

Research Article



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## 시설재배 근대 중 Neonicotinoid계 살충제 Acetamiprid 및 Thiamethoxam의 생산단계 잔류특성

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가

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

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#### 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

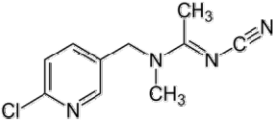
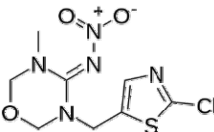
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**Table 1. Chemical structures and physico-chemical properties of acetamiprid and thiamethoxam (Turner J. A., 2015)**

Pesticide	Acetamiprid	Thiamethoxam
Chemical structure		
Vapor pressure (mPa)	< 0.001 (25°C)	6.6×10 <sup>-6</sup> (25°C)
log K <sub>ow</sub>	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 m<sup>2</sup> , 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 <sup>b)</sup> (days)	MRL <sup>c)</sup> (mg/kg)
	Type	%AI <sup>a)</sup>	Spray concentration (kg ai/hl)	Max. No.	Interval (days)		
Acetamiprid	SL <sup>d)</sup>	5	0.005	2	7	3	7.0
Thiamethoxam	WG <sup>e)</sup>	10	0.005	2	7	7	10.0

<sup>a)</sup> Active ingredient, <sup>b)</sup> Pre-harvest interval, <sup>c)</sup> Maximum residue limit, <sup>d)</sup> Soluble concentrate, <sup>e)</sup> 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 $\mu$ 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 $\mu$ 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  
(r<sup>2</sup>) 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  
N<sub>2</sub> 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

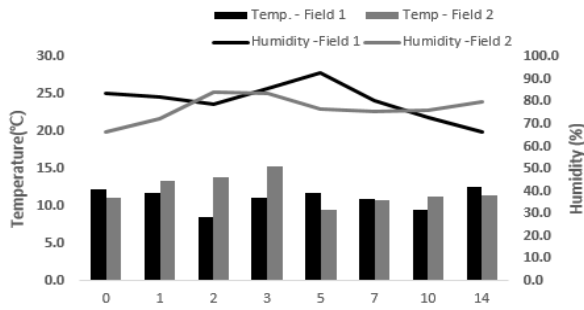


Fig. 1. Temperature and humidity of residue field trials for Swiss Chard.

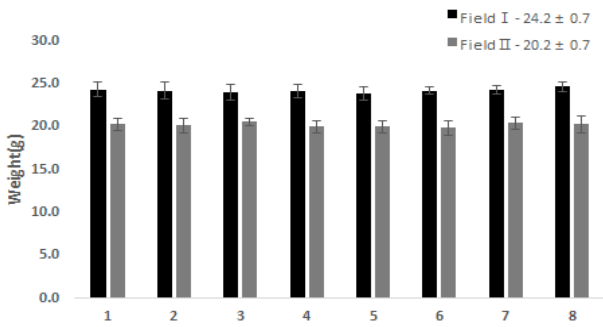


Fig. 2. Changes of Swiss Chard weight at sample harvest intervals.

,  $F$   $t$ -  
, 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)  
( $r^2$ ) ,  $y=1.44338x-0.60804$   
( $r^2=0.999$ )  $y=1.64724x-1.00638$  ( $r^2=0.999$ )  
. 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 <sup>b)</sup>	LOQ <sup>c)</sup> (mg/kg)
		Replicate			Mean±SD <sup>a)</sup>		
		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	

<sup>a)</sup> Standard deviation, <sup>b)</sup> Coefficient of variation, <sup>c)</sup> Limit of quantification

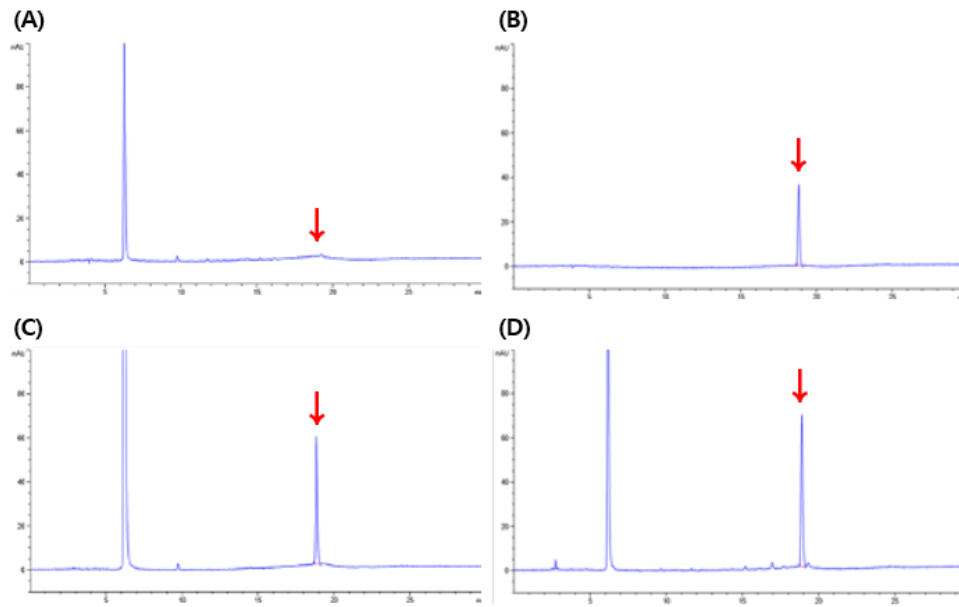


Fig. 3. Representative chromatograms of acetamiprid by HPLC-DAD analysis(A; blank sample, B; standard 2.0 mg/kg, C; recovery 1.0 mg/kg, D; swiss chard sample at 10 days after application).

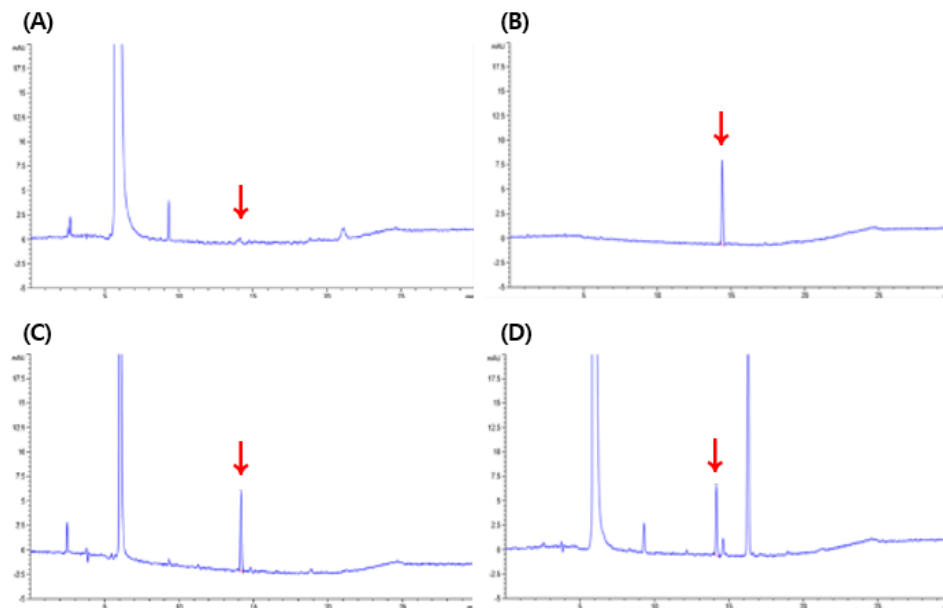


Fig. 4. Representative chromatograms of thiamethoxam by HPLC-DAD analysis (A; blank sample, B; standard 0.5 mg/kg, C; recovery 0.2 mg/kg, D; swiss chard sample at 14 days after application).

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

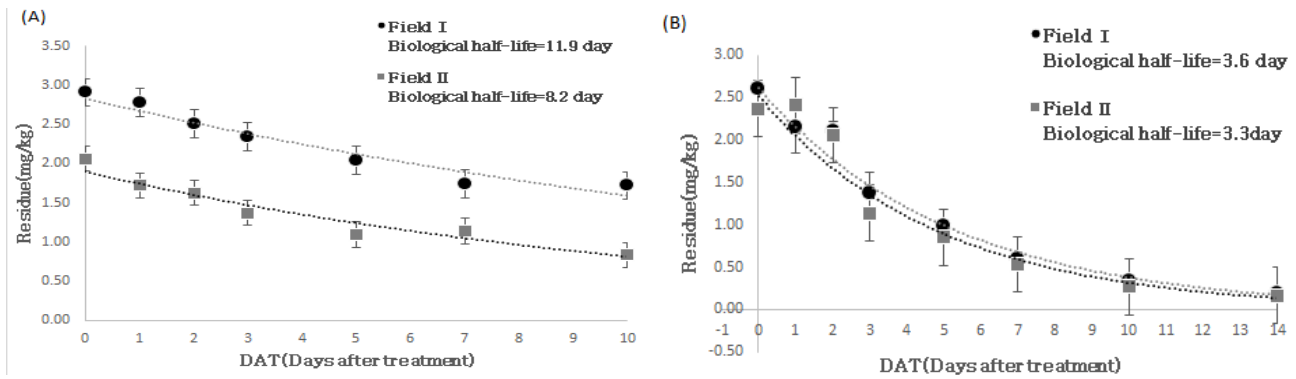


Fig. 5. Dissipation curves and half-lives of acetamiprid(A) and thiamethoxam(B) in Swiss Chard.

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

Pesticide	Acetamiprid		Thiamethoxam	
Field No.	Field I	Field II	Field I	Field II
Dissipation regression equation <sup>a)</sup>	$y=2.8361e^{-0.0578x}$ ( $r^2=0.9391$ )	$y=1.8980e^{-0.0848x}$ ( $r^2=0.9385$ )	$y=2.6131e^{-0.1935x}$ ( $r^2=0.9870$ )	$y=2.5236e^{-0.2077x}$ ( $r^2=0.9747$ )
Dissipation rate constant <sup>b)</sup>	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

<sup>a)</sup> Significant at  $p<0.05$  by the *F*-test, <sup>b)</sup> 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.

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**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.

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- 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.