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Dissipation kinetics of spiromesifen on tea (*Camellia sinensis*) under tropical conditions

K.K. Sharma [a,*], J.K. Dubey [b], S.C. Deka [c], S. Chandrasekaran [d], Kalpana [a], Pratigya Gupta [a], Anoop Kumar [a], Vandana [a], M. Jaya Devi [a], B. Singh [a], A.A.L.H. Baruah [c], J.S. Kennedy [d], I.D. Sharma [b], S.K. Patyal [b], A. Nath [b]

[a] *All India Network Project on Pesticide Residues, Division of Agricultural Chemicals, IARI, New Delhi 110 012, India*
[b] *Dr. Y.S. Parmar University of Horticulture and Forestry, Nauni, HP 173 230, India*
[c] *Department of Entomology, AAU, Jorhat, Assam 785 013, India*
[d] *Department of Agricultural Entomology, TNAU, Coimbatore, Tamil Nadu 641 003, India*

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Abstract

Spiromesifen (Oberon®) is a new insecticide and miticide of chemical class ketoenol active against white flies (*Bemisia* spp., *Trialeuroides* spp.) and spider mites (*Tetranychus* and *Panonychus* spp.). Due to its potential significance in insect resistance management, it is important to establish its behaviour on crop and environment. In the present study, the degradation/dissipation of spiromesifen on tea crop under tropical environmental conditions was studied and its DT_{50} ($t_{1/2}$), and DT_{90} (time to reduce to 90% of the initial value) were estimated. Spiromesifen was sprayed on tea crop after first rain flush at four different locations @ 96 and 192 g a.i. ha^{-1}. Samples of tea leaves were drawn at 0, 1, 3, 5, 7, 10, 15, 21 and 30 days after treatment and that of soil at 10 days after treatment and at harvest from 0 to 15 and 15 to 30 cm layers. After crude extraction of tea leaves for spiromesifen residues with acetone:water, the contents were partitioned with cyclohexane:ethyl acetate and cleaned up on Florosil column. Soil residues were also extracted similarly. Quantification of residues was done on GC–MS in Selected Ion Monitoring (SIM) mode in mass range 271–274 *m/z*. The LOQ of this method was found to be 0.05 μg g^{-1} while LOD being 0.015 μg g^{-1}. The DT_{50} of spiromesifen when applied at recommended doses in tea leaves was found to be 5.0–8.5 days. Ninety-nine percent degradation was found to occur within 33–57 days after application. In soil, no residues of spiromesifen were detectable 10 days after treatment.

Keywords: Spiromesifen; Degradation; First-order kinetics; DT_{50}; DT_{90}

1. Introduction

In the present scenario when most of the persistent pesticides are in the process of being phased out, focus is shifting towards more effective, ecofriendly new molecules with novel mode of action. Tea is a major cash crop of India and it is one of the leading exporters of tea to Japan, USA and various European countries. Most of the insecticides/acaricides presently recommended on tea like dicofol, ethion, tetradifon, chlorpyrifos, etc. are persistent in nature and thus their high residues in the crop may pose risks to human health. India has suffered serious setbacks as some major export consignments have been rejected due to the presence of pesticide residues higher than the prescribed Maximum Residue Limits (Jha et al., 1999).

Spiromesifen [3-(2,4,6-trimethylphenyl)-4-(3,3-dimethylbutyl-carbonyloxy)-5-spirocyclo-pentyl-3-dihydrofuranon-2], a spirocyclic phenyl substituted tetronic acid derivative (Fig. 1) is a good alternative for these persistent pesticides. In India, spiromesifen is presently under consideration of

* Corresponding author. Fax: +91 11 25846396.
E-mail address: kksaicrp@yahoo.co.in (K.K. Sharma).

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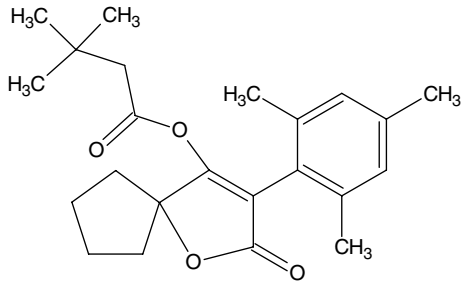

Fig. 1. Chemical structure of spiromesifen.

approval for use on plantation crops including tea and is in the process of being registered under the trade name Oberon® by Bayer Crop Science. It is a lipid biosynthesis inhibitor and has low mammalian toxicity (Dekeyser, 2005). Its acceptable daily intake is 0.022 mg kg^{-1}. Spiromesifen is very active against white flies (*Bemisia* spp., *Trialeuroides* spp.) and numerous mite species (*Tetranychus* and *Panonychus* spp.) at very low dosages of 100–150 g a.i. ha^{-1} (Bretschneider et al., 2003). Owing to its unique structure and novel mode of action, it is a useful tool in resistance management in many cropping systems including cotton, tea, vegetables, fruits and ornamentals (Nauen et al., 2002).

Dissipation rate is one of the most important parameters in predicting the fate of pesticides in the environment. The behaviour of spiromesifen in tomato, cotton and lettuce crops under simulated field conditions has been reported (Weber, 2005). In all the crops, spiromesifen has not been found to tanslocate to the fruits. First metabolite of spiromesifen is formed by hydrolysis of the ester group to form enol, which is further metabolized by hydroxylation of the methyl groups or cyclopentyl ring. Degradation rate of spiromesifen in aerobic and anaerobic conditions (soil and water/sediment system) was determined under laboratory conditions. The DT_{50} in aerobic soil was reported in the range of 3–18 days, and in water/sediment as 4–11 days, the enol and 4-carboxy being the major metabolites (Babczinski and Arthur, 2005).

Relevant data on the behaviour of spiromesifen in plants and environment is scanty in the literature. Therefore, the present studies have been undertaken with the objective of determining the dissipation behaviour of spiromesifen in the tea cropping system. Field trials have been conducted in the major tea growing locations of India with variable weather parameters (Table 1). Its kinetic parameters (dissipation constant, DT_{50}, DT_{90}) have also been established (Table 3).

2. Materials and methods

2.1. Chemicals

All solvents were of analytical grade obtained from Merck, India. Spiromesifen technical (99% purity) and formulation (Oberon® 240 SC) were obtained from M/s Bayer Crop Science Limited. The stock solution of spiromesifen was prepared at 100 μg ml^{-1} in acetone:hexane (0.5:9.5 v/v). This solution was diluted to 10.0, 1.0, 0.1 and 0.01 μg ml^{-1} in hexane. Formulation was used in field trials after dilution in tap water (pH 7.2–7.5). Florosil for column chromatography (Pesticide Residue Grade) was procured from Fluka, Germany. Anhydrous sodium sulfate was used as drying agent and washed with acetone and heated at 650 °C in muffle furnace for 4 h before use.

2.2. Instrument

The quantification of residues was done by Thermo Finnigan (Trace) GC coupled with mass detector (Fisons MD 800). The GC was equipped with capillary column (J&W, DB-17) of 30 m × 0.32 i.d. × 0.25 mm dimension. Helium was used as carrier gas with flow rate of 1 ml min^{-1}. The sample was injected in a split mode with split ratio 1:50. The injector temperature was maintained at 260 °C. The column temperature was programmed at 175° (1 min hold) to 250 °C @ 20 °C min^{-1}. The mass detector was of quadrupole mass analyzer type and used at 70 eV for ionization. Residues were estimated in SIM (Selected Ion Monitoring) mode in mass range of 271–274 m/z. The solvent delay was 2 min and retention time of spiromesifen under these conditions was 6.95 min. Data acquisition was through MS-Lab workstation.

2.3. Field experiment

Following good agricultural practices, field experiments were conducted at four different locations viz, Experimental farm, Palampur, AAU, Jorhat, Teok Tea Estate (TTE), Jorhat, and TNAU, Coimbatore, India, using Randomized Block Design (RBD).

Each treatment was made in plots of size 90 m^2 in triplicate. A control plot where no pesticide was sprayed was kept aside. Spiromesifen 240 SC (suspension concentrate) was sprayed @ 96 and 192 g a.i. ha^{-1} using knapsack sprayer. Applications of insecticides were made when first flush was appearing on tea plant after rain.

Table 1
Weather parameters during field experiment

Climatic conditions	Palampur	AAU, Jorhat	TTE, Jorhat	Coimbatore
Average minimum temperature (°C)	18.65	25.5	25.0	18.0
Average maximum temperature (°C)	26.87	31.3	32.4	22.0
Rainfall (mm)	65.2	74.0	46.5	85.0
Average relative humidity (%)	81.05	92.1	91.0	80.0