Dissipation Behavior of $^{14}$C-Deltamethrin in Egyptian Soil Columns in Absence and Presence of Chlorpyrifos under Subtropical Conditions

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Abstract

The dissipation of deltamethrin in silt clay under subtropical climate conditions was studied. $^{14}$C-Deltamethrin labeled at gem-dimethyl groups of cyclopropane ring was used alone in one sets of columns and in presence of chlorpyrifos in the other sets and kept under field conditions for eleven months. Radioactivity was concentrated in the soil in the upper zone of the columns 0-10 cm. The total dissipation of the insecticide amounted to 31%; 52% of the applied dose in silt clay soil in absence and presence of chlorpyrifos, respectively. The soil binding capacity increased with time whereby the extractable $^{14}$C-residues simultaneously decreased. The nature of methanolic extract of soils was determined by chromatographic analysis. Deltamethrin was the main degradation product of the extractable residues in addition to 3-phenoxymethyl alcohol, 3-phenoxycarboxylic acid and 3-phenoxymethyl alcohol.

Keywords: $^{14}$C-Deltamethrin; Chlorpyrifos; Soil columns; Dissipation

Introduction

The persistence of pesticides in soil has both economic and environmental significance and is often used as a key parameter in pesticide risk assessment. An appreciable proportion of the insecticides applied to plants often reaches the soil and eventually become incorporated into it [1]. Dispersion of pesticides and their transformation products within the soil, or from the soil to the environment, is influenced not only by the properties of the pesticides and the soil but also by the climatic conditions. Soil properties known to influence the persistence of pesticides include soil pH [2] moisture [3] organic matter content [4-6], redox status [7], and mineral constituents [8]. The synthetic pyrethroids are among the most potent and effective insecticides, accounting for more than 30% of the world market of insecticides. The low toxicity of these insecticides to mammals, birds and their limited soil persistence has encouraged their widespread use in agriculture [9,10] as a substitute for more toxic or recalcitrant organochlorines or organophosphates [11]. The combination of insecticides from different groups may overcome the resistance of insects to pesticides. Several organophosphate insecticides have been mixed with pyrethroids [12,13]. For example, pyrinex quick (deltamethrin+chlordane) has a reduced volatility, inhalation toxicity, phototoxicity and is safe for the operators. Grain protectants including fenithion, malathion, pirimifos-methyl (organophosphorus compounds), deltamethrin (a synthetic pyrethroid), diatomaceous earth (DE), had proven effective against grain insects when used alone and in combination [14-15] Deltamethrin [8]-α-cyano-3-phenoxybenzyl-(1R,3R)-3-(2,2-dibromo-vinyl)-2,2-dimethylcyclopropane-1-carboxylate is a synthetic α-cyano pyrethroid insecticide. This insecticide is considered to be useful insecticide due to its high insecticidal activity with low mammalian toxicity and limited soil persistence [16-18]. Most investigations done efforts focused on the photochemistry and metabolism of deltamethrin in plants and animals. Limited information is available about the fate and movement of deltamethrin and its residues in soil, this is probably due to its extremely low solubility in water [19-21]. Chlorpyrifos, a broad spectrum chemical, is the most extensively used organophosphate insecticide in agriculture [22]. It is registered for the control of soil insects and some foliar insects on a wide range of economic crops, as well as for house hold use [23].

The aim of the present work is to study the movement, degradation and dissipation of $^{14}$C-deltamethrin in absence and presence of the organophosphorus insecticide.

Materials and Methods

Soil

A silt clay soil having different characteristics were used in this study (clay 33.60%; silt 55.15%; sand 11.25%; organic matter 0.95%; pH7.78). The used soil was air-dried and passed through a 2-mm sieve before use. The soil was stored below 0°C until use. At the start of the experiment, soil was thawed and air dried overnight.

Experimental Set-up

Hard polyvinylchloride cylinders (PVC) (50 cm length×5 cm i.d.) open at both ends, were used for the present study. Columns were inserted in soil in the field, two weeks prior to applications. Soil columns received regular inputs of fertilizer and were kept moist by adding water when necessary, and left in the open air under field conditions. Two sets of PVC columns were used; the radiochemical was appropriately diluted with the pure compound. Each column was spiked at the top of the soil column using a micro pipette with 10 mg of the diluted preparations /kg soil (containing) (1.0 µCi) of the radiochemical dissolved in 100 µl of water or acetone and two sets of columns received the above dose of $^{14}$C-deltamethrin in addition to 50 mg of pure chlorpyrifos. The experiment was run over 11 successive months.

Chemicals

$^{14}$C-Deltamethrin radiolabeled at gem-dimethyl groups of the cyclopropane ring was supplied by Roussel-Uclaf, Paris, France. It had a specific activity 695.6MBq/mg and a radiometric purity of 98%. Pure- non labelled deltamethrin and its main degradation products determined by chromatographic analysis. Deltamethrin was the main degradation product of the extractable residues in addition to 3-phenoxymethyl alcohol, 3-phenoxycarboxylic acid and 3-phenoxymethyl alcohol.
products were synthesized according to known procedures [24]. Pure chlorpyrifos, on the other hand was prepared according to Fakhr et al [25]. All chemicals used in this study were of analytical grade. Pure deltamethrin was synthesized by condensing thiophosphoryl chloride with two equivalents of (1:1, v/v) (Scheme 1). Pure chlorpyrifos was prepared by condensation of thiophosphoryl chloride with two equivalents of ethanol in presence of pyridine as acid binding reagent to give O,O-diethyl phosphorochloridothioate as colourless oil. The latter was stored at below 0 °C till analyzed. Samples (30g × 3) from each section of columns were extracted in a Soxhlet apparatus with methanol for 3 h at room temperature in presence of sodium carbonate and freshly distilled dimethylformamide to give chlorpyrifos (O,O-diethyl- O-3,5,6-trichloro-2-pyridyl phosphorothioate) which was crystallized from methanol to give pure white crystals which melted at 42-43 °C. The mixture was extracted with ethyl acetate, washed with water, dried over anhydrous magnesium sulphate, and concentrated in a vacuum. The solid residue was crystallized from ethanol to give white crystals (1) m.p.100-102 °C (Scheme 1). Pure deltamethrin was synthesized by condensing thiophosphoryl chloride with two equivalents of ethanol in presence of pyridine as acid binding reagent to give O,O-diethyl phosphorochloridothioate as colourless oil. The latter was condensed with an equimolecular amount of 3,5,6-trichloropyridinol for 3 h at room temperature in presence of sodium carbonate and freshly distilled dimethylformamide to give chlorpyrifos (O,O-diethyl- O-3,5,6-trichloro-2-pyridyl phosphorothioate) which was crystallized from methanol to give pure white crystals which melted at 42-43 °C. as shown in scheme 1.

**Sampling and extraction**

Samples were taken at various intervals over 11 months at 1, 30, 60, 90, 120, 150, 180, 210, 240, 270 and 330 days after treatment with insecticides. Each time, the columns were removed and sliced into 0-5, 5-10, 10-20, 20-30, and 30-45 cm sections carefully at random for analysis. Soil was air dried, thoroughly mixed and then three subsamples were analyzed from each section of column. Soil was usually stored at below 0 °C till analyzed. Samples (30g x 3) from each section of columns were extracted in a Soxhlet apparatus with methanol for 6 hours. Further extraction of the soil gave no further extractable residues of the pesticide.

**Analysis of Extractable 14C-Residues**

The nature of 14C-residues in the methanolic extract was determined by thin layer chromatography (TLC) and high performance liquid chromatography (HPLC) of samples taken over 11 months following application of the radioactive insecticide. The TLC analysis was conducted on precoated silica-gel plates (F-254, Merck, Germany) with 25 mm gel thickness. Authentic substances were run alongside as references. Spots of deltamethrin and its metabolites appear yellowish brown spots against white background. The following systems were used for development:

- System A: n-Hexane-ether (4:1, v/v)
- System B: Benzene-chloroform (1:1, v/v)

The HPLC analysis was performed on a Waters-Association Model 510 equipped with a U6K Loop injector and a Model 484 variable wave length detector was used. For the identification, 10 µCi, 14C, columns protected with a pre -column filter was used. HPLC grade acetonitrile and water were degassed in an ultrasonic bath just before use. The mobile phase consisted of acetonitrile and water, (8: 4, v/v), (System D) and the flow rate was 1 ml/min. The detection was set by monitoring the UV absorbance at 2190 nm.

**Radioactivity measurement**

The obtained extracts (1mL x3) were mixed with dioxyane-based Scintillator and determined in a liquid scintillation counter (LSC) [27]. Bound 14C-residues in extracted soil were determined by combustion (100mg) in a Harvey Biological Oxidizer (OX-600). For quench correction, an internal standard technique was used. For radio scanning of TLC plates, the plates were scraped at 1cm increments into vials, mixed with scintillation cocktail and counted by LSC. For each column, the overall residue load, and hence persistence, was calculated by summing increment loads of the column.

**Results and Discussion**

**Dissipation of 14C-Deltamethrin in Silt Clay Soil**

The data given for 14C-deltamethrin dissipation in silt clay soil over 11 months using in-situ soil columns are shown in Table 1. The initial concentration of 14C-deltamethrin was found to be 98.5% after one day of application (zero time). Most of the radioactivity was concentrated in the upper zone (0-5 cm) in control columns. This layer contained about 89 and 67% after 6 and 11 months, respectively. The amount of extractable 14C-deltamethrin residues in the upper 0-5cm zone decreased from 98.5% at zero time to 94.5, 86.7 and 52% after 3, 6 and 11 months, respectively. After 10 months, a trace of extractable insecticide residues (0.44%) was observed in the 5-10cm zone. The amount of bound residues (non-extractable) showed a gradual slow increase during the time of experiment. The binding became clear after 4 months especially in the upper zone (0-5cm) and reached its maximum 9% and 14% after 10 and 11 months, respectively. The recovery percent ranged between 67-98.5% in the upper 0-10 cm zone. The percentage of dissipation represented 31% of the total applied dose at the end of the experiment (Table 1).

-Radioactivity applied per column =1 µ Ci (37 MBq) +10 mg non-labelled deltamethrin /kg silt clay soil (control). Results are mean of two columns

On the other hand, the presence of chlorpyrifos insecticide mixed with deltamethrin in silt clay soil columns, led to a faster downward movement of deltamethrin. The percentage of dissipation represented 52% of the total applied dose in 11 months as shown in Table 2. The extractable deltamethrin residues in the upper 0-5 cm zone decreased from 97.8% at zero time to 19%, after 11 months. After 3 months, a trace of extractable insecticide residues (1.2%) was observed in the 5-10 cm zone and reached its maximum (10%) at the end of the experiment. The binding became clear after 3 months (2%) and reached (15 and 17%) in the 0-10 cm zone at 10 and 11 months respectively. After 6 months, a trace of the insecticide residues was observed in 10-15 cm zone.

-Radioactivity applied per column =1 µ Ci (37 MBq ) +10 mg non-labelled deltamethrin + 50 mg non-labelled chlorpyrifos /kg silt clay soil (treated)

Results are mean of two columns

The obtained data as shown in Tables 1 and 2, revealed that deltamethrin dissipated more readily in the presence of chlorpyrifos. These data are in agreement with other reported findings where deltamethrin was immobile in soil that had a higher organic matter content and / or higher clay content than sand [28]. Moreover 93% of the applied deltamethrin remained within the 0-2cm layer, and only 0.5-1% of the applied dose could be extracted from the subsequent lower depths 2-6cm layers [29-32]. It is known that the pyrethroid insecticide deltamethrin is classified as a low mobile compound in soil according to the pesticide mobility classification system [28]. Kaufman et al. [33] found that deltamethrin was practically immobile in soil...
columns, where 97% of the ¹⁴C-activity remained in the upper 0-2.5 cm layer and these results are in line with the obtained results. Its immobility in the environment is attributed to its strong adsorption on particles and its insolubility in water [28-32]. On the other hand, the bound ¹⁴C-residues increased gradually as time of incubation increased due to hydrophobic property of pyrethroids, thus leading to formation of bound residues [28-34].

Generally, it is found that the loss in the amount of recovery is probably caused by surface runoff transport, leaching of the pesticide from the sampled top soil layer, and enhanced microbial/chemical degradation due to variable soil temperature and moisture conditions. The soil surface photolysis may also accelerate the dissipation of the pesticide under field conditions [35]. Also, the soil microorganisms are believed to play an important role in the release and further degradation of bound residues of organochlorine (DDT) [36,37], organophosphorus (chlorpyrifos) [38] and herbicides (prometryn) [39].

In the presence of chlorpyrifos, the percentage of the obtained insecticide residues is 46% of the applied dose in silt clay (Tables 2).
### Table 2: Dissipation of 14C-deltamethrin in presence of chlorpyrifos in silt clay soil columns during 11 months

<table>
<thead>
<tr>
<th>Sampling Date (month)</th>
<th>Column Zone (Cm)</th>
<th>Extractable 14C-deltamethrin residues</th>
<th>Bound 14C-deltamethrin residues</th>
<th>Total 14C-deltamethrin residues</th>
<th>Recovery, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>µg ± S.D %</td>
<td>µg ± S.D %</td>
<td>µg ± S.D %</td>
<td></td>
</tr>
<tr>
<td>1 day</td>
<td>0 – 5</td>
<td>978 ± 0.01 97.8</td>
<td>0.02 ± 0.00 0.2</td>
<td>9.80 ± 0.01 98.0</td>
<td>98.00</td>
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<tr>
<td>1</td>
<td>0 – 5</td>
<td>9.35 ± 0.05 93.5</td>
<td>0.06 ± 0.01 0.6</td>
<td>9.41 ± 0.06 94.1</td>
<td>94.70</td>
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<tr>
<td>1</td>
<td>5 – 10</td>
<td>0.06 ± 0.01 0.6</td>
<td>0.02 ± 0.03 0.2</td>
<td>0.062 ± 0.09 0.6</td>
<td>60.60</td>
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<tr>
<td>2</td>
<td>0 – 5</td>
<td>8.81 ± 0.03 88.1</td>
<td>0.08 ± 0.04 0.8</td>
<td>8.89 ± 0.05 88.9</td>
<td>90.30</td>
</tr>
<tr>
<td>2</td>
<td>5 – 10</td>
<td>0.08 ± 0.02 0.8</td>
<td>0.06 ± 0.05 0.6</td>
<td>0.14 ± 0.06 1.4</td>
<td>88.20</td>
</tr>
<tr>
<td>3</td>
<td>0 – 5</td>
<td>8.51 ± 0.03 85.1</td>
<td>0.1 ± 0.03 1.0</td>
<td>8.61 ± 0.01 86.1</td>
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<tr>
<td>3</td>
<td>5 – 10</td>
<td>0.12 ± 0.01 1.2</td>
<td>0.09 ± 0.02 0.9</td>
<td>0.21 ± 0.00 2.1</td>
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<tr>
<td>4</td>
<td>0 – 5</td>
<td>7.60 ± 0.06 78.0</td>
<td>0.30 ± 0.01 3.0</td>
<td>8.1 ± 0.04 81.0</td>
<td>85.00</td>
</tr>
<tr>
<td>4</td>
<td>5 – 10</td>
<td>0.30 ± 0.05 0.3</td>
<td>0.10 ± 0.00 1.0</td>
<td>0.4 ± 0.01 4.0</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>0 – 5</td>
<td>7.10 ± 0.04 71.0</td>
<td>0.45 ± 0.01 4.5</td>
<td>7.55 ± 0.05 75.5</td>
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<tr>
<td>5</td>
<td>5 – 10</td>
<td>0.4 ± 0.01 4.0</td>
<td>0.20 ± 0.02 2.0</td>
<td>0.6 ± 0.04 6.0</td>
<td></td>
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<tr>
<td>6</td>
<td>0 – 5</td>
<td>6.50 ± 0.02 65.0</td>
<td>0.52 ± 0.03 5.2</td>
<td>7.02 ± 0.01 70.2</td>
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<tr>
<td>6</td>
<td>5 – 10</td>
<td>0.4 ± 0.03 4.0</td>
<td>0.25 ± 0.01 2.5</td>
<td>0.65 ± 0.06 6.5</td>
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<td>7</td>
<td>0 – 5</td>
<td>5.82 ± 0.05 58.2</td>
<td>0.65 ± 0.01 6.5</td>
<td>6.47 ± 0.05 64.7</td>
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<tr>
<td>7</td>
<td>5 – 10</td>
<td>0.50 ± 0.03 5.0</td>
<td>0.29 ± 0.03 2.9</td>
<td>0.79 ± 0.03 7.9</td>
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<tr>
<td>7</td>
<td>10 – 15</td>
<td>0.003 ± 0.04 0.03</td>
<td>0.001 ± 0.04 0.01</td>
<td>0.004 ± 0.01 0.04</td>
<td></td>
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<tr>
<td>8</td>
<td>0 – 5</td>
<td>5.0 ± 0.06 50.0</td>
<td>0.75 ± 0.02 7.5</td>
<td>5.75 ± 0.04 57.5</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>5 – 10</td>
<td>0.7 ± 0.01 7.0</td>
<td>0.30 ± 0.03 3.0</td>
<td>1.00 ± 0.06 10.0</td>
<td></td>
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<tr>
<td>8</td>
<td>10 – 15</td>
<td>0.005 ± 0.02 0.05</td>
<td>0.001 ± 0.01 0.01</td>
<td>0.006 ± 0.05 0.06</td>
<td></td>
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<tr>
<td>9</td>
<td>0 – 5</td>
<td>3.8 ± 0.01 38.0</td>
<td>0.83 ± 0.05 8.3</td>
<td>4.63 ± 0.01 46.3</td>
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<tr>
<td>9</td>
<td>5 – 10</td>
<td>0.8 ± 0.00 8.0</td>
<td>0.40 ± 0.04 4.0</td>
<td>1.20 ± 0.04 12.0</td>
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<tr>
<td>9</td>
<td>10 – 15</td>
<td>0.009 ± 0.02 0.09</td>
<td>0.002 ± 0.01 0.02</td>
<td>0.011 ± 0.03 0.1</td>
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<td>10</td>
<td>0 – 5</td>
<td>2.80 ± 0.03 28.0</td>
<td>0.95 ± 0.00 9.5</td>
<td>3.75 ± 0.02 37.5</td>
<td></td>
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<td>10</td>
<td>5 – 10</td>
<td>0.90 ± 0.05 9.0</td>
<td>0.50 ± 0.05 5.0</td>
<td>1.40 ± 0.03 14.0</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>10 – 15</td>
<td>0.01 ± 0.04 0.1</td>
<td>0.003 ± 0.06 0.03</td>
<td>0.013 ± 0.01 0.13</td>
<td></td>
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<tr>
<td>11</td>
<td>0 – 5</td>
<td>1.85 ± 0.01 18.5</td>
<td>1.10 ± 0.01 11.0</td>
<td>2.95 ± 0.05 30.0</td>
<td></td>
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<tr>
<td>11</td>
<td>5 – 10</td>
<td>1.00 ± 0.03 10.0</td>
<td>0.55 ± 0.02 5.5</td>
<td>1.55 ± 0.01 15.5</td>
<td></td>
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<tr>
<td>11</td>
<td>10 – 15</td>
<td>0.05 ± 0.02 0.5</td>
<td>0.005 ± 0.00 0.05</td>
<td>0.055 ± 0.04 0.55</td>
<td></td>
</tr>
</tbody>
</table>

**Figure 1:** Main Degradation Products of Deltamethrin in Soil Columns
Table 3: R<sub>f</sub> and R<sub>v</sub> values of deltamethrin and its degradation products

These data indicate that movement of deltamethrin and dissipation is faster in the presence of chlorpyrifos under the field condition. It is worth mentioning that significant interactions between pesticides applied in combination, in terms of their persistence in soils and toxicity to crops and insects, have been documented [40, 41]. The nature of extractable residues showed that deltamethrin represents 60-70% of the applied dose by TLC and HPLC analysis, in addition to, at least three degradation products (25%) at the end of experiment as shown in Figure 1 and Table 3. It is obvious that the preferred degradation pathway of deltamethrin occurs via hydrolysis of the ester linkage followed by oxidation. These metabolites appear to have no tendency to accumulate in soils [42].

References


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