

**DISSIPATION RATE AND RESIDUES OF ACETAMIPRID AND
IPRODIONE IN SWEET CHERRY FRUITS**

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ABSTRACT

A neonicotinoid insecticide acetamiprid and dicarboximide fungicide iprodione, are used in sweet cherry for control of the major pest (*Rhagoletis cerasi* L.) and pathogen (*Monilia laxa*). For the purpose of the safe consumption of agricultural products after pesticide application, studies on their dissipation kinetics are essential to work out their half-lives (DT_{50}) and pre-harvest intervals (PHI). However, there is a lack of information on the persistence of acetamiprid and iprodione in sweet cherry fruits in different climatic conditions of production. Therefore, the objectives of this study were to investigate the dissipation and residues of acetamiprid and iprodione in sweet cherry fruits, as well as to evaluate the validity of prescribed PHI for these pesticides. Field experiments were conducted in a sweet cherry orchard, near Novi Sad, where acetamiprid and iprodione were applied at a recommended concentration. At various time intervals, from treatment to harvest, having in mind PHI (14 days for acetamiprid and 7 days for iprodione) representative samples of sweet cherry fruits were collected. Extraction of pesticides was carried out by QuEChERS method, followed by HPLC-DAD analysis. The method was validated in accordance with the SANCO/12571/2013 document and was used the determination of pesticides in real sweet cherry samples. During the study period, the concentration of acetamiprid and iprodione decreased from 0.52 mg/kg to 0.11 mg/kg and from 0.29 mg/kg to 0.07 mg/kg, respectively. The dissipation of acetamiprid and iprodione residues over the time fitted to the equation $C_t=0.52^{-0.22t}$ and $C_t=0.29^{-0.20t}$, with DT_{50} of 3.15 and 3.47 days, respectively. Finally, the content of acetamiprid and iprodione in sweet cherry samples, at the end of PHI, were below the maximum allowed level specified by the Serbian (1.5 mg/kg and 3 mg/kg) and EU MRLs (1.5 mg/kg and 10 mg/kg).

Keywords: *sweet cherry, Acetamiprid, Iprodione, dissipation rate.*

INTRODUCTION

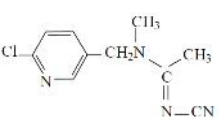
Pesticides use in agriculture is necessary for control a variety of pests in order to ensure higher yields and to improve the quality of agricultural products (Lazi et al., 2016). Monitoring of pesticide residues and check of the accuracy of the

required pre-harvest interval (PHI) proved to be necessary. This is especially important for fruits and vegetables that are mostly consumed fresh, such as sweet cherry. For the control of sweet cherry's major pest (*Rhagoletis cerasi* L.) and pathogen (*Monilia laxa*), a neonicotinoid insecticide acetamiprid and dicarboximide fungicide iprodione, are used.

Management of pests in sweet cherry orchards largely depends on the use of conventional, neurotoxic, broad-spectrum, synthetic chemical pesticides, such as organophosphates. However, good agricultural practice requires use of products with shorter PHI and more convenient ecotoxicological properties than previously used insecticides (Lazi et al., 2012), such as neonicotinoids.

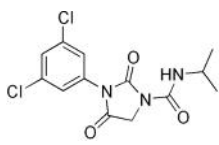
A neonicotinoid insecticide acetamiprid has been introduced as an alternative to organophosphate insecticides for control of major sweet cherry pests (Table 1). In recent years, a number of researches have dealt with the behavior of acetamiprid in different plant (Pramanik et al., 2006; Gupta et al., 2008; Sanyal et al., 2008; Park et al., 2011; Shams El Din et al., 2012; Wu et al., 2012; Romeh et al., 2013). To the best of our knowledge, there is no information related to acetamiprid behaviour in sweet cherry fruits.

Table 1. Physico-chemical properties of acetamiprid

Common name/ molecular formula/CAS No.	IUPAC name	Structure
Acetamiprid C ₁₀ H ₁₁ ClN ₄ (160430-64-8)	(E)-N1-[(6-chloro-3-pyridyl)methyl]-N2-cyano-N1-Methylacetamide	

On the other hand, for the control of one of the major sweet cherry pathogen, *Monilia laxa*, the causal agent of blossom and brown rot of stone fruit, iprodione based fungicides are used (Table 2). Iprodione was first manufactured in the 1990s. In cherry orchards, it is used usually in a single pre-harvest application (Savi - Petri, 2015). Nowadays, iprodione residues are one of the commonly detected residues in agricultural products (Lentza-Rizos, 1995; Lopez and Riba, 1999; Stensvand and Christiansen, 2000).

Table 2. Physico-chemical properties of iprodione

Common name/ molecular formula/ CAS No.	IUPAC name	Structure
Iprodione C ₁₃ H ₁₃ Cl ₂ N ₃ O ₃ (36734-19-7)	3-(3,5-dichlorophenyl)-N-isopropyl-2,4-dioximidazolidine-1-carboxamide	

With the aim of consumer's protection, it becomes necessary to know the residual level, the rate of dissipation and half-lives (DT_{50}) of pesticides in agricultural products. However, there is a lack of information on the persistence of these pesticides in sweet cherry fruits in different climatic conditions of production. Therefore, the objectives of this study were to investigate the dissipation rate and residues of acetamiprid and iprodione in sweet cherry fruits, as well as to evaluate the validity of prescribed PHI for these pesticides.

MATERIAL AND METHODS

Field trials

The field trials were carried out in the orchards in the surrounding of Novi Sad city (Vojvodina province, Serbia). The trials were designed according to OEPP standard for experimental design and data analysis (Anonymous, 2004; Anonymous 2006). Acetamiprid was applied as aqueous solutions of commercial formulation Mospilan 20 SP with 200 g/kg a.i., with a hand sprayer at the manufacturer's recommended concentration of 0.025%. Iprodione was applied as a suspension of commercial formulation Dional 500-SC with 500 g/l a.i. with a hand sprayer at the manufacturer's recommended doses of 1.5 l/ha, during ripening (Savić-Petrić, 2015).

Sampling was performed by randomly collecting from various places of the experimental plots according to the FAO/WHO recommendations. Around 0.5 kg of the sweet cherries fruit was collected from each replicate and brought to the laboratory. Samples were collected immediately before and after acetamiprid application (when the spraying mixture has dried), and 2, 4, 6, 8, 10, 12 and 14 days after the application. For the iprodione residue analysis, samples were taken immediately before and after fungicide application (when the spraying mixture has dried), and 2, 3, 4, 5, 6 and 7 days after the application.

Every single analytical sample was considered in triplicates. The untreated sweet cherry trees were the sources of the blank sweet cherry samples, used for method validation.

Extraction and determination

Extraction and determination of acetamiprid and iprodione residues from sweet cherry fruits were performed using previously validated QuEChERS-based methods (Lazić et al., 2014; Lazić et al., 2016), followed by HPLC/DAD analysis. Applied methods were completely fulfilled SANCO/12571/2013 criteria. Chromatogram of iprodione from sweet cherry fruit is presented at Figure 1.

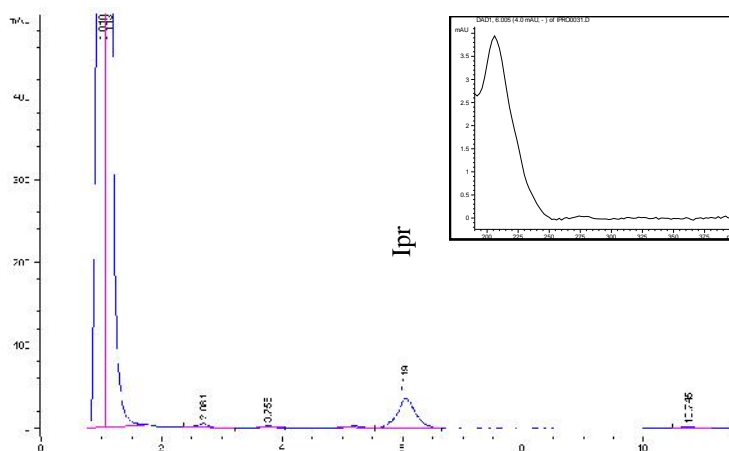


Figure 1. Chromatogram and UV spectra of iprodione in sweet cherry fruit samples

RESULTS AND DISCUSSION

These pesticides provided many obvious benefits in agriculture their inappropriate use can result in unacceptably high levels of these compounds in fruits and vegetables. Although in cases when applied in accordance with good agricultural practices, pesticides may leave residues (Lazi et al., 2014). Since the presence of pesticide residues in fruits and vegetables can affect consumer health, the regulatory authorities have established maximum residue levels of pesticides for most common vegetables and fruits. The European Union and Serbian legislation have specified a maximum residue levels (MRLs) for acetamiprid in sweet cherries of 1.5 mg/kg. From the other hand, till 2015, MRL for iprodione in sweet cherry fruits was 3.0 mg/kg (149/2008), while now it is 10.0 mg/kg (2015/400). Iprodione residue in sweet cherry allowed by Serbian legislation (Official Gazette 29/2014) is 3.0 mg/kg.

The results of the field studies conducted in our research are shown in figure 2 and 3.

The initial deposit of acetamiprid in sweet cherry fruits was 0.52 mg/kg. In this case, as well as during iprodione application, immediately after drying deposit the concentration of acetamiprid in sweet cherries was lower than the MRL of 1.5 mg/kg, according to EU and Regulations of the Republic of Serbia from 2014 (Official Gazette 29/2014). The average content of acetamiprid residues determined in samples collected on the second day after its application was 0.36 mg/kg with standard deviation of 0.01 mg/kg. Subsequently, residues decreased slowly and at the intervals of 4, 6, 8, 10, 12 and 14 days after treatments, the estimated residues were from 0.31 mg/kg to 0.11 mg/kg.

Acetamiprid content below the maximum permitted level of 0.2 mg/kg, defined by Regulations of the Republic of Serbia from 2010 (Official Gazette 25/2010), was established in samples collected eight days after the insecticide application.

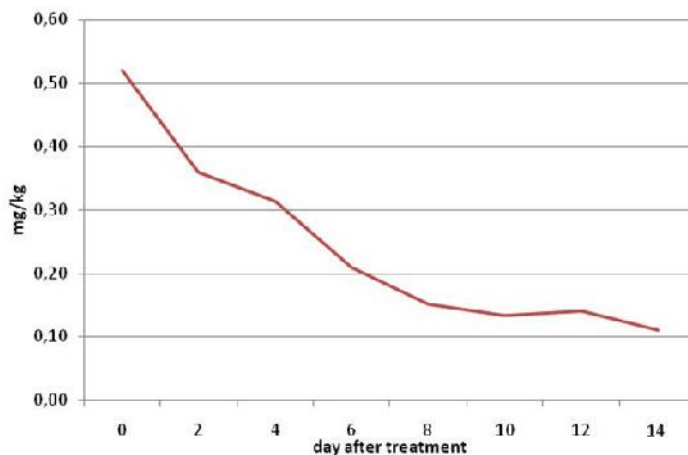


Figure 2. Residues of acetamiprid in sweet cherry fruits during PHI

The highest residue level of iprodione was found in samples taken in the first sampling time, 1 h after the fungicide application. Throughout the experiment residue levels of iprodione had been decreasing, reaching levels below 0.29 and 0.09 mg/kg.

Having in mind newly prescribed, as well as the previous MRLs, the highest quantity of the present iprodione was significantly below these values. In samples collected on the first day after the treatment, the average value of iprodione residues in sampled sweet cherries was 0.23 mg/kg. Further analysis established reduction in iprodione content in sampled fruits, and after the PHI, iprodione quantity was reduced for 0.07 mg/kg.

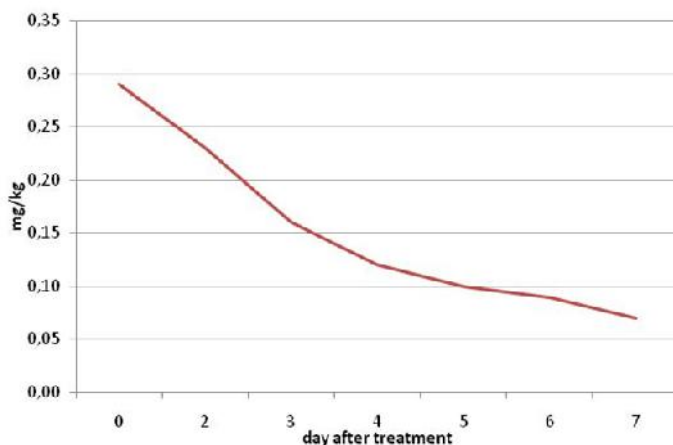


Figure 3. Residues of iprodione in sweet cherry fruits during PHI

The dissipation kinetic of the acetamiprid and iprodione in sweet cherry was determined by plotting residue concentration against time. The half-life of pesticides calculated using the first order rate equation:

$$C_t = C_0 e^{-kt}$$

where C_t represents the concentration of the pesticide residue at time t , C_0 represents the initial concentration and k is the rate constant per day. Half-lives (DT_{50}) were determined from the k value, $DT_{50} = \ln 2/k$ (Gupta et al., 2008).

The dissipation of acetamiprid residues over the time fitted to the equation $C_t = 0.52 \cdot 0.22^t$, with DT_{50} of 3.15. In recent years, a number of researches have dealt with the behaviour of acetamiprid in plant products, with lack of information about acetamiprid in sweet cherries. Pramanik et al. (2008) established that acetamiprid half-life in mustard plants is 1.02 days, while acetamiprid half-life in made tea was 1.84–2.33 days (Gupta et al., 2008). Half-lives of acetamiprid determined in tomato and cucumber fruits were 1.04 and 1.18 days, respectively (Shams El Din et al., 2012). Analysis of acetamiprid residues in zucchini grown under greenhouse conditions were performed by Park et al. (2010). DT_{50} of acetamiprid achieved in this experiment was 1.9 days.

In this study, the first-order kinetic equations determination coefficient (R^2) for iprodione in sweet cherry was 0.929 ($C_t = 0.29 \cdot 0.20^t$). The change in iprodione residue concentrations in cherry samples indicated half-life of 3.47 days. Wang et al. (2012) established that the half-life of iprodione in green tobacco leaves was 5.64–8.80 days. In the study performed by Salghi et al. (2013), iprodione residue levels in the peach fruits ranged between 0.52 and 0.06 mg/kg and after the PHI were below the legal limits. Analysis of iprodione residues in tomato grown under greenhouse conditions was performed by Omirou et al. (2009), with DT_{50} of 6.8 days.

CONCLUSIONS

In this study, dissipation rates of acetamiprid and iprodione in sweet cherry fruits were evaluated under field conditions, after pesticides application at recommended doses. The highest residue levels of iprodione and acetamiprid, found in cherry samples taken in the first sampling time, 1 h after pesticides application, was 0.29 mg/kg and 0.52 mg/kg, respectively and were far below established MRLs. In addition, the results showed that the insecticide acetamiprid and fungicide iprodione in sweet cherry fruits declined rapidly, and had relatively short half-life values.

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