

Research Article



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시설 내 오이(*Cucumis sativus* L.) 재배 중 Penthiopyrad 및 Pyriofenone의 잔류특성과 생산단계 잔류허용기준 설정

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Establishment of Pre-Harvest Residue Limits and Residue Characteristics of Penthiopyrad and Pyriofenone in Cucumber (*Cucumis sativus* L.) Under Greenhouse Condition

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Abstract

BACKGROUND: Greenhouse crops are one of agricultural products consumed largely in Korea. Cucumber is a typical example as main vegetables of greenhouse crops. Thus, pesticide residue analysis is an important requirement to guarantee pesticide safety of cucumber. This work was aim to investigate the residues of penthiopyrad and pyriofenone in cucumber after harvest.

METHODS AND RESULTS: Cucumber was subjected to treat with penthiopyrad and pyriofenone at a level of recommended dose 0, 1, 2, 3, 5, 7 and 10 days before harvest under greenhouse conditions. The samples were extracted with organic solvent by using a homogenizer and purified on solid phase cartridge column followed by LC-MS/MS analysis. The recovery levels of penthiopyrad and pyriofenone ranged from approximately 81 to 93% with the method limit of 0.005 mg/kg and coefficient of variation less than 10%. Penthiopyrad and pyriofenone were detected at a

level less than maximum residue limit in cucumber at 10 days before. The half-lives of penthiopyrad and pyriofenone were determined to 2.4 ~ 2.6 days.

CONCLUSION: Penthiopyrad and pyriofenone are suggested to use in cucumber 10 days before harvest to reach their levels less than maximum residue limit.

Key words: Biological half-life, Cucumber, Penthiopyrad, Pyriofenone, Pre-harvest residue limits (PHRLs)

서론

2015 271,040 ton 가
85% (240,212
ton) (MAFRA, 2016).

가

가

(Lee *et al.*, 2005).

가

가

가

(Lee

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Table 1. Safe use guidelines for penthiopyrad and pyriofenone in *Cucumis sativus* L

Pesticides	Formulation	A.I. ^{a)} (%)	Dilution	Safe use guidelines		MRL ^{d)} (mg/kg)
				PHI ^{b)} (day)	MNA ^{c)} (time)	
Penthiopyrad	EC ^{e)}	20	4,000	2	3	0.5
Pyriofenone	SC ^{f)}	10	2,000	2	3	0.7

^{a)}A.I.: Active ingredient, ^{b)}PHI: Pre-harvest interval, ^{c)}MNA: Maximum number of application, ^{d)}MRL: Maximum residue limit, MFDS, ^{e)}EC: Emulsifiable concentrate, ^{f)}SC: Suspension concentrate

et al., 2009; Nam *et al.*, 2010).

penthiopyrad pyriofenone 64
가
(Lee *et al.*,
2005).
(Kim and park,
2002).
penthiopyrad pyriofenone
가
(KCPA,
2015).
(Maximum Residue Limit, MRL) 0.5 mg/kg, 0.7
mg/kg

(Pre-Harvest Residue Limit, PHRL)

가
(Park. *et al.*,
2011; Ha *et al.*, 2012; MAFRA, 2016).

penthiopyrad
pyriofenone

가

재료 및 방법

시험농약 및 시험포장

20% penthiopyrad
(: , ()) 10% pyriofenone
(: , ())

가 1 (1) 21
(2)
50 m

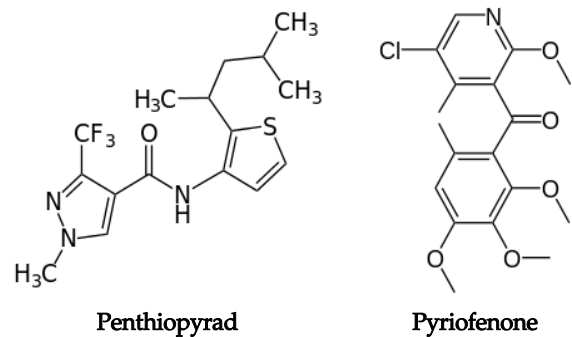


Fig. 1. Chemical structure of penthiopyrad and pyriofenone.

3
1 m
4 15 14
2016 4 2

1
(Table 1, KCPA, 2015).

시약, 재료 및 기구

penthiopyrad pyriofenone
Dr. Ehrenstorfer GmbH (Germany)
98.2%, 97.33%
Fig. 1 (Turner, 2015).
Junsei Chemical (Japan) acetonitrile
dichloromethane , methanol water
Merck (Germany) GR . Sodium
sulfate anhydrous, sodium chloride DAE JUNG
(Korea) , NH2 solid
phase extraction (SPE) cartridge (1 g) Phenomenex
(USA) . Homogenizer vacuum
rotary evaporator Nissei EYELA
HPLC, DIONEX
UltiMate 3000 (Thermo Scientific, USA) ,
TSQ Quantum Max (Thermo Science, USA)

시료채취 및 잔류분석

2 0 0, 1, 2, 3, 5, 7, 10
2 kg

Table 2. Analytical conditions for the determination of penthiopyrad and pyriofenone in *Cucumis sativus* L

HPLC	DIONEX UltiMate 3000 (Thermo Scientific, USA)		
Detector	TSQ Quantum Access Max (Thermo science, USA)		
Column	Shiseido Capcell Core-C ₁₈ (2.7 μm, 2.1 mm I.D.×150 mm)		
Oven temp.	40°C		
Flow rate	0.3 mL/min.		
Injection vol.	1.0 uL		
	0.1% formic acid+0.5 mM ammonium formate in Water:0.1% formic acid in Acetonitrile=A:B		
Mobile phase	Time (min.)	A (%)	B (%)
	0.0	95	5
	2.0	95	5
	3.0	10	90
	6.0	10	90
	6.5	95	5
	10.0	95	5
Ion source	ESI +		
Spray voltage	3,500 V		
temperature	Vaporizer: 350°C, Capillary: 320°C		
gas pressure (N ₂)	Ion sweep: 1.0 unit, Sheath: 35.0 unit, Aux: 10.0 unit		

Table 3. Selected Reaction Monitoring (SRM) condition of penthiopyrad and pyriofenone

Compound	Precursor ion	Product ion	CE	Q1 PW	Q3 PW	Retention time
Penthiopyrad	360.158	177.068	30	0.7	0.7	7.77 min.
		256.061	19	0.7	0.7	
		276.067	13	0.7	0.7	
Pyriofenone	366.100	166.110	35	0.7	0.7	8.17 min.
		184.060	23	0.7	0.7	
		209.120	23	0.7	0.7	

가 , cartridge , Dichloromethane 5 mL
 -20°C , pre-washing cartridge
 Penthiopyrad pyriofenone loading , (dichloromethane:methanol=95:5, v/v)
 acetonitrile 20 g , penthiopyrad pyriofenone
 acetonitrile 100 mL 가 , homogenizer 3 , acetonitrile 2 mL
 (10,000 rpm) , LC-MS/MS (0.2 µm membrane filter) ,
 100 mL 50 mL chromatography peak
 가 separatory funnel dichloromethane 50, (Table 2, 3).
 50 mL 2 분석법 검증
 anhydrous sodium sulfate ,
 dichloromethane 5 mL , Penthiopyrad (Method Limit of Quantification,
 pyriofenone SPE , NH₂ 1 g MLOQ) 10 (0.05 mg/kg), 50 (0.25 mg/kg)

Table 4. Linear equation of calibration curve for the quantification of the pesticide residues in *Cucumis sativus* L.

Pesticide	Linear equation	R ²
Penthiopyrad	y=23,312,661.04x+51,749,80821	0.9987
Pyriofenone	y=43,761,803.01x+237,167.5128	0.9997

Table 5. Recovery rate and MLOQ for penthiopyrad and pyriofenone in *Cucumis sativus* L

Pesticide	Fortification level (mg/kg)	Recovery (%)				MLOQ ^{a)} (mg/kg)
		1	2	3	AVG±C.V. ^{b)}	
Penthiopyrad	0.05	92.8	94.9	95.4	94.3±1.5	0.005
	0.25	94.9	93.1	93.2	93.7±1.1	
Pyriofenone	0.05	87.3	89.8	83.4	86.8±3.8	0.005
	0.25	81.2	82.7	81.0	81.7±1.1	

^{a)}Method of Limit of Quantification, ^{b)}Coefficient of variation

pyriofenone 20 g penthiopyrad
1 mg/kg, 5 mg/kg 1
mL 가 3 , 30
시설 내 기상조건 및 중량
1, 2
19.8~26.9℃, 17.6~24.8℃
63.8%~88.1%, 46.5%~88.6%
1, 2 179.1~234.2
g, 165.0~209.7 g

결과 및 고찰

표준검량선 작성

penthiopyrad
(98.2%) pyriofenone (97.33%) acetonitrile
1,000 mg/kg stock solution
(Minimum Detectable Amount, MDA) 0.05
mg/kg 2.0 mg/kg
matrix
matched
(R²) 0.99
(Table 4).

분석정량한계 및 회수율

(Lee *et al.*, 2009).
penthiopyrad pyriofenone
0.005 mg/kg , MRL
0.5 mg/kg, 0.7 mg/kg
2
(10 MLOQ, 50 MLOQ) 3
70~120% (/
x100) 10% (Table 5). LC-MS/MS
penthiopyrad
pyriofenone 7.77 min., 8.17 min.

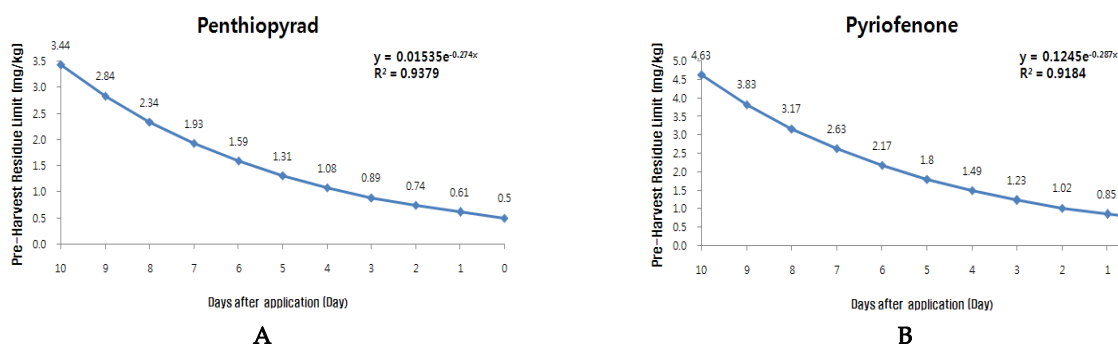
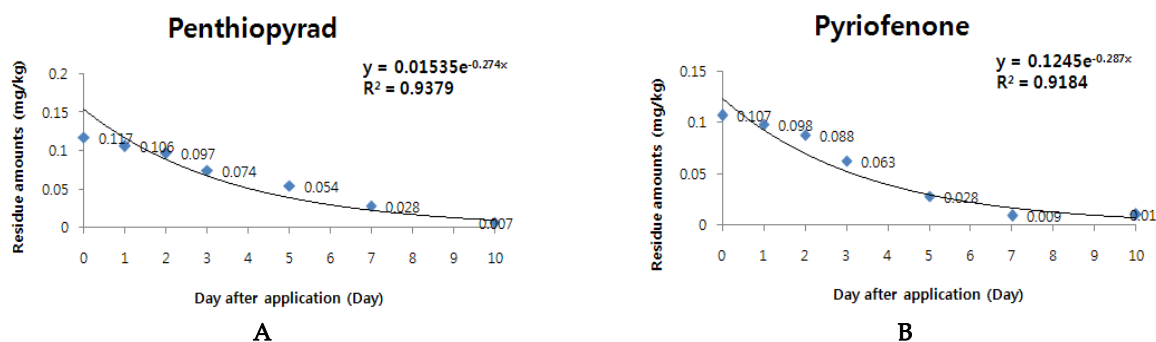
(Lee *et al.*, 2009).

잔류특성과 생물학적 반감기

penthiopyrad
pyriofenone
Penthiopyrad 1 2
0.122 mg/kg, 0.117 mg/kg ,
pyriofenone 1 0.091 mg/kg, 2
0.107 mg/kg .

(Kanazawa, 1992). Moon (2016)

(Lee *et al.*, 2009).
가
가
(Kim *et al.*, 2003; Lee *et al.*,
가 ,
(Moon *et al.*,
2016).



10 1 2

penthiopyrad 0.008 mg/kg, 0.007 mg/kg

, pyriofenone 0.008 mg/kg, 0.010 mg/kg

가 10 20

가 (Lee *et al.*, 2009).

,

,

가 (Kim *et al.*, 2003; Lee *et al.*, 2003; Park *et al.*, 2011).

(Fig. 2).

가

가

가

(Kim *et al.*, 2002).

penthiopyrad pyriofenone pH 4~9 가

가

(RDA,

2013). Lee (2005)

,

(Lee *et al.*,

2009; Hwang *et al.*, 2012; Han *et al.*, 2013).

	0.639/k	k	(Kim <i>et al.</i> , 2013;
MFDS, 2016).		penthiopyrad	pyriofenone
1	2	2.6	2.5 , 2.5 ,
2.4			.
boscalid	amisulbrom	1.9	3.6
Lee (2008)	Hwang (2012)		,

Pre-Harvest Residue Limit (PHRL) 설정
(Pre-Harvest Residue Limit, PHRL)

가

MRL 가

가

(Park *et al.*, 2005).
 penthiopyrad pyriofenone
 1,
 2 $y=0.1433e^{-0.266x}$ ($R^2=0.9461$), $y=0.1535e^{-0.274x}$ ($R^2=0.9379$)
 $y=0.0999e^{-0.277x}$ ($R^2=0.9543$), $y=0.1245e^{-0.287x}$ ($R^2=0.9184$)
 PHRL
 10
 3.44 mg/kg, 4.63 mg/kg
 penthiopyrad
 pyriofenone MRL 0.5 mg/kg, 0.7 mg/kg
 (Fig. 3).

요약

penthiopyrad pyriofenone
 가
 Penthiopyrad
 pyriofenone
 1, 1 2
 2 0 0, 1, 2, 3, 5,
 7, 10
 acetonitrile, dichloromethane, SPE NH₂ cartridge
 LC-MS/MS
 0.005 mg/kg 10, 50
 penthiopyrad
 pyriofenone 92.8~95.4%, 81.0~89.8%
 10%
 1, 2
 penthiopyrad 2.6 2.5, pyriofenone
 2.5 2.4 Penthiopyrad
 pyriofenone 10
 3.44 mg/kg, 4.63 mg/kg
 MRL (Penthiopyrad: 0.5 mg/kg,
 Pyriofenone: 0.7 mg/kg)
 penthiopyrad pyriofenone
 가

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