PERSISTENCE OF ENDOSULFAN AND ITS METABOLITES IN TOMATO PLANTS AND SOIL

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Abstract

Tests were conducted to study the persistence of ^{14}C-labelled α and β -endosulfan in tomato plants and soil under the greenhouse conditions when applied at the rate and number of applications used by tomato growers in Costa Rica. Two applications, at 30 and 55 days after planting were made. Plant and soil samples were extracted 37, 49, 71 and 125 days after planting and analyzed by LSC, TLC and GC-ECD. At 37 days after planting the compounds identified were α-endosulfan, β-endosulfan and endosulfan sulphate with a combined concentration of 3.6 mg/kg in plant and 0.6 mg/kg in the soil. At 49 days after planting the same three compounds were found at the combined concentration of 1.51 mg/kg in the plant and at 0.34 mg/kg in the soil. After 71 days low levels of α-endosulfan, β-endosulfan, endosulfan sulphate and endosulfan lactone were found in plants and soil. Similarly, at 125 days low levels of these compounds as well as low levels of two other metabolites, endosulfan alcohol and endosulfan ether were detected. Under the conditions of the experiment endosulfan residues do not seem to be significant or persistant.

1. INTRODUCTION

Endosulfan is an broad spectrum organochlorine insecticide and comes in α and β isomers, both of which are found in commercial formulations. It is practically insoluble in water, but is soluble in organic solvents. In the biological tissues and the environment it is known to degrade into various metabolites, which include endosulfan sulphate, endosulfan alcohol, endosulfan ether and endosulfan lactone. The only metabolite toxicologically important is the endosulfan sulphate.

In Costa Rica endosulfan is widely used on tomato to control lepidopterous larvae and whiteflies. The most common formulation used on tomato crop is 0.1 to 0.2% suspension of Thiodan® 35 EC. The present work was intended to study the persistence, degradation and residues of endosulfan in tomato plants and soil after applications made similar to those used by tomato growers in Costa Rica.

2. MATERIAL AND METHODS

A seedbed with tomato var. Hayslip (Asgrow Seed Co., Michigan, USA) was planted under greenhouse conditions (25 ± 5°C); fertilized with 14-14-14 (N-P-K), fungicides were applied to protect the seedlings. On emergence each seeding was tranplanted into a plastic cup with soil treated with organic fertilizer and fungicides. The plants were covered with a special cloth

to protect them from an early whiteflies attack. After transplanting at 30 days to bigger pots (10 L) with loam soil (7.8% OM, 4.7 pH), the plants were fertilized with 10-30-10 (N-P-K). The insecticide treatment was a 0.1% suspension of Thiodan 35 EC (AgrEvo-Hoecht) fortified with 120 KBq of ^{14}C-α-endosulfan (Sp. act. 2962.3 MBq/g) and 90 KBq of β-endosulfan (Sp. act. 2921.4 MBq/g). The isomers were labelled in the 6,7,8,9,10 carbon positions with ^{14}C. Each plant was treated with an average of 1.2 mL suspension using a De VilBiss applicator. At 7 and 19 days after the first application, six plants were sampled to give three replicate of a composite sample of leaf tissue from two pots. Soil sampling was done after pulling the plants out and removing visible roots with tweezers; the soil was collected from the top 15 cm of the two pots and combined to get 1 kg of composite sample, which was sieved through a 2 mm sieve.

The second application of the insecticide solution was made 55 days after planting. As describe before, a 0.1 % suspension of the insecticide, containing 86 KBq of α-^{14}C-endosulfan and 150 KBq β-^{14}C-endosulfan was applied per plant. Sixteen and 70 days after the second application, six plants and pots were sampled, each time.

A US FDA method based on the method 301 from the Pesticide Analytical Manual [1] validated by Mejías *et al.*[2] was used to analyze the residues in soil and plant by GC-ECD. A Shimadzu Model 14A gas chromatograph (GC) equipped with an electron capture detector (ECD) was used and the operational conditions were as following:
Carrier and make up gas : Nitrogen at a rate of 40 mL/min
Injector Temperature: 275 °C
Detector Temperature: 235 °C
Column: SPB-1 30 m x 0.32 cm x 0.25 μm
Injection volume: 1 μL
T° program: T_1= 200°C t_1= 2 min R_1= 2°C/min
T_2= 250°C t_2= 1 min R_2= 0°C/min

One sample of the extract was counted by liquid scintillation counter (LSC) and another was analysed on a Silica gel G_{F254} TLC plate. The plates were developed in acetone : hexane (1 + 4, v/v) solvent mixture. The plates were autoradiographed on X-OMAT Kodak XRay film for identification of the metabolites.

3. RESULTS

The GC retention times for the compounds were: 6.8 min for α-endosulfan, 8.3 min for β-endosulfan, 9.9 min for endosulfan sulphate, 5.9 min for endosulfan alcohol, 5.3 min for endosulfan ether and 3.7 min for endosulfan lactone

The detection and quantification limits for analysis of endosulfan and metabolites in tomato plant are shown in Table I, and the detection and quantitation limits for analysis of these compounds in soil are shown in Table II.

The R_f's on the Silica gel G_{F254} plates for the α-endosulfan, β-endosulfan, endosulfan sulfate, endosulfan lactone, endosulfan alcohol and endosulfan ether were 0.98, 0.89, 0.62, 0.60, 0.43 and 0.95, respectively.

The amounts of residues (mg/kg) found for all the compounds are shown on Table III.

Table I. Detection Limit and Quantification Limit of endosulfan and metabolites analyzed by CG-ECD in plant tissue.

	Endosulfan α	Endosulfan β	Endosulfan Sulfate	Endosulfan Alcohol	Endosulfa n Ether	Endosulfan Lactone
Detection Limit (mg/kg)	0.002	0.001	0.001	0.01	0.002	0.001
Quantif. Limit (mg/kg)	0.006	0.003	0.003	0.03	0.006	0.003

Table II. Detection Limit and Quantification Limit of endosulfan and metabolites analyzed by CG-ECD in soil.

	End. Alpha	End. Beta	End. Sulfate	End Alcohol	End. Ether	End. Lactone
Detection Limit (mg/kg)	0.0004	0.0003	0.0003	0.0027	0.0004	0.0003
Quantif. Limit (mg/kg)	0.0012	0.0009	0.0009	0.0080	0.006	0.003

Table III. Residues of endosulfan and its metabolites (mg/kg) in soil and plant samples[1].

Time	α-Endosulfan	β-Endosulfan	Endosulfan Sulfate	Endosulfan Lactone	Endosulfan Ether	Endosulfan Alcohol
$t_{1\text{-Plant}}$	0.704 ± 0.380	1.921 ± 0.266	0.968 ±	N.D.	N.D.	N.D.
$t_{1\text{- Soil}}$	0.236 ± 0.134	0.267 ± 0.202	0.296	N.D.	N.D.	N.D.
			0.106 ± 0.072			
$t_{2\text{-Plant}}$	0.114 ± 0.028	0.537 ±	0.915 ±	N.D.	N.D.	N.D.
$t_{2\text{-Soil}}$ •	0.110 ± 0.084	0.141	0.175	*	*	N.D.
		0.128 ± 0.045	0.010 ± 0.061			
$t_{3\text{-Plant}}$	0.086 ±	0.370 ±	0.430 ±	**	N.D.	N.D.
$t_{3\text{-Soil}}$	0.058	0.364	0.402	0.291 ± 0.119	N.D.	N.D.
	0.281 ± 0.052	0.334 ± 0.066	0.127 ± 0.036			
$t_{4\text{-Plant}}$ ••	***	0.042 ± 0.038	0.093 ±	***	***	***
$t_{4\text{-Soil}}$ •••	0.064 ± 0.010	0.213 ± 0.245	0.047	****	0.248 ±	****
			0.080 ± 0.043		0.042	

[1] Average of three composite samples

* One of the samples showed residue of 0.24 mg/kg endosulfan ether and 0.01 mg/kg endosulfan lactone.

** One of the samples showed residue of 0.05 mg/kg endosulfan lactone.

*** One of the samples showed residue of 0.03 mg/kg endosulfan lactone, another showed 0.02 mg/kg endosulfan ether, 0.17 mg/kg endosulfan alcohol and 0.01 mg/kg α endosulfan.

****One of the samples showed residue of 0.33 mg/kg endosulfan lactone and 0.10 mg/kg endosulfan alcohol.

t_1= time 1, 37 days after planting, 7 days after first application.

t_2= time 2, 49 days after planting, 19 days after first application.

t_3= time 3, 55 days after planting, 16 days after second application.

t_4= time 4, 125 days after planting, 70 days after second application.

4. DISCUSSION

After 7 days the first application (t_1), the total residue found was 3.6 mg/kg in plants and 0.6 mg/kg in soil. The residue in plants was mainly of β-endosulfan, but α-endosulfan and endosulfan sulphate were present, no other endosulfan metabolites were found.

At time 19 days after the first application (t_2) of the total residues in plants were half of the level found at 7 days after application in plants and soils; in plants, mainly, endosulfan sulphate was found; endosulfan α and endosulfan β were present at low levels. In soil the levels of the α and β endosulfan and endosulfan sulphate were low.

At time 16 days after the second application (t_3), in plants, residues of endosulfan β and endosulfan sulphate were similar, the residues of α endosulfan were lower. In soil, at this time, residues of α and β endosulfan were similar and the residues of endosulfan sulphate were lower; residues of endosulfan lactone were found only in one of the replicates.

After 70 days the second application (t_4) residues on plants, were low, (endosulfan α and β as well as endosulfan sulphate were the compounds identified). Very low concentrations of endosulfan lactone, endosulfan ether and endosulfan alcohol were found in one of the samples. In soil small amounts of α and β endosulfan and endosulfan sulphate were found but endosulfan ether was found at higher levels in one of the sample concentrations of endosulfan lactone (0.3 mg/kg) and endosulfan alcohol (0.10 mg/kg) were found.

The residues in plants and soils disappear quickly as was mentioned before elsewhere [3, 4, 5, 6, 7] due in part specially to the greenhouse conditions where the temperature is relatively high (25 ± 5°C) and the appreciably volatility of the main compound (endosulfan) seems to be important on the behavior of the residues. The same volatility property, according to Gorbach [8], is responsible for the composition of the terminal residue that shifts first to β endosulfan and at the end, towards endosulfan sulfate that is less volatile.

We conclude that under the experimental conditions endosulfan residues do not seem to be important, due to the low concentration found and low persistence.

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