

Research Article



CrossMark

Open Access

시설재배 근대 중 Neonicotinoid계 살충제 Acetamiprid 및 Thiamethoxam의 생산단계 잔류특성

장희라^{1*}, 유정선¹, 도정아²

¹

, ²

가

Residue Dissipation Patterns of Neonicotinoid Acetamiprid and Thiamethoxam in Swiss Chard for the Harvest Periods under Greenhouse Conditions

Hee-Ra Chang^{1*}, Jung-Sun You¹ and Jung-Ah Do² (¹Department of Food & Pharmaceutical Engineering, Graduate School of Hoseo University, Asan 31499, Korea, ²Pesticide and Veterinary Drug Residues Division, Food Safety Evaluation Department, Ministry of Food and Drug Safety, Cheongju 28159, Korea)

Received: 15 June 2018/ Revised: 20 June 2018/ Accepted: 25 June 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: Dissipation of acetamiprid and thiamethoxam in greenhouse grown chard samples was evaluated at 5 intervals including the pre-harvest interval after application. This study was conducted to determine the residue levels, the biological half-lives and dissipation rate of acetamiprid and thiamethoxam in chard under controlled conditions.

METHODS AND RESULTS: Acetamiprid and thiamethoxam were applied in accordance with good agricultural practices for chard. Chard samples were collected at 0, 1, 2, 3, 5, 7, 10 and 14 days after application. Quantitation was performed by HPLC-DAD system with C18 column. Limit of quantification (LOQ) of acetamiprid and thiamethoxam were both 0.02 mg/kg for chard. The recovery of acetamiprid and thiamethoxam were 77.8~107.5% and 94.3~108.6% at two concentration levels. The half-lives of pesticide dissipation in chard for two fields were 11.9 and 8.2 days for acetamiprid and 3.6 and 3.3 days for thiamethoxam respectively. The dissipation rate of acetamiprid and thiamethoxam were estimated according to

the statistics method with a 95% confidence.

CONCLUSION: Dissipation of acetamiprid and thiamethoxam in chard were determined under greenhouse. The concentration of acetamiprid and thiamethoxam in chards at 0 days after application were below specified by Korean MRL. Dissipation rate constant will be useful to set the pre-harvest residue limit for public health and consumer protection.

Key words: Acetamiprid, Dissipation, Residue, Swiss Chard, Thiamethoxam

서론

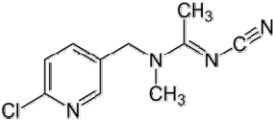
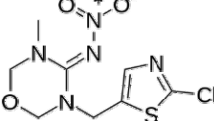
2019

(Positive list system, PLS)가

가 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 acetamiprid and thiamethoxam (Turner J. A., 2015)

Pesticide	Acetamiprid	Thiamethoxam
Chemical structure		
Vapor pressure (mPa)	< 0.001 (25°C)	6.6×10 ⁻⁶ (25°C)
log K _{ow}	0.8	-0.13
Water solubility (mg/L, 20-25°C)	<4,250	4,100
Organic solubility (mg/L, 20-25°C)	Soluble in acetone, methanol, ethanol, dichloromethane, chloroform, acetonitrile and tetrahydrofuran	Soluble in acetone (48), ethyl acetate (7.0), dichloromethane (110), toluene (0.68), methanol (13), n-octanol (0.62), hexane (<0.001)

가 , (Kwon et al., 2009; Jang et al., 2011; Park et al., 2015). 1996 2007 25.7% , 2009 13.3%, 2013 1 (Seung et al., 2010; Kime t al., 2014). 2010 ~2012 16 3 , 2016 18 , 21017 (Woo et al., 2013; NAPQMS, 2016 & 2017). Neoticotinoide acetamiprid thiamethoxam 2016 3.2% 2.0%, 8 6 , , 1.7% 가 5.6% 가 (NAPQMS, 2016). neonicotinoide acetamiprid thiamethoxam

(99.5%, Chem Service, USA) Thiamethoxam (99.7%, Sigma-Aldrich, USA) Table 1 (Turner, 2015). HPLC acetone, acetonitrile, dichloromethane, water n-hexane Merck (Germany), Sodium sulfate sodium chloride Junsei chemical(guaranteed reagent grade, Japan), Solide phase extraction cartridge(florisil, 5 g, 30 cc) Agilent Technologies(USA)

포장시험

가 20 km 가 2 (1, :) (2, :) 10 m² , 3 1 (KCPA, 2014) (YAMATO, DY-435Y, Japan) (Table 2). 0, 1, 2, 3, 5, 7, 10 14 1 kg polyethylene bag , ice box 24

시료 조제

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

재료 및 방법

시험약제 및 시약

Acetamiprid 5% (, (주)), Thiamethoxam 10% (, (주)) Acetamiprid

분석법 확립

가

Table 2. Good agricultural practice and maximum residue limit of acetamiprid and thiamethoxam on Swiss Chard in Korea

Pesticide	Formulation		Application			PHI ^{b)} (days)	MRL ^{c)} (mg/kg)
	Type	%AI ^{a)}	Spray concentration (kg ai/hl)	Max. No.	Interval (days)		
Acetamiprid	SL ^{d)}	5	0.005	2	7	3	7.0
Thiamethoxam	WG ^{e)}	10	0.005	2	7	7	10.0

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

Table 3. HPLC gradient conditions for the analysis of acetamiprid and thiamethoxam in Swiss Chard

Pesticides	Acetamiprid			Thiamethoxam		
Instrument	Agilent 1260 Infinity Series HPLC					
Column	Phenomenex Luna 5 μ C18 (250 \times 4.60 mm)					
Detector	Diode Array Detector (DAD)					
Flow rate	1.0 mL/min					
Mobile phase	Time (min)	Acetonitrile (%)	Water (%)	Time (min)	Acetonitrile (%)	Water (%)
	0	5	95	0	5	95
	15	30	70	15	30	70
	20	5	95	20	5	95
	25			25	5	95
Wavelength	258 nm					
Injection volume	40 μ L					

(Limit of Quantification, LOQ)
Signal to noise ratio(S/N)가
10 (MFDS, 2016). Acetamiprid
Thiamethoxam HPLC
Table 3 . Acetamiprid (99.5%) 10.05 mg
Thiamethoxam (99.7%) 10.03 mg
/water(5/95, v/v) 10 mL 1,000 mg/L stock
solution , acetonitrile/water(5/95, v/v)
0.05, 0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 7.0 10.0
mg/L
chromatogram peak area
(r²) 0.99

sodium sulfate , 40 $^{\circ}$ C
rotary vacuum evaporator (V-700, BUCHI, Switzerland)
dichloromethane
10 mL , dichloromethane 25 mL
florisil SPE cartridge (5 g, 30 cc)
florisil SPE cartridge 10 mL ,
acetone/ dichloromethane (4/96, v/v) 50 mL
acetone/dichloromethane (45/55, v/v) 70 mL
N₂ gas , acetonitrile/ water
(5/95, v/v) 4 mL HPLC-DAD (Agilnet
1200 Infinity Series, Agilent Technologies, USA)
(Table 3).

저장안정성 및 일자별 잔류량

회수율시험
Acetamiprid thiamethoxam
10 (0.2 mg/kg) 50 (1.0 mg/kg)
2 3 . 25 g
, acetonitrile
/water (80/20, v/v) 100 mL 가 250 rpm 20
50 mL Volumetrick
flask , 20 mL
n-Hexane 20 mL 2 , dichloromethane
20 mL 2 .

3 25 g acetamiprid
thiamethoxam 1.0 mg/kg
, (-20 $^{\circ}$ C) , 87
acetamiprid Thiamethoxam

생물학적 반감기 및 감소상수

acetamiprid thiamethoxam

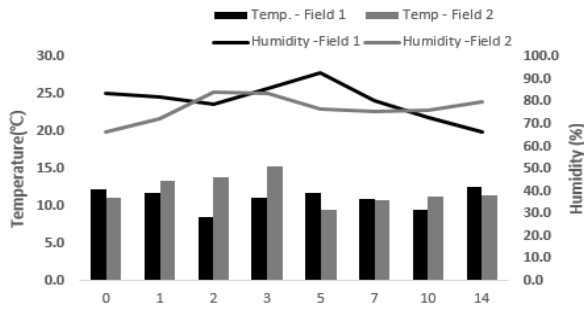


Fig. 1. Temperature and humidity of residue field trials for Swiss Chard.

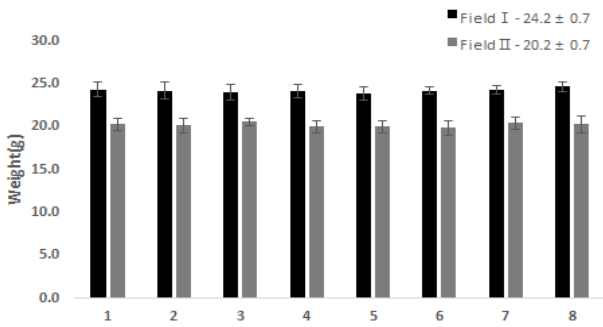


Fig. 2. Changes of Swiss Chard weight at sample harvest intervals.

, F t-
, 95%
(MFDS, 2014).

결과 및 고찰

포장시험

1 2
9.9±1.8°C 11.6±1.6°C , 77.4±7.2%
81.2±5.7% .(Fig. 1).
I II 24.2±0.7 g
20.2±0.7 g , 0
14 2.9% 3.7% .(Fig. 2).

분석법 검증

Acetamiprid thiamethoxam
0.02 mg/kg , 7
(0.2, 0.5, 1.0, 2.0, 5.0, 7.0 10.0 mg/L)
(r²) , y=1.44338x-0.60804
(r²=0.999) y=1.64724x-1.00638 (r²=0.999)
. Acetamiprid
80.6±2.8% 103.8± 5.6%, thiamethoxam
100.2±7.5% 98.9±4.9% , (% coefficient
of variation) acetamiprid 3.4% 5.4% ,
thiamethoxam 7.5% 5.0%
70~
110% 20% (Table 4, MFDS,
2014). Acetamiprid thiamethoxam HPLC-DAD
peak
(Fig. 3, 4).

일자별 잔류량 변화

acetamiprid thiamethoxam
, 0 acetamiprid 1
2 2.91 mg/kg 2.06 mg/kg,
thiamethoxam 2.60 mg/kg 2.37 mg/kg ,
acetamiprid thiamethoxam
7.0 mg/kg 10.0mg/kg
(MFDS, 2018). acetamiprid
thiamethoxam 5% 10%,
1,000 2,000 , 1 2
acetamiprid가
0.223g 0.207 g, thiamethoxam 0.243 g 0.233 g
. Acetamiprid
1 7.1 mg/kg
10 mg/kg ,
3 1.63 mg/kg 10 mg/kg
, 0 ~3
(Park et al., 2010; Hur et al., 2012).
thiamethoxam

Table 4. Limit of quantification and recoveries of acetamiprid and thiamethoxam in Swiss Chard

Pesticide	Fortification level (mg/kg)	Recovery (%)				CV ^{b)}	LOQ ^{c)} (mg/kg)
		Replicate			Mean±SD ^{a)}		
		1	2	3			
Acetamiprid	0.2	80.8	77.8	83.3	80.6±2.8	3.4	0.02
	1	106.5	97.4	107.5	103.8±5.6	5.4	
Thiamethoxam	0.2	94.3	108.6	97.6	100.2±7.5	7.5	0.02
	1	94.9	97.4	104.4	98.9±4.9	5.0	

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

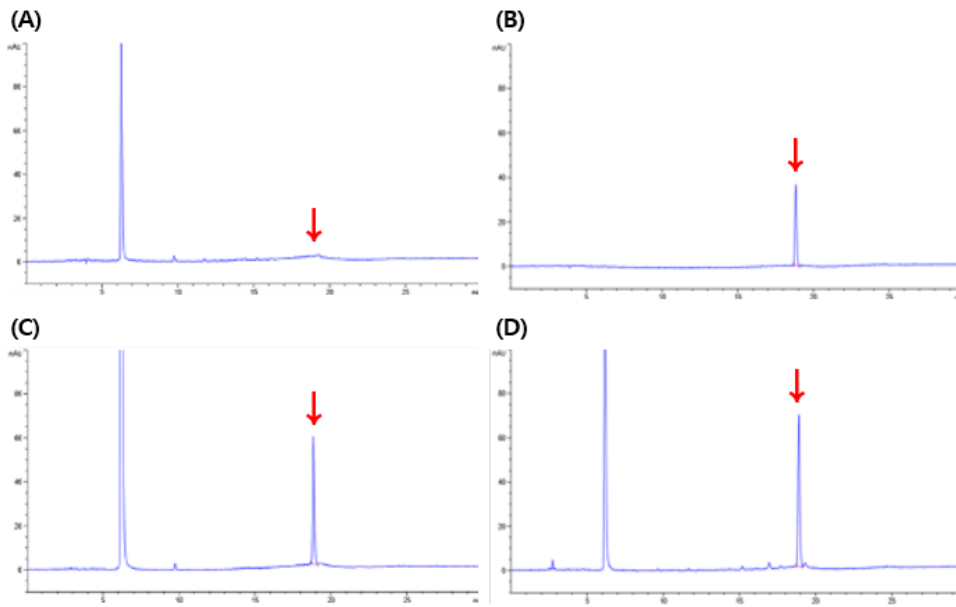


Fig. 3. Representative chromatograms of acetamiprid by HPLC-DAD analysis(A; blank sample, B; standard 2.0 mg/kg, C; recovery 1.0 mg/kg, D; swiss chard sample at 10 days after application).

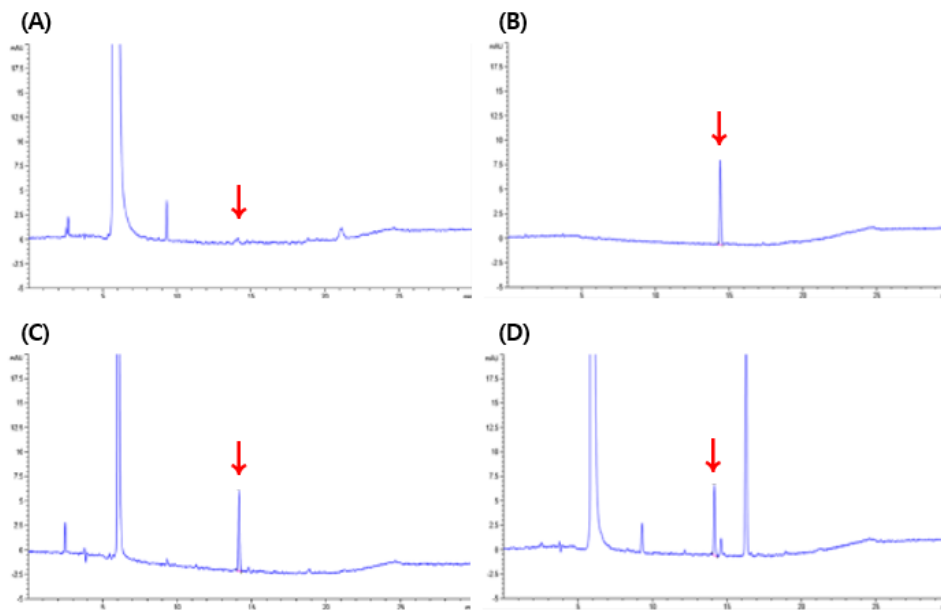


Fig. 4. Representative chromatograms of thiamethoxam by HPLC-DAD analysis (A; blank sample, B; standard 0.5 mg/kg, C; recovery 0.2 mg/kg, D; swiss chard sample at 14 days after application).

1	0	2.35 mg/kg	생물학적 반감기 및 감소상수
~3.16 mg/kg		(Rahman et al., 2015).	
tiamethoxam		7	acetamiprid
0	80%	, 7	12.0 8.2
2	0	가	(Fig. 5).
		, thiamethoxam	acetamiprid thiamethoxam
			3.6 3.3

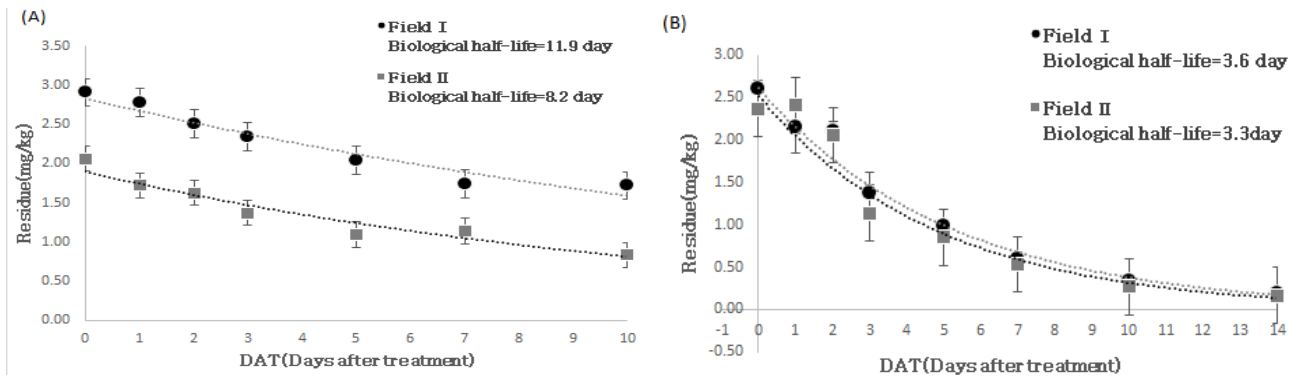


Fig. 5. Dissipation curves and half-lives of acetamiprid(A) and thiamethoxam(B) in Swiss Chard.

Table 5. Regression analysis for the dissipation of acetamiprid and thiamethoxam on Swiss Chard

Pesticide	Acetamiprid		Thiamethoxam	
	Field I	Field II	Field I	Field II
Dissipation regression equation ^{a)}	$y=2.8361e^{-0.0578x}$ ($r^2=0.9391$)	$y=1.8980e^{-0.0848x}$ ($r^2=0.9385$)	$y=2.6131e^{-0.1935x}$ ($r^2=0.9870$)	$y=2.5236e^{-0.2077x}$ ($r^2=0.9747$)
Dissipation rate constant ^{b)}	0.0409 ~ 0.0747	0.0598 ~ 0.1098	0.1713 ~ 0.2157	0.1744 ~ 0.2410
Lower limit of dissipation rate constant	0.0409	0.0599	0.1714	0.1744

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

(95% confidence level) acetamiprid가 1 2 0.0409 ~ 0.0747 0.0598 ~ 0.1098, thiamethoxam 0.1713 ~ 0.2157 0.1744 ~ 0.2410 (Table 5). Acetamiprid 가 1.94 2.54 , , , acetamiprid sunlight 가 (Gupta et al., 2008; Park et al., 2010). 1 clothianidin thiamethoxam 2 6.3 4.2 , codex thiamethoxam , Rahman et al. thiamethoxam 2 3.6 (Rahman et al., 2015). acetamiprid thiamethoxam

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 : 17162MFDS010).

References

Gupta, S., Gajbhiye, V. T., & Gupta, R. K. (2008). Effect of light on the degradation of two neonicotinoids viz acetamiprid and thiacloprid in soil. *Bulletin of Environmental Contamination and Toxicology*, 81(2), 185-189.

Jang, M. R., Moon, H. K., Kim, T. R., Yuk, D. H., Hwang, I. S., Kim, M. S., Kim, J. H., & Chae, Y. Z. (2011). Exposure assessment for pesticide residues in vegetables using korea national health and nutrition examination survey data for seoulites. *Korean Journal of Nutrition*, 44(5),443-452.

Jang, M. R., Moon, H. K., Kim, T. R., Yuk, D. H., Hwang, I. S., Kim, M. S., Kim, J. H., & Chae, Y. Z. (2011). Exposure assessment for pesticide residues in vegetables

- using korea national health and nutrition examination survey data for seoulites. *Korean Journal of Nutrition*, 44(5), 443-452.
- Kim, N. H., Lee, J. S., Kim, W. H., Choi, Y. H., Han, S. H., Kim, Y. H., Kim, H. S., Lee, S. R., Lee, J. M., Yu, I. S., & Jung, K. (2014). Monitoring of pesticide residues and risk assessment on agricultural products in the northern area of seoul. *Journal of Food Hygiene and Safety*, 29(3), 170-180.
- Kwon, H. Y., Lee, H. D., Kim, J. B., Jin, Y. D., Moon, B. C., Park, B. J., Son, K. A., Kwon, O. K., & Hong, M. K. (2009). Reduction of Pesticide residues in field-sprayed leafy vegetables by washing and boiling. *Journal of Food Hygiene and Safety*, 24(2), 182-187.
- Park, D. W., Kim, A. G., Kim, T. S., Yang, Y. S., Kim, G. G., Chang, G. S., Ha, D. R., Kim, E. S., & Cho, B. S. (2015). Monitoring and safety assessment of pesticide residues on agricultural products sold via online websites. *The Korean Journal of Pesticide Science*, 19(1), 22-31.
- Park, H. R., Heo, S. P., Thapa, I. H., Yu, J. M., Cho, J. M., & Hur, J. H. (2012). Residual analysis and risk assessment of acetamiprid 5% sl in the amaranthus (*Amaranthus mangostanus* L). *Journal of Agricultural, Life and Environmental Sciences*, 24(2), 55-61.
- Park, J. Y., Choi, J. H., Kim, B. M., Park, J. H., Cho, S. K., Ghafar, M. W., Abd El-Aty, A. M., & Shim, J. H. (2011). Determination of acetamiprid residues in zucchini grown under greenhouse conditions: application to behavioral dynamics. *Biomedical Chromatography*, 25, 136-146.
- Rahman, M. M., Farha, W., Abd El-Aty, A. M., Kabir, M. H., Im, S. J., Jung, D. I., Choi, J. H., Kim, S. W., Son, Y. W., Kwon, C. H., Shin, H. C., & Shim, J. H. (2015). Dynamic behaviour and residual pattern of thiamethoxa and its metabolite clothianidin in Swiss chard using liquid chromatography-tandem mass spectrometry. *Food Chemistry* 174, 248-255.
- Seung, H. J., Park, S. K., Ha, K. W., Kim, O. H., Choi, Y. H., Kim, S. J., Lee, K. A., Jang, J. I., Jo, H. B., & Choi, B. H. (2010). Survey on pesticide residues in commercial agricultural products in the northern area of seoul. *Journal of Food Hygiene and Safety*, 25(2), 106-117.
- Turner, J. A (2015). *The pesticide manual*. pp.9 & 1092. 17th edition, British Crop Production Council, UK.
- Woo, N., Ko, S. H., & Park, Y. J. (2013). Monitoring of pesticide residues in vegetables collected in chungbuk, korea. *The Korean Journal of Food and Nutrition*, 26(4), 865-878.