JOURNAL OF
AGRICULTURAL AND
FOOD CHEMISTRY

Fate of Spinosad in Litter and Soils of a Mixed Conifer Stand in the Acadian Forest Region of New Brunswick

DEAN G. THOMPSON,*,† BRENDA J. HARRIS,‡ LEONARD J. LANTEIGNE,§ TERESA M. BUSCARINI,† AND DEREK T. CHARTRAND†

Canadian Forest Service, Great Lakes Forestry Centre, 1219 Queen Street East, Sault Ste. Marie, Ontario, P6A 2ES Canada, Dow AgroSciences Canada Inc., No. 201, 1144 29th Avenue N.E., Calgary, Alberta, T2E 7P1 Canada, and Canadian Forest Service, Atlantic Forestry Centre, P.O. Box 4000, Fredericton, New Brunswick, E3B 5P7 Canada

Spinosad is a natural insecticide, produced via fermentation culture of the actinomycete *Saccharopolyspora spinosa*, with potential use against a number of forest pests including spruce budworm (*Choristoneura fumiferana* [Clem]). Persistence of spinosad was determined in terrestrial fate experiments conducted within a semimature stand of black spruce (*Picea mariana* [Mill.]) and balsam fir (*Abies balsamea* [L]) in the Acadian forest region of New Brunswick, Canada. Results of experiments established under full coniferous canopy and in a canopy opening indicated that spinosad dissipated rapidly following hyperbolic kinetics in both litter and soils and was not susceptible to leaching. Time to 50% dissipation estimates for spinosyn A ranged from 2.0 to 12.4 days depending upon matrix and experimental conditions. Spinosyn D dissipated to levels below quantitation limits (0.02 μg/g of dry mass) within 7 days in all cases. Sporadic low-level detection of the demethylated metabolites suggested that parent compounds were degraded in situ.

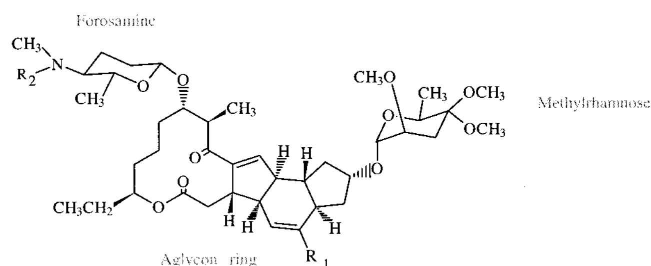
KEYWORDS: **Spinosad; spinosyns; degradation; leaching; soils; fate; forestry**

INTRODUCTION

Restrictions on the use of fenitrothion, historically the principal insecticide used for spruce budworm control (*1*), have piqued scientific interest in the discovery and development of more environmentally acceptable pest control products. One area of intense research interest involves investigations of natural active metabolites derived from microbial and higher plant sources commonly referred to as biopesticides (e.g., refs *2*−*5*).

Spinosad is a biopesticide formulation produced by fermentation culture of the actinomycete *Saccharopolyspora spinosa* (*4*). The commercial formulation is composed of a mixture of two macrolide active ingredients referred to as spinosyns A and D (**Figure 1**), in a ratio approximating 85% to 15%, respectively (*4*). Spinosad persistently activates the central nervous system of insects through interaction with the nicotinic acetylcholine receptors. Although the exact mechanism of activity is incompletely understood, it is distinct from that of other nicotinic agonists (*6*, *7*). To date, cross-resistance with other known classes of insecticidal compounds has not been observed (*8*).

Spruce budworm (*Choristoneura fumiferana* [Clem]) is commonly considered to be the most destructive defoliator of spruce and fir species in North American forests (*9*). This is



Spinosyn A: $R_1 = H$ $R_2 = CH_3$ **Spinosyn D:** $R_1 = CH_3$ $R_2 = CH_3$

Spinosyn DM-A: $R_1 = H$ $R_2 = H$ **Spinosyn DM-D:** $R_1 = CH_3$ $R_2 = H$

Figure 1. Molecular structure of the principal active ingredients (spinosyns A and D) and their respective primary metabolites (DM-A and DM-D).

particularly true in eastern Canada, where episodic infestations may decimate valuable stands of mature and semimature black spruce (*Picea mariana* [Mill.]), white spruce (*Picea glauca* [Moench]), and balsam fir (*Abies balsamea* L. [Mill.]). Spinosad has demonstrated activity against forest insect pests including spruce budworm (B. Helson, personal communication; *10*) as well as other pests of economic importance in agriculture (*11*). Spinosad shows minimal acute toxicity to mammals [LD_{50} (rats) > 5000 mg/kg], birds [LD_{50} (bobwhite and mallard duck) > 2000 mg/kg], fish (LC_{50} = 1−100 mg/L), and aquatic invertebrates (LC/EC_{50} = 10−100 mg/L) and shows no carcinogenic,

* Author to whom correspondence should be addressed [telephone (705) 949-9461, ext 2424; fax (705) 759-5700; e-mail dthompso@nrcan.gc.ca].
† Canadian Forest Service, Great Lakes Forestry Centre.
‡ Dow AgroSciences Canada Inc.
§ Canadian Forest Service, Atlantic Foresty Centre.

10.1021/jf011319l CCC: $22.00 © 2002 American Chemical Society
Published on Web 01/19/2002

teratogenic, or reproductive effects in laboratory tests (*12*). In addtion, spinosad has reportedly low toxicity to beneficial insects in comparison to several other insecticides (*13*, *14*).

Previous studies (*15*−*17*) demonstrate that only a small portion (typically <20%) of the active ingredient (ai) released from the aerial insecticide applications in forestry typically reach the ground surface under coniferous tree canopies. However, where natural openings or gaps within such canopies exist, higher ground deposits may occur (*16*). Dissipation of pesticide residues from the forest floor compartment is a function of both degradation and movement, which in turn are controlled principally by adsorption−desorption equilibria (*18*, *19*) that are chemical and matrix specific. As noted by Mackay and Stiver (*20*), the fate of a compound in an environmental compartment is predictable given sufficient knowledge of the physicochemical characteristics of the compound and the matrices with which it is interacting. Spinosyns A and D (**Figure 1**) have low to moderate water solubility (235 and 0.329 mg/L, respectively, at pH 7), are characterized by relatively high log K_{ow} values (4.0−5.2) under neutral to basic (pH 7−9) conditions, and are essentially nonvolatile (vapor pressure < 2.4×10^{-10} mm) (*10*, *21*). Soil sorption coefficient (K_d) values range from 5 to 323, indicating moderate to strong sorption, depending upon the characteristics of the soils studied. Typically, stronger sorption occurs on finer textured soils with higher organic matter content or cation exchange capacity. Overall, the physicochemical characteristics and available experimental evidence suggest that spinosad will sorb to cation exchange sites and organic components of soils, is unlikely to volatilize from litter or soil surfaces, and is unlikely to leach. Photolysis is recognized as the primary degradation mechanism for spinosyns A and D in the environment with photolytic half-lives on soil surfaces ranging from 8.68 to 9.44 days (*12*). Photolysis results in the formation of mono-demethylated products, referred to herein as DM-A and DM-D (**Figure 1**). A combination of both degradative and dissipative mechanisms control overall persistence in natural environments. In agricultural soils of the southern United States, very short time to 50% dissipation (DT_{50}) values have been observed (e.g., for spinosyn A, DT_{50} < 1 day; *22*), but estimates generally range between 9 and 17 days for spinosyns A and D in silt loam and sandy loam soils (*23*). The degree to which degradation and dissipation may be inhibited under the low light, temperature, and pH regimes typical of northern coniferous forest sites is largely unknown. In this context, concurrent comparative field experiments were established in a mixed black spruce/balsam fir stand located in the Acadian forest region in eastern Canada. The experiments were designed to address the following specific objectives: (a) to determine and compare the persistence of spinosad (spinosyns A and D) and their primary demethylated metabolites in the litter and underlying soils typical of mature spruce/fir forests in the Acadian forest region of New Brunswick under conditions of both closed and open canopies and (b) to determine the vertical movement of spinosad (spinosyns A and D) and their primary demethylated metabolites through litter and underlying soils.

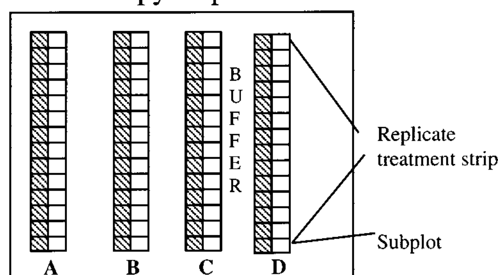
MATERIALS AND METHODS

Site Selection and Experimental Design. The experimental site was chosen to be representative of mature, closed canopy, mixed spruce/fir stands, which are of high value, susceptible to defoliation by spruce budworm, and typical of those that might receive insecticide applications for control of spruce budworm. Located in the Acadia Forest Experimental Station near Fredericton, NB, the site was characterized as a mature (60 years old) black spruce/balsam fir stand established on deep (>100 cm), well-drained soils, with a relatively thin (<5 cm) litter horizon. Soils in the area are classified as Harcourt compact tills (*24*). Detailed soil characteristics are provided in **Table 1**.

Table 1. Characteristics of Litter and Soil Matrices from the Experimental Site[a]

characteristic	litter	organic soil (0–5 cm)	mineral soil (5–15 cm)
loss on ignition	92.24	50.24	2.42
organic matter (%)	68.32	42.47	1.65
pH	3.59	3.31	3.73
sand %	NA	NA	74
silt %	NA	NA	23
clay %	NA	NA	3.0
N %	0.80	0.62	0.04
P %	0.09	0.11	0.05
K %	1.52	2.18	0.76
Ca %	1.10	1.72	0.49
Mg %	0.0.98	0.80	0.46
CEC (mequiv/100 g)	46.11	48.93	6.66

[a] All values are expressed in terms of air-dry mass. Litter composed largely of mosses.



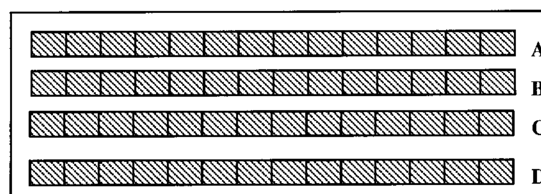


Figure 2. Experimental layout for spinosad fate and persistence in the Acadia Experimental Forest, New Brunswick, Canada.

Within the site, two experimental areas of ∼190 m^2 (**Figure 2**) were established: one under a full coniferous canopy closure and another in a canopy opening. The latter was created by felling and clearing several trees with care taken to minimize disturbance of the forest floor. In both experiments, all branches and ground vegetation impairing uniform spray delivery to the ground surface were removed. In the full canopy experiment, lower (dead) branches from the mature spruce and fir trees were pruned to ∼2 m above ground level. Each site was subdivided into four replicate treatment strips (1 m width), separated by nonsprayed buffers (1 m width). In the full canopy experiment only, the litter layer was removed from half of each treatment strip to expose underlying organic soils. Finally, each treatment strip was subdivided into 14 subplots (0.8 × 2 m) and randomly assigned sampling times [0.1, 1, 3, 5, 7, 15, 22, 28, 35, 42, and 47 days after treatment (DAT)] such that each subplot was sampled only once during the course of the experiment.

Chemical Application. Spinosad (NAF-85 formulation; Dow Agro-Sciences USA; 480 g of ai/L), was used in both the open and canopy

experiments. Chemical applications were made on June 20, 1996, using a calibrated CO_2-pressurized backpack sprayer (model 4F, R&D Sprayers Inc., Opelousas, LA) equipped with a hand-held boom and Teejet SS8002 nozzles. During the applications, ground speed was controlled using a calibrated metronome. The spray system was calibrated to deliver a rate of 200 g of ai/ha with a volume rate of 100 L/ha to the ground surface of each replicate spray strip. Following the applications, residual volumes were measured and duplicate subsamples were taken for analytical confirmation of active ingredient concentrations.

Litter and Soil Residue Sampling. The experimental design allowed for 14 discrete sampling events. Greater sampling frequency was undertaken initially to clearly define the pattern of dissipation. Samples from untreated control plots were taken prior to those from treated strips, and all samples were handled to minimize potential cross-contamination, exposure to sunlight, and time at ambient temperature. Soil samples were obtained using a JMC Zero Contamination stainless steel soil-sampling probe (Ben Meadows Co., Atlanta GA) fitted with a butyrate sleeve liner. Six cores, each 2.3 cm diameter × 30 cm length, were taken from randomly assigned split plots within each replicate treatment strip of both experimental sites on each sampling day. Each soil core was capped, labeled, and placed on ice in insulated boxes until sampling was complete. Following sample collection for a given split plot, all sampling instruments were thoroughly cleaned with a soap solution, followed by distilled water and acetone rinses to eliminate potential cross-contamination between replicates. Samples were transported and stored frozen (−18 °C, in the dark) until analyzed.

Analytical Chemistry. Sample cores were sorted, thawed, and divided into litter, 0−5, 5−15, and 15−30 cm soil layers reflecting the average soil horizon levels. For each sampling event, subsamples of each layer were pooled by split plot, replicate strip, and experiment. Pooled layers were then extruded from the butyrate sleeves into the pans, transferred to a stainless steel Hobart chopper, and thoroughly mixed. All equipment was rinsed and wiped clean with acetone to eliminate cross-contamination between layers or replicates. A subsample (20 g for soil; 15 g for litter) was obtained for extraction and residue analysis. A second subsample (1−8 g depending upon matrix) was dried in a convection oven for 24 h at 130 °C to determine percent moisture content. All reported residue concentrations were calculated on a dry mass basis (micrograms per gram of dry mass).

Spinosad residues (spinosyns A and D), as well as their primary degradation products DM-A and DM-D, were extracted, purified, and analyzed simultaneously, essentially following the techniques described by West (*25*). Briefly, the method involved extraction of analytes from litter and soil matrices with basic methanol, purification by liquid−liquid partitioning into hexane followed by solid phase isolation on silica cartridges and quantitation by reversed phase high-performance liquid chromatography (RP-HPLC). Modifications to the original method included use of a diode array detector (DAD) to allow for peak purity assessment and use of a Supelcosil ABZ Plus (5 μm; 250 × 4.6 mm i.d.) analytical column to maximize resolution. Analytes were quantified by ultraviolet detection at 247 nm with a reference wavelength of 322 in comparison to an external standard containing equivalent concentrations (1, 0.5, or 0.1 μg/mL) of all four analytes (spinosyns A, D, DM-A, and DM-D). External standards were prepared from certified neat samples of individual analytes (97, 98, 94, and 97.4% purity, respectively) as provided by Dow AgroSciences, Indianapolis IN.

In-house validation and test samples run concurrently for quality control showed no coextractive interferences for spinosyns A and D in blank samples. Particularly in the more organic matrices, small peaks interfering with quantitation of DM-A and DM-D were occasionally observed, necessitating fortification with known amounts of pure standard to confirm the presence or absence of the metabolites. Analytical quality control (QC) measures included concurrent extraction, processing, and analysis of two fortified matrix blanks per batch of 10−15 field samples. QC results generally mirrored those of the prior method validation study and were characterized by good recovery efficiency (>80%) and precision (CV < 12%) for all analyte/matrix combinations with the exception of DM-A in the litter matrix where CV was 18.7%. Mean recovery values were used to calculate differential correction factors (100/mean percent recovery efficiency) that were applied to correct raw data for processing losses. Validated limits of quantitation (LOQ) were established as 0.02 μg/g of dry mass for soils, slightly higher than the 0.01 μg/g dry mass value calculated by West (*25*). Limits of detection (LOD) calculated as residue levels equivalent to a 3:1 S/N ratio of blank matrix samples were estimated as 0.01 μg/g of dry mass. Analytical quality control results for soils demonstrate recovery efficiencies and precision comparable to those reported by West (*25*) for soils and by Yeh et al. (*26*) for vegetative samples.

Statistical Analyses. Corrected data for the spinosad compounds (spinosyns A and D) were subjected to nonlinear, least-squares regression analysis with time (DAT) as the independent variable and parent spinosyn concentration (micrograms per gram of dry mass) as the dependent variable. Separate analyses were conducted for each experiment, analyte, and layer combination. Models were fitted to the data using standard statistical software (*27*). All models were assessed to ensure standard assumptions of regression analysis (*28*) were met. An α level of 5% was used as a criterion for the significance of the regression, and persistence endpoints (DT_{50}) were estimated from best fit regressions as follows:

Exponential Decline Model

$$Y = ae^{(-bX)} \qquad DT_{50} = 0.69/b$$

where a = intercept, b = slope, Y = spinosyn A or D residue concentration (μg/g of dry mass), X = time (days after treatment), and e = euclid = 2.7183.

Hyperbolic Decline Model

$$Y = (ab)/(b + x) \qquad DT_{50} = [(ab)/Y_{i/2}] - b$$

where $1/a$ = intercept, $1/ab$ = slope, Y = spinosyn A or D residue concentration (μg/g of dry mass), Y_i = mean initial concentration of spinosyn A or D concentration at DAT = 0.1 day, $Y_{i/2}$ = half of mean initial concentration, and X = time (days after treatment).

RESULTS

Meteorological Conditions. Meteorological data were obtained from the Fredericton monitoring station located ∼5 km from the experimental site. The data indicate that on the day of application, conditions were warm (mean air temperature = 17 °C) and sunny, with no rain. Relatively minor rainfall events occurred 1 DAT (∼13 mm) and again at 5−6 DAT (8−9 mm). The most significant rainfall events occurred at 23 DAT (∼70 mm) and 29 DAT (∼42 mm). Average afternoon soil temperatures at 5 cm depth were 19.6 °C for June and 21.1 °C for July. Average daily hours of bright sunshine varied significantly, with August being generally sunnier than June and July. Consistently sunny days did not occur until ∼1 week after treatment in June and may have been somewhat inhibitory to photodegradation potentials.

Full Canopy Experiment: Intact Split Plots. Maximum concentrations (mean ± SE) of the parent spinosyns A and D in litter were 0.71 ± 0.21 and 0.10 ± 0.017 μg/g of dry mass, respectively, both occurring on the day of application. These values equate to an A/D ratio of 88:12, closely approximating ratios (85:15) reported by Thompson et al. (*4*) for the commercial formulation. Subsequently, residues of both spinosyns A and D dissipated rapidly from the litter matrix. Residues of spinosyn D dissipated to below LOQ levels within 7 days after treatment, negating effective modeling of the dissipation curves. Dissipation of spinosyn A in the litter layer of intact split plots is shown graphically in **Figure 3A**. Results of the nonlinear regression analysis demonstrate that spinosyn A dissipated following a hyperbolic decline model with an estimated DT_{50} value of 2.0 days. The dissipation rate slowed markedly with

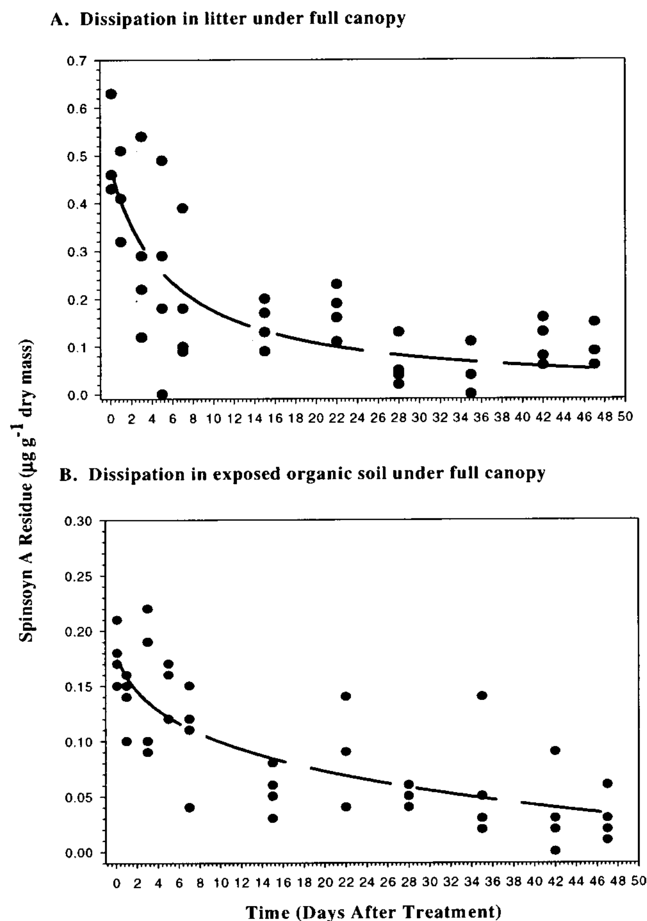


Figure 3. Dissipation of spinosyn A in litter and exposed soils following spinosad application in the full canopy experiment.

increasing time. Although 73% of spinosyn A residue had dissipated during the period of observation, small but detectable quantities remained in the litter matrix at 47 DAT. Throughout the period of observation, only 2 of the 88 samples contained quantifiable levels of DM-A and DM-D metabolites. The single observations for DM-A (0.1 μg/g) and DM-D (0.04 μg/g) occurred on the day of application and 47 DAT, respectively. No residues of either the parent spinosyns or their demethylated metabolites were observed in the 5−15 cm organic soil layer underlying the treated litter, confirming that spinosad residues were retained in the highly organic litter layer.

Full Canopy Experiment: Exposed Split Plots. In the exposed split plots of the full canopy experiment, mean initial concentrations of spinosyns A and D in the upper treated soil layer (0.18 ± 0.01 and 0.022 ± 0.002 μg/g of dry mass, respectively) were also maximal on the day of application. Mean initial concentrations were substantially lower than those observed in the litter layer, reflecting differential bulk density of the litter and exposed soil matrices but again approximated the expected 85:15 ratio of the two analytes. In a pattern similar to that observed for the litter matrix, both spinosyns A and D dissipated rapidly from the treated exposed soil. Dissipation of spinosyn A (**Figure 3B**) was somewhat slower in exposed soils as compared to that in litter but was also effectively modeled with a hyperbolic decline function, accounting for 63% of the variation and yielding an estimated DT_{50} of 12.4 days. By the end of the 47-day observation period, mean spinosyn A concentrations in exposed organic soils had declined to <17% of their initial mean levels. In contrast to the findings for the litter matrix, quantifiable levels of DM-A were consistently observed in all replicates of the 0−5 cm exposed soil layer through the first 5 days after treatment. Maximal mean concentrations of DM-A (0.07 ± 0.04 μg/g of dry mass) were observed 1 day after treatment, declining monotonically thereafter and reaching levels below LOQ by day 7. As observed in the litter matrix, spinosyn D residues dissipated too rapidly to allow for effective modeling of dissipation kinetics. No spinosad residues above LOQ levels were observed in the underlying 5−15 cm soil layer, confirming a general nonleaching tendency for all spinosyn analytes under these experimental conditions.

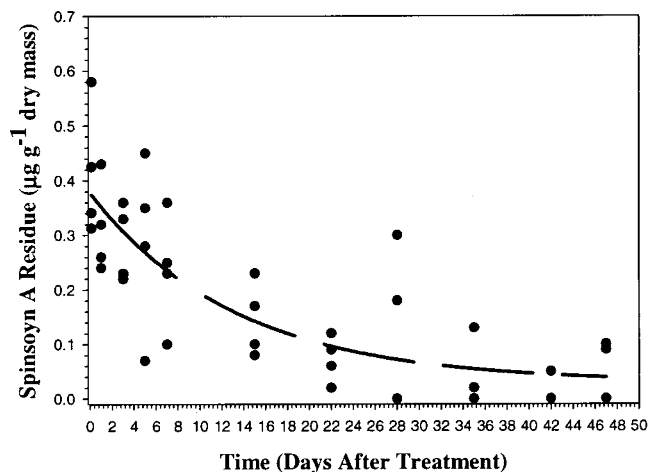


Figure 4. Dissipation of spinosyn A following spinosad application to litter in the open experiment.

Open Experiment. Initial means of spinosyn A and D residues in the litter layer receiving direct chemical application were 0.415 ± 0.06 and 0.049 ± 0.011 μg/g of dry mass, respectively. In the litter matrix under open conditions, spinosyn A residues dissipated following a slow curvilinear pattern (**Figure 4**) modeled most effectively with a two-parameter exponential function. The model accounted for 68% of the data variation and resulted in an estimated DT_{50} value of 11.7 days. By the end of the 47-day period of observation, mean residues of spinosyn A were <12% of mean initial values for this matrix. In the upper treated layer, spinosyn D residues again dissipated rapidly, reaching levels consistently below LOQ limits within 7 days after treatment. Only 2 of 44 litter samples contained quantifiable levels of DM-A. In both cases, one on DAT 7 and one on DAT 22, concentrations were at the LOQ (0.02 μg/g of dry mass). Residues of DM-D above the LOQ were not observed in the litter layer, nor were there quantifiable residues of any spinosyn analyte in the underlying 5−15 cm mineral soil layer.

DISCUSSION

Results of this study demonstrate that spinosad residues dissipate rapidly from forest floor matrices of black spruce/balsam fir stands typical of the Acadian forest region in New Brunswick, Canada. Calculated DT_{50} estimates for spinosyn A ranged from 2.0 to 12.4 days, with persistence depending primarily upon matrix characteristics and being greatest in exposed organic soils under full coniferous canopy. Spinosyn D residues dissipated very rapidly to levels below validated LOQ levels (0.02 μg/g of dry mass) within 7 days after treatment irrespective of light condition or matrix type. Lack of quantifiable residues in the underlying 5−15 cm soil layers confirms that spinosad residues are not susceptible to leaching. This result

Table 2. Dissipation Model Statistics and Estimated DT_{50} Values for Spinosyn A Dissipation

site	subplot[a]	layer	Y_i	$Y_{i/2}$	model[b]	r^2	SEE	F	p	coeff	est	p	DT_{50}
canopy	I	litter	0.72	0.355	H	0.65	0.103	73.98	<0.0001	a	0.48	<0.0001	2.0
										b	5.79	<0.001	
canopy	E	0–5 cm	0.18	0.089	H	0.63	0.037	69.99	<0.0001	a	0.17	<0.0001	12.4
										b	13.58	0.0002	
open	I	litter	0.42	0.028	E	0.68	0.089	88.76	<0.0001	a	0.37	<0.0001	11.7
										b	0.059	<0.0001	

[a] I = litter intact, E = exposed mineral soil (litter removed). [b] All models met criteria of $p < 0.05$ for tests of normality and homogeneity assumptions; H = hyperbolic, E = exponential.

is consistent with both the physicochemical characteristics for these compounds and the highly organic nature of the litter and exposed soil matrices with which they are interacting.

Results from this study are generally consistent with both prior laboratory (*12*, *23*) and agricultural field studies from the United States (22). Results also mirror those of a parallel study conducted in a white spruce stand of Ontario, Canada (*29*) where estimated DT_{50} values ranged from 2.0 to 7.8 days. In both the New Brunswick and Ontario studies, residue dissipation patterns were strongly curvilinear, a phenomenon common to pesticide dissipation in environmental matrices (*30*). Curvilinear patterns of dissipation may reflect intensified binding of molecules within the soil matrix over time, resulting in reduced susceptibility to biodegradation, photolysis, or other dissipation mechanisms. In both studies, transient detection of demethylated metabolites confirms that parent molecules (spinosyns A and D) were being degraded in situ and that neither of the demethylated metabolites was persistent. The fact that spinosad residues did not persist or leach in either of the soil dissipation studies conducted suggests that findings may be generally extrapolated to similar soils and environmental conditions in northern climates.

ABBREVIATIONS USED

DAT, days after treatment; LOD, limit of detection; LOQ, limit of quantitation; DM-A, demethylated metabolite of spinosyn A; DM-D, demethylated metabolite of spinosyn B; K_{ow}, octanol−water partition coefficient; QC, quality control; OM, organic matter; S/N, signal-to-noise ratio.

ACKNOWLEDGMENT

Technical assistance in soil sampling was provided by Shawn Farrell, Fredericton, NB. Assistance in soil sectioning and laboratory sample preparation was provided under subcontract to D. Martis, Sault Ste. Marie, ON. We thank J. Ramakers of the Canadian Forest Service, Sault Ste. Marie, for characterization of litter and soil matrices.

LITERATURE CITED

(1) Pauli, B. D.; Holmes, S. B.; Sebastien, R. J.; Rawn, G. *Fenitrothion Risk Assessment*; Canadian Wildlife Service Technical Report Series No. 165; Environment Canada: Ottawa, ON, Canada, 1993; p 75.

(2) Helson, B. Naturally derived insecticides: Prospects for forestry use. *For. Chron.* **1992**, *68*, 349−354.

(3) Pillmoor, J. B.; Wright, K.; Terry, A. S. Natural products as a source of agrochemicals and leads for chemical synthesis. *Pestic. Sci*. **1993**, *39*, 131−140.

(4) Thompson, G. D.; Dutton R.; Sparks, T. C. Spinosad−A Case Study: An example from a natural products discovery programme. *Pest. Manag. Sci.* **2000,** 56, 696−702.

(5) Hedin, P. A.; Hollingworth, R. M.; Masler, E. P.; Miyamoto, J.; Thompson, D. G. *Phytochemicals for Pest Control*; ACS Symposium Series 658; American Chemical Society: Washington, DC, 1997; p 372.

(6) Sparks, T. C.; Kirst, H. A.; Mynderse, J. S.; Thompson, G. D.; Turner, J. R.; Jantz, O. K.; Hertlein, M. B.; Larson, L. L.; Baker, P. J.; Broughton, M. C.; Busacca, J. D.; Creemer, L. C.; Huber, M. L.; Martin, J. W.; Nakatukasa, W. M.; Pashal, J. W.; Wordon, T. V. Chemistry and biology of the spinosyns: Components of spinosad (Tracer), the first entry into DowElanco's naturalyte class of insect control products. In *Proceedings of the Beltwide Cotton Conferences*; Dugger, P., Richter, D., Eds.; National Cotton Council of America: Memphis, TN, 1996; Vol. 2, pp 692−696.

(7) Salgado, V. L Studies on the mode of action of spinosad: Insect symptoms and physiological correlates. *Pestic. Biochem. Physiol.* **1998**, *60*, 01−102.

(8) Busacca, J. D.; Jantz, O. K.; Ertlein, M. B.; Shaw, M. C.; Dintenfass, L. P.; Nolting S. P.; Stockdale, G. D. Summary of the field performance of spinosad against insect pests of crops. In *Abstracts of the 50th North Central Branch of the Entomological Society of America*; Weinzierl, R. A., Compiler; University of Illinois: Urbana−Champaign, IL, 1995.

(9) Rose, A. H.; Linquist, O. H. *Insects of Eastern Spruces, Fir and Hemlock*; Department of the Environment, Canadian Forest Service Technical Report 23; Government of Canada: 1997.

(10) DowElanco. *Spinosad Technical Guide*; DowElanco: Indianapolis, IN, undated; p 25.

(11) Stockdale, G. D. Field performance of spinosad against insect pests of vegetables. In *Abstracts of the 50th North Central Branch of the Entomological Society of America*; Weinzierl, R. A., Compiler; University of Illinois: Urbana−Champaign, IL, 1995.

(12) Dow AgroSciences. *Material Safety Data Sheet. Tracer Naturalyte Insect Control MSDS 005499*; Dow AgroSciences LLC: Indianapolis, IN, 1998; p 4.

(13) Murray, D.; Lloyd, R. The effects of spinosad (Tracer) on pests and beneficials. *Aust. Cottongrower* **1997**, *18*, 62−64.

(14) Boyd, M. L.; Boethel, D. J. Residual toxicity of selected insecticides to heteropteran predaceous species (Heteroptera: Lygaeidae, Nabidae, Pentatomidae) on soybean. *Biol. Contr.* **1998**, *237*, 154−159.

(15) Sundaram, K. M. S.; Sundaram, A.; Nott, R. Mexacarbate deposits on simulated and live fir needles during an aerial spray trial. *Trans. ASAE* **1986**, *29*, 382−392.

(16) Sundaram, K. M. S.; Helson, B. V.; Payne, N. J. Distribution and persistence of aerially sprayed permethrin in some terrestrial components of a boreal plantation forest. *J. Agric. Food Chem.* **1992**, *40*, 2523−2529.

(17) Picot, J. J. C.; Kristmanson, D. D.; Mickle, R. E.; Dickison, R. B. B.; Riley, C. M.; Wiesner, C. J. Measurements of foliar and ground deposits in forestry aerial spraying. *Trans. ASAE* **1993**, *36*, 1013−1024.

(18) Thompson, D. G.; Fate and movement of pesticides in the environment. In *Pesticides and the Environment*; Stephenson, G. R., Solomon, K. R., Frank, R., Hsiang, T., Thompson, D. G.,

Eds.; University of Guelph: Guelph, ON, Canada, 2000; pp 11-1−11-12.

(19) Cheng, H. H. *Pesticides in the Soil Environment: Processes, Impacts and Modeling*; Soil Science Society of America Book Series; Madison, WI, 1990; p 530.

(20) Mackay, D.; Stiver, W. Predictability and environmental chemistry. In *Environmental Chemistry of Herbicides*; Grover, R., Cessna, A. J., Eds.; CRC Press: Boca Raton, FL, 1991; Vol. II, pp 281−294.

(21) DeAmicis, C. V.; Dripps, J. E.; Hatton, C. J.; Karr, L. L. Physical and biological properties of the spinosyns: novel macrolide pest-control agents from fermentation. In *Phytochemicals for Pest Control*; Hedin, P. A., Hollingworth, R. M., Masler, E. P., Miyamoto, J., Thompson, D. G., Eds.; ACS Symposium Series 658; American Chemical Society: Washington, DC, 1997; pp 144−154.

(22) Borth, P. W.; McCall, P. J.; Gischoff, R. F.; Thompson, G. D. The environmental and mammalian safety profile of naturalyte insect control. In *Proceedings of the Beltwide Cotton Conferences*; Dugger, P., Richter, D., Eds.; National Cotton Council of America: Memphis, TN, 1996; Vol. 2, pp 690−692.

(23) Hale, K. A.; Portwood, D. E. The aerobic soil degradation of spinosad−a novel natural insect control agent. *J. Environ. Sci. Health* **1996**, *B31*, 477−484.

(24) Colpitts, M. C.; Fahmy, S. H.; MacDougall, J. E.; Ng, T. T.; McInnis, B. G.; Zelazny, V. F. *Forest Soils of New Brunswick*; New Brunswick Department of Natural Resources and Energy: Fredericton, NB, Canada, 1995; p 51.

(25) West, S. D. Determination of the naturally derived insect control agent spinosad and its metabolites in soil, sediment and water with UV detection. and water by HPLC with UV detection. *J. Agric. Food Chem.* **1997**, *45*, 3107−3113.

(26) Yeh, L.; Schwedler, D. A.; Schelle, G. E.; Balcer, J. L. Application of Empore disk extraction for trace analysis of spinosad and metabolites in leafy vegetables, peppers, and tomatoes by HPLC with UV detection. *J. Agric. Food Chem.* **1997**, *45*, 1746−1751.

(27) Jandel Scientific. *Sigma Plot 4 for Windows. User's Manual*; Jandel Scientific: San Rafael, CA, 1997.

(28) Draper, N. R.; Smith, H. *Applied Regression Analysis*, 2nd ed.; Wiley: New York, 1981; p 709.

(29) Thompson, D. G.; Harris, B. J.; Buscarini, T.; Chartrand, D. Fate of spinosad in litter and soils of a white spruce plantation in central Ontario. *Pest Manag. Sci.* **2001**, in press.

(30) Faber, M. J.; Thompson, D. G.; Stephenson, G. R. Persistence and leachability of glufosinate-ammonium in a northern Ontario terrestrial environment. *J. Agric. Food Chem.* **1997**, *45*, 3672−3676.

Received for review October 3, 2001. Revised manuscript received November 28, 2001. Accepted December 3, 2001. We gratefully acknowledge the financial assistance provided by Dow AgroSciences Inc. Canada in support of this study.

JF011319L