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Preharvest Interval Periods and their relation to fruit growth stages and pesticide formulations

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ABSTRACT

The aim of this study was to evaluate the effect of pesticide formulations and fruit growth stages on the Pre-harvest Interval Period (PHI). Results showed that pesticide formulations did not affect the initial deposit and dissipation rate. However, the fruit growth stage at the application time showed a significant effect on the above-mentioned parameters. Fruit diameter increases in one millimeter pesticide dissipation rates were reduced in -0.033 mg kg^{-1} day^{-1} ($R^2 = 0.87$; $p < 0.001$) for grapes and -0.014 mg kg^{-1} day^{-1} ($R^2 = 0.85$; $p < 0.001$) for apples. The relation between solar radiation, air humidity and temperature, and pesticide dissipation rates were dependent on fruit type. PHI could change according to the application time, because of the initial amount of pesticide deposit in the fruits and change in the dissipation rates. Because Maximum Residue Level are becoming more restrictive, it is more important to consider the fruit growth stage effects on pesticide when performing dissipation studies to define PHI.

1. Introduction

Although a raw product or its primary processed food can satisfy the requirements of Maximum Residue Level (MRLs), consumers demands healthy foods with non-detectable pesticide residues. However, to accomplish this important goal, the producers need specific information about the real effect of pesticide application conditions on residue dissipations, considering local productive conditions.

According to studies performed in Italy, approximately 30% of foods showed residues below MRLs, and the main products that provide residues to a person's diet were fruits and wine, comprising 77 and 15% of intake residues, respectively (Lorenzini, 2007; Pasarella, Elia, Guarino, Bourlot, & Négre, 2009).

Several experimental researches conclude that factors like species, fruit growth, climatic conditions, pesticide formulation, application method, and pesticide physicoo-chemical properties could affect pesticide residue dissipations and therefore the residues at harvest (Balsari & Marucco, 1989; Cabras & Angioni, 2000; Cabras et al., 1997; Huo, Salazar, Hyder, & Xu, 2007; Mandal, Das, & Bhattacharyya, 2010; Marin, Oliva, Garcia, Navarro, & Barba, 2003). However, under producer conditions or at the orchard application (commercial field application), not all of the above mentioned factors have a really high significance on dissipation processes, like fruit cultivar, formulation or application methods (Banerjee et al., 2006; Cabras et al., 2001; Pasarella et al., 2009; Alister et al., 2014; Liu, Wan, Huang, Wang, & Wang, 2012; Shirra et al., 2010). Because of this, there are still doubts about how field application factors, as pesticide formulations or application timing (fruit growth), would affect the Pre-harvest Interval Period (PHI).

For these reasons, the aims of this study were to elucidate the real effect of apple and wine grape fruits growth stage at application time on pesticide dissipations and PHI estimations, and to evaluate if the mentioned above parameters are affected by pesticide formulations.

2. Materials and methods

2.1. Pesticide field dissipation studies

The present study was performed from January to April 2014 in an orchard located at Casablanca Valley, Valparaiso region, Chile (Latitude 33°17′ S and Longitude 71°24′ W). Apple and wine grape cultivars corresponded to Pink Lady and Sauvignon Blanc respectively. Six orchard rows of 60 m-large of each fruit species was

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selected to be treated with each selected formulated pesticide (Table 1). Two rows without pesticide application (untreated) were left as controls. Also, buffer zones between each treated and untreated row were left to avoid contamination drift. Each 60 m-long row were divided in three plots of 20 m-long to apply the selected pesticides and their respective formulations in three fruit diameter stages to apple and wine grape fruits.

The insecticides acetamiprid ((E)-N1[(6-chloro-3-pyridyl)methyl]-N′-cyano-N1-methylacetamidine), formulated as Acetamiprid SL (200 g ia L^{-1}) and Hurricane 70 WP (700 g ai kg^{-1}), buprofezin ((Z)-2-*tert*-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one), formulated as Applaud 40 SC (400 g ai L^{-1}) and Buprofezin 25 WP (250 g ai kg^{-1}), and the fungicide fenhexamid (2′,3′-dichloro-4′-hydroxy-1-methylcyclohexanecarboxanilide), formulated as Teldor 50 WP (500 g ai kg^{-1}) and Altivo 500 SC (500 g ai L^{-1}) were applied to apple fruits in the following diameters of fruit set: 12.1–18.4; 29.8–36.2 and 40.5–54.0 mm (Table 2) and to grape at full bloom, buckshot berries and veraison (Table 3). The application was made using an experimental turbo-nebulizer mounted to a tractor, equipped with an Albuz ADR 80 nozzles, calibrated to sprayed a water volume of 695 L ha^{-1} and 706 L ha^{-1} to apple and vine grape plants, respectively, at 10 bar pressure. Application was performed under no wind conditions (<2 km ha^{-1}). The pesticide sprayed rates were: acetamiprid 58 g ia ha^{-1}, Buprofezin 200 g ia ha^{-1} and fenhexamid 420 g ia ha^{-1}, independently of the formulation.

As soon as applications dried out (approximately forty min later), apple and wine grape fruit samples were collected, at 3, 10, 20, 40 and 60 days after application (DAA) for the first two application stages, and 3, 10, 20 and 40 for the last stage. This was done from each experimental plot following a random sampling for each replication (three samples for each pesticide, formulation and fruit growth stages). Samples of ±200 g were collected for grape at the initial fruit growth stage, after that ±400 g were collected. For apples ± 400 g samples were collected at the initial fruit growth stages and after ±600 g. The samples were kept in plastic bags at 4 ± 1 °C until they were carried to the laboratory and maintained at −19 ± 2 °C until residue analysis. The climatic conditions at the study period were: average air temperature of 16.7 °C (8.2–27.6 °C) and relative humidity of 67.4% (30.6–96.7%). Only light rain occurred during the study (0.66 mm) and the average solar radiation was 560.8 w m^{-2}.

2.2. Pesticide extraction and analysis

All fruit samples were homogenized using a Grindomix® Knife Mill, and sub samples of 10 g were taken for analysis. The analysis of pesticide residues was performed using QuEChERS method. Ten grams of samples were put in 50 mL conic polipropilene tubes (Jet Biofil®) and each received 20 mL of acetonitrile (LiChrosolv® Merck). After agitation (30 min at 180 rpm) (VWR Orbital Shaker DS-500E), the polipropilene tubes with the samples were put into an Ultrasonic bath (Branson model 3510) for 10 min, and QuEChERS UCT® sachet which contains: 4*g* Magnesium Sulfate ($MgSO_4$), 0.5*g* of Disodium citrate ($C_6H_6Na_2O_7$), 0.5*g* of trisodium citrate ($Na_3C_6H_5O_7$) and 1*g* of Sodium Chloride (NaCl), were added to the tubes and manually shacked (10 s). All samples were centrifuged (HERMLE® Z 200A) at 4500 rpm for 5 min and after that aliquot of 10 mL was taken from each centrifuged sample and 1.5*g* $MgSO_4$ (EMSURE®ACS MerckMillipore) and 0.25*g* of PSA (UCT Selectra®) were added to the samples and then transferred to an ultrasonic bath for 10 min, and centrifuged at 4500 rpm for 5 min. For buprofezin and fenhexamid (Sigma-Aldrich analytical standard), an aliquot of 1.5 ml was put into a glass vial and analyzed using gas chromatography (Shimadzu Model GC-2010 Plus) with mass detector (Shimadzu GCMS-QP 2010 Ultra), equipped with a Rtx-5MS 30 m × 0.25 μm column (Restek). The gas carrier was He (Alphagaz® Helio 1Airliquide), at a flow rate of 1 mL min^{-1} and the injector temperature was 250 °C. The samples were injected at 1 μL into the autosampler in a split-less mode, with an injection pulse of 250 kpa at 2 min. The oven temperature was: 70 °C (1 min), increased to 150 °C (at 25 °C min^{-1}), followed by an increase to 200 °C (at 3 °C min^{-1}), and finally raised to 280 °C (at 8 °C min^{-1}). Recovery from spiked samples and retention times are shown in Table 1.

For acetamiprid (Sigma-Aldrich analytical standard), an aliquot of 5 mL of acetonitrile extract was concentrated to dryness in a rotary evaporator, re-suspended in 1.5 mL acetonitrile and transferred to a glass vial, and analyzed using high performance liquid chromatography (Hitachi LaChrom Elite Model L-2300) with diode array detector (Hitachi LaChrom Elite Model L-2450), equipped with a Kromasil® 100-5-C18 5 μm 4.6 × 250 mm column and Kromasil KR100-5C18 pre-column. The liquid phase used was water (LiChrosolv® Merck) –acetonitrile (LiChrosolv® Merck) at a flow rate of 1 mL min^{-1} with a gradient from water-acetonitrile (95/5

Table 1
Recoveries, limit of quantification (LOQ), limits of detection (LD) and selected physic-chemical properties* of acetamiprid, buprofezin and fenhexamid.

Pesticide	Fortification levels	Recovery	LOQ	LD	Molecular weight (g mol^{-1})	*pKa*	*Log kow*	Solubility (mg L^{-1} at 20 °C)	Vapor pressure (mPa)
	(mg kg^{-1}) (n = 3)†	(Average ± SD)	(mg kg^{-1}) (n = 6)†						
Acetamiprid (Chemical family: neonicotinoid)	0.01 0.05 0.1 0.5 1.0	93.5 ± 3.3 88.2 ± 6.2 91.8 ± 4.0 93.5 ± 3.3 91.4 ± 2.6	0.022	0.007	222.67	0.7	0.8	2,950.0	1.74×10^{-4}
Buprofezin (Chemical family: thiadiazine)	0.01 0.05 0.1 0.5 1.0	101.0 ± 5.4 97.7 ± 3.9 94.1 ± 3.3 96.9 ± 4.8 94.0 ± 1.5	0.016	0.005	449.85	–	4.93	0.46	4.20×10^{-2}
Fenhexamid (Chemical family: anilide)	0.01 0.05 0.1 0.5 1.0	89.9 ± 5.3 93.5 ± 3.3 91.1 ± 2.4 95.1 ± 4.8 94.7 ± 2.2	0.049	0.014	302.2	7.3	3.51	24.0	4.0×10^{-4}

* Pesticide Properties Database in http://sitem.herts.ac.uk/aeru/footprint/es/index.htm
† n = number of replications.