

Fate and transport of ethoprophos in the Jamaican environment

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Abstract

The hydrolytic half lives of ethoprophos in distilled, river, brackish and open sea water were 25, 133, 65 and 81 days, respectively. Under laboratory conditions, volatilisation of the residues after 12 h was 1.4–3.6, 2.3–4.5 and 6.5–20.2% from a sandy loam soil with 1, 10 and 20% moisture levels, respectively. Photolysis in soil was significantly faster ($P < 0.05$) in direct sunlight ($T_{1/2}$ of 4.7 days) than in the shade ($T_{1/2}$ of 12.3 days). The microbial degradation of ethoprophos was more than two-fold faster in unsterile soil ($T_{1/2}$ of 10.9 days) than in sterile soil ($T_{1/2}$ of 28.8 days). The runoff of ethoprophos from unweeded plantation soil at 23° slope was significantly ($P = 0.015$) less than at 38° slope; the amounts lost after 9 weeks and 27.5 mm of rainfall were 89.4 and 91.2%, respectively, of the applied amount from the two respective slopes. In the weeded plots, 93.6 and 92.4% of the applied insecticide were lost from 23° and 38° slopes, respectively. Under laboratory conditions, between 67.0 and 85.1% of ethoprophos leached through the soil columns. Under field conditions, after 9 weeks and 25 mm of rainfall, only 2.8 and 2.0% residues were recovered at a depth of 10–15 cm from unweeded and weeded slopes, respectively at 23° slope, and 2.2 and 1.9% from the two respective plots at 38° slope. © 1999 Elsevier Science B.V. All rights reserved.

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1. Introduction

Ethoprophos is widely used in banana and coffee plantations in Jamaica and is becoming increasingly popular as a soil pesticide. Since coffee

with banana as a shade plant is widely cultivated on steep slopes, the residues eventually run off to rivers and sea coasts contaminating sediment, water and aquatic fauna. Indeed, a rapid survey of pesticide residues in the major rivers of Jamaica revealed 1.38 and 1.98 $\mu\text{g kg}^{-1}$ of ethoprophos residues in the sediment of a river which traverses two areas heavily cultivated with bananas (Witter

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et al., 1999). In spite of the fairly heavy use of the insecticide in the Caribbean, Central and South America, there is little information on its fate, transport and ecological impact under tropical conditions.

The present investigations were therefore carried out to provide basic data on the fate of ethoprophos in a tropical island agro-ecosystem. The results would be useful in environmental risk assessment of the insecticide and in developing strategies for the management of its residues.

2. Materials and methods

Hydrolysis of ethoprophos (Mocap 10G[®]) in distilled, river, brackish (2.0% salinity) and open sea (salinity 3.3%) waters was studied in the three replicates of a 500 ml solution of 10 ppm a.i. per replicate. Each replicate was held in open 1-l narrow-mouthed brown bottles under laboratory conditions at 30°C. At regular intervals, for 130 days (Fig. 1), 25-ml aliquots were removed for residue analyses.

Volatilisation from Cuffy Gully Gravelly Sandy Loam soil (CGGSL; 64% sand, 22% silt, 14% clay, 4.45% organic matter and pH 6.96) taken from a Blue Mountain plantation was studied under laboratory conditions in a closed system of flasks with treated soil over which air was passed and the residues trapped in methylene chloride. The soil was completely dried in an oven and nine 100-g samples were weighed and required volumes of water added (where needed) to obtain 1, 10 and 20% moisture levels. Each sample was mixed thoroughly with 1 g of Mocap 10G and placed at the bottom of a horizontal glass column and air passed over it at a rate of 9.26 ml s⁻¹ from one end and bubbling it through methylene chloride in two Erlenmeyer flasks at the other end to trap the residues (Singh et al., 1991). The solvents were removed every 2 h for 12 h for residue analyses. The experiments were conducted in three replicates.

Photolysis was conducted by mixing 20 ppm a.i. of Mocap 10G with 100 g of sterilised CGGSL soil at 10% moisture level, in large petri dishes. Each of the three replicates of petri dishes were

held under direct sunlight or constant tree shade on a plantation. On days 0, 5, 8, 16, 32, 64 and 82 of the experiment the soil in each dish was mixed thoroughly and a 10-g subsample withdrawn for residue determination.

For microbial degradation of ethoprophos, 500 g of plantation soil was autoclaved at 120°C for 8 h. Both the sterilised and unsterilised soils were mixed with water to provide 10% moisture level and then with 20 ppm a.i. of ethoprophos. Microbial degradation was determined by removing aliquots of sample from each of the three replicates at 4-h intervals for a period of 36 h.

Run-off and leaching of ethoprophos were studied in sloping sections of the plantation with CGGSL soil which were at 23° and 38°. A 2 × 6 m strip of each slope was cleaned of weeds and grasses (weeded). Mocap 10G (20 g) was incorporated into the soil on a 0.3 × 2 m weeded band at the top of each 2 × 6 m strip at each slope. Soil samples were collected from 1 to 5 and 5 to 10 cm depths at 1 h and 2, 4, 6 and 9 weeks after treatment at distances of 1.5, 3, 4.5 and 6 m down the slope from the treated band, for residue analysis. Leaching was also investigated in the laboratory in 30-cm soil columns kept at 20% moisture through which one litre of water was passed and every 200 ml portion of eluate collected for analysis.

Residues were extracted from soil and water according to the procedure described earlier (Robinson et al., 1997). Residues were extracted from water in methylene chloride and dried in an anhydrous sodium sulphate column. Soil samples were extracted in methylene chloride by soxhlet for 8 h and cleaned by passing through a florisil column. A Shimadzu 9A gas chromatograph equipped with a FPD was used to identify and quantify the residues. Analytical conditions were; glass column, 1.6 m × 2 mm packed with OV-17; carrier gas, nitrogen, at a flow rate of 30–35 ml min⁻¹; temperature settings: column 250°C, injector and detector 280°C. Detection levels ranged from 0.001 to 0.002 ng and recovery ranged from 75.8 to 80.4% for soil samples and from 89.2 to 91.7% for water samples. Reproducibility of results was 95.5 ± 1.5%.

3. Results

The dissipation of ethoprophos was fastest (significant at $P = 0.01$) in distilled water ($T_{1/2} = 25$ days), followed by brackish ($T_{1/2} = 65$ days) and sea ($T_{1/2} = 81$ days) waters (not significantly different at $P > 0.05$), and slowest ($T_{1/2} = 133$ days; significantly different at $P = 0.01$) in river water (Fig. 1).

Volatilisation flux of ethoprophos from soil was 23.1, 40.6 and 186.9 ng cm^{-2} during the first 2 h, but declined after 12 h to 7.6, 8.9 and 32.9 ng cm^{-2} , at 1, 10 and 20% soil moisture levels, respectively (Fig. 2). The total 12-h dissipation of 2.73 ± 0.42 , 3.42 ± 0.79 and $10.51 \pm 0.88\%$, respectively, of the residues from the soil at 1, 10 and 20% moisture levels were significantly ($P < 0.001$) different from each other.

Shaded and unshaded conditions did not have a significant ($P > 0.05$) impact on the persistence of ethoprophos in the soil (Fig. 3), the $T_{1/2}$ values being 4.7 days in direct sunlight and 12.3 days in tree shade. The degradation of ethoprophos in non-sterile soil was significantly ($P = 0.045$) faster than in sterile soil (Fig. 4); the $T_{1/2}$ value in non-sterile soil was 10.9 days compared to 28.8 days in sterile soil.

Under field conditions, weekly and total 6-week losses of ethoprophos residues from the treated plots in the weeded and unweeded slopes were

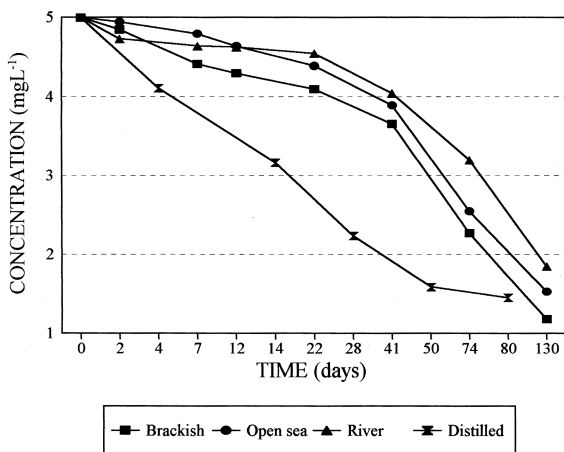


Fig. 1. Persistence of ethoprophos in distilled, river, brackish and open sea waters in Jamaica.

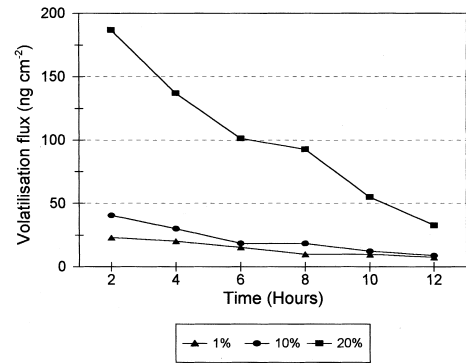


Fig. 2. Volatilisation of ethoprophos from soil of a Blue Mountain plantation, Jamaica, at different moisture levels.

steady and always significantly ($P = 0.015$) less at 23° than 38° slopes (Fig. 5). The loss of residues from the weeded slopes was significantly ($P = 0.05$) faster than from the unweeded slopes during weeks 1–3 after treatment, when only 0.4 mm of rain fell. However, there was no significant ($P > 0.05$) difference in loss from the weeded and unweeded slopes during weeks four to nine when 27.1 mm of rain fell. The overall 9-week losses of 93.6 and 92.4% from the treated bands in the weeded 23° and 38° slopes, respectively, were not significantly ($P > 0.05$) more than the 89.5 and 91.2% losses from unweeded plots at the two respective slopes.

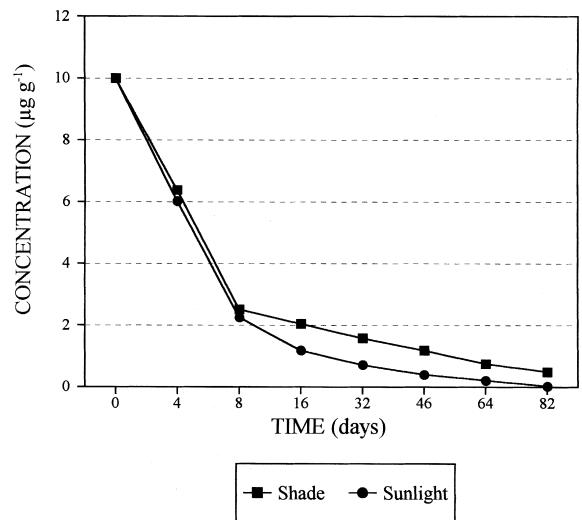


Fig. 3. Persistence of ethoprophos in soil under tree shade and direct sunlight.

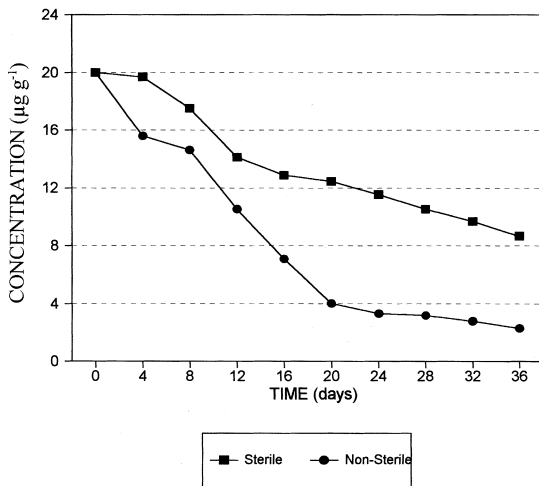


Fig. 4. Persistence of ethoprophos in natural and sterilised soils.

Under laboratory conditions, $78.4 \pm 6.3\%$ of the applied ethoprophos leached with one litre of water from soil columns packed with CGGSL soil. Of the $21.6 \pm 1.1\%$ which remained in the soil column, $10.7 \pm 1.81\%$ was recovered from the top 10 cm while $5.2 \pm 0.9\%$ and $5.8 \pm 0.9\%$ were recovered from 10 to 20 and 20 to 30 cm depths of the column, respectively. Leaching was significantly ($P = 0.032$) more at 23° than at 38° slopes

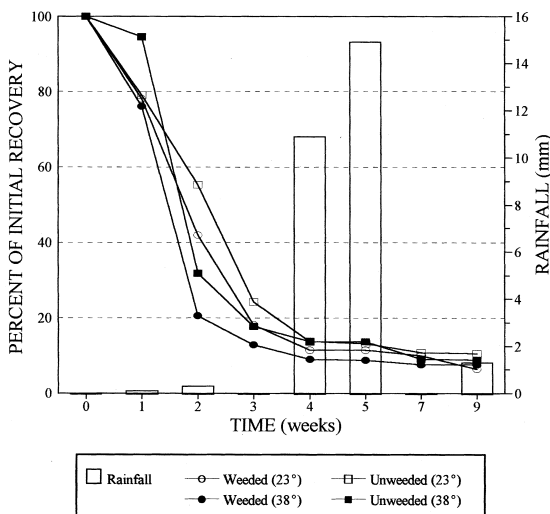


Fig. 5. Loss of ethoprophos residues from treated bands in the weeded (A) and unweeded (B) plots at 23° and 38° slopes.

in both the weeded and unweeded plots but there was no significant ($P = 0.364$) difference between them. The recovery of residues from a depth of > 5 to 15 cm was 0.34 and 0.33% of the applied insecticide in the weeded, and 0.68 and 0.61% in the unweeded plots at 23° and 38° slopes, respectively.

4. Discussion

The persistence of ethoprophos in the three natural waters of pH 7.76–8.15 ($T_{1/2} = 65$ –133 days) is not different from the $T_{1/2}$ of 70 days reported by Linders et al. (1994). It is known to be very stable in water at pH 7 but is rapidly hydrolysed at pH 9 (Worthing, 1987). The faster hydrolytic rate of the insecticide in distilled water may be attributed to the lack of any organic matter for adsorption of the residues, as suggested by Singh et al. (1991) for endosulfan. In aquatic ecosystems, hydrolysis rate is affected by complex adsorption and degradation processes due to organic impurities and salts which make the residues less available for hydrolysis (Haque et al., 1977).

The volatilisation of granular ethoprophos from the soil was significantly ($P < 0.001$) lower than that of endosulfan EC 35 under similar conditions (Robinson et al., 1997), obviously because moisture is needed to release the active ingredient from the granules, as evidenced by 4.5-fold higher volatilisation of ethoprophos at 20% than 10% moisture level. Our data is also consistent with Henry's law constant (K_h) which states that the K_h of a pesticide is directly proportional to its vapour pressure and inversely proportional to the soil solution concentration of the insecticide (Spencer et al., 1988), the water solubility of ethoprophos being 750 mg l^{-1} .

Photolysis may be another route of dissipation of ethoprophos, although the 2.6-fold difference in its persistence in sunlight and shade was not significant ($P > 0.05$). Soil microbes play a definite role in the degradation of the residues as the $T_{1/2}$ in non-sterile soil ($T_{1/2} = 11$ days) was significantly ($P = 0.03$) lower than in sterile soil ($T_{1/2} = 29$ days). Microbial degradation of insecti-

cide residues in soil is well documented (Hill and Wright, 1978; Brady, 1984).

The rapid loss of ethoprophos, though at significantly ($P < 0.001$) different rates from both the weeded and unweeded slopes is not surprising as its high solubility in water would result in it running off both in solution and through erosion of residue-adsorbed soil particles. The higher loss from the weeded slope can be attributed to the vegetative cover, as the plants take up some residues from the soil (Beall and Nash, 1972), reduce and redistribute them in the top soil (Hill and Wright, 1978) and check soil erosion (Morgan, 1979).

The relatively high level of leaching of ethoprophos is consistent with its high solubility (750 mg l^{-1}) which is an important factor in the leachability of insecticides (Nicholls, 1988). Increased leaching in soil columns than in field may be due to differences in the compaction of soil, volume of water available for leaching, and microbial degradation of leachate as it percolates slowly under field conditions. Gentle rainfall also encouraged leaching, as an increase from $2.6 \text{ mm h}^{-1} \text{ day}^{-1}$ to $10.5 \text{ mm h}^{-1} \text{ day}^{-1}$ can result in a fourfold decrease in the volume of water leaching in the soil (Johnson, 1995). Vegetation also increases percolation of water into the soil (Beall and Nash, 1972), though intermittent wet and dry periods determine the downward and upward movement of residues in soil, particularly in fields without vegetative cover (Nicholls, 1988).

It is obvious that about 30% of the applied ethoprophos is likely to be removed by runoff to rivers, depending upon the distance of the water body from the site of application. However, the residues are not as persistent in the environment as endosulfan (Robinson et al., 1997). Ethoprophos is not as persistent in soil as endosulfan (Robinson et al., 1997), as most of it (30%) may be lost by run-off, followed by hydrolysis, microbial degradation, volatilisation and to some extent, photolysis. However, ethoprophos granule formulation is quite persistent in water and may pose a threat to aquatic fauna. There is no information available on the transfer of ethoprophos to humans via diet but the communities which

depend on river water for bathing, drinking and cooking may be exposed to health risk. WHO/FAO have not established any Acceptable Daily Intake levels for the residues, but the Environmental Protection Agency (USA) maximum recommended residue levels in fruits and crops is 0.02 ppm is encouraging to not that only low levels of ethoprophos (0.02–1.38 ppb) residues have been detected occasionally in a few rivers compared to frequent and often high levels of endosulfan (Witter et al., 1999), obviously because the residues were degraded in soil before reaching the rivers.

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