Effect of Decontamination and Processing on Insecticide Residues in Grape (Muscat Hamburg)

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Abstract

Field and laboratory experiments were conducted to study the effect of simple decontamination methods and processing on imidacloprid, dimethoate, and emamectin benzoate residues in grapes and their processed products using Liquid-Chromatograph Mass Spectrometer validated method. Among the decontamination methods evaluated, sodium chloride (2%) solution was found effective and contributed to the reduction of imidacloprid (77.55%), dimethoate (83.27%) and emamectin benzoate (77.28%) residues in mature grapes. Grapes were processed into various products *viz*., fresh juice, squash and raisin as per standard effective steps for each product. Based on decontamination experiment findings, washing with sodium chloride (2%) solution was included as an additional step in the standard protocol and has resulted in substantial removal of surface residues of selected insecticides. The processing factor calculated was less than one for all the products.

Introduction

Grape (*Vitis vinifera L*.) is one of the important fruit crops and it is a non-climacteric fruit that grows on the perennial and deciduous woody climbing vines. Globally, India ranks seventh with the production of 2.93 MT during 2019-20 with an area of 1, 47,000 ha and productivity of 21 MT ha^{-1}. In Tamil Nadu state, it is cultivated in 2,200 hectares with a production of 58.93 MT and productivity of 27.27 MT ha^{-1} (DAC & FW, 2019). It can be consumed in the form of raw or processed such as squash, juice, wine and raisins (Heshmati et al. 2020). Out of the total production of grapes, 74.5% is consumed as fresh (raw) and more than 22.5% is used for fresh juice, raisin and wine production (Adsule et al. 2012). In commercial cultivation, numerous insect pests cause damage to the vineyards. As many as 60 different insects attack grapes, and farmers most commonly use pesticides to battle these pests (Wadhi & Batram 1964). Evidence showed that grapes consume nearly 7% of pesticides used in agriculture (Zengln & Karaca 2018).

Due to the high consumption of grapes, a survey on pesticide usage patterns was conducted in vital grape-growing districts of Tamil Nadu (India) and found that farmers use dimethoate (93.33%) and imidacloprid (75%) as primary plant protection chemicals (Jayabal *et al*. 2020). Imidacloprid is recommended for pest management in grapes by the Central Insecticide Board and Registration Committee of India (CIB & RC 2021). It is also widely used by grape farmers across the world (Hogg et al. 2021; Daane et al. 2020). Dimethoate is registered under CIB & RC to control aphids, mealybugs, hoppers and stem borer in various fruit crops *viz.,* mango, banana, citrus, apple, fig and apricot (CIB & RC 2021). However, a survey conducted showed that farmers used it extensively in grapes. Unsurprisingly, emamectin benzoate is often used indiscriminately against a diverse array of grape insect pests and also registered, recommended for usage in grapes for thrips by CIB & RC (Yadav et al. 2016; Patil et al. 2017).

Insecticides thus applied during the fruit growth period may evaporate more quickly because of the growth dilution effect and those applied later in the process are more likely to occur in the economically valuable part (fruit), which is defined by the pesticide nature. There have been several reports on the prevalence of pesticide residues in grapes (Arora et al. 2008; Mohapatra et al. 2011). Generally, the processing of the fresh commodity into value-added products and ultimately affects the nature and magnitude of residues and may increase or decrease in the transformed product (Rizos et al. 2006). The processing factor (PF) is used to quantify the risk of pesticide residue intake, notably for processed food products (Christensen *et* al. 2003). The extent of reduction or removal of pesticide residues is determined by elements such as chemical characteristics of pesticides, kind of food commodity, processing stage, and time spent in contact with the food. Earlier studies have reported that processing (washing, peeling, boiling, and juicing) considerably reduced pesticide residues (Aguilera et al. 2014; Han et al. 2013; Lopez-Fernandez et al. 2013).

In grapes, the majority of studies on pesticide residues focused on the vine-to-wine conversion process. Given the large-scale use of the above-mentioned insecticides, wide use of its processed products as fresh juice, squash, raisin and scarcity of published literature on the effect of processing on pesticides in grapes, the study was undertaken to focus on simple decontamination approaches and the impact of processing on residues of selected insecticides.

Materials And Methods

Chemical and reagents

Reference Standard of imidacloprid (98.3%), 6-chloronicotinic acid (98.9%), dimethoate (99.5%), omethoate (96.8%), emamectin benzoate (98.0%) and anhydrous sodium citrate dibasic sesquihydrate (≥ 99% purity) were procured from Sigma Aldrich, India. Sisco Research Laboratories (Mumbai, India) supplied the HPLC grade of acetonitrile (≥ 97%), hexane (≥ 95%), ethyl acetate (≥ 99.7%), and hexane (≥ 95%). Sodium chloride analytical grade (99%), tri-sodium citrate dihydrate (99%) and Lichrosolv (LCMS) grade acetonitrile (> 99.9%) were acquired from Merck (Mumbai, India) and anhydrous magnesium sulphate (≥ 99%) was supplied by Himedia Laboratories, Mumbai, India. Agilent Technologies (USA) provided Graphitised Carbon Black (GCB) and Primary Secondary Amine (PSA, 40 µm). Formic acid (≥ 99%) was supplied by Fisher Scientific Limited (Czech Republic). The commercial formulation of imidacloprid 17.8 SL, dimethoate 30 EC and emamectin benzoate 5 SG was purchased locally from a pesticide vendor in Theni, Tamil Nadu, India.

Preparation of standard solutions

Individual stock solutions containing 400 mg/L of imidacloprid, 6- CNA and emamectin benzoate were prepared in HPLC grade acetonitrile by measuring 10.17, 10.11 and 10.24 mg of respective analytical standards into the volumetric flask (25mL), separately. Stock solutions of dimethoate and omethoate (400 mg/L) were made in LCMS grade methanol by independently weighing 10.05 and 10.33 mg of the analytical standards. To prepare secondary stock solutions (40 mg/L) of each pesticide, about 2.5 mL each stock solution was relocated into a volumetric glass measuring 25 mL. A working standard mixture (10 mg/L) was made from the secondary stock solution. From the mixed standard solution, linearity and spiking standard solutions in the range of 0.005–0.1 mg/L were prepared using serial dilution. All standard solutions were stored at a temperature of -20^{o}C in a deep freezer until utilised.

Field experiments

Experiments were conducted during February 2021 at farmers' field in Theni district of Tamil Nadu, India (9^{o} N latitude, 76^{o} E longitude and 375m above mean sea level) with all good agricultural practices. The trials were conducted separately in a 50m^{2} plot that had not been treated with selected insecticides before, and the treatments consisted of three replicated plots. A buffer zone of 10m was maintained between each treatment. The commercial formulations of imidacloprid 17.8 SL, dimethoate 30 EC and emamectin benzoate 5 SG was applied using Spraywell-SW16C-2 battery power operated knapsack sprayer on grapes (Muscat Hamburg variety) at the time of harvest to study decontamination in mature grapes and the impact of processing on residues in commodities made from fresh grapes at the single dose (53, 445 and 11 g a.i ha^{-1}) and double dose (106, 890 and 22 g a.i ha^{-1}), respectively (Table. S5).

Collection and preparation of samples

The grape berries (0.5 kg) were picked from vines at random for analysis of residues of selected insecticides. Samples were collected after two hours of spraying, transported to the laboratory in the icebox and stored at -5^{o}C temperature. The berries were processed (Srivastava and Kumar, 2005) and produced into juice, squash, and raisins (Figure. 1a). Samples were homogenised using a high-volume blade homogeniser (Robot-Coupe).

Optimisation of analytical methods used in the estimation of residues

Different compositions of solvents and salts were tried in the extraction and clean-up of selected insecticide residues are detailed in Table S6.

Extraction and clean-up of imidacloprid and emamectin benzoate residues

Mature berries

The modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) procedure was adopted and validated for analysis of residues in grapes (Anastassiades et al. 2003). To 10g of a homogenised sample taken in a centrifuge tube (50 mL), 10 ml of acetonitrile was added and vigorously agitated for one minute. After adding 4 g of anhydrous magnesium sulphate and 1 g of sodium chloride, the mixture was gently mixed before being centrifuged at 6000 rpm for ten minutes. Following centrifugation, 6 mL was relocated to a new 15mL polypropylene centrifuge tube containing GCB, PSA, MgSO4 with 10, 100 and 600 mg, respectively, vortexed for one minute followed by centrifugation at 3000 rpm for 10 minutes. A total of 1.0 mL was collected into autosampler vials filtered through a 0.2µ membrane syringe filter without evaporation.

Juice, squash and raisin

The samples were processed using the QuEChERS (Quick, Easy, Cheap, Effective, Rugged and Safe) approach, which was developed by (Pohorecka et al. 2012). A representative sample of 10g from each product (juice, squash, and raisin) was loaded in a 50 ml centrifuge tube and agitated for one minute with a vortexer after adding 10 ml ultrapure water. After vortexing, 10mL acetonitrile and 2mL n-hexane were added subsequently and again gently vortexed for 1 minute. Approximately 4 g anhydrous MgSO4, 1 g NaCl, 1 g sodium citrate dibasic sesquihydrate and 1 g anhydrous tri-sodium citrate dihydrate was added, vortexed, and centrifuged at 7600 rpm for five minutes. The upper supernatant of 6mL after centrifugation was transferred to a 15 mL centrifuge tube consisting of 100 mg PSA, 600 mg anhydrous MgSO4, and 20 mg GCB. The mixture was vortexed for one minute before being centrifuged at 8100 rpm for one minute. Finally, 1.0 mL was recovered and subsequently filtered using a 0.2 µ membrane syringe filter before transfer into 1.0 mL autosampler vials for LC-MS analysis of imidacloprid and emamectin benzoate residues.

Extraction and clean-up of dimethoate and omethoate residues

Mature berries

A modified QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe) technique (Anastassiades et al. 2003) similar to the procedure adopted for imidacloprid and emamectin benzoate residues in mature berries except for use of 20 mL ethyl acetate instead of acetonitrile in the initial steps. Finally, 2mL of aliquot was evaporated to near dryness under a gentle stream of nitrogen gas in a low volume concentrator at 40 ^{o}C and the residue was redissolved in 1.0 mL methanol, filtered using 0.2 µ membrane syringe filter and transferred into 1.0 mL autosampler vials.

Juice, squash and raisin

The method developed by Pohoreckaet al. (2012) used for the extraction of imidacloprid and emamectin benzoate residues was followed. Acetonitrile was replaced with 20 mL ethyl acetate for extraction of residues. The final 2 mL of aliquot was evaporated to near dryness under a gentle stream of nitrogen gas in a low volume concentrator at 40 ^{o}C. The residue was redissolved in 1.0 mL methanol, filtered through a 0.2 µ membrane syringe filter and transferred into 1.0 mL autosampler vials.

LC-MS apparatus and chromatographic conditions

Residues were detected, estimated, and confirmed using Shimadzu 2020 series LCMS equipped with a reverse phase C_{18} (Eclipse plus- Agilent) column (250 mm length x 4.6 mm internal diameter, 5µm particle size) at a column oven temperature of 40˚C. The mobile phase, flow rate and instrument parameters were detailed in Table. S4.

Method validation parameters

For estimating residues in grapes, the method was validated using SANTE guidelines (SANTE 2019) and evaluated in terms of factors such as linearity, limit of quantification (LOQ), limit of detection (LOD), recovery, precision, repeatability, and matrix effect. Method acceptability in terms of reproducibility is shown by HorRat (Horwitz ratio) for intra-laboratory precision, calculated using the formula below (Horwitz & Albert 2006).

$$\text{HorRat} = \text{RSD}/\text{PRSD}$$

Using the formula $\text{PRSD} = 2\ C^{-0.15}$, the expected RSD is calculated, where C is the mass fraction

Matrix Effect (ME) was assessed based on the formula given below (Dong et al. 2018).

$$\text{Matrix effect (\%)} = \frac{\text{Matrix match standard peak area} - \text{Solvent standard peak area}}{\text{Matrix match standard peak area}} \times 100$$

Decontamination of residues

Grape berries were subjected to simple decontamination approaches for one minute (T_1- tap water washing, T_2- washing in sodium chloride water (2%), T_3- dipping in tamarind water (2%), T_4- dipping in lemon water (2%), T_5- dipping in lukewarm water, T_6- dipping in ozonised water (0.2ppm) and no treatment (control). The solutions of sodium chloride, tamarind, and lemon juice were prepared by mixing 20 g of each in a 1000 ml beaker. Ozonised water was produced using an ozone generator (L30G model manufactured by Faraday Ozone Products Private Limited) by high-frequency corona discharge technology using oxygen as feed gas that was supplied by the oxygen generator. Following treatment, the berries were air-dried and processed for analysis of residues.

Processing factor

For each step of processing, PF is computed as the ratio of pesticide residue level in processed products to pesticide residue level in raw commodities. (Scholz et al. 2017). The PF less than one, indicates a reduction in the residue in the processed product, whereas a PF greater than one implies a concentration effect (BfR 2021).

Risk assessment

To evaluate the safety of studied insecticides for the grapes and raisin consumers especially children, maximum permissible intake [MPI (mg person^{-1} day^{-1})] was compared with their dietary exposure [TMDI (mg person^{-1} day^{-1})]. The MPI is estimated by multiplying the acceptable daily intake (ADI) of pesticide by the average body weight (NIN 2021) of the child (16kg) adult (60kg). The dietary exposure was arrived at by multiplying an average per capita consumption of 0.15 kg of grapes (NIN 2021) and 0.0043 kg raisins per day (NSSO 2001) with residue levels in the sample. Since no standard data for consumption of juice and squash is available; risk assessment was not calculated for juice and squash.

Results And Discussion

Different methods were tried for the extraction of residues of imidacloprid and dimethoate in grapes and their processed products (Table. S6). The mobile phase for dimethoate and imidacloprid extraction was also optimized with different formic acid compositions (0, 0.01%, 0.05% and 0.1%). In the mobile phase of 0.05% formic acid with methanol, the peak shape of dimethoate improved well. However, at 0.1% formic acid concentration with acetonitrile mobile phase, the imidacloprid peak shape and signal intensities were good than at 0.01% and 0.05%.

Optimized LCMS Parameters

Instrument conditions were optimised using single quadrupole LC-MS to identify, confirm, and quantify the selected insecticide residues in mature grapes, grape juice, squash and raisin. At standardised chromatographic conditions, imidacloprid, 6-CNA, dimethoate, omethoate and emamectin benzoate eluted at a retention time of 7.76, 7.72, 8.47, 5.31 and 3.93 minutes, respectively [Figure 1(b), 1(c), 1(d)]. Positive Selective Ion Monitoring (SIM) was used for quantification of imidacloprid, dimethoate, omethoate and emamectin benzoate with a target m/z of 256, 230, 214 and 887 and 6-CNA was quantified in negative SIM mode with a target m/z of 156.

Method Validation

Linearity, LOQ, LOD, recovery, precision and matrix effect were estimated as per SANTE (2019) guidelines for the validation of the analytical method used to identify and quantify the imidacloprid, 6-CNA, dimethoate, omethoate and emamectin benzoate residues in grapes.

(a) Linearity: The linearity of the method was assessed at concentrations (0.005, 0.01, 0.025, 0.05, 0.075 and 0.1 mg/kg) with three replicate injections per concentration for all grape matrices. Matrix-matched and solvent standards (Table S1, S2 & S3) had correlation coefficient (r^2) values greater than 0.99 for imidacloprid, 6-CNA, dimethoate, omethoate and emamectin benzoate.

(b) Limit of detection (LOD) and Limit of quantification (LOQ): LOD and LOQ were established by comparing the signal-to-noise ratio of three and 10 to a blank sample's background noise. LOD and LOQ were confirmed as 0.005, 0.01 µg/g, respectively. The proposed LOQ (0.01 mg/kg) of the method was below the maximum residue limit (MRL of 1.0 mg/kg & 2.0 mg/kg for imidacloprid and dimethoate) fixed by FSSAI and 0.05 mg/kg for emamectin benzoate fixed by European Union (FSSAI/EU Database 2020).

(c) Recovery: The obtained recoveries of imidacloprid, 6-CNA, dimethoate, omethoate and emamectin benzoate in mature grapes, grape juice, squash and raisin falls within the satisfactory range of 70 -20% (Table 1, 2 & 3).

(d) Precision: Precision was quantified in terms of RSD, which varied between 0.17 and 12.33 per cent across all grape matrices (Table 1, 2 & 3). The HorRat (Horwitz ratio) of imidacloprid, 6-CNA, dimethoate, omethoate and emamectin benzoate was less than 0.5 at all the spiked levels in grape matrices and was within the permitted range of 0.5 to 2.0 as suggested by SANTE (2019) standards. As a result, the analytical method exhibited acceptability concerning intra-laboratory precision and accuracy.

(e) Matrix effects: The matrix-matched standard solutions were prepared with different grape matrices *viz.,* mature grapes, juice, squash and raisin separately to obtain more realistic results. The calculated matrix effect was < 20%, ranging from 1.68 to 8.73 per cent in the spiked mature grapes, juice, squash, raisin samples.

Decontamination of insecticide residues in mature grape berries

Various decontamination methods were used to study their effect on insecticide residues by exposing the mature grape berries for one minute (Figure S1, S2 and S3). Among the decontamination methods employed, washing with 2% sodium chloride solution removed the maximum of 68.30% and the next best treatment was lukewarm water (60.00%) at the recommended dose (53 g a.i ha^{-1}) of imidacloprid. Similarly, in the case of double dose (106 g a.i ha^{-1}) also, 2% sodium chloride solution (77.55%) and lukewarm water (72.94%) were found effective. At a single dose (445 g a.i ha^{-1}) of application, dimethoate residues were effectively removed by 2% sodium chloride solution (83.24%), 2% tamarind water (75.14%) and lukewarm water (74.49%). A double dose (890 g a.i ha^{-1}), 2% sodium chloride solution (74.45%),2% tamarind water (64.45%) and 0.2ppm ozonised water (64.38%) were effective. Maximum removal (77.48%) of emamectin benzoate residues was observed in 2% NaCl solution residues while lukewarm water affected 68.06% removal at a single dose (11 g a.i ha^{-1}). Alike in single-dose, in double dose (22 g a.i ha^{-1}) also 2% sodium chloride solution removed the maximum of 73.45% residues followed by 62.71% in lukewarm water treatment. The present study indicated that treating for a minute using 2% sodium chloride solution was highly effective in the reduction of all the selected insecticides *viz.,* imidacloprid, dimethoate and emamectin benzoate residues for tested doses in mature grape berries.

Sodium chloride solution is a potent electrolyte solution that interacts with pesticide residues, reducing their concentration and providing an attractive source for pesticide residue removal. Pesticides with high water solubility were easily detached from the fruits in the salt medium when dipped in the solution (Pallavi et al. 2021). Washing with salt water (2%) solution for 10 minutes was recorded as an effective decontaminant in the removal of acephate, chlorpyriphos, quinalphos, bifenthrin residues in the range of 51.80-72.80% and acephate (72.74%), chlorpyrifos (67.52%), quinalphos (65.0%), respectively in grapes (Reddy and Rao 2004; Reddy and Rao 2005; Reddy and Rao 2002). The oxidant nature of the utilised washing solution (alkaline, acidic, or neutral), the surfactant activity, the pH, and negatively or positively charged ion interference might have influenced the removal of residues from berries.

Impact of processing on residues during juice, squash and raisin preparation

During product preparation, samples were taken at each step of processing and analysed for residues. The PFs obtained for juice, squash and raisin preparation for the imidacloprid, dimethoate and emamectin benzoate are given in Table 4.

Imidacloprid

In this study, imidacloprid residues were removed in the range of 65.16 - 66.29% from grapes during washing with tap water and it is inferred that there is a strong correlation between water solubility (600 mg L^{-1}) and removal of imidacloprid (Malhat et al. 2021). Crushing/homogenisation does not impact residues, but it speeds up processes like hydrolysis and releases isolated enzymes, acids from the cuticle layer more quickly, reducing residues in the juice. During clarification of juice, a reduction of 14.32-21.55% of residues was recorded. It might be due to the elimination of residues in the suspended particles due to partitioning characteristics of insecticide between pulp and juice. The residues found were less than the FSSAI and EU MRLs of 1.0 mg/kg. A negligible amount of systemic insecticides might be absorbed by pulp or fruits (Malhat et al. 2021). In the case of juice preparation, pasteurisation (80^{o}C for 10 minutes) was led to the loss of imidacloprid residue (10.49%) and it might be due to evaporation, hydrolysis, or thermal destruction during heating. Pasteurisation was found to reduce imidacloprid residues (32.45%) in strawberry juice preparation (Hendawi et al. 2010) and 60.42 - 100% of imidacloprid in tomato juice and paste (Romeh et al. 2009). A total of 89.13-97.17% residues were removed due to the processing of grapes into fresh juice. Studies reported 93.26-97.85% removal of imidacloprid residues during the processing of apples into juice (Wang et al. 2016). Pesticide residues were significantly reduced during juice processing also reported from apple, carrot and lemons (Zabik et al. 2000; Burchat et al. 1998; Holland et al. 1994; Pappas et al. 2003; Rasmussen et al. 2003).

Tap water washing removed imidacloprid residues in the range 61.35-67.94% during squash preparation. Further, clarification of pure juice eliminated residues in the range of 14.34-19.60%. The addition of sugar syrup to the pure juice reduced residues (94.32%) as the water was added to sugar syrup resulted in dilution of residues. Imidacloprid residue reduction (82.66% and 66.55%) was studied in sugared pulp and paste of winter jujube (Peng et al. 2014), strawberry syrup and jam preparation (50.64 and 84.41%) respectively (Hendawi et al. 2010). A total of 92.43-94.68% residues were reduced after the production of squash.

In the current study, tap water washing (59.75-65.29%) and dipping in sugar syrup for 24 hrs (86.99-89.60%) reduced the residues cumulatively up to 90%. Residues of imidacloprid in raisin were below the detectable level (<0.01 mg kg^{-1}) in a single-dose and 0.038 mg/kg detected in double dose (106 a.i ha^{-1}). Tap water washing (59.75-65.29%) and dipping in sugar syrup for 24 hrs (86.99-89.60%) reduced the residues cumulatively up to 90%. Evaporation and degradation process during drying might have been the factors for significant reduction of imidacloprid residues (Bajwa & Sandhu 2014). Concerning imidacloprid residues, 70% reduction in pomegranate anardana by hot oven air drying (Utture et al. 2012), 36.73% reduction in zucchini processing (Oliva et al. 2017), 53% in lettuce (Camara et al. 2017) and 37% in chilli peppers (Noh et al. 2015) were reported during drying processes. In raisin preparation, removal of phosalone (68.04%) and ethion (69.55%) residues were reported (Rahimi et al. 2021). The PF achieved for hexythiazox and bifenazate were 0.36 and 0.15 in grapes for raisin (Shabeer et al. 2020).

In the present study, PFs were in the range of 0.01 to 0.35, 0.04 to 0.39 and 0.03 to 0.40 for juice, squash and raisin, respectively. It is concluded that pesticides with low K_{ow} might be removed through volatilization after drying and this is correlated with studied chemical imidacloprid where the K_{ow} is low (0.57).

Dimethoate

Tap water washing reduced the dimethoate residues in the range of 28.22 – 41.70% for all the processed products. Washing reduced chlorpyrifos residues (21%) in apple processing (Kong et al. 2012). An increase in the residue was observed during pulping of berries from 0.397 to 0.425 mg/kg and 0.89 to 1.177 mg/kg at single and double doses, respectively in grape juice preparation. Increased residue in filtered juice is attributed to higher water solubility (23300mg/litre at 20°C) and low octanol-water partition co-efficient (0.7) of dimethoate. Moreover, dimethoate is xylem mobile due to its low log K_{ow} value of 0.7 and phloem mobile due to its pK_a of 2 (British Crop Protection Council, 2014). This is probably why washing and peeling are less effective at removing dimethoate than other organophosphates such as chlorpyriphos and parathion and thereby ending up in the filtered juice. However, it was previously reported that residue levels increased in juicing when insecticides having high solubility in water and a low K_{ow} value would leave residues in juices (Ramezani & Shahriari 2015; Saber et al. 2016). Burchat et al. (1998) reported that the water solubility of a pesticide is critical during the juicing process, and pesticides with the maximum water solubility were found in relatively larger concentrations in juiced carrots, tomatoes, and strawberries. The concentration of insecticides was reported like dimethoate in wine (Pazzirota et al.2013), chlorpyrifos in apple juice (Kong et al. 2012), quinalphos and chlorpyrifos in apple juice (Rasmussen et al. 2003). Most of the dimethoate, omethoate and quinalphos residues from made tea (80.5 - 84.9%) were transferred into the tea infusion easily as transfer rate was positively correlated with water solubility and negatively correlated with octanol-water partition coefficient. Pesticides with high water solubility (quinalphos, dimethoate and hexaconazole) and low octanol-water partition coefficient get easily accumulated in tea (Manikandan et al. 2009; Pan et al. 2015).

Washing with running tap water recorded a reduction of 32.42-38.75% of dimethoate residues during squash preparation. Pulping followed by clarification increased the residues (0.393 to 0.435 at the recommended dose), (0.767 to 0.846 mg/kg at double dose) similar to juice preparation and it is due to high water solubility. Mixing sugar syrup in squash production diluted the dimethoate residues by 63.08% in the current study. Sugar dipping was reported to reduce the dimethoate (88%) and triazophos (46%) residues in kumquat production (Chen et al. 2016).

Reduction of residues achieved through tap water washing (45.35%) followed by sugar dipping (85.51%) cumulatively. The residues of dimethoate in raisin production through oven drying increased from 0.441 to 0.499 and 1.07 to 1.623 mg/kg at single and double doses, respectively due to moisture loss indicating the concentration of residues. The first reason for this concentration can be explained that water loss in grapes was higher than the degradation rate of dimethoate during drying and secondly, the left-over residue present after sugar syrup soaking treatment could be more bound in the matrix and may not be available for degradation during drying resulting in concentration of dimethoate. A higher PF for hexythiazox (1.64) and bifonazole (1.12) was observed during raisin production (Thekkumpurath et al. 2020), methamidaphos residues increased by three times higher in dried grapes through oven drying (Athanasopoulos et al. 2005), cypermethrin residues increased to 0.46 in raisin from 0.40 mg/kg (Lentza-rizos and Kokkinaki, 2002). Dimethoate increased by 11% in dried kumquat fruit production (Chen et al. 2016), bifenthrin, lambda-cyhalothrin and beta-cyfluthrin in dried shiitakes (Liu et al. 2016). Pesticide residue levels were reduced during the processing of food commodities but those pesticides (dimethoate, azoxystrobin and pyrimethanil) were not having a preferential partitioning between liquid and solid phase may be concentrated in the final processed product (Cus et al. 2010). PFs arrived in the range of 0.44 to 0.94, 0.22 to 0.74 and 0.14 to 1.51 for juice, squash and raisin, respectively.

Emamectin benzoate

Tap water washing resulted in a reduction of residues (43.15-61.82%) at single and double doses for all products. Filtration of pure juice by discarding the pulp, seed reduced the residues in the range of 55.08-68.94 per cent over unprocessed samples for both juice and squash. The poor transfer/ presence of lower residues in filtered juice might be due to low water solubility (0.1 mg/L) and high octanol co-efficient (K_{ow}=5.0) and reported for emamectin benzoate, fenpropathrin and propargite in tea brewing (Manikandan et al. 2009; Zhou et al. 2016). Pasteurisation resulted in a reduction of 24.74% of residues during juice preparation. The residues were below BDL at the recommended dose and 0.02 mg/kg detected at a double dose for fresh juice with an overall reduction of 92.68%.

Mixing sugar syrup with pure juice for squash production diluted the residues by 87.67. Most of the residues (93.01%) during raisin preparation were removed during dipping/soaking in sugar syrup, thereby resulted in the residue below BDL after drying in a hot air oven. No literature is available on the fate of emamectin benzoate during processing in grapes as well as other fruit. It was reported in other crops, post-harvest processing and decoction of the Chinese medicinal plant mugua resulted in a 99.94 per cent reduction of emamectin benzoate (Xiao et al. 2021) and in Chenese peony (PF=0.06) reported by Xiao et al. (2021b). The above findings concluded that physicochemical properties might strongly decide how far residues are leached into by-products of any food commodity. The PFs were less than one and in the range of 0.11-0.49, 0.06-0.57 and 0.07-0.48 for juice, squash and raisin, respectively.

Impact of processing on residues with the addition of 2% sodium chloride washing

Based on results obtained in the decontamination experiment, washing with 2% sodium chloride solution for one minute was concluded as the best effective decontaminant in the removal of all the selected insecticide residues *viz.,* imidacloprid, dimethoate and emamectin benzoate. A separate experiment was carried out to observe the effect of processing on residues in juice, squash and raisin by including sodium chloride washing before tap water washing in standard protocol for preparation of processed products and was summarized in Table 5.

The results depicted that sodium chloride washing strongly influenced the residues and showed removal of imidacloprid (64.70%), dimethoate (71.64%) and emamectin benzoate (62.76%). Subsequent tap water washing resulted in > 80% cumulative reduction of imidacloprid (89.59%), dimethoate (88.93%) and emamectin benzoate (84.41%) over control. In juice preparation, the subsequent pulping and filtration of pure juice reduced 94.61 and 91.40 per cent of

imidacloprid, emamectin benzoate residues. Dimethoate residues increased from 0.106 to 0.174 mg/kg (recommended dose) and 0.141 to 0.198 mg/kg (double dose) and might be due to its high-water solubility, as in the earlier experiment. Pasteurisation of filtered juice resulted in 96.08, 95.82, 91.40 per cent removal of imidacloprid, dimethoate and emamectin benzoate residues, respectively. The addition of sodium benzoate ultimately reduced the residues below the detectable level (<0.01 mg kg^{-1}) in juice for all the products except for the double dose of dimethoate.

In squash preparation, a total of 68.44, 70.82, 65.50 per cent residues of imidacloprid, dimethoate and emamectin benzoate were reduced due to sodium chloride (2%) washing over control. Further tap water washing removed a substantial quantity of residues of imidacloprid (89.59%), dimethoate (86.88%) and emamectin benzoate (77.59%). Pulping of juice reduced imidacloprid (94.60%), emamectin benzoate (90.52%) and increased dimethoate residues from 0.115 to 0.218 (recommended dose) and 0.152 to 0.234 (double dose). The addition of sugar syrup resulted in the imidacloprid and emamectin benzoate residues to below BDL at the recommended dose and 96.59, 97.65 per cent less of initial residues at double dose. A total of 97.33 per cent of dimethoate residues were removed due to mixing sugar syrup with filtered juice. The addition of tonovin and sodium benzoate reduced residues to BDL at the recommended dose for all insecticides except for dimethoate squash (0.014 mg/kg) at a double dose. Dilution of residues after the addition of sodium benzoate is mainly due to the strong electrolytic nature of sodium.

During raisin preparation, a total of 69.06, 63.18 and 57.92 per cent imidacloprid, dimethoate and emamectin benzoate residues, respectively, were eliminated due to 2% sodium solution washing. Further washing with tap water reduced imidacloprid (89.59%), dimethoate (87.76%) and emamectin benzoate (75.73%) residues. Dipping in sugar syrup recorded the maximum reduction (95.56, 98.58, 93.82%) of imidacloprid, dimethoate and emamectin benzoate residues, respectively and concentration of residues in raisin was noticed in a double dose of dimethoate. However, overall PF was less than one in raisin for all the insecticides studies. When compared to the previous experiment, the use of a 2% sodium chloride solution for washing grapes as part of the standard protocol provided a maximum reduction of residues in final products. Findings reveal that as transfer of residues into processed products of grapes is positively correlated with water solubility and negatively correlated with octanol-water partition (log K_{ow}) co-efficient.

Safety evaluation

Since grape is often taken by the consumers, risk assessment is calculated for fresh grapes, decontaminated grapes [sodium chloride (2%)] and raisin. Consumption of fresh grapes after application of dimethoate is not safe (MPI<TMDI) and found safer (MPI>TMDI) for imidacloprid and emamectin benzoate. After washing with sodium chloride solution, grapes were safe (MPI>TMDI for consumption. Data revealed that TMDI (Table S7) of all three insecticides for raisin was less than MPI at both doses and indicating safety to children as well as adults too. However, considering dimethoate MRL (2.0 mg kg^{-1}) fixed by FSSAI, the raisin was found safe and regarding EU MRL (0.01 mg kg^{-1}) raisin might be a risk for the raisin consumers.

Conclusion

LC-MS analytical methods were validated for the detection of imidacloprid, 6-CNA, dimethoate, omethoate and emamectin benzoate residues in grapes and their processed products. Sodium chloride (2%) solution was found to be an effective decontaminant for reducing the imidacloprid, dimethoate and emamectin benzoate residues in grapes. The residues in commercially prepared products were at below quantification level after the inclusion of sodium chloride washing in the standard protocol. This study suggests including sodium chloride washing as an essential step in the preparation of processed products from grapes for the reduction of imidacloprid, dimethoate and emamectin benzoate residues in grapes, consequently a low risk for consumers.

Declarations

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Tables

Table 1. Recovery, precision (RSD) and Horwitz ratio (HorRat) of imidacloprid, 6-CNA and emamectin benzoate residues in grape juice, squash and raisin at different spiking levels (n=7)

Matrix	Spiked concentration (mg/kg)	Imidacloprid			6-chloronicotinic acid			Emamectin benzoate		
		Recovery (%) ± SD	RSD (%)	HorRat	Recovery (%) ± SD	RSD (%)	HorRat	Recovery (%) ± SD	RSD (%)	HorRat
Juice	0.010	100.55 ± 9.33	9.28	0.29	91.56 ± 2.04	2.23	0.07	102.33	3.19	0.10
	0.025	98.10 ± 4.09	4.17	0.15	87.98 ± 2.16	2.45	0.09	94.54	5.69	0.21
	0.050	99.24 ± 2.86	2.88	0.12	92.99 ± 1.50	1.61	0.06	95.67	5.51	0.22
	0.075	95.84 ± 2.98	3.11	0.13	89.42 ± 1.36	1.52	0.06	97.39	3.65	0.16
	0.100	93.99 ± 3.30	3.51	0.16	90.55 ± 2.11	2.33	0.10	105.03	2.80	0.12
Squash	0.010	99.00 ± 10.20	10.31	0.33	100.02 ± 1.59	1.59	0.05	97.55	3.70	0.12
	0.025	81.68 ± 2.80	3.42	0.12	102.02 ± 0.51	0.50	0.02	102.63	4.04	0.15
	0.050	80.17 ± 2.63	3.28	0.13	105.19 ± 0.18	0.17	0.01	102.58	2.77	0.11
	0.075	75.18 ± 1.27	1.69	0.07	98.33 ± 0.53	0.54	0.02	104.46	4.05	0.17
	0.100	78.33 ± 2.51	3.20	0.14	99.93 ± 0.25	0.25	0.01	97.50	3.24	0.14
Raisin	0.010	107.03 ± 13.20	12.33	0.39	93.79 ± 6.49	6.92	0.22	100.73	5.39	0.17
	0.025	105.10 ± 6.45	6.14	0.22	108.77 ± 1.02	0.94	0.03	99.71	5.21	0.19
	0.050	80.07 ± 4.38	5.47	0.22	110.82 ± 3.90	3.52	0.14	102.47	3.71	0.15
	0.075	83.23 ± 8.53	10.25	0.44	111.71 ± 2.88	2.58	0.11	101.93	4.04	0.17
	0.100	105.80 ± 1.17	1.11	0.05	99.39 ± 4.68	4.71	0.21	102.80	3.51	0.16

SD-Standard deviation, HorRat- Horwitz ratio, RSD- Relative standard deviation

Table 2. Recovery, precision (RSD) and Horwitz ratio (HorRat) of dimethoate, omethoate residues in grape juice, squash and raisin at different spiking levels (n=7)

Matrix	Spiked concentration (mg/kg)	Dimethoate			Omethoate		
		Recovery (%) ± SD	RSD (%)	HorRat	Recovery (%) ± SD	RSD (%)	HorRat
Juice	0.010	84.18 ± 1.70	2.02	0.06	81.61 ± 2.18	2.67	0.08
	0.025	85.39 ± 1.63	1.91	0.07	86.09 ± 1.10	1.28	0.05
	0.050	82.96 ± 3.11	3.75	0.15	92.92 ± 2.51	2.70	0.11
	0.075	81.83 ± 1.17	1.43	0.06	88.08 ± 2.22	2.52	0.11
	0.100	84.42 ± 2.52	2.99	0.13	90.43 ± 2.90	3.21	0.14
Squash	0.010	94.86 ± 1.10	1.15	0.04	97.95 ± 2.02	2.06	0.06
	0.025	91.91 ± 1.06	1.15	0.04	81.02 ± 0.90	1.12	0.04
	0.050	100.53 ± 2.19	2.18	0.09	88.59 ± 1.51	1.70	0.07
	0.075	98.02 ± 4.06	4.15	0.18	90.10 ± 1.96	2.18	0.09
	0.100	90.40 ± 2.59	2.86	0.13	80.53 ± 1.63	2.02	0.09
Raisin	0.010	84.58 ± 3.38	4.00	0.13	94.86 ± 1.57	1.66	0.05
	0.025	95.17 ± 2.35	2.47	0.09	83.70 ± 3.45	4.12	0.15
	0.050	93.16 ± 1.32	1.41	0.06	81.29 ± 1.71	2.10	0.08
	0.075	88.12 ± 2.50	2.84	0.12	97.86 ± 1.50	1.54	0.07
	0.100	85.58 ± 1.49	1.74	0.08	90.25 ± 2.35	2.61	0.12

SD-Standard deviation, HorRat- Horwitz ratio, RSD- Relative standard deviation

Table 3. Recovery, precision (RSD) and Horwitz ratio (HorRat) of imidacloprid, 6-CNA, dimethoate, omethoate and emamectin benzoate in mature berries at different spiking levels (n=7)

Insecticide	Spiked concentration (mg/kg)	Mature grapes		
		Recovery (%) ± SD	RSD (%)	HorRat
Imidacloprid	0.010	107.29 ± 5.63	5.25	0.17
	0.025	106.64 ± 6.25	5.86	0.21
	0.050	89.72 ± 2.56	2.85	0.11
	0.075	99.66 ± 7.84	7.87	0.34
	0.100	90.62 ± 3.91	4.32	0.19
6-CNA	0.010	85.57 ± 7.41	8.66	0.27
	0.025	78.73 ± 5.13	6.51	0.24
	0.050	92.68 ± 3.15	3.40	0.14
	0.075	88.27 ± 3.40	3.85	0.16
	0.100	91.56 ± 2.66	2.91	0.13
Dimethoate	0.010	95.68 ± 1.72	1.80	0.06
	0.025	90.10 ± 1.50	1.66	0.06
	0.050	85.04 ± 1.68	1.98	0.08
	0.075	92.08 ± 2.61	2.83	0.12
	0.100	95.28 ± 3.17	3.33	0.15
Omethoate	0.010	85.28 ± 3.09	3.62	0.11
	0.025	98.58 ± 1.48	1.51	0.05
	0.050	93.54 ± 1.96	1.02	0.04
	0.075	97.82 ± 2.88	2.94	0.13
	0.100	94.19 ± 1.91	2.02	0.09
Emamectin benzoate	0.010	92.19 ± 2.89	3.13	0.10
	0.025	100.41 ± 2.37	2.36	0.09
	0.050	95.65 ± 4.49	4.70	0.19
	0.075	98.99 ± 2.11	2.13	0.09
	0.100	103.07 ± 3.46	3.36	0.15

SD-Standard deviation, HorRat- Horwitz ratio, RSD- Relative standard deviation

Table 4. Residues and processing factor of imidacloprid, dimethoate and emamectin benzoate in grape juice, squash and raisin

Product		Imidacloprid (n=3)				Dimethoate (n=3)				Emamectin benzoate (n=3)			
		53 g a.i ha^{-1}		106 g a.i ha^{-1}		445 g a.i ha^{-1}		890 g a.i ha^{-1}		11 g a.i ha^{-1}		22 g a.i ha	
Grape juice		Residues* (mg/kg)	PF	Residues* (mg/kg)	PF	Residues* (mg/kg)	PF	Residues (mg/kg)	PF	Residues* (mg/kg)	PF	Residues* (mg/kg)	
	J1	0.267	-	0.531	-	0.681	-	1.240	-	0.161	-	0.287	
	J2	0.093(65.16%)	0.35	0.179(66.29%)	0.32	0.397(41.70%)	0.58	0.890(28.22%)	0.71	0.063(60.86%)	0.39	0.141(50.	
	J3	0.065(75.65%)	0.24	0.064(87.84%)	0.11	0.425(37.59%)	0.62	1.177(5.80%)	0.94	0.050(68.94%)	0.31	0.119(58.	
	J4	0.037(86.14%)	0.13	0.047(91.14%)	0.07	0.383(43.75%)	0.56	1.030(16.93%)	0.83	0.019(88.19%)	0.11	0.048(83.	
	J5	0.029(89.13%)	0.10	0.015(97.17%)	0.01	0.304(55.35%)	0.44	0.970(21.77%)	0.78	BDL	-	0.021(92.	
Grape Squash	S1	0.251	-	0.546	-	0.642	-	1.135	-	0.146	-	0.236	
	S2	0.097(61,35%)	0.39	0.175(67.94%)	0.31	0.393(38.75%)	0.61	0.767(32.42%)	0.67	0.083(43.15%)	0.57	0.125(47.	
	S3	0.061(75.69%)	0.24	0.068(87.54%)	0.11	0.435(32.24%)	0.67	0.846(25.46%)	0.74	0.061(58.21%)	0.42	0.106(55.	
	S4	0.023(90.83%)	0.09	0.031(94.32%)	0.05	0.284(55.76%)	0.44	0.419(63.08%)	0.36	0.018(87.67%)	0.12	0.031(86.	
	S5	0.019(92.43%)	0.07	0.029(94.68%)	0.04	0.143(77.72%)	0.22	0.351(69.07%)	0.30	BDL	-	0.015(93.	
Grape raisin	R1	0.246	-	0.510	-	0.441	-	1.070	-	0.186	-	0.301	
	R2	0.099(59.75%)	0.40	0.177(65.29%)	0.03	0.241(45.35%)	0.55	0.836(21.86%)	0.78	0.071(61.82%)	0.38	0.147(51.	
	R3	0.032(86.99%)	0.13	0.053(89.60%)	0.09	0.089(79.81%)	0.20	0.155(85.51%)	0.14	0.013(93.01%)	0.07	0.028(90.	
	R4	BDL	-	0.038(92.54%)	0.05	0.499(+13.1%)	1.13	1.623(+51.6%)	1.51	BDL	-	0.011(96.	

J_1-Treated and unwashed, J2- washed, J3- Filtered juice, J4-Pasteurised juice, J5- Final juice

S1- Treated and unwashed, S2- washed, J3- Filtered juice, J4- Juice + Sugar syrup, J5- Final squash

R1- Treated and unwashed, R2- washed, R3- sample dipped in brix solution, R4- Final raisin

Figures in parenthesis are percent reduction of residues

BDL- below detectable level, PF- processing factor

Table 5. Residues and processing factor of imidacloprid, dimethoate and emamectin benzoate in grape juice, squash and raisin

Product		Imidacloprid (n=3)				Dimethoate (n=3)				Emamectin benzoate (n=3)			
		53 g a.i ha^{-1}		106 g a.i ha^{-1}		445 g a.i ha^{-1}		890 g a.i ha^{-1}		11 g a.i ha^{-1}		22 g a.i ha	
Grape juice		Residues* (mg/kg)	PF	Residues* (mg/kg)	PF	Residues* (mg/kg)	PF	Residues (mg/kg)	PF	Residues* (mg/kg)	PF	Residues* (mg/kg)	
	J1	0.235	-	0.475	-	0.862	-	1.269	-	0.131	-	0.370	
	J2	0.083(64.70%)	0.35	0.200(57.89%)	0.42	0.307(64.38%)	0.36	0.360(71.64%)	0.28	0.053(59.06%)	0.40	0.138(62.	
	J3	0.028(88.20%)	0.12	0.049(89.59%)	0.10	0.106(87.74%)	0.12	0.141(88.93%)	0.11	0.020(84.41%)	0.15	0.080(78.	
	J4	0.019(91.90%)	0.08	0.026(94.61%)	0.05	0.174(79.81%)	0.20	0.198(84.38%)	0.16	0.011(91.40%)	0.08	0.046(87.	
	J5	0.018(92.25%)	0.07	0.019(96.08%)	0.04	0.026(95.82%)	0.03	0.106(91.62%)	0.08	BDL	-	0.028(92.	
	J6	BDL	-	0.010(97.88%)	0.02	BDL	-	0.043(96.61%)	0.04	BDL	-	BDL	
Grape Squash	S1	0.217		0.439	-	0.813	-	1.159	-	0.139	-	0.393	
	S2	0.068(68.44%)	0.31	0.198(54.81%)	0.45	0.285(64.98%)	0.35	0.338(70.82%)	0.29	0.066(52.79%)	0.47	0.136(65.	
	S3	0.030(86.33%)	0.14	0.046(89.59%)	0.10	0.115(85.81%)	0.14	0.152(86.88%)	0.13	0.031(77.59%)	0.22	0.095(75.	
	S4	0.012(94.56%)	0.05	0.024(94.60%)	0.52	0.218(73.19%)	0.27	0.234(79.84%)	0.20	0.023(83.71%)	0.16	0.037(90.	
	S5	BDL	-	0.015(96.59%)	0.03	0.031(97.33%)	0.03	0.042(96.34%)	0.03	BDL	-	0.012(97.	
	S6	BDL	-	BDL	-	BDL	-	0.014(98.77%)	0.01	BDL	-	BDL	
Grape raisin	R1	0.231	-	0.468	-	0.610	-	1.155	-	0.141	-	0.314	
	R2	0.072(69.06%)	0.31	0.210(55.12%)	0.45	0.225(63.18%)	0.37	0.444(61.52%)	0.38	0.068(51.47%)	0.48	0.132(57.	
	R3	0.027(88.20%)	0.12	0.049(89.59%)	0.10	0.075(87.76%)	0.12	0.313(72.86%)	0.27	0.035(75.41%)	0.24	0.076(75.	
	R4	0.013(95.46%)	0.06	0.025(94.60%)	0.05	BDL	-	0.016(98.58%)	0.01	0.011(92.02%)	0.08	0.019(93.	
	R5	BDL	-	BDL	-	BDL	-	0.085(92.63%)	0.07	BDL	-	BDL	

J_1-Treated and unwashed, J2- Salt water washed, J3- Tap water washed, J4- Filtered juice, J5-Pasteurised juice, J6- Final juice

S1- Treated and unwashed, S2- Salt water washed, S3- Tap water washed, S4- Filtered juice, S5- Juice + Sugar syrup, S6- Final squash

R1- Treated and unwashed, R2- Salt water washed, R3- Tap water washed, R4- Sample dipped in brix solution, R5- Final raisin

Figures in parenthesis are percent reduction of residues

BDL- below detectable level, PF- processing factor

Figures

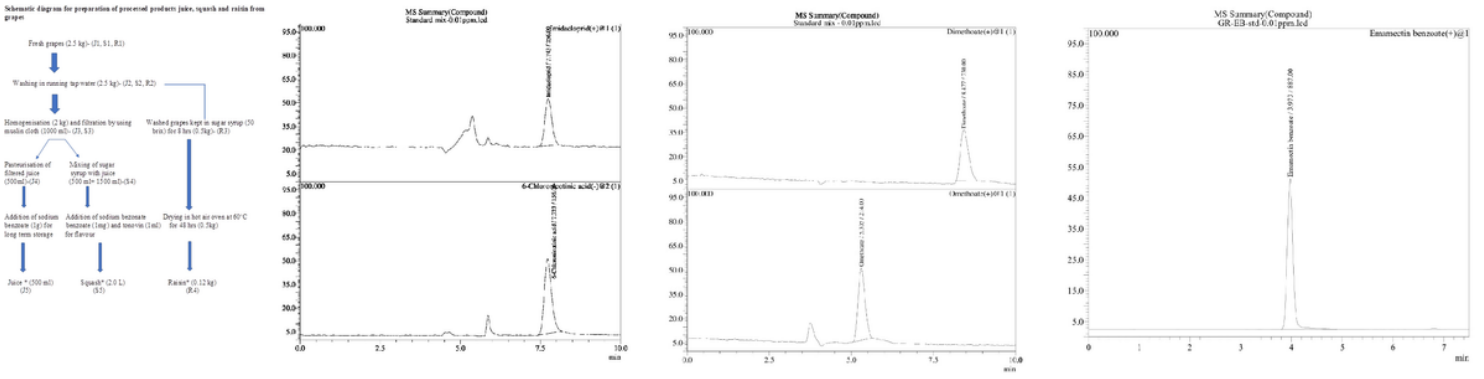

Figure 1

(a) Schematic preparation of juice, squash and raisin from grapes

(b) LCMS standard chromatogram of imidacloprid and 6-CNA

(c) LCMS standard chromatogram of dimethoate and omethoate

(d) LCMS standard chromatogram of emamectin benzoate

Supplementary Files

This is a list of supplementary files associated with this preprint. Click to download.

- SupplementarymaterialGrapes10.01.2022.doc