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Dissipation and Residues of Spinosad in Eggplant and Soil

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Spinosad is a natural biopesticide developed by Dow AgroSciences as an excellent alternative reagent to classic organophosphorus pesticides (Thompson et al., 2000). The commercial formulation of spinodsad contains two primary active compounds, spinosyn A and spinosyn D, which were derived from the bacterium *Saccharopolyspora spinosa* isolated from soil. Spinosad has a unique mode of action against a variety of target pests and shows relatively low toxicity to mammals and birds. Since its introduction to the market in 1997, spinosad has been applied in many countries to many corps, including cotton, soybean, fruits and vegetables.

Eggplant is a popular vegetable crop in China, which is produced in two growth seasons. Thrips *palmi Karny* is a significant economic pest of eggplants in China. Originally from south Asia, this pest is becoming widely distributed in south China and causes serious damage to eggplant production (Gu et al., 2000). Recent studies have shown that spinosad could be a valuable reduced-risk pesticide against thrips in integrated pest management (Jones et al., 2005).

Previous studies on the environmental fate of spinosad focused on the degradation of spinosad in aqueous systems (Cleveland et al., 2002a; Liu et al., 2005), and assessment of the ecological risk of spinosad application on cotton and white spruce (Thompson et al., 2002a, 2002b; Cleveland et al., 2002b). The purpose of the present work was to study the dissipation rate and ultimate residue of spinosad in an eggplant field ecosystem, and thereby provide an evaluation for scientific, safe use of spinosad.

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Materials and Methods

The analytical standards for spinosyns A and spinosyns D and the Success 25SC formulations (25g of ai/L) were obtained from Dow AgroSciences, USA. High-performance liquid chromatography (HPLC)-grade *n*-hexane, dichloromethane, acetonitrile, and methanol were supplied by Tedia (Fairfield, OH, US). Analytical-grade petroleum ether, hydrochloric acid, sodium chloride, sodium hydroxide, and ammonium acetate were purchased form the Beijing Reagent Company (Beijing, China).

All analysis was conducted with an Agilent 1100 HPLC equipped with ultraviolet (UV) detection (Agilent, Palo Alto, CA USA). A reverse-phase C18 HPLC column (150 × 4.6 mm i.d., 5 μm particle size) was used as the separation column and was maintained at 25°C The mobile phase consisted of acetonitrile/2% aqueous ammonium acetate (80:20) with a flow rate of 1 mL/min. The injection volume was 100 μL, and the UV wavelength was 250 nm. The retention times for spinosyans A and spinosyns D were 12.8 and 16.5 min, respectively.

The field trials, including the dissipation experiment and ultimate residue experiment, were carried out in Beijing. Each experiment field consisted of three replicate plots with an area of 30 m^2 and was separated by irrigation channels.

After the maturation of the first eggplant' spraying with success 25SC was carried out. The applied dose was 6000 mL/hm^2. This level, which is four times the recommend dosage level, was used in order to reach the detection limits in the experiment. Representative eggplant and soil samples were collected about 2 h, 8 h, 1 d, 2 d, 3 d, 5 d, 7 d, 10 d and 14 d after spraying. The collected eggplant samples were comminuted with a blender (Philips, China). All

collected samples were stored in a freezer at –4°C for further analysis.

The ultimate residue experiment was performed at a lower dosage level of 1500 mL/hm^2 (the recommended dosage) as well as at a higher dosage level of 3000 mL/hm^2 (twice the recommended dosage), respectively. One week after the first eggplant maturation, the first treatment was conducted; the second treatment took place after an interval of seven days. Representative eggplant and soil samples were collected one day, three days, and five days after the application of the success 25SC.

10 g soil and 5 g eggplant samples were subjected to ultrasonic extraction by adding a 50-mL aliquot of methanol/5% aqueous sodium chloride/4% sodium hydroxide (65:27:8) mixture in an ultrasonic cleaner for about 5 min. After ultrasonic extraction, the samples were shaken in a reciprocating shaker for 30 min. The samples were filtered through a Whatmen number 1 filter paper in a Büchner funnel into a 250-ml side-arm flask under vacuum; the filter residue was extracted again as described above. When the second extraction was completed, the filtrate was combined in a 250-ml separatory funnel for the liquid–liquid extraction (LLE).

A 70-mL aliquot of acidic salt solution (0.16N hydrochloric acid and 5% sodium chloride) was added to the separatory funnel to adjust the pH to less than or equal to ≤ 2, and a 50-mL aliquot of light petroleum was added to funnel. The separatory funnel was shaken vigorously for about 30 s, and used to separate for 5 min. The aqueous layer was drained into a 250-mL beaker. A 10-mL aliquot of 1N sodium hydroxide was added to the separatory funnel to ensure the pH was equal to or above ≥9. The analytes were extracted by vigorously shaken for about 30 s with the addition of 50-mL of light petroleum, and collecting the organic layer in a 500-mL flask. This extraction was repeated three times. The organic phase was evaporated to dryness using a rotary vacuum evaporator over a water bath at a temperature of 45–50°C. The residue in the flask was dissolved in 10 mL of hexane for further cleaning by column chromatography.

A column (30 × 1.5 mm i.d., 50 ml reservoir) was packed with a plug of glass wool and a 1-cm layer of anhydrous sodium sulfate at the bottom. A 1 g aliquot of silica gel sorbent was added to the column, and another 1 cm layer of anhydrous sodium sulfate was placed above the sorbent. The column was conditioned with the following sequence of solvents: 10 mL of dichloromethane/methanol (75:25), 10 mL of acetonitrile, 10 mL of dichloromethane and 20 mL of hexane. The hexane solution was added to the column. After the hexane had eluted, the evaporating flask was rinsed with a 10-mL aliquot of hexane, and the hexane solvent was added to the column. After the hexane had eluted, the evaporating flask was rinsed with 10 mL of dichloromethane, and the rinsate was added to the column. The column was then eluted with 2 × 4 mL of acetonitrile and 10 mL of dichloromethane/methanol (75:25). The last elution was collected in a 50 mL evaporating flask and evaporated to dryness using the rotary vacuum evaporator. The residue was dissolved in 1.0 mL of acetoniltrile/2% ammonium acetate (80:20), and the solution was transferred to an HPLC sample vial for instrumental analysis.

Results and Discussion

This study was carried out to determine the recovery levels, precision and limits of detection of the analytical method. Spinosyn A and D were added to untreated eggplant and soil samples at three concentration levels. The fortified samples were analyzed using the procedure described with three reptitions. The results were shown in Table 1. The limits of detection (LOD) of all the target analytes in eggplant and soil samples were below 10 μg/kg at a signal-to-noise ratio of 3. The precision of the method in terms of relative standard deviations (RSD) ranged from 3.06–6.68. The recovery and precision results were acceptable according to the residues analysis quality control guide (General Administration of Quarantine of the People's Republic of China, 2002).

The results of dissipation data in eggplant are shown in Fig. 1. Spinosyn A and D dissipated rapidly after application. The concentration of spinosyns A and D 2 h after treatment with Success 25SC was 0.5712 and 0.1040 mg/kg, respectively. The amount of spinosyna A and D residue was below the LOD of the method seven days after the treatment. The dissipation dynamics of spinosyns A and D could be described by the following first-order rate equation: $C = 0.3817e^{-0.3827t}$ and $C = 0.0771e^{-0.435t}$, respectively. The half-life time of sinosyns A and D in eggplant was 1.81 d and 1.61 d, respectively.

Table 1 Recovery data of spinosyns A and D in eggplant and soil samle

Sample type	Spinosyn A			Spinosyn D		
	Added μg/g	Recovery[a] %	RSD %	Added μg/g	Recovery %	RSD %
Eggplant	0.010	88.8	6.35	0.002	87.6	7.67
	0.100	87.9	5.50	0.020	88.6	3.06
	1.000	85.0	4.32	0.200	90.3	4.25
Soil	0.020	92.2	6.00	0.004	85.8	8.68
	0.100	86.9	6.41	0.002	86.7	5.57
	1.000	88.8	4.81	0.002	90.8	6.88

[a] Recovery means the average recovery of the three repetitions

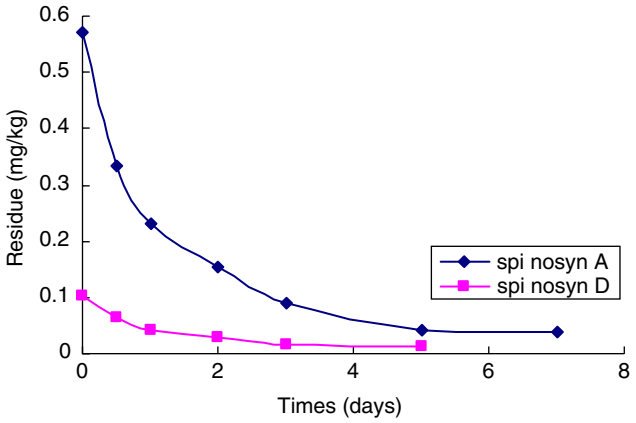

Fig. 1 Dissipation of spinosyn A and D in eggplant in Beijing, 2005

Figure 2 shows the dissipation data for spinosad in the soil samples. The initial concentration level of spinosyn A and D in soil was higher than in the eggplant.

This can be explained by the fact that most of the spinosad after application drifted to the soil. The concentration of spinosyn A and D in the soil two hours after application was 1.5021 and 0.3310 mg/kg.. The amount of spinosyn A was below the LOD after 10 days of the treatment, and spinosyan D was undetectable after seven days. A sharp decline of spinosyn A and D within two days of treatment can be observed from Fig. 2. The dissipation dynamics of spinosyn A and D could also be described by the equations $C = 0.5511e^{-0.3708t}$, $C = 0.2714e^{-0.7313t}$, respectively, with a half-life of 1.87 and 0.95 days, respectively. Spinosyn D has a shorter half-life time than spinosyns A, which may be explained by the fact that spinosyns D may be degraded rapidly by bacterium in the soil.

The ultimate residue data are shown in Table 2. The concentration level of spinosyn A and D in eggplant and soil could be detected after the application of Success 25SC at levels of 1500 mL/hm^2 (recommended dosage) and 3000 mL/hm^2 (twice the recommended dosage), respectively. As shown in Table 2, the concentration of spinosyn A and D in eggplant were below 0.2 mg/kg 1 day after the treatment. No available maximum residue limits (MRL) for spinosad in eggplant have been established by the World Health Organization (WHO), Food and Agricultural Organization (FAO) or other governmental agencies. However, it is acceptable to spray Success 25SC at the recommended dosage due to its lower toxicity to non-target species and very short half-life. Therefore, spinosad could be considered as a good alternative to high-toxicity pesticides in China, and can be used in eggplant fields safely.

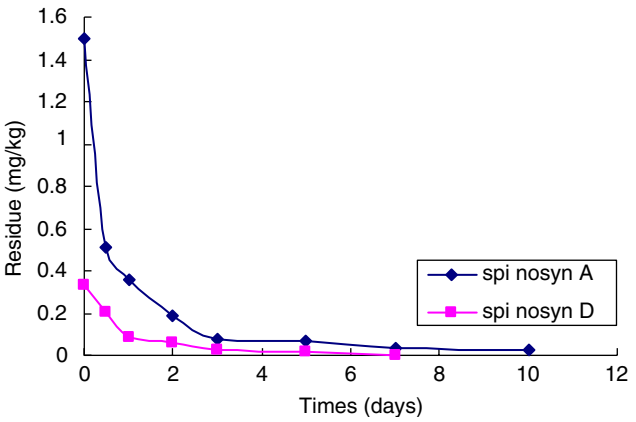

Fig. 2 Dissipation of spinosyn A and D in soil in Beijing, 2005

Table 2 Ultimate residue of spinosad in eggplant and soil

Dosage (ml/hm^2)	Spray times	Interval (days)	Residue (mg/kg)			
			Spinosyn A		Spinosyn D	
			eggplant	soil	eggplant	soil
1500 mL/hm^2	1	1	0.0180	0.0859	0.0040	0.0018
		3	0.0050	0.0450	ND	0.0088
		5	0.0040	0.0237	ND	0.0058
	2	1	0.0150	0.1100	0.0043	0.0270
		3	0.0131	0.0790	0.0039	0.0160
		5	0.0050	0.0159	0.0027	0.0039
3000 mL/hm^2	1	1	0.1200	0.1934	0.0180	0.0395
		3	0.0110	0.1006	0.0030	0.0190
		5	ND	0.0842	ND	0.0110
	2	1	0.0570	0.0350	0.0010	0.0626
		3	0.0420	0.1006	ND	0.0232
		5	0.0460	0.0344	ND	0.0132
CK	-		ND	ND	ND	ND

ND: means below the LOD of the method

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