Ecotoxicology and Environmental Safety 73 (2010) 183–188

Contents lists available at ScienceDirect

Ecotoxicology and Environmental Safety

journal homepage: www.elsevier.com/locate/ecoenv

Famoxadone residue and dissipation in watermelon and soil

Congyun Liu [a], Dongmei Qin [b], Yuzhen Zhao [a], Canping Pan [a], Shuren Jiang [a], Fengmao Liu [a,*]

[a] College of Science, China Agricultural University, Beijing 100193, PR China
[b] Institute for the Control of Agrochemicals, Ministry of Agriculture, Beijing 100026, PR China

ARTICLE INFO

Article history:
Received 3 July 2008
Received in revised form
15 June 2009
Accepted 11 August 2009

Keywords:
Famoxadone
Pesticide residue
Dissipation
Watermelon
Soil

ABSTRACT

The residue levels and dissipation rate of famoxadone in watermelon and soil were determined by HPLC-UVD. The LODs for famoxadone in watermelon, peel, flesh and soil were 0.002 mg/kg (0.004 mg/kg in leaf). The fortified recoveries ranged from 84.91% to 99.41% with relative standard deviations (RSDs) of 0.06–4.50%. The dissipation of famoxadone residue over the time in watermelon leaf and soil fitted to the equation $C_T = 19.695e^{-0.078T}$ and $C_T = 1.369e^{-0.129T}$. The half-lives ($T_{1/2}$) of famoxadone in watermelon leaf and soil were 9.7 and 5.5 days, respectively. The final residue in watermelon was lower than 0.1 mg/kg at harvest, which suggested the use of this fungicide to be safe to both human and environment. This work would be helpful in establishing the maximum residue limit (MRL) for famoxadone in watermelon in China, and provide guidance to the proper and safe use of this pesticide in agriculture.

1. Introduction

Watermelon is one of the most common types of melon. It is mainly used for the production of fresh fruit, juices, nectars, fruit cocktails, etc. Even the by-product such as peel and seed can be made into pickle, preserve and food (Wani et al., 2008). Many kinds of pesticide were applied to protect the watermelon from pests and fungi.

Famoxadone, 5-methyl-5-(4-phenoxyphenyl)-3-(phenyl amino)-2, 4-oxazolidinedione (Fig. 1) is a relatively new pesticide produced by DuPont (USA). It is widely used for the control of plant pathogenic fungi (Zhu, 2004). Famoxadone is particularly effective against grape downy mildew, potato and tomato late and early blights wheat leaf and glume blotch, and barley net blotch (Zhu, 2004). It is also applied on watermelon to prevent anthracnose.

The analytical methods for famoxadone have been reported in recent years. A gas chromatography with electron-capture detection (GC-ECD) method and a gas chromatography with mass spectrometric detection (GC–MS) screening method were compared for the analysis of famoxadone in grapes and wines (Abreu et al., 2006). A rapid gas chromatography method was reported for the determination of famoxadone residue in tomato, grape and wine samples (Likas et al., 2007). A selective fungi-toxicity study of famoxadone tebuconazole and trifloxystrobin in mushroom showed that famoxadone was much more effective than the other two fungicides in a fungicidal evaluation against *Verticillium fungicola* on *Agaricus bisporus* (Chrysayi-Tokousbalides et al., 2007). Li and Yang (2006) described the behavior and toxicology of famoxadone in the environment. A residue dynamics study in citrus showed that the half-life of famoxadone in citrus peel was 9.2 days (Xu et al., 2006).

The MRLs of famoxadone in watermelon have been legislated in some countries. In Japan, the MRL is set at 0.1 mg/kg in watermelon (Ge, 2006), in European Union, the MRL is set at 0.3 mg/kg in melon (Commission Directive 2004/95/EC of 24 September, 2004), in South Korea, the MRL is set at 0.5 mg/kg in Korean melon (http://www.chinapesticide.gov.cn). However, in China, to our knowledge there is no regulation on the MRL in watermelon, and no work has been done to determine the famoxadone residues and to estimate the dissipation behavior of famoxadone residue in watermelon.

In this work, a simple HPLC-UVD method was established to detect the residue of famoxadone in watermelon and soil. A field study was done to investigate the dissipation of famoxadone in watermelon leaf and soil. This work would help the government to establish the MRL of famoxadone in watermelon and to provide guidance on the proper and safe use of this pesticide.

2. Materials and methods

2.1. Materials and reagents

Famoxadone standard and formulation (68.75% of water dispersible granule WG) were supplied from DuPont Company; acetone (analytical reagent AR), dichloromethane (AR), petroleum ether (AR) and anhydrous magnesium sulfate

* Corresponding author. Fax: +86 10 62733620.
E-mail address: liufengmao@yahoo.com (F. Liu).

0147-6513/$ - see front matter © 2009 Elsevier Inc. All rights reserved.
doi:10.1016/j.ecoenv.2009.08.003

(AR) were purchased from Beijing Chemical Reagents Company, China; Acetonitrile for chromatography was purchased from Dikma Co., America; Florisil was purchased from Beijing Chemical Reagents Company and deactivated under 130° C for 6 h before use. The shaker (HZQ-C) was from Haerbin Donglian Electron Technology Exploiter Co., Ltd., Heilongjiang Province, China; and the vacuum rotary evaporator (N-1000) was from Tokyo Rikakikai Co., Ltd, Tokyo, Japan.

2.2. Field experiment design

The experiment was conducted in Beijing in two consecutive years. Beijing is located in the north of China, and it has a temperate monsoon climate. The soil is clay loam with the pH value of 7.23 and the organic matter content of 2.28%. The experiment was designed according to Guideline on Pesticide Residue Trials issued by the Institute for the Control of Agrochemicals, Ministry of Agriculture (ICAMA), People's Republic of China. Eight field plots each with 5×6 (30) m^2 area were prepared; 1 m distance was used as a buffer area to separate each plot in the same field.

To investigate the dissipation of famoxadone in plant and soil, watermelon leaf and soil were sprayed with famoxadone formulation (68.75% of water dispersible granule) in the experiment plots each with three replicates, the dosage was 2250 g a.i. ha^{-1} (gram of active ingredient per hectare). A plot with the same size but no famoxadone application was compared simultaneously.

To investigate the final residue of famoxadone in watermelon and soil, both high (1160 g a.i. ha^{-1}, with two treatments: spray 4 times and 5 times) and low (580 g a.i. ha^{-1}, with two treatments: spray 4 times and 5 times) dosages were conducted in two plots, separately. There was an interval of 5 days between each application. A plot with the same size but no famoxadone application was compared simultaneously.

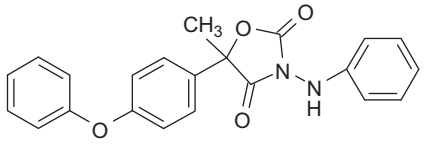

Fig. 1. Structure of famoxadone.

Table 1
The average recovery and the LODs ($n = 3$).

Samples	Fortified level (mg/kg)	Average recoveries (%)	RSD (%)	LOD (mg/kg)
Watermelon	0.10	92.19	2.35	0.002
	0.50	94.91	3.14	
	1.00	96.83	4.93	
Peel	0.10	84.91	1.38	0.002
	0.50	98.40	0.83	
	1.00	95.36	0.94	
Flesh	0.10	94.91	1.56	0.002
	0.50	94.85	0.65	
	1.00	97.30	1.09	
Leaf	0.10	97.25	0.06	0.004
	0.50	87.46	4.77	
	1.00	93.80	1.27	
Soil	0.10	96.11	4.50	0.002
	0.50	96.98	2.17	
	1.00	99.41	0.98	

2.3. Sampling and storage

Representative samples were collected from each plot at different time intervals. To investigate the dissipation of famoxadone, the watermelon leaf and the soil in which the watermelon grows were collected on days 0, 1, 3, 5, 7, 14, 24 and 35 after spraying. To determine the final residue of famoxadone, both watermelon and soil samples were collected at days 7 and 14 before harvest. All the samples were stored at −20°C before further analysis.

2.4. Analytical procedure

2.4.1. Sample preparation

Watermelon: The whole watermelon after removing the seeds was divided into watermelon, the peel and flesh. Each matrix of these samples was mixed in a blender separately, and then stored in a deep freezer at −20° C.

Leaf: The leaves were comminuted and then stored in a deep freezer at −20° C.

Soil: The soil was dried in shade, sieved through a 40-mesh sieve, and then stored in a deep freezer at −20° C.

2.4.2. Sample extraction

Twenty grams of watermelon, peel, flesh and soil samples (10 g for leaves) were placed in a 250 mL conical flask and 40 mL acetone was added (2 mL water was mixed with the soil samples). The flask was capped and shaken on a shaker for 30 min. The extracts were filtered with a filter paper and washed with another 40 mL acetone. The filtrate was transferred to a 500 mL separator funnel containing 200 mL 2% sodium chloride solution. The sample solution was then extracted by liquid–liquid partition with 2×20 mL dichloromethane. The dichloromethane layers were combined, dehydrated with anhydrous sodium sulfate, filtered through a funnel and evaporated to near dryness with a vacuum rotary evaporator at 40°C. After the extract was made to dryness under a gentle nitrogen stream, 1 mL of acetone/petroleum ether mixture (v/v = 1:9) was added to re-dissolve the sample before cleanup.

2.4.3. Sample cleanup

A glass cleanup column (250 mm × 10 mm i.d.) packed with 5 g basic alumina in between two layers of 2 cm anhydrous sodium sulfate was used. The column was preconditioned with 10 mL petroleum ether in order to remove impurities in basic alumina and anhydrous sodium sulfate. The concentrated extract was transferred to the column and eluted by 80 mL acetone/petroleum ether mixture (v/v = 1:9). The first 30 mL was discarded and the following 50 mL elute was collected and evaporated under vacuum at 40°C, made to dryness under a gentle nitrogen stream. The residue was redissolved in 2 mL acetonitrile for HPLC analysis.

2.4.4. HPLC condition

HPLC was performed using an Agilent 1100 series liquid chromatography system (Agilent Technologies, USA) with a UVD detector. A C18 column, 250 mm × 4.6 mm (Agilent), was operated at a flow rate of 1.0 mL min^{-1}. The

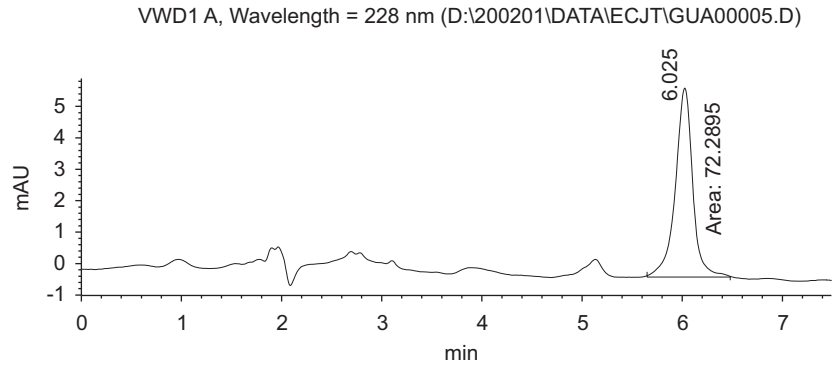

Fig. 2. The chromatogram of famoxadone standard (0.1 mg/kg).