Asian Journal of Water, Environment and Pollution, Vol. 5, No. 2, pp. 49-52.

Dissipation Behaviour of Spinosad Insecticide in Chilli and Soil

Anjali Sharma, Anjana Srivastava*, Bali Ram and P.C. Srivastava[1]

Department of Chemistry, [1]Department of Soil Science
G.B. Pant University of Agriculture and Technology, Pantnagar-263145
Uttarakhand, India
✉ anj612003@yahoo.co.in

Received July 27, 2006; revised and accepted July 31, 2007

Abstract: The persistence of Spinosad insecticide in chilli fruits was evaluated at two application rates (73.0 g a.i./ha and 146.0 g a.i./ha) by high performance liquid chromatography. The dissipation of the insecticide from chilli fruits appeared to occur in two phases. Each phase followed first-order kinetics. Half life values of Spinosad for the first and second phase on green chilli were found to be 1.48 d and 0.70 d respectively for 73.0 g a.i./ha application rate, and 6.72 d and 5.55 d respectively for 146.0 g a.i./ha application rate. No detectable residues (<0.05 µg/g) were found in red chilli and soil, sampled on the 15th day of application which depicts that spinosad is environmentally safe as regards soil pollution.

Key words: Spinosad, persistence, dissipation, chilli, biphasic, hplc, soil pollution.

Introduction

The indiscriminate use of broad spectrum chemicals has resulted in reduction of natural enemies, contamination of food and fodder, ecosystem and hazards to environment including human beings through food chain and ground water (Arora, 2006). The use of eco-friendly bio-pesticides is a distinct possibility in the modern agriculture within the framework of Integrated Pest Management system, with no harm to any component of the ecosystem (Mukhopadhyay et al., 2003).

Spinosad is a mixture of Spinosyn A and D which are tetracyclic macrolide secondary metabolites produced by an actinomycete, *Saccharopolyspora spinosa* (Kirst et al., 1992). It represents a new class of insecticides for use in agriculture with favourable mammalian and off-target toxicity profiles (Sparks et al., 1995). Spinosad is registered in many countries for use on a variety of crops, including cotton, corn, soyabean, fruits and vegetables (West et al., 2000).

Chilli (*Capsicum annuum* L.) is one of the most valuable crops of India. There are a number of insects like aphids, pepper weevils and pepper maggot (Chaudhary, 2000) which attack chilli but only thrips are often serious. The most common method of pest control in crops is the application of insecticides. Soil also acts as a major sink for the bulk of pesticides used in agriculture. These pesticides are subjected to various transformation and transportation processes which are responsible for air and soil pollution (Flury, 1996). As the crops invariably retain some residues of the insecticides, the health hazards depend on the quantity of such residues in the consumable product. The present investigation was carried out to determine the residues of spinosad in chilli and soil by high performance liquid chromatography (HPLC) to ensure human and environmental safety from the crop and soil pollution point of view.

*Corresponding Author

Materials and Methods

Insecticide Treatment

A field trial of chilli (cv. Pant C-1) was conducted in a randomized block design with three replications during the winter season of 2005-06. Seedlings were planted in a geometry of 45 × 60 cm as interplant and inter-row distances, respectively. Spinosad 45 SC was sprayed @ 73.0 g a.i./ha and 146.0 g a.i./ha in a spray volume of 800 L solution/ha using a hand sprayer after 22 d of planting without any protection to plants. Two more sprays were given each at 15 d interval. For control treatment (0 g a.i. Spinosad/ha), equivalent volume of plain water was sprayed on the same dates.

Sampling

Fruits of chilli in triplicate were sampled starting from the last day of spray at different time intervals viz. 0 (1 hr after application), 1, 2, 5, 7, 10 and 15 d. Samples were collected randomly from each plot. Red chilli and soil samples were collected on the 15th day of application.

Weather Conditions

During the crop season, the maximum and minimum temperatures varied in the range of 19°C to 36°C and 7°C to 16°C, respectively with average humidity of 65.2%. Average annual rainfall was about 150 cm.

Extraction

Fifty gram sample of chilli fruit was blended in 100 mL of acetonitrile-water mixture (8:2, v/v) for two minutes and the contents were transferred to a conical flask. Thereafter, the samples were subjected to 30 min. shaking on a mechanical shaker. The contents were then filtered through a buchner funnel and washed with acetonitrile-water mixture (8:2, v/v).

Soil sample (50 g), without blending, was also extracted in 100 mL of acetonitrile-water mixture (8:2, v/v) for 30 min. on a mechanical shaker, filtered through buchner funnel and washed with acetonitrile-water mixture. The combined filtrate was concentrated and partitioned with dichloromethane and the organic phase was collected. Ten mL methanol and 1 mL (1N) sodium hydroxide along with additional dichloromethane was added to the aqueous phase and the mixture was again partitioned. The pooled organic phase was evaporated to dryness in a rotary vacuum evaporator at 40°C and the residue was dissolved in n-hexane.

Clean-up

The hexane extract was purified using silica SPE (Solid Phase Extraction) cartridge which was conditioned with n-hexane under vacuum. The sample solution in n-hexane was added to the silica SPE cartridge and eluted. The flask was also rinsed with n-hexane and eluted as above. The cartridge was then dried under vacuum. The flask was again rinsed with acetonitrile and the rinsate was added to the dried cartridge. The acetonitrile solution was eluted, collected and immediately evaporated to dryness on a rotary vacuum evaporator. The residue was reconstituted in 1 mL of methanol : acetonitrile : 2% ammonium acetate solution (1:1:1, v/v) for final HPLC analysis.

Analysis of Spinosad

Spinosad residues were determined by high performance liquid chromatography (HPLC, a Beckman model 322) equipped with UV detector (250 nm). The column used was C_{18} (250 mm × 4.6 mm i.d). and the mobile phase was acetonitrile : methanol : 2% ammonium acetate (21:21:8) at a flow rate of 2.0 mL min^{-1}. A 5 µL aliquot of each sample was injected each time for residue analysis. The representative retention times of Spinosyn A and D were 9.5 min and 11.0 min, respectively.

Recovery Studies

Fifty gram samples of chilli and soil were fortified in triplicate with Spinosad at 2 µg g^{-1}. The samples were extracted and cleaned up following the procedure described in the preceding sections.

Results and Discussion

The percent recovery values of Spinosad 45 SC from soil and chilli samples were 75 ± 0.6 and 94 ± 0.8 percent, respectively.

The persistence and dissipation data of Spinosad recovered from chilli fruits are depicted in Table 1. Percent persistence values at different time intervals were calculated considering the amount of insecticide recovered on the 0th day (1 h after application) as 100%.

As evident from Table 1, the persistence of Spinosad in green chilli for the lower application rate (73.0 g a.i./ha) decreased from 100% on the 0th d to 19.27% on the 10th d. The persistence of Spinosad applied @ 146.0 g a.i./ha decreased to 28.33% on the 10th d. No detectable residues (<0.05 µg/g) were found after the 15th d of application. Graphically determined DT_{50} values of

Table 1: Amount of Spinosad in Chilli fruits applied at 73.0 g a.i./ha and 146.0 g a.i./ha of Spinosad

Days of Application	*Amount of Spinosad recovered (µg/g)**			
	73.0 g a.i./ha		*146.0 g a.i./ha*	
	Persis-tence	*% dissi-pation*	*Persis-tence*	*% dissi-pation*
0 (1 hr)	5.014		6.626	
	(100)	0	(100)	0
1	2.584		5.632	
	(51.54)	48.46	(85.00)	15.00
3	1.966		4.804	
	(39.21)	60.79	(72.50)	27.50
5	1.325		2.617	
	(29.43)	73.57	(39.50)	60.50
7	1.060		2.231	
	(21.15)	78.85	(33.67)	66.33
10	0.966		1.877	
	(19.27)	80.73	(28.33)	71.67
15	N.D.	N.D.	N.D.	N.D.

Values in the parenthesis show % persistence of the insecticide. (N.D. < 0.05 µg/g)

*Standard deviation values for the amount of Spinosad recovered varied in a range of 2.0-4.5%.

Spinosad (50% dissipation) in the present study were 1.5 d at 73.0 g a.i./ha and 3.1 d at 146.0 g a.i./ha application rate.

The data on the amount of Spinosad recovered from soil and chilli samples for both application rates, were fitted to a first order kinetic equation:

$$C = C_0 e^{-\lambda t}$$

where C is amount of Spinosad recovered from the samples at time t. C_0 is amount of Spinosad recovered at $t = 0$, λ is degradation constant and t is time in d.

For both the rates of Spinosad application (73.0 and 146.0 g a.i./ha), natural logarithm of Spinosad residues was plotted against time (Figure 1). The distribution of points for chilli for both the levels suggested that dissipation of Spinosad occurred through two distinct phases with each phase conforming to the first order kinetics. Statistically significant (at $p = 0.05$) values of coefficient of determination (R^2) between log residues and time indicated that dissipation of Spinosad could be accounted by the first order kinetics.

The computed half lives for the first and second phases were found to be 1.48 d and 0.70 d, for the lower application rate (73.0 g a.i./ha) and 6.72 d and 5.55 d for the higher application rate (146.0 g a.i./ha). The half lives for both Spinosyns have been reported to vary with the rate of application; lower persistence at the lower application rates (Turnbull, 2003).

No detectable residues (<0.05 µg/g) were found in the red chilli and soil, sampled on the 15th d of application, for both the application rates (73.0 and 146.0 g a.i./ha). Spinosyn A and D had been reported to dissipate rapidly from plant surfaces predominantly by photolysis and the reported half-lives for foliar applied chemical varied in the range of 2.0 to 12 d (Thompson et al., 2002). The proposed photodegradation/metabolism pathway for Spinosyn A and D involves the initial formation of

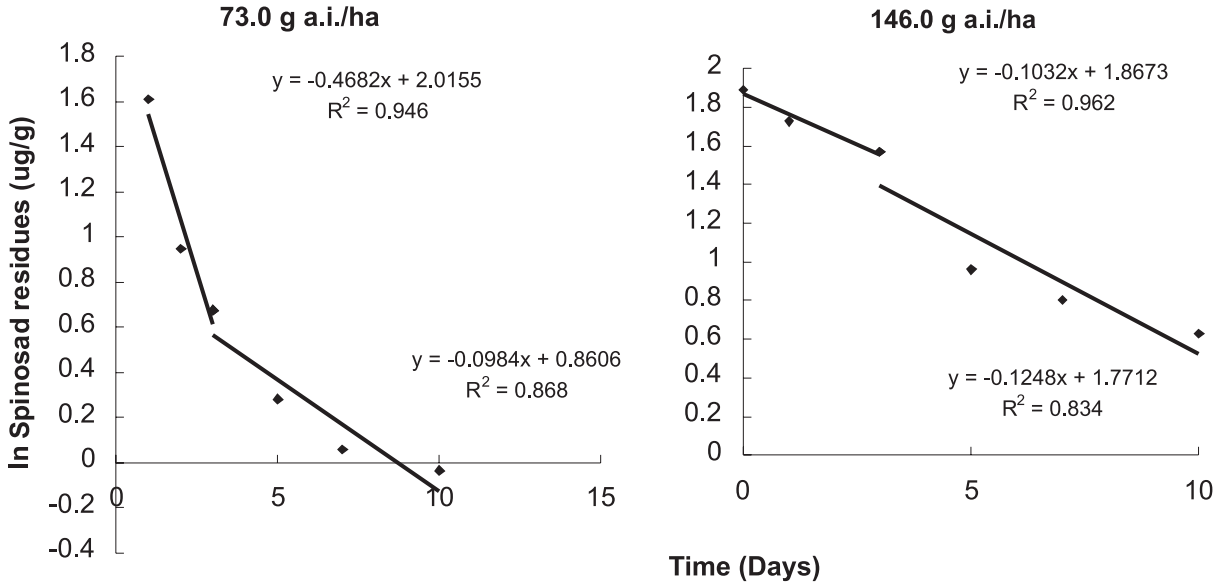

Figure 1: Plots of natural logarithm of Spinosad concentration in Chilli versus time at two rates of application (73.0 g a.i. /ha and 146.0 g a.i.ha).

nonpolar photoproducts through N-demethylation of the forsamine sugar of O-demethylation of the rhamnose sugar. With further photodegradation, polar and non-extractable metabolites are formed which are subject to biochemical processes and incorporation into natural components of plants (Saunders et al., 1997). Turnbull et al., (2003) found that under field conditions Spinosad dissipated rapidly from soil surfaces with observed half-lives of less than 1 d. Spinosad present in deeper soil layers or shaded soil also degraded rapidly with a half-life of 9-17 days at 25°C.

Thus, the dissipation of Spinosad in chilli occurred through two phases with each one conforming to first order kinetics. As Spinosad does not persist in the soil and crop at the time of harvest it does not appear to cause any sort of environmental pollution.

References

Mukhopadhyay, A.N. (2003). Innovations in Plant Pest Management by ecofriendly biopesticides. *In:* Pesticide usage scenario in India and variable alternatives. Voluntary Health Association of India, New Delhi, pp. 45-55.

Chaudhury, B. (2000). Solanaceous fruits and cole crops. *In:* Vegetables. National Book Trust, pp. 63-84.

Thompson, D.G., Harris, B.J., Buscarini, T.M. and D.T. Chartrand (2002). Fate of Spinosad in litter soils of a mixed conifer stand in the Acadian forest region of New Brusnwick. *Journal of Agriculture and Food Chemistry*, **50(4):** 790-795.

Turnbull, G.C. (2003). Success 480 SC – New Class Insecticide for use in potatoes. Proceedings of the 3rd Canadian Workshop on Fusarium Head Blight held at Delta Winnipeg, Winnipeg Manitoba, Dec. 9th to 12th, 2003, pp. 220-222.

Kirst, H.A., Michel, K.H., Mynderse, J.S., Choco, E.H., Yao, R.C., Nakatsukasa, W.M., Boeck, L.D., Occlowitz, J., Paschel, J.W., Deeter, J.B. and G.D. Thompson (1992). Discovery, isolation and structure elucidation of a family of structurally unique fermentation derived tetracyclic macrolide. *In:* D.R. Baker, J.G. Fenyes and J.J. Steffens (Eds), Synthesis and Chemistry of Agrochemicals. III. Am. Chem. Soc., Washington, D.C., pp. 214-215.

Flury, M. (1996). Experimental evidence of transport of pesticides through field soils. *J. Envi. Qual*., **25:** 25-45.

Saunders, D.G. and B.L. Bret (1997). Fate of Spinosad in the environment. *Down to Earth*, **52(1):** 14-20.

Arora, S. (2006). Pesticides and Environment in Today's Context. *Agriculture Today*, pp. 53-56.

West, S.D., Yeh, L.T., Shwedler, D.A., Turner, L.G., Thomas, A.D. and D.O. Duebelbeis (2000). Determination of spinosad and its metabolite in food and environmental matrices. 1. High-performance liquid chromatography with ultraviolet detection. *J. Agric. Food Chem*., **48:** 5131-5137.

Sparks, T.C., Thompson, G.D., Larson, L.L., Kirst, H.A., Jantz, O.K., Worden, T.V., Hertlein, M.B. and J.D. Busacca (1995). Biological characteristics of the spinosyns: New naturally derived insect control agents. Proc. Beltwide cotton conf., pp. 903-907.