

Research Article



CrossMark

Open Access

노지재배 복숭아 중 Bistrifluron과 Cyenopyrafen의 생산단계 잔류특성에 따른 감소추이

황은진¹, 박정은¹, 권찬혁², 김진숙², 장희라^{1*}

¹ , ²

Residue Dissipation Behavior of Bistrifluron and Cyenopyrafen in Peach for the Cultivation Periods under Field Conditions

Eun-Jin Hwang¹, Jung-Eun Park¹, Chan-Hyeok Kwon², Jin-Sook Kim² and Hee-Ra Chang^{1*} (¹Department of
Pharmaceutical Engineering·Applied Biotoxicology, Graduate School of Hoseo University, Asan 31499, Korea,
²Ministry of Food and Drug Safety, Osong 28159, Korea)

Received: 9 March 2018 / Revised: 14 March 2018 / Accepted: 25 March 2018

Copyright © 2018 The Korean Society of Environmental Agriculture

This is an Open-Access article distributed under the terms of the Creative Commons Attribution
Non-Commercial License (<http://creativecommons.org/licenses/by-nc/3.0>) which permits unrestricted
non-commercial use, distribution, and reproduction in any medium, provided the original work is
properly cited.

ORCID

Hee-Ra Chang

<http://orcid.org/0000-0002-0307-7703>

Abstract

BACKGROUND: This study was performed to calculate the biological half-lives and regression coefficient of bistrifluron and cyenopyrafen dissipation in peach and to estimate the Pre-Harvest Residue Limits (PHRLs).

METHODS AND RESULTS: The bistrifluron and cyenopyrafen were prepared on the basis of good agricultural practice for peach and treated with a single application. Peaches were harvested at 0, 1, 3, 5, 7, 10 and 14 days after application, prepared for analysis, and analyzed by HPLC-DAD. The limits of quantitation (LOQ) of bistrifluron and cyenopyrafen were 0.02 mg/kg and 0.04 mg/kg, respectively. The recoveries of bistrifluron and cyenopyrafen were 99.5~108.7% and 88.4~98.9% at two different concentration levels. The biological half-lives of field I (Sejong) and field II (Pyeongtaek) were 6.1 and 7.0 days for bistrifluron, and 6.3 and 7.0 days for cyenopyrafen, respectively. The 95% confidence intervals of dissipation rate constants of bistrifluron in peach were 0.0805~0.1457 and 0.0577~0.1417 for field I and field II, respectively, and those of

cyenopyrafen were 0.0911~0.1278 and 0.0576~0.1417, respectively.

CONCLUSION: Residue dissipation of bistrifluron and cyenopyrafen in peach were similar to that of correction to sample weight difference during the harvest periods. This study suggests that residue dissipation rate would be helpful to set the PHRLs that protect public health.

Key words: Bistrifluron, Cyenopyrafen, Dissipation, Pre-harvest residue limit, Peach

서론

1 (Kim, 2007; Woo *et al.*, 2010).

35%가

가

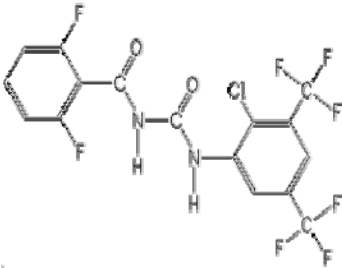
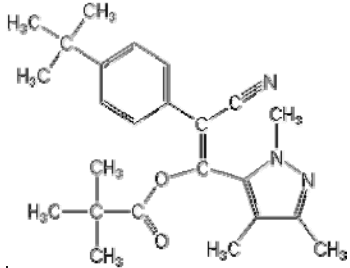
Kim, 2001; Kim and Kim, 2011).

2016 166,473 ha

2.2% 가 , 1,165 ha
237,711 7.5% 13.0% 가

*Corresponding author: Hee-Ra Chang
Phone: +82-41-540-9696; Fax: +82-41-540-9696;
E-mail: hrchang@hoseo.edu

Table 1. Chemical structures and physico-chemical properties of bistrifluron and cyenopyrafen (Turner J. A., 2015)

Pesticide	Bistrifluron	Cyenopyrafen
Chemical structure		
Vapor pressure (mPa)	0.0027 (25°C)	5.2E-4 (25°C)
log Kow	5.74	5.6
Water solubility (mg/l, 20-25°C)	<0.03	0.3
Organic solubility (g/l, 20-25°C)	Soluble in dichloromethane (64.0), hexane (3.5), methanol (33.0)	-

(KOSTAT, 2016a; 2016b).

가 , 가
가 , 가
5~10 , 가
가
(Jeon *et al.*, 2000; Woo and Park, 2001; Kim *et al.*, 2002; Ha *et al.*, 2012).

가 42
km 가 2 ,
(Kim *et al.*, 2002). 145
(Maximum Residue Limit, MRL)
(Pre-Harvest Residue Limit, PHRL) 49
(MFDS, 2017a, 2017b).
bistrifluron
(IGR) , cyenopyrafen 30) 1
(KCPA, 2014; RDA 2018).
bistrifluron)
cyenopyrafen ,
polyethylene bag , ice box
24

재료 및 방법

시험약제 및 시약

bistrifluron 10%
(, (주)), cyenopyrafen 25%
(, (주))

bistrifluron (97.6%, Sigma-Aldrich, USA) cyenopyrafen (97.3%, Sigma-Aldrich, USA)
acetone, acetonitrile, dichloromethane, *n*-hexane ethyl acetate Merck(Germany), Sodium sulfate sodium chloride Junsei chemical(guaranteed reagent grade, Japan), Solide phase extraction cartridge(florisil, 1 g, 6 cc) Agilent Technologies(USA)

포장시험

가 42
km 가 2 ,
(I, :)
(II, :)
1 , 3
1
(KCPA, 2014)
(YAMATO, DY-435Y)
I(2015 07 28) II(2015 07
(Table 2).
0, 1, 3, 5, 7, 10 14
1 kg (5
polyethylene bag , ice box
24

시료 조제

가 ,
deepfreezer (-70°C) 48
, homogenizer . 가
(-15°C)

Table 2. Good agricultural practice and maximum residue limit of bistrifluron and cyenopyrafen on peach in Korea

Pesticide	Formulation		Application			PHI ^{b)} (days)	MRL ^{c)} (mg/kg)
	Type	%AI ^{a)}	Spray concentration (kg ai/hl)	Max. No.	Interval (days)		
Bistrifluron +Flubendiamide	EC ^{d)}	10+13	0.0025	3	10	14	1.0
Cyenopyrafen	EC	25	0.0125	3	-	14	0.5

a) Active ingredient
b) Pre-harvest interval
c) Maximum residue limit
d) Emulsifiable concentrate

Table 3. Instrumental conditions for the analysis of bistrifluron and cyenopyrafen in peach

Pesticide	Bistrifluron	Cyenopyrafen			
Instrument	Agilnet 1260 Infinity Series HPLC				
Column	Phenomenex Luna 5μ C18 (250×4.60 mm)				
Detector	Diode Array Detector (DAD)				
Flow rate	1.0 mL/min				
Mobile phase	Acetonitrile/Water (75/25, v/v), Isocratic	Acetonitrile/Water (80/20, v/v), Gradient			
		Time(min)	Acetonitrile	Water	Flow
		13	80	20	1.0
		15	100	0	2.0
		39	100	0	2.0
		41	80	20	1.0
Wavelength	250 nm	294 nm			
Injection volume	30 μL	40 μL			

분석법 정량한계				회수율 시험 및 잔류분석			
(Limit of Quantification, LOQ)				Bistrifluron			
Signal to noise ratio				10 g			
(S/N)가 10				(0.02 mg/kg)			
				10 (0.2 mg/kg)			
				(Maximum			
(Park <i>et al.</i> , 2017). Bistrifluron				Residue Limit, MRL)			
HPLC				(0.5 mg/kg)			
cyenopyrafen				(2.0 mg/kg)			
Table 3				3			
				가 250 rpm 20			
				1,000 mL			
직선성				300 mL			
Bistrifluron (97.6%) 10.25 mg				100 mL 가 bistrifluron			
mL 1,000 mg/L				dichloromethane 100 mL 50 mL 2			
acetonitrile 0.05, 0.1, 0.2, 0.5, 1.0, 2.0				cyenopyrafen dichloromethane 100 mL 1			
5.0 mg/L				sodium sulfate			
Cyenopyrafen (97.3%) 5.14 g				, 40°C rotary vacuum evaporator (V-700,			
mL 500 mg/L				BUCHI, Switzeland)			
acetonitrile 0.1, 0.5, 1.0, 2.0 5.0 mg/L				n-hexane 4 mL . n-Hexane 4 mL			
bistrifluron				florisil SPE cartridge (1 g, 6 cc) 2			
cyenopyrafen chromatogram peak				mL , bistrifluron n-hexane/ethyl acetate (85/			
area				15, v/v) 10 mL , cyenoprafen n-hexane 10			
(r ²)				mL n-hexane/ethyl acetate (95/5, v/v) 2 mL			

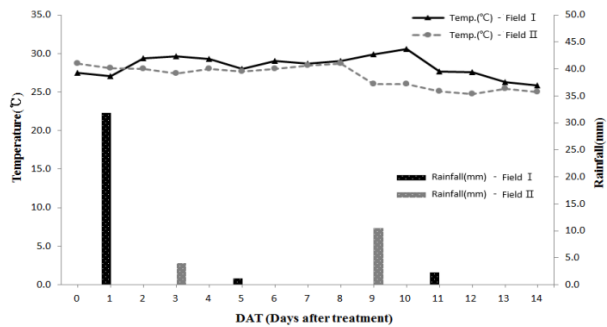


Fig. 1. Climatic conditions in residue field trials for peach.

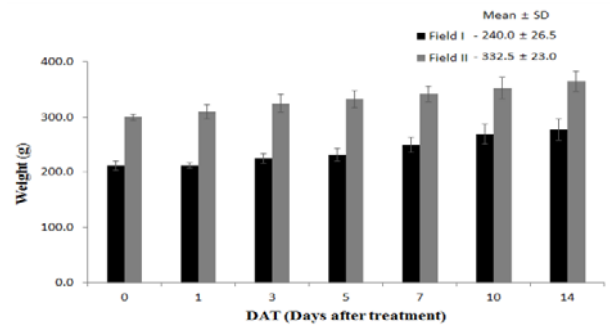


Fig. 2. Changes of peach weight at sample harvest intervals.

n-hexane/ethyl acetate (95/5, v/v) 5 mL *n*-hexane/ethyl acetate (90/10, v/v) 8 mL N₂ gas acetonitrile 2 mL HPLC-DAD (Agilnet 1260 Infinity Series, Agilent Technologies, USA) (Table 3).
(-20°C)
3 10 g bistrifluron
cyenopyrafen 1.0 mg/kg
, bistrifluron 83 , cyenopyrafen
25

Bistrifluron cyenopyrafen

복숭아 시료의 개체 중량 차이에 의한 희석 영향 산출
bistrifluron
cyenopyrafen
(Lee *et al.*, 2013).

$$\frac{\text{(mg/kg)}}{\text{(mg/kg)}} = \frac{\text{(kg)}}{\text{(kg)}} \times \frac{\text{(kg)}}{\text{(mg/kg)}}$$

생물학적 반감기 산출 및 생산단계 잔류허용기준(안)
bistrifluron cyenopyrafen
, *F* *t*
, 95%
(MFDS, 2014).

결과 및 고찰

포장시험

I II
28.4°C 27.0°C , 1.0 mm
3 2 (Fig. 1, KMA, 2015). I
1 ,
,
,
(RDA, 2011).
가 ,
I
240.0±
II
26.5 g 332.5±23.0 g . I II
가 ,
14
30.6% 21.6% (Fig. 2).

Table 4. Limit of quantification and recoveries of bistrifluron and cyenopyrafen in peach

Pesticide	Fortification level (mg/kg)	Recovery (%)				CV ^{b)}	LOQ ^{c)} (mg/kg)
		Replicate			Mean±SD ^{a)}		
		1	2	3			
Bistrifluron	0.02	99.5	108.7	101.8	103.3±4.8	4.7	0.02
	0.2	100.3	101.2	102.1	101.2±0.9	0.9	
Cyenopyrafen	0.5	90.2	91.6	88.4	90.1±1.6	1.8	0.04
	2.0	95.4	98.9	97.8	97.7±1.2	1.3	

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

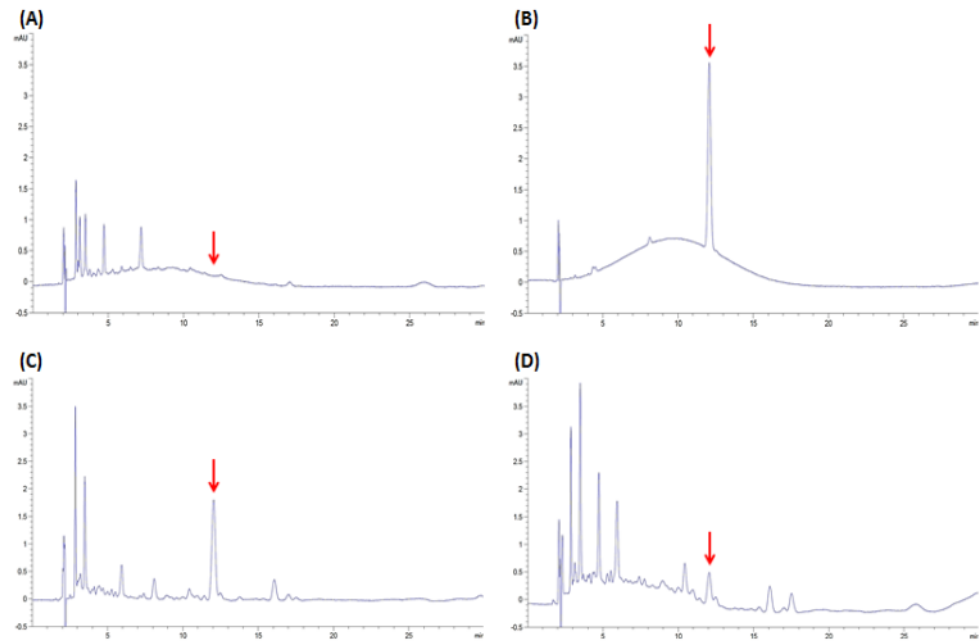


Fig. 3. Representative chromatograms of bistrifluron by HPLC-DAD analysis (A; blank peach, B; standard 1.0 mg/kg, C; recovery 2.0 mg/kg, D; sample 0 day (Field II)).

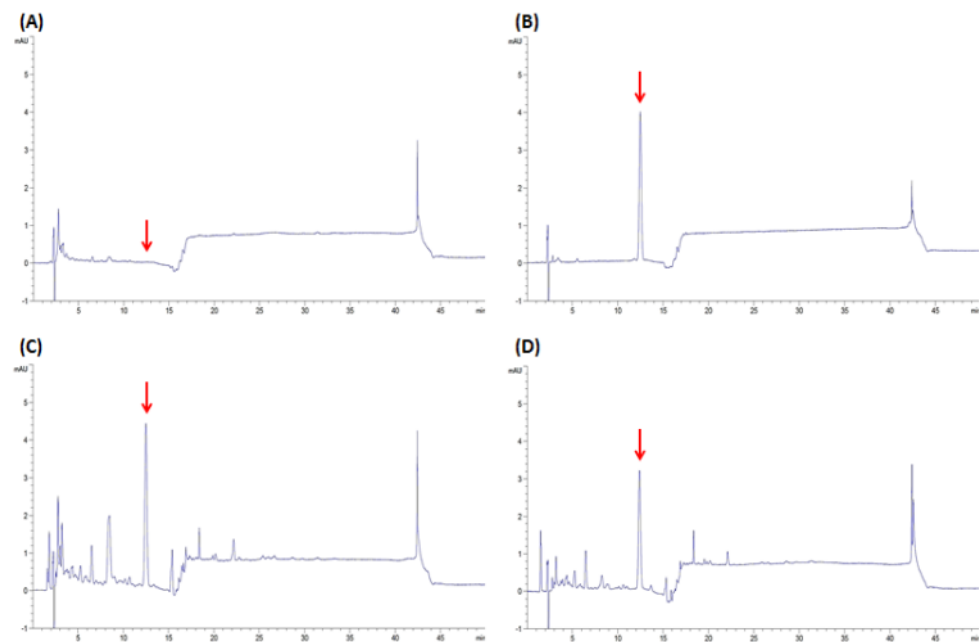


Fig. 4. Representative chromatograms of cyenopyrafen by HPLC-DAD analysis (A; blank peach, B; standard 1.0 mg/kg, C; recovery 0.5 mg/kg, D; sample 3 day (Field II)).

분석법 검증		0.999)		. Bistrifluron cyenopyrafen	
Bistrifluron	cyenopyrafen	99.5~108.7%		88.4~98.9%,	(%
0.02 mg/kg	0.04 mg/kg	coefficient of variation)		0.9~4.7%	1.3~1.8%
7	(0.05~5.0 mg/L)	5			
(0.1~5.0 mg/L)		70~110%		20%	(Table 4,
y=1.44338x-0.60804 (r ² =0.999)	y=1.64724x-1.00638 (r ² =	MFDS, 2014). Bistrifluron		cyenopyrafen	HPLC-

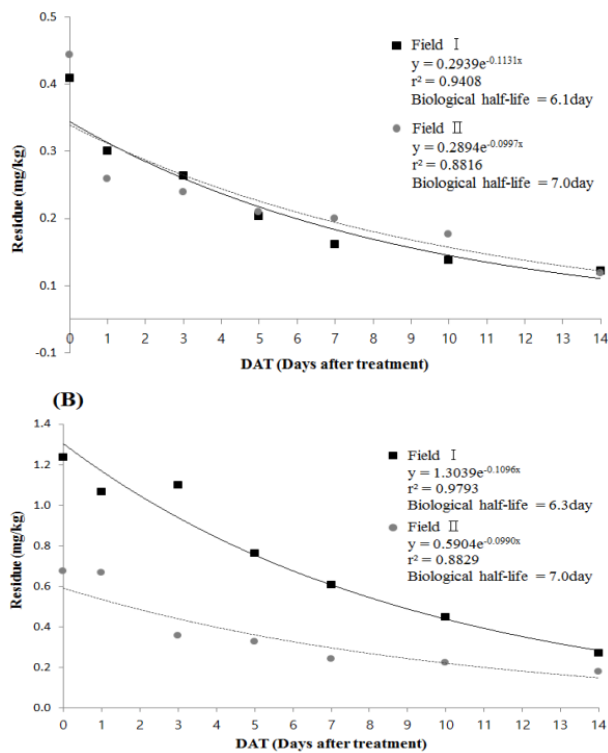


Fig. 5. Dissipation curves and half-lives of bistrifluron (A) and cyenopyrafen (B) in peach.

DAD
peak (Fig. 3, 4).

일자별 잔류량 변화

Bistrifluron cyenopyrafen
Fig. 5
bistrifluron I II 0.36 mg/kg
0.39 mg/kg , cyenopyrafen 1.24 mg/kg
0.67 mg/kg . Cyenopyrafen I II 0
1.24 g 0.77 g 2 가
Bistrifluron I II
0 1.0 mg/kg
cyenopyrafen I 10 , II
3 0.5 mg/kg
(MFDS, 2017a).
bistrifluron I 0.097~0.36 mg/kg,
II 0.079~0.39 mg/kg , cyenopyrafen
I 0.34~1.24 mg/kg, II 0.22~0.67
mg/kg , bistrifluron cyenopyrafen
I II

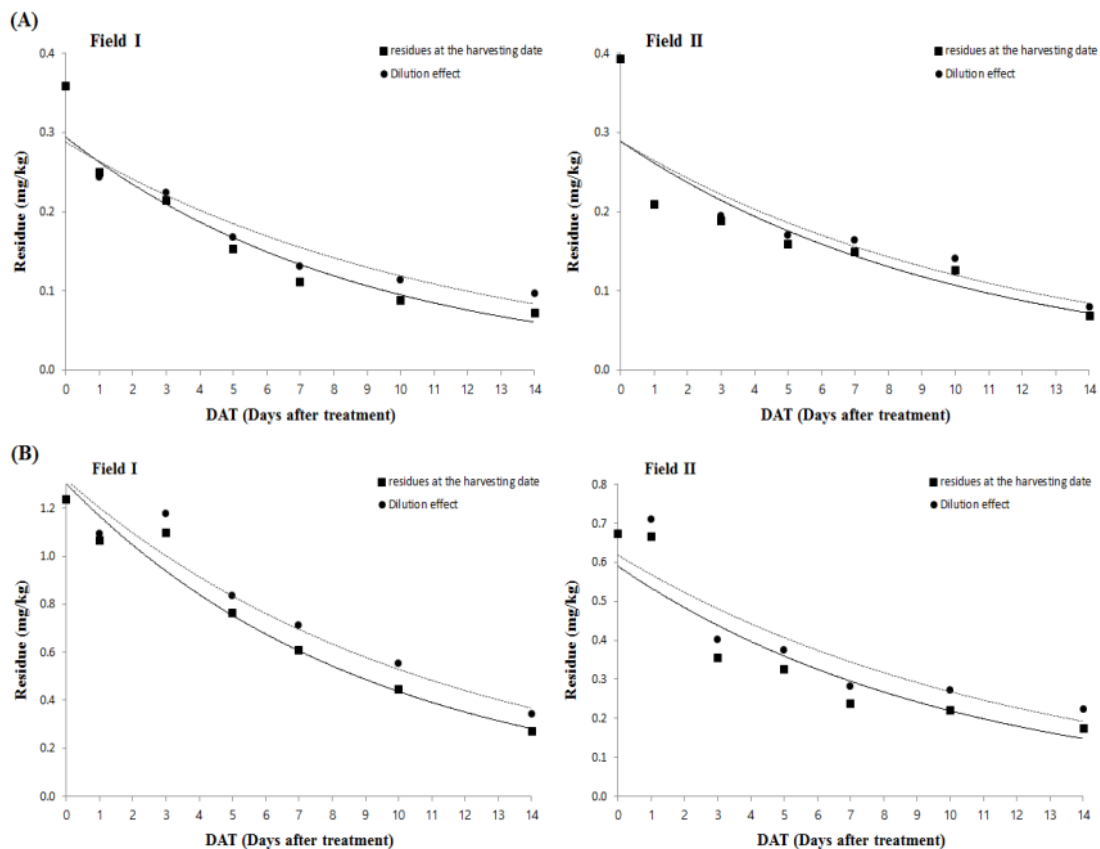


Fig. 6. Dissipation curves of bistrifluron (A) and cyenopyrafen (B) for dilution effects by increasing peach weights.

Table 5. Regression analysis for the dissipation of bistrifluron and cyenopyrafen on peach

Pesticide	Bistrifluron		Cyenopyrafen	
Field No.	Field I	Field II	Field I	Field II
Dissipation regression equation ^{a)}	$y=0.2939e^{-0.1131x}$ ($r^2=0.9408$)	$y=0.2894e^{-0.0997x}$ ($r^2=0.8816$)	$y=1.3039e^{-0.1095x}$ ($r^2=0.9793$)	$y=0.5904e^{-0.0990x}$ ($r^2=0.8829$)
Dissipation rate constant ^{b)}	0.0805~0.1457	0.0577~0.1417	0.0911~0.1278	0.0576~0.1417
Lower limit of dissipation rate constant	0.0805	0.0577	0.0911	0.0576

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

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

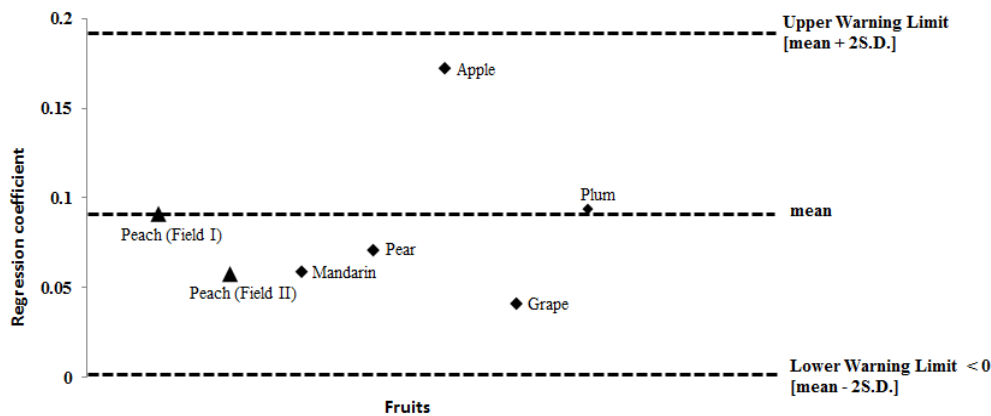


Fig. 7. Dissipation rate constants evaluation of cyenopyrafen on peach with fruits proposed by MFDS.

가 (Fig. 6). 95% bistrifluron I II 0.0805
~0.1457 0.0577~0.1417 , cyenopyrafen
10 16 0.0911~0.1278 0.0576~0.1417 . 95%
가 , bistrifluron I II
가 (Lee *et al.*, 2008). 0.0805 0.0577 , cyenopyrafen 0.0911
15 29.6% 가 0.0576 (Table 5).
가
가
(Kim *et al.*, 2009).
I II 0 14 가 bistrifluron
21.6~30.6% 가 0.0400 0.0316,
cyenopyrafen , , , , 0.0589,
0.0709, 0.1723, 0.0411 0.0934 (MFDS, 2017b).
Cyenopyrafen 5
±2SD(standard deviation) 0.0362~0.187
생물학적 반감기 및 감소상수
bistrifluron I II (Fig. 7, Moser H. and J. Römbke, 2009; Lee *et al.*,
6.1 7.0 cyenopyrafen 6.3 2015; Park *et al.*, 2017). Bistrifluron
7.0 (Fig. 5). 가 2
bistrifluron cyenopyrafen 1
F- t-

Note

The authors declare no conflict of interest.

Acknowledgement

This research was supported by the Ministry of Food and Drug Safety, Republic of Korea (grant number : 00-15-8-0399-00).

References

- Ha, H. Y., Ra, D. S., Shin, W. C., Im, G. J., & Park, J. E. (2012). Survey of pesticide use in fruit vegetables, fruits, and rice cultivation areas in Korea. *The Korean Journal of Pesticide Science*, 16(4), 395-400.
- Han, S. S., Lo, S. C., & Ma, S. Y. (2004). Effect of some variation factors on dissipation of tebuconazole in grape. *Korean Journal of Environmental Agriculture*, 23(3), 142-147.
- Jeon, H. Y., Kim, D. S., Cho, M. R., Yiem, M. S., & Chang, Y. D. (2000). Recent status of major fruit tree pest occurrences in Korea. *Journal of the Korean Society for Horticultural Science*, 41(6), 607-612.
- Kim, H. C., & Kim, M. R. (2001). Consumers' recognition and information need about food safety-Focused on pesticide residues, foodborne illness, and food additives. *Journal of the Korean Society of Food Culture*, 16(4), 296-309.
- Kim, Y. S., Park, J. H., Park, J. W., Lee, Y. D., Lee, K. S., & Kim, J. E. (2002). Persistence and dislodgeable residues of chlorpyrifos and procymidone in lettuce leaves under greenhouse condition. *Korean Journal of Environmental Agriculture*, 21(2), 149-155.
- Kim, S. S. (2007). A study on consumer's attitude for food safety and purchase of environment friendly agricultural products. *Journal of Korean Home Management Association*, 25(6), 15-32.
- Kim, S. W., Lee, E. M., Lin, Y., Park, H. W., Lee, H. R., Riu, M. J., Na, Y. R., Noh, J. E., Keum, Y. S., Song, H. H., & Kim, J. H. (2009). Establishment of pre-harvest residue limit (PHRL) of insecticide bifenthrin during cultivation of grape. *The Korean Journal of Pesticide Science*, 13(4), 241-248.
- Kim, H. J., & Kim, M. R. (2011). Concerns about hazardous elements on foods and recognition of the roles of government, food producers, and consumers in securing food safety. *Journal of the East Asian Society of Dietary Life*, 21(3), 401-417.
- Lee, H. D., Kyung, K. S., Kwon, H. Y., Ihm, Y. B., Kim, J. B., Park, S. S., & Kim, J. E. (2004). Residue characteristics of hexaconazole and chlorothalonil in several fruits. *The Korean Journal of Pesticide Science*, 8(2), 107-111.
- Lee, J. H., Park, H. W., Keum, Y. S., Kwon, C. H., Lee, Y. D., & Kim, J. H. (2008). Dissipation pattern of boscalid in cucumber under greenhouse condition. *The Korean Journal of Pesticide Science*, 12(1), 67-73.
- Lee, D. Y., Kim, Y. J., Park, M. H., Lee, S. H., Kim, S. G., Kang, N. J., & Kang, K. Y. (2013). Establishment of pre-harvest residue limit (PHRL) of fungicides azoxystrobin and difenoconazole on prunus mume fruits. *The Korean Journal of Pesticide Science*, 17(4), 307-313.
- Lee, D. K., In, J., & Lee, S. (2015). Standard deviation and standard error of the mean. *Korean journal of anesthesiology*, 68(3), 220-223.
- Moser, H., & Römbke, J. (2009). Ecotoxicological characterization of waste: results and experiences of an international ring test. pp. 73-75, Springer Science & Business Media, Germany.
- Park, J. E., Hwang, E. J., & Chang, H. R. (2017). Sediment toxicity assessment of pesticides using *Chironomus riparius* acute and chronic effect. *Korean Journal of Environmental Agriculture*, 36(2), 80-86.
- Park, J. S., Yang, S. H., & Choi, H. (2017). Residue patterns and biological half-lives of pyridalyl and fluopicolide in watermelon. *Korean Journal of Environmental Agriculture*, 36(1), 50-56.
- Turner, J. A. (2015). *The Pesticide Manual*. pp.117-261, 17th edition, British Crop Production Council, UK.
- Woo, J. H., & Park, S. H. (2001). Production-distribution system in a fruit-grwoing farming community and the role of a community-based endogenous farming organization : the case of nulmi-ri, chungdo-kun, kyoungbuk province. *Journal of The Korean Association of Regional Geographers*, 7(4), 1-16.
- Woo, H. D., Lee, J. K., Hang, G. D. (2010). Consumer awareness survey on safety management of pesticide residue. *Food Science and Industry*, 43(2), 24-40.