

Research Article



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시설재배 숙갓 및 피망의 작물특성에 따른 Boscalid 및 Spinetoram의 잔류량 감소추이

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Residual Dissipation based on Crop Commodities Classification of Boscalid and Spinetoram on Crown Daisy and Sweet Pepper under Green Houses

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Abstract

BACKGROUND: This study was performed to evaluate the residue dissipation of boscalid and spinetoram on crown daisy and sweet pepper affected by the morphology of the crop. The half-lives and dissipation rate constants for boscalid and spinetoram on crown daisy and sweet pepper were calculated. And then lower limit of 95% confidence interval for dissipation rate constant could be used to propose the pre-harvest residue limit.

METHODS AND RESULTS: The pesticide products diluted according to the pesticide label were applied one time on crown daisy and sweet pepper at 2 field sites, respectively. Initial concentration of boscalid and spinetoram on crown daisy after application were in the range of 72.80~117.15 mg/kg and 2.82~4.67 mg/kg, respectively. And Initial concentration of boscalid and spinetoram on sweet pepper were in the range of 1.58~1.62 mg/kg and 0.10~0.21 mg/kg, respectively. Boscalid and spinetoram for crown daisy dissipated below the maximum residue limit(MRL) at 10 and 2 days after application,

respectively. All residues concentration of boscalid and spinetoram for sweet pepper below the MRL at 0 day after application. The half-lives based on dissipation rate constant for boscalid and spinetoram on crown daisy were 4.2~4.9 days and 3.0~2.4 days respectively. And the half-lives for boscalid and spinetoram on sweet pepper were 6.7~7.0 days and 2.8~4.0 days respectively.

CONCLUSION: The difference in initial concentration of boscalid and spinetoram among crop commodities were due to different crop morphology with larger surface areas. This study was suggested that pre-harvest residue limit would be calculated from lower limit of 95% confidence interval for dissipation rate constant and would be useful to protect consumers by controlling the pesticide residues in crop.

Key words: Crown daisy, Pesticide residues, Pre-harvest residue limit, Sweet pepper

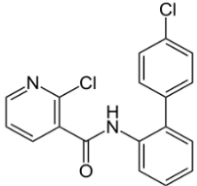
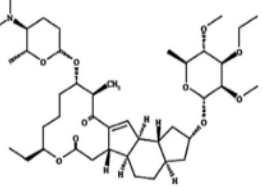
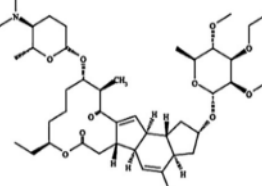
서론

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(RDA, 2012).
1979 1.7

2015 1,681,000 ha

Table 1. Chemical structures and physico-chemical properties of boscalid and spinetoram (Tumer J. A., 2015)

Pesticides	Boscalid	Spinetoram	
		XDE-175-J	XDE-175-L
Chemical structure			
Vapor pressure (mPa)	0.0072 (20°C)	0.053 (20°C)	0.021 (20°C)
log K _{ow}	2.96	4.09 (pH 7)	4.49 (pH 7)
Water solubility (mg/L, 20-25°C)	4.6	11.3 (pH 7)	46.7 (pH 7)

ha 11.6 kg , 2.3 가 (MAFRA, 2016). 가 (KCPA, 2005). RDA, 2017). (MFDS, 2016, boscalid spinetoram , 2010 2015 1.7 ~5.0%, 0.7~2.0% , (NAPQMS, 2010-2015).

재료 및 방법

시험약제 및 시약

(Oh *et al.*, 2003, Lee *et al.*, 2010, NAPQMS, 2010-2015). (Pre-Harvest Residue Limit, PHRL) 220 338 16 14 , (Maximum Residue Limit, MRL) 41 161 (MFDS, 2016). (NAPQMS, 2010-2015).

boscalid 23.5% (, ()), spinetoram 5% (, ()) boscalid 49.3% (, ()), spinetoram 5% (, ()) boscalid (98.4%) Dr. Ehrenstorfer GmbH (Germany), spinetoram (XDE-175-J (97.6%) XDE-175-L (100.0%)) Dow chemical (USA) Table 1 . Acetone, acetonitrile, dichloromethane, *n*-hexane ethyl acetate residue analysis grade HPLC grade Merck (Germany) , sodium sulfate anhydrous sodium chloride Guaranteed reagent grade Junsei chemical (Japan) . Solid-phase extraction cartridge (florisil silica, 1 g, 6 mL) Agilent Technologies (USA)

포장시험

90 km 가 2

Boscalid , spineotram

Table 2. Good agricultural practice and maximum residue limit of boscalid and spinetoram on crown daisy and sweet pepper in Korea

Crops	Pesticide	Formulation			Application			PHI ^{b)} (days)	MRL ^{c)} (mg/kg)
		Type	%AI ^{a)}	Dilution	Spray concentration (kg ai/hl)	Max. No.	Interval (days)		
Crown daisy	Boscalid +Fludioxonil	SC ^{d)}	28.5 (23.5+5)	1,000	0.235	2	7	14	20.0
	Spinetoram	SC	5	2,000	0.025	3	7	7	2.0
Sweet pepper	Boscalid	WG ^{e)}	49.3	1,500	0.329	2	7	2	3.0
	Spinetoram	SC	5	2,000	0.025	3	7	2	0.5

a) Active ingredient, b) Pre-harvest interval, c) Maximum residue limit, d) Suspension concentrate, e) Water-dispersible granule

0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0 10.0 mg/L

(I, :) (II, . Spinetoram XDE-175-J (97.6%) 10.25
:) , (I, mg XDE-175-L (100.0%) 10.00 mg acetonitrile
: ,) (II, : 10 mL 1,000 mg/L .
 ,) . XDE-175-J XDE-175-L (1,000 mg/L) 1
10 m² 3 mL N₂ gas acetonitrile
1 10 mL 100 mg/L
(KCPA, 2016) . Matrix matched
 , (() , EL969-1) acetonitrile 0.0005, 0.001,
1 (Table 2). 0, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1, 0.2, 0.5 0.8 mg/L,
0, 1, 3, 5, 7, 10 14 , 0.0005, 0.001, 0.002, 0.005, 0.01, 0.02, 0.05, 0.1
kg 0.2 mg/L , 1
bag ice box polyethylene mL N₂ gas
24 1 mL
 . chromatogram
시료조제 peak area
(r²) .
 , 5 cm 회수율 시험 및 잔류분석
 , 5 Boscalid 3 10 g
가 deepfreezer(-70°C) 48 10 (0.4 mg/kg), (20.0 mg/kg)
homogenizer , (100.0 mg/kg), 10
(-15°C) . (0.2 mg/kg) (3.0 mg/kg)
 . Spinetoram
분석법 정량한계 10 (XDE-175-J XDE-175-L, 0.2 mg/kg
(Limit of quantification, LOQ) 0.02 mg/kg) (XDE-175-J XDE-175-L,
chromatogram 2.0 mg/kg), 10 (XDE-175-J
(signal to noise ratio, S/N)가 10 XDE-175-L, 0.02 mg/kg) (XDE-175-J
, , XDE-175-L, 0.5 mg/kg)
(Park *et al.*, 2017). .
분석법 직선성 acetone 100
Boscalid (98.4%) 10.16 mg acetone 10 mL mL 가 20 , 250 rpm (BBT-2, JEIO
1,000 mg/L , acetone 1,000 mL 200 mL .
0.1, 0.2, 0.5, 50 mL 가 dichloromethane 100 mL 50 mL 2
1.0, 2.0, 5.0, 10.0, 20.0, 50.0, 60.0 70.0 mg/L, sodium sulfate

Table 3. GC-ECD conditions for the analysis of boscalid on crown daisy and sweet pepper

Instrument	Agilent 7860 series GC
Detector	Electron Capture Detector (ECD)
Column	DB-5, Capillary column (30 m×320 µm×0.25 µm)
Temperature	Inlet port : 260°C Detector : 300°C Oven : 200°C (2 min) → 10°C/min → 280°C (10 min)
Gas flow	Carrier (N ₂) : 1.0 mL/min Make-up (N ₂) : 60 mL/min
Inlet mode	Split (50:1)
Injection volume	1 µL

, rotary vacuum evaporator(V-700, BUCHI, Switzerland) 40°C . Boscalid

Spinetoram
n-hexane 4 mL *n*-hexane/acetone(70/30, v/v) 4 mL
 . Boscalid *n*-hexane 5 mL
 florisil SPE cartridge(1 g, 6 mL)
 4 mL 2 mL , *n*-hexane/ethyl acetate
 (90/10, v/v) 5 mL , *n*-hexane/ethyl acetate
 (80/20, v/v) 10 mL . N₂ gas
 acetone 2 mL GC-ECD
 (Table 3). Spinetoram *n*-hexane
 4 mL silica SPE cartridge (1 g, 6 mL)
 4 mL 2 mL , *n*-hexane/acetone
 (95/5, v/v) 5 mL *n*-hexane/acetone (70/30,
 v/v) 20 mL . N₂ gas
 acetonitrile 2 mL , XDE-175-J 100
 XDE-175-L 10 HPLC-MS/MS
 (Table 4).

3 10 g boscalid

Table 4. HPLC-MS/MS conditions for the analysis of spinetoram in crown daisy and sweet pepper

Instrument	Agilent 1200 series HPLC		
Column	Imtakt, Candenza CD-C18 (150 × 3 mm, 3 µm)		
Detector	AB SCIEX QTRAP® 5500 LC/MS/MS/ system		
Flow rate	0.4 mL/min		
	A: 0.1% formic acid, 5 mM ammonium formate in methanol B: 0.1% formic acid, 5 mM ammonium formate in water A/B (50/50, v/v), Gradient		
	Time (min)	A (%)	B (%)
	0	50	50
Mobile phas	1	70	30
	3	95	5
	6	95	5
	8	70	30
	10	50	50
	20	50	50
Injection volume	10 µL		
Retention time	XDE-175-J : 7.6 min		XDE-175-L : 7.9 min
	Target analyte	XDE-175-J	XDE-175-L
	Precursor ion, Q1	748.518	760.485
	Product ion, Q3	142.200	142.200
	Collision energy (V)	45	43
	Ionization	ESI positive	
MS/MS condition	Ionspray voltage	+ 4500V	
	Nebulizer gas pressure	50 psi	
	Heater gas	55 psi	
	Curtain gas	30 psi	
	Drying gas temp.	400°C	
	Scan type	MRM mode	

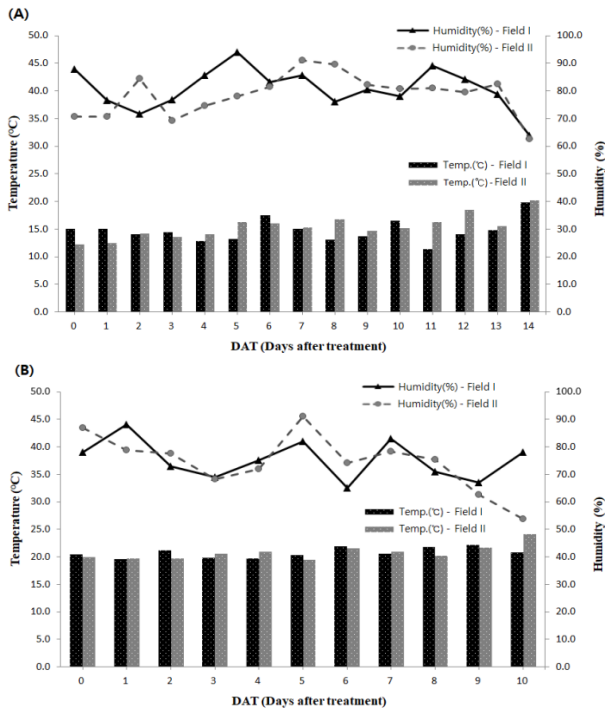


Fig. 1. Temperature and humidity of field sites for crown daisy (A) and sweet pepper (B).

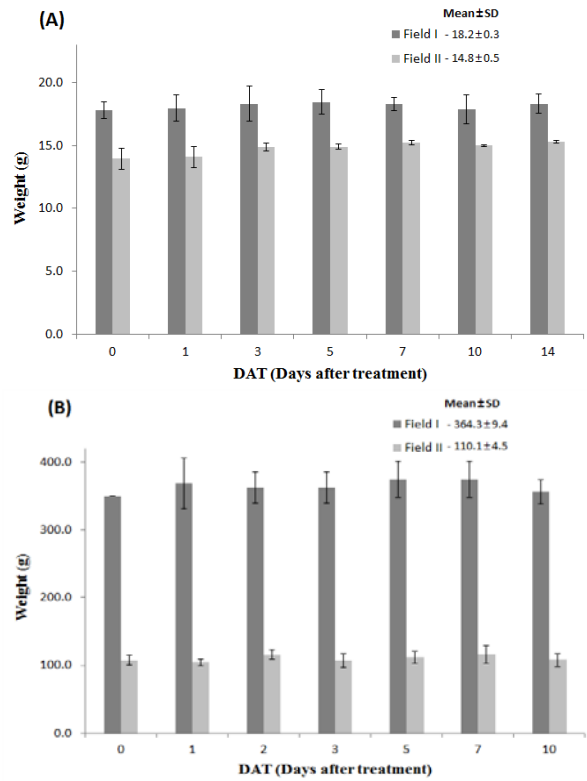


Fig. 2. Average sample weights of crown daisy (A) and sweet pepper (B) at harvest date.

spinetoram 1.0 mg/kg
 , -20°C
 . Boscalid 175 162 ,
 spinetoram 174 181
 .
 boscalid spinetoram
 , XDE-175-J
 (3'-O-ethyl-5,6-dihydro spinosyn J) XDE-175-L(3'-O-ethyl spinosyn L)
 spinetoram
 XDE-175-J XDE-175-L (Sparks,
 2008; MFDS, 2017).

생물학적 반감기 산출

boscalid spinetoram

(Lee, 1998; MFDS, 2017).

, F

t-

95%
 (MFDS, 2014).

결과 및 고찰

포장시험

14.7°C 15.4°C, 78.5% 80.8% ,
 I II

I II 20.7°C 20.8°C,
 75.4% 74.4% (Fig. 1). 가
 15~20°C 10°C 가 ,
 22~25°C, 16~18°C ,
 (RDA, 2007).
 I II 18.2
 ±0.3 g 14.8±0.5 g , 364.3±9.4 g
 110.1 g±4.5 (Fig. 2).
 10%
 가

I II
 , I
 , II
 100 g , 가 (Lee,
 2001).

분석법 검증

boscalid 0.04
 mg/kg 0.02 mg/kg , spinetoram
 XDE-175-J XDE-175-L 0.02 mg/kg
 0.002 mg/kg, 0.002 mg/kg

Table 5. Limit of quantification and Recovery of boscalid and spinetoram in crown daisy and sweet pepper

Crops	Pesticide	Fortification level (mg/kg)	Recovery(%)					LOQ ^{c)} (mg/kg)
			Replicate			Mean±SD ^{a)}	CV ^{b)}	
			1	2	3			
Crown daisy	Boscalid	0.4	76.4	80.1	81.3	79.3±2.6	3.2	0.04
		20	103.3	104.7	102.0	103.3±1.3	1.3	
		100	99.7	92.1	101.7	97.8±5.1	5.2	
	XDE-175-J	0.2	94.7	100.9	99.1	98.2±3.2	3.3	0.02
		2	85.2	96.0	87.8	89.7±5.6	6.3	
		0.02	85.0	95.3	94.1	91.5±5.6	6.1	
XDE-175-L	2	109.3	108.9	102.6	106.9±3.7	3.5	0.002	
	0.2	86.0	88.6	83.7	86.1±2.5	2.9		
	3	96.5	100.3	96.9	97.9±2.1	2.1		
Sweet pepper	Boscalid	0.2	86.0	88.6	83.7	86.1±2.5	2.9	0.02
		3	96.5	100.3	96.9	97.9±2.1	2.1	
		0.02	85.8	90.6	86.7	87.7±2.6	2.9	
	XDE-175-J	0.5	90.7	89.5	92.3	90.8±1.4	1.6	0.002
		0.02	89.3	90.1	89.1	89.5±0.5	0.6	
		0.5	86.9	87.5	88.7	87.7±1.0	1.1	

a) Standard deviation, b) Coefficient of variation, c) Limit of quantification

0.05 mg/kg (Table 5, MFDS, 2014).
 Boscalid 7 (0.1
 ~10.0 mg/L) 5 (10.0~70.0 mg/L) 2
 $y=973.85087x-311.12292$ ($r^2=0.99395$)
 $y=1506.88790x-7039.51392$ ($r^2=0.99846$) , 8
 (0.05~10.0 mg/L) $y=1395.51102x-56.42835$ ($r^2=$
 0.99981) . Spinetoram
 XDE-175-J 8 (0.0005~0.1 mg/L)
 $y=101811934.25969x+72318.79901$ ($r^2=0.99992$),
 XDE-175-L 6 , 2 (0.0005~0.02 mg/L) 0
 0.02~0.8 mg/L) , $y=34976545.53479x+2775.$
 49949 ($r^2=0.99948$) $y=48906919.99303x-1004292.$ 73139
 ($r^2=0.99888$) , 9 (0.0005~0.2 mg/L)
 XDE-175-J XDE-175-L $y=$
 $81147830.20776x+67853.10714$ ($r^2=0.99972$) $y=21304343.$
 $53742x+7264.72619$ ($r^2=0.99996$) .
 Boscalid 76.4~104.7%
 86.0~100.3% , spinetoram XDE-
 175-J XDE-175-L 85.2~100.9% 85.0
 ~109.3%, 85.8~92.3% 86.9~90.1%
 , boscalid spinetoram 0.6
 ~6.3% ,
 70~110% (% coefficient of
 variation) 20% (Table 5, MFDS, 2014).
 일자별 잔류량 변화
 boscalid 0 I

II 72.80 mg/kg 117.15 mg/kg,
 1.58 mg/kg 1.62 mg/kg ,
 spinetoram 0 I
 II 2.82 mg/kg 4.67 mg/kg, 0.21
 mg/kg 0.10 mg/kg . Boscalid
 가 23.5% ,
 49.3% ,
 boscalid 0.235 kg ai/hl 0.329 kg
 ai/hl, spinetoram 5%
 0.025 kg ai/hl (Table 2).
 boscalid spinetoram
 0 , boscalids
 가 1.5 , 2%
 . boscalid spinetoramd
 0
 ,
 (Nam *et al.*, 2007; Park *et al.*, 2009).
 boscalid I II
 10 19.29 mg/kg 15.64 mg/kg
 20 mg/kg , spinetoram
 3 1.50 mg/kg 1.13 mg/kg
 2.0 mg/kg ,
 boscalid spinetoram I II
 0 boscalid 1.58 mg/kg 1.62
 mg/kg, spinetoram 0.10 mg/kg 0.21 mg/kg
 3.0 mg/kg 0.5 mg/kg (Fig. 3).
 boscalid spinetoram

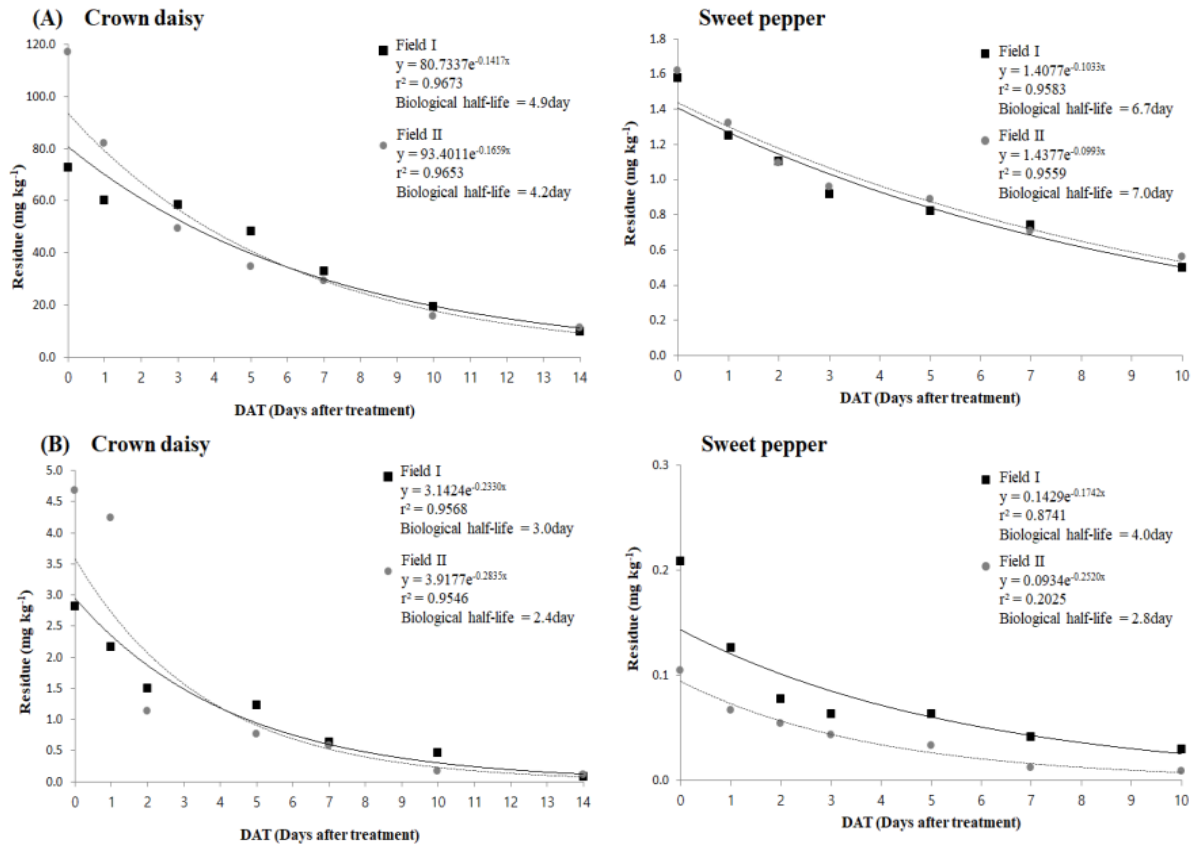


Fig. 3. Dissipation curves of boscalid (A) and spinetoram (B) on crown daisy and sweet pepper.

Table 6. Regression analysis for the dissipation of boscalid on crown daisy and sweet pepper

Crops	Crown daisy		Sweet pepper	
	Field I	Field II	Field I	Field II
Dissipation regression equation ^{a)}	$y=80.7337e^{-0.1417x}$ ($r^2=0.9673$)	$y=93.4011e^{-0.1659x}$ ($r^2=0.9653$)	$y=1.4077e^{-0.1033x}$ ($r^2=0.9583$)	$y=1.4377e^{-0.0993x}$ ($r^2=0.9559$)
Dissipation rate constant ^{b)}	0.1417±0.0300	0.1659±0.0361	0.1033±0.0248	0.0993±0.0245
Lower limit of dissipation rate constant	0.1118	0.1297	0.0785	0.0748

^{a)} Significant at $p<0.05$ by the *F*-test, ^{b)} Significant at $p<0.05$ by the *t*-test

생물학적 반감기 및 감소상수 (MFDS, 2014). boscalid spinetoram (Lee, 1998; Cho *et al.*, 2011). boscalid spinetoram (Fig. 3).

14 7 가 , 2 가 , 3.0 2.4 , 4.0 2.8 (Fig. 3). I II 1 2 F- t- 95% boscalid spinetoram 0.1417±0.0300 0.1659±

Table 7. Regression analysis for the dissipation of spinetoram on crown daisy and sweet pepper

Crops	Crown daisy		Sweet pepper	
Field No.	Field I	Field II	Field I	Field II
Dissipation regression equation ^{a)}	$y=3.1424e^{-0.2330x}$ ($r^2=0.9568$)	$y=3.9177e^{-0.2835x}$ ($r^2=0.9546$)	$y=0.1429e^{-0.1742x}$ ($r^2=0.8741$)	$y=0.0934e^{-0.2520x}$ ($r^2=0.2025$)
Dissipation rate constant ^{b)}	0.2330±0.0570	0.2835±0.0710	0.1742±0.0760	0.2520±0.0495
Lower limit of dissipation rate constant	0.1761	0.2124	0.0982	0.2025

^{a)} Significant at $p < 0.05$ by the *F*-test, ^{b)} Significant at $p < 0.05$ by the *t*-test

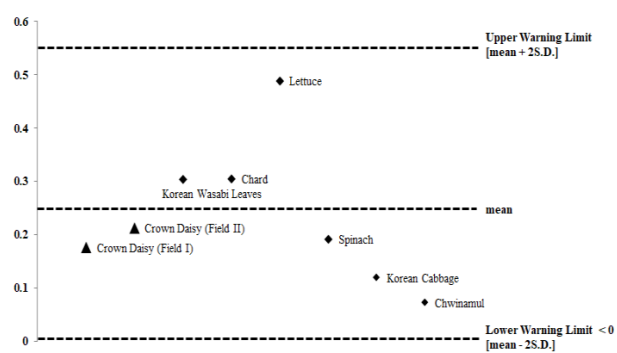


Fig. 4. Dissipation rate constants evaluation of spinetoram on crown daisy with leafy vegetables proposed by MFDA.

0.0361 , 0.1033±0.0248 0.0993±0.0245
 , spinetoram I II
 0.2330±0.0570 0.2835±0.0710 , 0.1742±
 0.0760 0.2520±0.0495 (Table 6, 7).

95%
 , boscalid

가 0.1071 0.1688 ,
 0.0608 0.0533

, spinetoram

(), , , , ,
 0.3036, 0.3045, 0.4883, 0.1912, 0.1197 0.0718

, 0.0270
 0.0863 (MFDS, 2016b). Spinetoram

6

(standard deviation, SD) ±
 2SD (standard deviation) 95%

spinetoram (Fig. 4,
 Moser H. and J. Römbke, 2009; Lee *et al.*, 2015).

boscalid spinetoram

가 2 가

가 가 , 가

Notes

The author declare no conflict of interest.

Acknowledgement

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