were spinosad, pyrimethanil and boscalid respectively. Thirteen different pesticide active substances were detected below the MRL in the samples. All pesticides detected in the samples were fungicides (85%) and insecticides (15%).

Uşak İlinde İyi Tarım Uygulamaları Yapılan Bağ Alanlarındaki Üzümlerde Bulunan Pestisit Kalıntılarının Belirlenmesi

Anahtar Kelimeler
Kalıntı,
Pestisit,
Üzüm,
Uşak

Özet: Bu çalışma, 2017 üretim sezonunda Uşak'ta iyi tarım uygulamaları yapılan bağ alanlarında yetiştirilen üzümler üzerinde bulunan pestisitlerin kalıntı düzeylerinin belirlenmesi amacıyla yapılmıştır. Üç farklı ilçeden alınan toplam 51 adet üzüm numunesi, Sıvı Kromatografi/Kütle Spektrometresi (LC-MS/MS) ve Gaz Kromatografi/Kütle Spektrometresi (GC-MS/MS) cihazlarıyla analiz edilmiştir. Toplanan üzüm örneklerinin %45.1'inde herhangi bir pestisit kalıntısına rastlanmamıştır. Kalıntı tespit edilen örneklerin hiçbirinde kalıntı seviyesi, Türk Gıda Kodeksi'nce belirlenen maksimum kalıntı seviyelerini aşmamıştır. Kalıntılı üzüm örneklerinde tespit edilen en yaygın pestisitler sırasıyla spinosad, pyrimethanil ve boscalid olmuştur. Tespit edilen 13 farklı pestisitin %85'ini fungisitler, %15'ini de insektisitler oluşturmuştur.

1. Introduction

Grape and productions derived from grape are extensively consumed all over the world. The world grape production amounts about 75.8 million tons. Turkey is the sixth largest grape producing country in the world with a grape production 4 million tons [1].

As grape is very susceptible to insect attack and disease infestation, producers mostly rely on different chemical pesticides to control the pests. In 2016, approximately 50.000 tones pesticide were used in Turkey and 3500 tones (%7) of this figure were in vineyards [2].

Although the use of pesticides in agriculture has brought many benefits to the producer, the overuse and misuse of these chemicals has led to high levels of pesticide residues on the crops. This situation is to be a problem in international market. Recently, this problem has been relatively reduced with the spread of Good Agricultural Practices (GAP). Even if the pesticides are applied in accordance with principles of GAP, residues may remain on the crops [3].

This study was conducted to determine pesticide residue levels in grape samples collected from vineyards implemented GAP in Uşak province.

*Corresponding author: 0erdalzengin0@gmail.com

2. Material and Method

2.1. Chemicals and reagents

Pesticides given in the Table 1 were obtained from Dr. Ehrenstorfer (Augsburg, Germany) and all of them are >95% pure. Acetonitrile (MeCN), Magnesium sulphate (MgSO4), sodium acetate were analytical grade from Merck (Germany). Primary secondary amine (PSA) was from Sigma-Aldrich (England) and it also was analytical grade.

2.2. Instrumentation

An Agilent 1260 series coupled to a 6420 model triple quadrupole mass spectrometer (Agilent Technologies Inc., CA) was applied for chromatographic separation. The instrument settings were gas temperature 350 °C; gas flow, 12 L min^{-1}; nebuliser gas, 50 psi; sheath gas temperature, 350 °C; sheath gas flow, 12 L min^{-1}; capillary voltage, 2000 V. Mass Hunter Quantitative analysis software (Agilent Technologies, Palo Alto, CA, v.B.05) were used for all data analyses.

The chromatographic separation was performed on a Rapid Resolution reverse phase column-C18 2.7 µm, 2.1 × 100 mm column (Agilent Technologies). The mobile phases comprised of 100 % water in 5 mM ammonium formate containing 0.1 % formic acid for solvent A and acetonitrile in 5 mM ammonium formate containing 0.1 % formic acid for solvent B. LC and MS/MS conditions were injection volume, 5 µL; oven temperature, 55°C; flow rate of mobile phase, 0.5 mL min^{-1} and total elution time, 7.5 minutes.

Gas chromatography analysis were performed using an Agilent 7890A GC system with an Agilent 5975C Series GC/MSD (Agilent Technologies), equipped with capillary column HP-5MS (30 m × 0.25 mm × 0.25 µm); electron capture.

Besides LC-MS/MS and GC-MS/MS devices, a centrifuge, centrifuge tubes up to 50 mL and 15 mL capacity, a digital balance, vortex, blender, glass GC vials (1.5 mL) were used during laboratory studies.

2.3. Collection of the samples

Grape samples were collected from a total of 51 different vineyards across three different districts of Usak province where produced the most grapes according to data of Uşak Directorate of Provincial Food Agriculture and Livestock in September 2017 when was pre-harvest period. The grape samples which is material of the study were taken as 2 kg from each production field. Disposable polyethylene gloves were used to prevent contamination during collection of samples. The collected samples were sent to the laboratory on the same day without waiting.

2.4. Cleanup and extraction of the samples

The grape samples were extracted by QuEChERS method [4]. The samples were homogenized with steel blenders by shredding. 15 g of the homogenized sample was taken and placed into 50 ml falcon tube which contains 15 mL of acetonitrile with 1 % acetic acid. Afterwards, 6 g of anhydrous magnesium sulfate and 1.5 g of sodium acetate is added into falcon tubes and centrifugated for 5 min. For cleanup stage, 4 ml of the sample were transported into 15 ml falcon tubes which contain 1200 mg of anhydrous MgSO4 and 400 mg primary secondary amine (PSA) and centrifuged. Then, 1 ml of the extracts was transferred into viales and kept in a freezer [4]. The vials were taken from the freezer, waited under room conditions and analyzed by LC-MS/MS and GC-MS/MS. Figure 1 represent a schematic diagram illustrating the workflow of analysis.

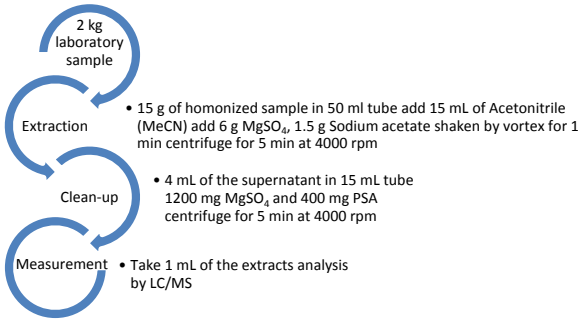

Figure 1. Workflow diagram for the analysis (Adapted from [5])

2.5. Analysis of the samples

Pesticide analyses of the samples were performed in three different laboratories accredited for all analytical methods. It was used liquid chromatography with mass spectrometry (LC-MS/MS) and gas chromatography with mass spectrometry (GC-MS/MS) devices for all analyses.

3. Results and Discussion

The matrix-matched calibration curves of all pesticides were found as linear ($R \geqslant 99$) in calibration limits. Consentration ranges, analytical functions, limit of quantification (LOQ) and MRLs of the pesticides detected on the samples are present Table 1.

Twenty three samples (45.1%) of the total of 51 grape samples had no detecable residue, while 28 samples (54.9%) contained residues lower than maximum residue limits given in Turkish Food Codex.

Table 1. Active substances detected in grape samples

Active substance	No. of samples detected residue	Frequency (%)**	Range (mg.kg^{-1})	MRL*** (mg.kg^{-1})	LOQ (mg.kg^{-1})	Analytical function	R^2
Azoxystrobin	2	7.1	0.029-0.039	2	0.01	y=7057.8+10503.74x	0.998
Boscalid	20	71,4	0.059-2.737	5	0.02	y=-623.93+727.96x	0.996
Bupirimate	1	3.6	0.012	1.5	0.01	y=-505.46+3563.53x	0.998
Cyprodinil	10	35.7	0.024-0.31	3	0.02	y=-2281.86+3560.98x	0.999
Famoxadone	2	7.1	0.03-0.25	2	0.01	y=66.257+204.01x	0.995
Fenhexamid	16	57.1	0.097-0.43	15	0.02	y=800.92+285.54x	0.996
Fludioxonil	14	50	0.015-0.57	5	0.01	y=116.45+87.023x	0.997
Imidacloprid	4	14.3	0.017-0.182	1	0.01	y=190.727+347.97x	0.998
Iprodione*	1	3.6	0.041	20	0.01	y=264.78+126.51x	0.999
Pyrimethanil*	24	85.7	0.025-0.77	5	0.01	y=-2988.26+1773.26x	0.998
Spinosad	27	96.4	0.011-0.18	0.5	0.01	y=2481.31+213.837x	0.997
Tebuconazole	6	21.4	0.019-0.218	0.5	0.01	y=4012.26+1833.67x	0.998
Triadimenol	13	46.4	0.021-0.22	2	0.01	y=-29.834+544.64x	0.998

*Active substances detected by GC-MS/MS. ** Frequency in samples with residue.*** Value of Turkish Food Codex.

Similarly, [6] analyzed grape samples taken from vineyards implemented integrated pest management (IPM) and organic farming in Manisa, Denizli and İzmir provinces, Turkey and detected no pesticide residue. In same region, a study conducted by [7] wasn't also found any pesticide residue in grape samples. 27 out of the total of 28 grape samples detected residue contained residues of two or more pesticides. As a result of analysis, 13 different pesticide active substances were detected. These pesticides, MRLs and consentration ranges are presented in Table 1. All the detected residues below the MRL.

All pesticides detected in the samples were fungicides (85%) and insecticides (15%). The frequency of the most detected pesticides in the grape samples are given in Figure 2. As shown in the graph, the most common pesticides detected in grape samples with residue were spinosad, pyrimethanil and boscalid respectively. Spinosad that found in 27 of 28 samples with residue is a bio-insecticide which commonly used against grapevine moths (*Lobesia botrana* Den. & Schiff.) in vineyard. In vineyards from Denizli, İzmir and Manisa provinces, a study conducted by [6] was detected lambda-cyhalothrin as the most common pesticide residue. In the same study, It was found insecticide residues more than fungicide residues in the samples. Whereas in this study, it was more fungicide residue. Folpet was the most detected pesticide in the study conducted by [8]. One of the grape samples analyzed had ten different pesticide residue. Similarly, [9] reported that two samples of grapes had nine pesticide residue in their study. This number found as seven per sample by [8].

In 23 of the samples analyzed were detected no residue, one sample had one residue, four samples had two residue, five samples had three residue, eight samples had four residue and ten samples had four and more residue. The residue percentage of the samples are shown in Figure 3.

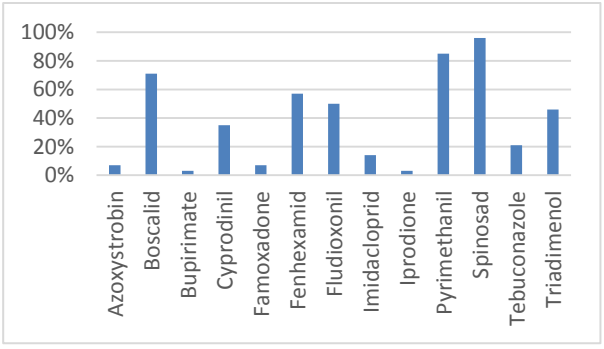

Figure 2. The frequency percentage of pesticide residue detected below MRL in the samples

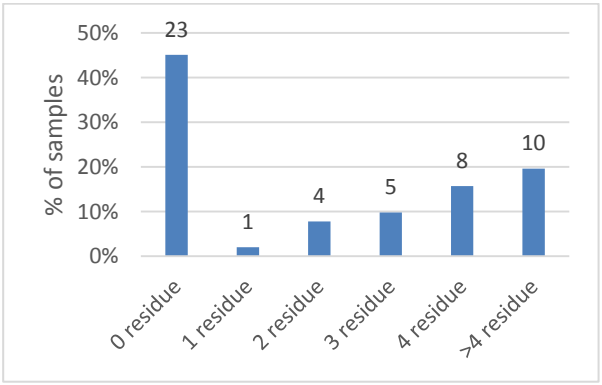

Figure 3. Percentage of the number of residue in the samples

4. Conclusion

This study was aimed to determine the level of pesticides residue in grape samples colleceted at preharvest. According to the analysis results, the most detected pesticide was spinosad which is a biological insecticide. None of 51 grape samples collected was detected a pesticide residue above MRL. This situation is one of the most important benefit of GAP which is a system adopting IPM. As it was found four and more pesticide residue in 18 of the grape samples, we have considered that practices, such as farmers' training and monitoring residue at preharvest, need to be continued.

References

[1] Anonymous, 2016. 2017 World Viti Viniculture Situation. OIV Statistical report on World Vitiviniculture, pp. 20, Paris.

[2] Dinçay, O., İsfandiyaroğlu, G., Aydın, A. 2017. Determination and Comparison of Pesticide Residues in Fresh Grapes Harvested From Different Vineyards and Raisins Obtained From Fresh Grapes After Two Different Drying Methods. Turkish Journal Of Agriculture - Food Science And Technology, 5(9), 1031 -1037.

[3] Stepán, R., Tichá, J., Hajslova, J., Kovalezuk, T., Kocourek, V. 2005. Baby food production chain: Pesticide residues in fresh apples and products. Food Additives and Contaminants, 22(12), 1231–1242.

[4] Lehotay, S. J. 2007. Determination of pesticide residues in foods by acetonitrile extraction and partitioning with magnesium sulphate colloborative study. Journal of AOAC International, 90, no:2.

[5] Tiryaki, O. 2016. Validation of QuEChERS method for the determination of some pesticide residues in two apple varieties. Journal of Environmental Science and Health, Part B, 51:10, 722-729.

[6] Turgut, C., Örnek, H., Cutright, T.J. 2011. Determination of pesticide residues in Turkey's table grapes: the effect of integrated pest management, organic farming, and conventional farming. Environ Monit Assess, 173, 315–323.

[7] Örnek, H. 2008. The investigation on residues of some pesticides and their risk possibilities in grapes and raisins obtained from vineyards in aegean region. Adnan Menderes University, Graduate School of Natural and Applied Sciences, Master Thesis, 57p, Aydın.

[8] Baša Česnik, H., Gregorčič, A., Čuš. F. 2008. Pesticide residues in g rapes from vineyards included in integ rated pest management in Slovenia. Food Additives and Contaminants, 25(4), 438–443.

[9] Hjorth, K., Johansen, K.,Holen, B., Andersson, A., Christensen, H.B., Siivinen, K., Toome, M. 2011. Pesticide residues in fruits and vegetables from South America - a Nordic project. Food Control, 22, 1701-1706.