Effects of Brining and Picking Time on The Degradation of Pesticide Residue in Grapevine Leaves

Rustem Cangi¹, Yusuf Yanar², Yagmur Dulgeroglu³

¹Department of Horticulture, Faculty of Agriculture, Tokat Gaziosmanpasa University, 60010 Tokat, Turkey
²Department of Plant Protection, Faculty of Agriculture, Tokat Gaziosmanpasa University, 60010 Tokat, Turkey
³Department of meadow, pasture and forage crops, Ministry of Agriculture and Forest, Erzincan Provincial Directorate 24050 Erzincan, Turkey

ARTICLE INFO

Research Article

Received : 26/02/2019
Accepted : 03/10/2019

Keywords:
Edible grapevine leaf
Fungicides
Brine
Degradation ratios
MRL

Abstract

Intensive pesticide use in vineyard resulted in residue problem on vine leaves that are used as food. This study was aimed at development of a proper chemical control program to reduce the pesticide residue problem on vine (cv. Narince) leaves in vineyards during the growing period. The residues of some fungicides were determined according to spraying time in the fresh (unprocessed) and preserved (brined) leaves. Additionally, the effects of preservation process on degradation of the fungicide residues were investigated. In this study three fungicides (Azoxystrobin, Triadimenol, Hexaconazole) were applied alternately for both powdery mildew and “Colomerus vitis” management, and two fungicides (Copper oxychloride, Metalaxyl + Mancozeb) for downy mildew control. Additionally, vine leaves were harvested at two different times: (i) before the half-life of the pesticides were reached and (ii) after the half-life of the pesticides have elapsed. Two different methods were applied to preserve the vine leaves. In first treatment, leaf samples were boiled in hot (98±2°C) tap water, then leaves were placed into jars, then filled with brine containing 8.0% salt + 0.25% lactic acid. In second treatment, vine leaves were placed into jars, then filled with tap water, then brine containing 8.0% salt+0.25% lactic acid. The residue levels of the fungicides were determined on leaves. Detectable copper and the other fungicide residues are compared according to Turkish Food Codex. Preserving applications were decreased fungicide and copper residue levels and hot water brining was decreased the levels of fungicide residues between 75.2% and 99.2%, according to the applications. As a result, systemic fungicides should not be used in vineyards in where pickled vine leaves are produced. It is proposed that better to use contact fungicides instead of systemic one and also viticulturists should be careful using the effective contact fungicides.

Introduction

Grape is used for different purpose while grapevine leaves have been traditionally used as a food in both fresh and brined forms in Turkey. The leaves are used to make stuffed grapevine leaves after gathering as fresh leaves or canned. Grape leaves contain several vitamins and minerals (El Nehir, et al., 1997; Gülçü and Demirci, 2011). Fresh grapevine leaves tend to decompose in a very short time during storage. Therefore, people generally prepare different kinds of brines to preserve the leaves for future use (Koşar et al., 2007). The grape variety affects the quality of pickled grape leaves. Thick and hairy leaves with lobes are not preferred by consumers. The leaves of ‘Narince’ and ‘Sultani Çekirdekız’ cultivars are widely used for pickled grapevine leaves products in Turkey (Göktürk et al., 1997). Harvest of brined grapevine leaves usually start when the summer shoot reach 50 cm long (after flowering) and continue till beginning of fruit maturity. According to the producer and region brined vine leaves are harvested 2 or 7 times a year.

The current model of agriculture is designed to maximize profit by increasing production yields and quality of agricultural products, while reducing costs for both producers and consumers. To reach this goal we should develop effective management programs for pests and diseases. Pesticides still play important role in a successful pest management program, despite their disadvantages such as toxicity to non-target organisms, environmental pollution and residue (Kaushik et al., 2009).
Intensive use of chemical pesticides for control of grape pests in commercial grape production is one of the main management practices. During the harvesting period of vine leaves, different contact and systemic fungicides are applied to control *Phomopsis viticola* Sacc., *Plasmopara viticola* “B. et. C. and *Erysiphe necator* “Schwein.” Burr. in vineyards. Both brined grape leaves and grape are produced in the same vineyards. This kind of production system resulted in reduced grape quality and pesticides residues on leaves and fruits. Tokat province is one of the main grape production areas of the Turkey and pesticides residues on grape leaves and fruits are the most important problem of vineyards of Manisa and Tokat provinces (Cangi et al., 2005; Yanar et al., 2015).

The pesticide residues, left to variable extent in the food materials after harvesting, are beyond the control of consumer and have deleterious effect on human health. There are several studies on pesticides residues on table grapes, raisin (Kaya et al., 2000; Pire, 2001; Turgut et al., 2011) and wine (Şen, 2005; Cus et al., 2010; Regueiro et al., 2015), on the other hand number of studies on pesticide residues on brined grapevine leaves are limited (Shokr et al., 2006; Ertürk, 2009; Cangi et al. 2014; Şensoy et al., 2017; Bakırçi et al., 2019; Kuşaksız and Çimer, 2019; Tutku and Tuna, 2019). In other study, indicate that fenarimol and flusilazole were determined more persistent in grape leaves than fruits of grape (Shokr et al., 2006).

Ahmad Sama’nneh (2003) investigated detection of Chlorpyrifos and penconazole in grape leaves by GSMS; Nasr et al. (2003) studied boiling and some environmental factors on residues behaviour of penconazole fungicide on grapevine leaves; Ertürk (2009) determined fungicide residues in fresh and pickled grape leaves (cv. Yapınçak) grown in Tekirdag province; Yanar et al. (2015) detected pesticide residues in fresh and pickled vine leaves in Tokat province. In a study conducted by Yanar et al. (2015), the residues of Triadimenol, Azoxystrobin and Metalaxyl were detected in most of brined grapevine leaf samples were over the MRL. Bakırçi et al. (2019), in their study in the province of Manisa 232 vine leaves investigated the pesticide residues. They found eighty-five (36.6%) pesticide residues in 52 samples (22.4%). They found that metalaxyl was the most active substance in the vine leaves, and that the active substance on the TGK MRL values was azoxystrobin.

Every pesticide needs time to reach half-life before harvesting a crop. If the conditions of good agricultural practice (GAP) such as applicable dose of the pesticide and the time interval between application and harvesting the crop are not met, harvested crops may contain unacceptable levels of pesticide residues (González-Rodríguez et al., 2011). Some studies have shown that certain types of postharvest treatments or household preparations may help to reduce pesticide residues (Ramesh et al., 1999; Zabik et al., 2000; Krol et al., 2000; Dhiman et al., 2006; Aktar et al., 2010). The washing with water or soaking in solutions of salt and some chemicals (chlorine, chlorine dioxide, hydrogen peroxide, ozone, acetic acid, hydroxy peracetic acid, and detergents) are reported to be highly effective in reducing the level of pesticides. Various thermal processing treatments like pasteurization, blanching, boiling, cooking, steaming, canning, scrambling etc. have been found valuable in degradation of various pesticides depending upon the type of pesticide and length of treatment (Shokr et al., 2006; Bajwa and Sandhu, 2014; Regueiro et al., 2015; Kuşaksız and Çimer, 2019). Also fermentation is often part of food-processing operations, which can reduce the pesticide residue on/in crops. (Pardez-L’opez et al., 1991). In a study conducted by Lu et al. (2013) reported that the pickling process had reduced the amount of pesticide residual in pickled cabbage.

In a vineyard pesticide application program, recommended by The Republic of Turkey Ministry of Agriculture and Forestry, was determined for grape not for grapevine leaves. So there is no data about the time should be elapse between spray and harvest for brined grapevine leaves. So that appropriate pesticide application program should be established for the vineyards which used for both grape and leaves productions.

The study was conducted to develop pesticide application program suitable for both grape and leaf production and to determine the effect of fermentation process on degradation of fungicide residue of grapevine leaves.

**Materials and methods**

**Material**

The study was conducted in 2011 growing season at a ten-year old *Vitis vinifera* L. cultivar ‘Narince’ grafted onto 1103 P in Tokat province of Turkey. The row and vine spacings were 3.0 and 1.75 m, respectively. Vines were trained as bilateral cordon onto single-curtain (wire) trellis system.

The brined leaves of ‘Narince’ grape cultivar are shown in Figure 1. Kara (1990), some of ampelographic characters determinate for ‘Narince’ grape cultivar. Colour of young leaf (4-6. leaf), Bronze speckled green; shape of mature leaf, pentagonal; mature leaf area, 232.67 cm²; colour of mature leaf, dark green (PL-XXIX-421); bunch weight, 227.65 g; berry weight, 3.34 g.

Figure 1 Upside and underside view of the brined grapevine leaf of Narince cultivar

**Pesticides Applications and Vine Leaves Pickling**

The pesticides doses and the time should be elapse were determined according to the manufacturer’s directions. Pesticides applications program and time interval between applications and leaves sampling were given in Table 1. All the vines were sprayed with micronized sulphur and metam in annual twins reach 20-25 cm long to control powdery and downy mildews. Experimental design was
randomized block design with four replication and each replication consist of 10 grapevines.

Grape leaves were taken at the half of time and at the end of the time which should elapse between application and harvest. Healthy undamaged leaves with normal appearance were harvested from the third to fifth leaf stage (up to two thirds of mature leaves) from the apex.

Fresh leaves (unprocessed) samples (500 g per treatment) were taken and stored in deep freeze at -18°C for pesticide residue analysis (Anonymous, 2002).

**Canning Process**

The leaves were cleaned and classified according to their size suitability for processing and their petioles were shortened to 2- cm, then leaves were placed into sealing glass jars (1000 cc). Two different methods were applied to preserve the vine leaves. First method, hot water brine, leaf samples were boiled in hot (98±2°C) tap water for 15 minutes, then filled with brine water containing 8% salt + 0.25% lactic acid. Second method, cold water brine, vine leaves were placed into jars, then filled with tap water (22±2°C) and brine containing 8% salt + 0.25% lactic acid. The leave samples were stored to fermentation for 3 months in ambient temperature (22±2°C).

**Residue Analyses**

Then residue analyses were made separately fresh and preserved vine leaves. Fresh and brined vine leaves residue analysis was performed in Manisa Province Control Laboratory. Extraction procedure was performed according to the methods of Lehotay (2005). Residue analysis were done by use of Liquid chromatography–tandem mass spectrometry (LC–MS/MS) LC-MS/MS Waters model ACQUITY UPLC-TQD(MS/MS) system and Perkin Elmer model Clarus 500 MS system.

Residue limits adopted for vine leaves were given Turkish Food Codex (TFC) according to (Anonymous 2016) in Table 2.

| Application code | Fungicide applied (**) | Time elapse between spray and harvest |
|------------------|------------------------|--------------------------------------|
| A                | Azoxystrobin           | 11° and 21th day                     |
| B                | Azoxystrobin + Metalaxyl + Mancozeb | 8° and 21th day                     |
| C                | Triadimenol            | 11° and 21th day                     |
| D                | Triadimenol + Metalaxyl + Mancozeb | 8° and 21th day                     |
| E                | Hexaconazole           | 8° and 14th day                      |
| F                | Hexaconazole + Metalaxyl + Mancozeb | 8° and 14th day                     |
| G                | Control                | 11th day                             |

**Table 1 Spray program and grapevine leaves sampling dates after spray**

*Fungicide applications were made when the berries reach the size of lentil.

**Table 2 Maximum residue limit (MRL) values of some pesticide on edible grapevine leaves according to the Turkish food codex (TFC) (Anonymous, 2016).**

| Active ingredient | MRL values (ppm) for vine leaves |
|-------------------|---------------------------------|
| Azoxystrobin      | 0.01                            |
| Hexaconazole      | 0.01+                           |
| Metalaxyl         | 0.05+                           |
| Metiram           | 0.05                            |
| Triadimefon ve triadimenol | 0.1+                          |
| Sulfur            | 50.0                            |
| Copper            | 20.0+                           |

*The lowest analytically detectable limit (LOD)

**Results and Discussion**

In Turkey, brined grapevine leaves become an important source of income for grape producers. But in a vineyard where grape is produced as a main crop Copper, sulphur and other pesticides residues occurring most frequently. In this study, level of pesticides residues on vine leaves were determined under controled pesticides application program.

In our study, copper (Copper oxychloride, 50%), metalaxyl, mancozeb, azoxystrobin and triadimenol were applied on grape vine and the leaves samples were collected at different times after applications. Based on the residue analysis results, copper oxychloride and the other fungicides residues in grapevine leaves harvested before half-life of the fungicide were higher than the limits of TFC. Sulphur and metiram residues were not detected on fresh and brined leaves in any samples. The fungicides residues were decreased by extending the harvesting time after spraying on fresh leaves in all treatments (Table 3). There were no pesticides residues in vine fresh leaves collected from control treatments, however, the residues of azoxystrobin, triadimenol, hexaconazole and copper in the fresh leaves from treatments have been above the MRL at all picking periods after applications. On the other hand, amounts of metalaxyl at leaves collected from treatment B 8 days after application was higher (0.05 ppm) then the limits of TFC, but there was no metalaxyl residue after half-life of the fungicide over. If we consider that the half-life of metalaxyl was 14 days in vine, this was the expected results. In treatment D, triadimenol and metalaxyl was applied in a mixture and residue level of metalaxyl was higher then the limits 8 days after metalaxyl application but 21 day after application metalaxyl residue was not determined (Table 3).
In treatment E amounts of Copper oxychloride were higher than MRL at 8 and 21 days after applications. However, metalaxyl residue in vine leaves in treatment F was above the limits 8 days after application, no samples contained metalaxyl at half-life of the fungicide (14 days after application). Mancozeb residue was not detected in fresh leaves in treatment (Table 3). This is evidence that the fungicide residues decrease by increasing time after spraying (Table 3). Similarly, the chlorpyrifos and penconazole residues were decreased by increasing time after spraying on grape flesh, cortex and leaves (Ahmad Samanah, 2004).

The level of pesticide residues is affected by cold and hot water brining applications and by increasing time after spraying on brined leaves in all treatments. But, residues of azoxystrobin and hexaconazole in the brined leaves have been above the MRL after spraying in all treatments. Residue of triadimenol on brined leaves was detected under the MRL. Metalaxyl residues were varied according to treatments. Hot water brining was the most effective method for degradation of pesticide residues in grapevine leaves (Table 4, 5, 6).

### Table 3 Copper and other fungicides residues detected in fresh grapevine leaves

| TC | HTS (day) | Amount of fungicide residues determined in fresh grape leaves (ppm) | Copper |
|----|-----------|-------------------------------------------------------------------|--------|
|    |           | Azoxytrobins | Triadimenol | Hexaconazole | Metalaxyl | Mancozeb |        |
| A  | 11        | 2.73         | 0.39        | 0.896        | ND        | ND       | 250.5  |
|    | 21        | 0.532        | 0.015       | ND           | ND        | ND       | 96.54  |
| B  | 8         | 3.789        | 1.654       | ND           | ND        | ND       | 42.57  |
|    | 21        |              |             |              |           |          | 14.08  |
| C  | 11        |              |             | 0.203        | ND        | ND       |        |
|    | 21        |              |             | 0.033        | ND        | ND       |        |
| D  | 8         |              |             |              | 0.505     | 0.689    | ND     |
|    | 21        |              |             |              | 0.310     | ND       | ND     |
| E  | 8         |              | 1.658       |              | 0.950     | ND       | 168.6  |
|    | 21        |              |             |              | 0.066     | ND       | 16.69  |
| F  | 8         | 1.896        | 1.089       |              | ND        | ND       |        |
|    | 14        |              |             |              |           |          |        |
| G  | 11        | ND           | ND          | ND           | ND        | ND       | ND     |

TC: Treatment codes, HTS: Harvesting time after spraying, ND: no detected

### Table 4 Copper and other fungicides residues detected on cold water brined grapevine leaves

| TC | HTS (day) | Amount of fungicides residues (ppm) | Copper |
|----|-----------|------------------------------------|--------|
|    |           | Azoxytrobins | Triadimenol | Hexaconazole | Metalaxyl |        |
| A  | 11        | 1.72        | 0.39        | 0.762        | 0.015     | 25.50  |
|    | 21        | 0.10        |             |             |           | 13.7   |
| B  | 8         | 0.190       | 0.140       | 0.145        | 0.010     | 150.7  |
|    | 21        | 0.120       | 0.099       |              |           | 12.67  |
| C  | 11        | 0.046       | 0.066       | 0.098        | 0.045     |        |
|    | 21        |              |             |              |           |        |
| D  | 8         | 0.389       | 0.039       | 0.088        | 0.015     |        |
|    | 21        | 0.011       |              |              |           |        |
| E  | 8         | 0.410       | 0.012       | 0.050        | 0.025     |        |
|    | 21        | 0.050       | 0.050       |              |           |        |
| F  | 8         | 0.389       | 0.039       | 0.088        | 0.015     |        |
|    | 14        | 0.059       | 0.011       |              |           |        |
| G  | 11        | ND          | ND          | ND           | ND        | ND     |

TC: Treatment codes, HTS: Harvesting time after spraying, ND: no detected

### Table 5 Copper and other fungicides residues detected on hot water brined grapevine leaves

| TC | HTS (day) | Amount of fungicides residues (ppm) | Copper |
|----|-----------|------------------------------------|--------|
|    |           | Azoxytrobins | Triadimenol | Hexaconazole | Metalaxyl |        |
| A  | 11        | 0.091       | 0.015       | 0.052        | 0.050     | 143.2  |
|    | 21        | 0.013       | 0.015       |              |           | 78.83  |
| B  | 8         | 0.012       | 0.050       | 0.011       | 0.015     |        |
|    | 21        | 0.090       | 0.011       |              |           |        |
| C  | 11        | 0.410       | 0.039       | 0.389        | 0.053     |        |
|    | 21        | 0.090       | 0.039       |              |           |        |
| D  | 8         | 0.039       | 0.059       | 0.038        |          |        |
|    | 14        |              |             |              |           |        |
| E  | 8         |              |             |              |           |        |
|    | 14        |              |             |              |           |        |
| F  | 14        |              |             |              |           |        |
| G  | 11        | ND          | ND          | ND           | ND        | ND     |

TC: Treatment codes, HTS: Harvesting time after spraying, ND: no detected
Maximum reduction rates of azoxystrobin residues in grapevine leaves (96.7-992%) was observed by hot water brining, however the reduction ratios were lower in cold water application. The residues of triadimenol were reduced by 822-965% by hot water brining in grapevine leaves. The reduction of hexaconazole residue was found in approximately the same ratios in both brine applications. The residues of metalaxyl were reduced by 15.19-94.4% with hot brining water application. The degradation ratios of copper residues with hot brining application were found between 15.6-44.8%, however the reduction ratios were lower in cold water application (Table 6). Similarly in a previous study, washing with water or soaking in solutions of salt and some chemicals e.g. chlorine, chlorine dioxide, hydrogen peroxide, ozone, acetic acid, hydroxy peracetic acid, iprodione and detergents are reported to be highly effective in reducing the level of pesticides (Bajwa and Sandhu, 2014).

There were many studies conducted to determine the pesticides residues in grapevine leaves are limited. In the study conducted in Slovakia vineyards to determine the metalaxyl residues which were applied at a rate of 0.25 kg/ha and 2.5 kg/ha there were no metalaxyl residues one month after applications (Vasilieva et al., 1991).

Based on the present study results, cold and hot water brining may result in reduction of residues pesticides in vine leaves. But it seems that this reduction will not be under the MRL levels for all active ingredients.

Similarly in a previous study brining reduced the residues of triadimenol, triadimethof and folpet on Yaprncak grape cultivar in Tekirdag-Turkey, and the residues of triadimenol, tritiamethof and folpet after brining were 7,348 ppm, 0.137 and 722 ppm, respectively. On the other hand residue levels of triadimenol, triadimefon and folpet in un-brined control were 2980 ppm, 137 ppm, and 1722 ppm respectively (Ertürk, 2009).

In another research, boiling process was reported that very effective in eliminating fenarimol residues on and in grape leaves than flusilazole residues. Whereas the reduction of fenarimol and flusilazole residues in the leaves due to boiling process were 47.06% and 24.76% for leaves picked one day after spraying, with residues decreased from 0.340 and 0.210 ppm in the fresh leaves to 0.180 and 0.158 ppm in the boiled leaves (Shokr et al., 2006).

Cangi et al. (2014), reported that brining application were generally decreased fungicides residue levels, but not all the time brining was not affected the carbendazim residue on brined grapevine leaves. Also it was reported that hot water brining method resulted in higher residue reduction (91% reduction compared to fresh leaves) than the cold water brining method (21% reduction compared to fresh leaves). In the similar study, it was determined that the pesticide residue values of grape leaves decreased in the cold brine by 69-73 % and in the hot brine by 73-91% (Kuşaksız and Çimer, 2019). Results of some studies shown that pesticides residues might be reduced when fresh vine leaves were washed, boiled and then brined (Nasr et al., 2003; Shokr et al., 2006; Ertürk, 2009; Cangi et al., 2014; Gülci and Demirci, 2014; Kuşaksız and Çimer, 2019), however washing did not reduce penconazole residues in vine leaves (Batta et al., 2005). Kang and Lee (2005) reported that brining had little impact on pesticide levels in cabbage apart from those of diazinon and dichlorvos, decreased by about 20%.

Residues of pesticides in food are influenced by processing such as fermentation. Reductions of pesticide levels during fermentation could mainly be due to chemical or biological degradation (Aislabie and Lloyd-Jones, 1995; Azizi, 2011; Lu et al., 2013), rather than the absorption onto the microbial cell walls (Ruediger et al., 2005).

In order to decrease the risk of taking high concentration of both pesticides during eating fresh leaves or brined leaves, it is important to respect to the time needed for degradation of these pesticides due to the action of internal metabolic processes depending on the time passed after spraying.

**Conclusions**

In general, systemic pesticides residues are found more frequently than the contact pesticides. However there is no record on the package of brined vine leaves when and where the leaves are collected. Therefore how soon the pesticides residues in vine leaves may fall below MRL levels. Present study revealed that how long the systemic pesticides may stay in vine leaves when the leaves harvested at different time after the pesticide application.

| TC | HTS (day) | Azoxystrobin | Triadimenol | Hexaconazole | Metalaxyl | Copper |
|---|---|---|---|---|---|---|
| | A | 11 | 36.9 | 96.7 | 21 | 30.8 | 42.9 |
| | | 21 | 26.7 | 97.2 | | 13.0 | 18.3 |
| | B | 8 | 48.3 | 98.7 | | 15.17 | 94.4 |
| | | 21 | 93.9 | 99.2 | | |
| | C | 11 | 6.4 | 94.1 | 21 | 40.14 | 44.8 |
| | | 21 | | 2.8 | 15.6 |
| | D | 8 | 76.2 | 82.2 | 21 | 78.9 | 87.2 |
| | | 21 | 68.1 | 96.5 | | |
| | E | 8 | 66.9 | 75.2 | 21 | 10.6 | 38.5 |
| | | 21 | 95.8 | 95.9 | | 23.9 | 40.1 |
| | F | 8 | 79.4 | 97.6 | 21 | 82.8 | 85.4 |
| | | 14 | 93.9 | 94.6 | | |

TC: Treatment codes, HTS: Harvesting time after spraying, CWB: Cold Water Brine, HWB: Hot Water Brine (%)
The growers whom grow grapevine for brined vine leaves production first of all they should prefer leaves production to grape production. Grapevine leaf producing manufacturers shouldn’t use systemic pesticides during leaves harvest period. We recommended the use of contact pesticide instead of systemic one.

Acknowledgements

The authors would like to thank to the Tokat Gaziosmanpasa University Scientific Research (2011/30) commission for the financial supports.

References

Akbar MW, Sengupta D, Purskait S, Chowdhury A. 2010. Risk Assessment and Decontamination of Quinolphos Under Different Culinary Processes in/on Cabbage. Env. mon. and ass., 163(1), 369-377. DOI: 10.1007/s10661-009-0841-9.

Ahmad Smanae AA. 2004. Detection of Chlorpyrifos and Panconazol Residues in Grape Leaves and Fruit by GCms. Master thesis. An najah nat. Univ. Fac. of Graduate studies, Nablus, Palestine, 46 p.

Aislajie J, Lloyd-Jones G A. 1995. Review of Bacterial Degradation of Pesticides. Aust. J. Soil. Res., 33:925–942.

Anonymous. 2002. Commission Directive 2002/63/EC of 11 July 2002 Establishing Community Methods of Sampling For The Official Control of Pesticide Residues in and on Products of Plant and Animal Origin and Regulating Directive 79/700/EEC. http://www.fsvps.ru/fsvps/docs/ru/usefulfiles/files/es2002-63.pdf.

Anonymous. 2016. Turkish Food Codex, mr Official Notification. http://www.resmigazete.gov.tr/eskiler/2016/11/201611125M1-1.htm.

Azizi A. 2011. Bacterial-degradation of Pesticides Residue in Vegetables During Fermentation. In: Pesticides – Formulations, Effects, Fate, M. Stoytcheva Ed., In Tech. Open Access Publisher, Rijeka, Croatia.

Bakirci GT, Çinlar E, Karakaya S. 2019. Pesticide Residues in Grape Leaves Collected from Manisa, Turkey Akad. Gida, 17(1): 55-60. DOI: 10.24323/akademik-gida.544073.

Bajwa U, Sandhu KS. 2014. Effect Of Handling And Processing on Pesticide Residues in Food-a Review. J. of food sci. and tech., 51(2), 201-220. DOI 10.1007/s13197-011-0499-5.

Batta Y, Zatar N, Safa S. 2005. Quantitative Determination of Chlorpyrifos and Penconazole Residues in Grapes Using Gas Chromatography/Mass Spectrometry, J. of Food Tech., 3(3): 284-285.

Cangi R, Kaya C, Kilic D, Yildiz M. 2005. The Brined-Vine Leaves Production in Tokat Province, The Problems Faced at Harvest and Processing and Solutions. VI. Viticulture Symp., 19-23 Sembetem, 2; 632-640. Tekirdag,Turkey.

Cangi R, Yanar Y, Yağcı A, Topçu N, Sücu S, Dilgeroğlu Y. 2014. The Effect of Picking Period and Brining Applications on Fungicide Residue Levels in Brined Vine Leaves Production. JAFAG, 31 (2): 23-30 (In Turkish). DOI: 10.13002/jafag724.

Cus F, Cesnik HB, Bolta SV, Gregoric A. 2010. Pesticide Residues in Grapes And During Vinification Process. Food Control, 21: 1512-1518. DOI:10.1016/j.foodcont. 2010.04.024.

Dhiman N, Jyot G, Bakhshi AK. 2006. Decontamination of Various Insecticides in Cauliflower and Tomato by Different Processing Methods, Mysores J. of Food Sci. and Tech., 43(1): 92-95.

El Nehir S, Kavas A, Karakaya S. 1997. Nutrient Composition of Stuffed Vine Leaves: A Mediterranean Dietary. J. of food quality., 20 (4), 337-341.

Ertrük A. 2009. Determination of Fungicide Residues in Grape Leaves (Cv Yaprancak) Grown in Tekirdag Province, Before and After Pickling. Namik Kemal Univ., Science Institute Plant Protect Department, Master Thesis, 29 s. (In Turkish).

Gökşürük N, Artik N, Yayav İ, Fidan Y. 1997. Research on The Possibilities of Using Leaves of Some Grape Varieties and Rootstocks as Canning Purposes. GIDA, 22 (1): 15-23.

Güleci M, Demirci AŞ. 2011. A Research on Quality Properties of Some Pickled Grape Leaves. J. of Tekirdag Agr. Fac., 8(3): 16-21.

Güleci M, Demirci AŞ. 2014. Pesticide Residue Problem in Brined Leaves Production and Marketing. 4. Traditional Foods Symposium, Adana,Turkiye, 17-19 Nisan 2014. Symp.Report Book (p.331).

González-Rodríguez R M, Rial-Otero R, Cancho-Grande B, González-Barreiro C, Simal- Gándara J. 2011. A Review On The Fate of Pesticides During the Processes within the Food-Production Chain. Crit. rev. in food sci. and nutr., 51(2): 99-114. DOI:10.1080/10408100903432625.

Kang SM, Lee MG. 2005. Fate of Some Pesticides During Brining and Cooking of Chinese Cabbage and Spinach. Food Sci Biotech, 14: 77–81.

Kara Z. 1990. Determination of the Ampelographic Characters of Grape Varieties Grown in Tokat, Turkish. (Doctorate Thesis). Ankara Univ. Science Institute, Horticulture Department, Ankara, p. 318.

Kauškiš G, Satysa S, Naik SN. 2009. Food Processing a Tool to Pesticide Residue Dissipation - A Review. Food Res. Int. 42:26–40. DOI: 10.1016/j.foodres.2008.09.009.

Kaya Ü, Erkan M, Altundişli Ö, Altunçar R. Duru AU. 2000. The Investigation on Residues of Some Pesticides and Their Risk Possibilities in Grapes and Raisins Obtained From Vineyards in Aegean Region. TAGEIM/BS/98/08/05/05. Bornova Agr. Res. Inst.

Koşar M, Küpeli E, Malyer U, Ulaşver S, Türkben C, Başer K HC. 2007. Effect of Brining On Biological Activity Of Leaves of Vitis vinifera L. (cv. Sultani Çekirdekizs) from Turkey. J. of Agr. and food chem., 55(11): 4596-4603. DOI:10.1021/jf070130s.

Krol WJ, Arsenault TL, Pylypiw HM, Mattina M J I. 2000. Reduction of Pesticide Residues on Produce by Rinsing, J. of Agr. and Food Chem., 48(10): 4666–4670. DOI: 10.1021/jf0002894.

Kuşaksız EK, Çimer H. 2019. Effect of Different Brine Media on Pesticide Residue Levels in Grapevine (Vitis vinifera var. Sultani çekirdekizs) Leaves. J. Of Agr. Fac. Of Ege Univ., 56(3), 267-272.DI.10.20289/zfdergi.464022.

Lehotay SJ. 2005 Quick Easy Cheap Effective, Rugged, and Safe Approach for Determining Pesticide Residues. Methods in Biotech. Vol. 19: 239-261 pp.

Lu Y, Yang Z, Shen L, Liu Z, Zhou Z, Diao J. 2013. Dissipation Behavior of Organophosphorous Pesticides During the Cabbage Pickling Process: Residue Changes with Salt and Vinegar Content of Pickling Solution. J. of Agr. and Food Chem., 61.9: 2244-2252. DOI:10.1021/jf304500f.

Nasr I N, Ahmed N S, Al-Maz M M. 2003. Effect of Boiling and Some Environmental Factors on Residues Behaviour of Penconazole Fungicide on Vine Leaves. Annals of Agr. Sci. (Cairo) 48: 365-372.

Pire R. 2001. Analysis of Some Pesticides Residues in Raisins by gc/ ecd (gas chromatography/ electron capture detector) and gc/ ms techniques E. Ü. Fen Bil. Eins. Food Eng. Master Thes., 179 S. (In Turkish).

Pardez-Lopez O, Gonzales-Casteneda J, Carabenz-Trejo AJ. 2011. Influence of Solid Substrate Fermentation on The Chemical Composition, J. Ferment. Bioeng. 71: 58–62.

Ramesh A, Balasubramanian M, Ramesh A, Balasubramanian M. 1999. The Impact of Household Preparation in The Residues of Pesticides in Selected Agricultural Commodities Available in India. J. of AOAC Int., 82(3), 725–737.
Ruediger G A, Pardon KH, Sas AN, Godden PW, Pollnitz AP. 2005. Fate of Pesticides During the Winemaking Process in Relation to Malolactic Fermentation. J. Agr. Food Chem. 53: 3023–3026. DOI: 10.1021/jf048388v.

Regueiro J, Lo’ pez-Fernández O, Rual-Otero R, Cancho-Grande B, Smal-Ga’ Ndara JA. 2015. Review on the Fermentation of Foods and the Residues of Pesticides Biotransformation of Pesticides and Effects on Fermentation and Food Quality. Critical Rev. in Food Sci. and Nutr., 55: 839–863. DOI: 10.1080/10408398.2012.677872.

Shokr IN Nasr IN, Mahmoud HA. 2006. Residual behaviour of fenarimol and flusilazole fungicides in grapes. J. Agric. Env. Sci. Alex. Univ, 5(2): 78-90.

Şen K. 2005. The Influence of Fining Agents on the Removal of Some Pesticides From Wine. Cukurova Univ., Science Institute, Food Engineering Science Department, Master Thes., 58 s. (In Turkish).

Şensoy RİG, Ersayar L, Doğan A. 2017. Determination of Pesticide Residue Amounts in Fresh Grapes, Raisins and Pickled Grape Leaves Sold in Van Province. Yuzuncu Yıl Univ. J. Of Agr. Sci., 27(3): 436-446.

Turgut C, Ornek H, Cutright TJ. 2011. Determination of Pesticide Residues in Turkey’s Tablegrapes: The Effect Of Integrated Pest Management, Organic Farming and Conventional Farming. Env. Monit Ass., 173: 315-323. DOI: 10.1007/s10661-010-1389-4.

Tutku K, Tuna, AL. 2019 Investigation of Pesticide Residue Levels in Fruit and Vegetables Collected from Three Farmers Market in İzmir Province. Turkish J. Of Agr. Res., 6(1): 32-38. DOI:10.19159/tutad.437474.

Vasilieva GK, Galiulin RV, Sukhparova V P, Galiulina R A, Bernat I, Shaly A, Kaluz S, Ragala P. 1991. Ecotoxicological Evaluation of The Fungiside Ridomil in Vineyards. Agrokhimiya, 4: 100-106.

Yanar Y, Cangi R, Ozata K. 2015. The Determination of Pesticide Residue Levels in Brined Vine Leaves Produced in Tokat Province, Selcuk Agr. and Food sci., Vol:27: 267-275.

Zabik MJ, El-Hadidi M FA, Cash JN, Zabik ME, Jones AL. 2000. Reduction of Azinophosmethyl, Chlorpyriphos, Esfenvalerate, and Methomyl Residues in Processed Apples. J. of Agr. and Food Chem., 48: 4199–4203., DOI:10.1021 /j90913559.