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Movement and Persistence of Methamidophos in Vegetable Agroecosystem

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In the scope of an environmental effects assessment, the transport of pesticides via surface runoff, leaching, and pesticide persistence in soil has to be viewed seriously. Pesticides may also be transported to adjacent areas together with soil particles as sediment. Not only are pesticide losses in surface runoff and leaching of concern in view of their impact on adjacent ecosystems, but their concentrations and persistence in soil can also be important. Data on pesticide losses in surface runoff (Wauchope 1978; Ahuja 1986; Klöppel et al. 1994), leaching (Ismail and Kalithasan 1997) and persistence (Talekar et al. 1978) have been published.

The presence of insecticide residues in runoff, sediment and leachate, as well as its mobility and persistence in soil, depends on such factors as chemical and physical properties of the compound, soil properties, amount of rainfall, bed construction and slope (Riley et al. 1994). Most pesticides, for example, persist longer in soil with high organic matter content (Oppong and Sagar 1992).

Field studies, like this one, which are conducted to assess the environmental fate of agriculturally applied pesticides, contribute to the informed prevention of environmental degradation associated with the use of pesticides. Such studies are also useful in gaining a clearer understanding of the processes governing the fate of pesticides. Data obtained from field studies are designed to complement data obtained from laboratory fate studies (Main 1995; Vereecken and Doring 1995).

In Malaysia, methamidophos is one of the organophosphorus insecticides used to control insect pests such as *Plutella xylostella* in the cultivation of cruciferous vegetables and tobacco (Cheah 1996; Cheah et al. 1994). Heavy use of this compound in combating insect pests may cause bioaccumulation in the environment and consequently may exert an adverse effect on non-target organisms.

Although field measurements of the environmental fate of this pesticide have been reported, only limited studies have been conducted in Malaysia (Cheah1996). Therefore, data on the fate of methamidophos under tropical conditions such as

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those found in Malaysia are important. The objective of this study was to determine the movement and persistence of methamidophos under field conditions in the Cameron Highlands.

MATERIALS AND METHODS

The field study was undertaken in the Cameron Highlands, Pahang, in Peninsular Malaysia. The Cameron Highlands is located at an altitude of between 1,280 m and 1,830 m above sea level. Its soils are predominantly sandy loam in texture (69% sand, 23% silt, 8% clay, pH 4.5-5.5, CEC 8.17 cmol kg^{-1}, 1.9% organic carbon). The average monthly rainfall is between 105 and 317 mm with an average yearly rainfall of 2474 mm. The Cameron Highlands' high altitude gives it a cool sub-tropical climate, with a mean daily temperature ranging from 14^0C to 21^0C, and an average daily relative humidity of 88%.

The experimental plot consisted of a rectangular area 15 x 10 m surrounded by wooden boards pushed into the soil to a depth of 5 cm with 30 cm protruding above the soil surface. The boards were covered with polyethylene plastic to ensure that only the surface flow generated within the confined plots was collected. A directional flow of runoff from the plot was effected by the construction of a concrete drain at the lower end of the plot and the installation of a 1.2 m-long metallic pipe leading into a collecting system. The bucket was installed under a shelter to prevent direct contribution to water volume by natural precipitation at the point of collection.

Two lysimeters were installed in each plot to collect pesticide leachate. The lysimeter was constructed in the shape of a trapezium with the rear end measuring 102 cm (length) x 56-cm (wide) x 35 cm (height). An opening was made on the floor at the deeper portion of the lysimeter where a 6-mm (i.d.) teflon tube was attached. Another opening was made at a central location 5 cm from the lower end of the lysimeter. A 15-mm (i.d.) plastic tube was connected to the opening. A 25 µm glass fibre filter was used to keep soil particles from falling directly into the leachate.

Cabbage (*Brassica oleraceae* var. *capitata*) and sweet peas (*Pisum sativum*) were cultivated in plots 1 and 2, respectively. Fourteen bunds, each measuring 10 m x 0.8 m, were prepared according to the usual conservation practice of farmers in the Cameron Highlands. The bunds were separated by furrows of 0.27 m.

Six-week-old seedlings were planted on the bunds of plot 1. Planting was carried out on 31 December 1997 at a distance of 30 - 40 cm within rows and about 70 cm between rows. Methamidophos (Tamaron®) was applied as normally practised by farmers at 1.76 g L^{-1} on 10 January, 4 February and 19 March 1998.

Runoff water (2.5 L) from plot 1 was sampled in the tipping bucket at 0

(immediately after treatment), 7, 21 and 24 days after treatment (DAT). Sediments were collected at 0, 4, 5, 7, 21 and 24 DAT. The leachates from plot 1 were sampled at 0, 1, 2, 3, 4, 5 and 7 DAT. In order to determine the persistence of methamidophos under these field conditions, cores of soil samples were taken with an auger to depths of 10 cm, 20 cm, 30 cm, 40 cm and 50 cm at 0, 3, 4, 5 and 7 DAT. All samples were stored in the refrigerator at -5 °C prior to analysis, which was carried out within 3-7 days.

In plot 2, samples of runoff (at 10, 29, 44, 54, 79, 111, 112 and 125 DAT), sediment (at 5, 10, 14, 20, 29, 44, 61, 80, 114 and 143 DAT), leachate (at 7, 54, 82, 86 and 113 DAT) and soils at five different depths (at 27, 60 and 82 DAT) were stored and analyzed as in plot 1.

The USEPA multi-residue method (EPA 1977) was used in the analysis of methamidophos residues in soils. A 10-g sub-sample was weighed and placed in a Soxhlet extraction thimble (Whatman, 80 mm long x 25 mm i.d.). Anhydrous sodium sulphate was added to the sample and thoroughly mixed using a glass stirring rod. A mixture of acetone and hexane (100 ml, 1:1 v/v) together with two glass beads were added to each round-bottom flask of the Soxhlet extraction assembly. All the components of the apparatus including the 125 mL capacity round-bottom flask, extraction tube and the condenser were assembled on a heating mantle. The sample was extracted for 8 hr. The flask was allowed to cool and the solvent was evaporated to about 5 mL using a rotary evaporator.

Florisil (60/100 mesh), which had previously been activated at 130°C for 16 hr, was transferred while hot into a glass column (300 mm long x 25 mm i.d.) until a 4-inch column was obtained. A 1.5-cm layer of anhydrous sodium sulphate was placed on top of the florisil without mixing. The column was allowed to cool to room temperature and pre-wet with 40 - 50 mL of petroleum ether (at boiling point 40-60°C) to flow through the column. Subsequent operations were carefully monitored so that the column did not run dry.

The extract was transferred from the concentrator tube to the column using a disposable Pasteur pipette. The transfer was timed to coincide to just when the pre-wetting agent receded to the top of the layer of anhydrous sodium sulphate. The concentration tube was rinsed with two successive 5 mL portions of hexane and the rinsings were transferred to the column with the pipette.

When the last of the solvent reached the top of the sodium sulphate, a total of 200 mL of the eluting mixture of 6% diethyl ether in petroleum ether was added. The elution rate was maintained at 5 mL min^{-1}. When the 6% elution mixture receded to the top of the sodium sulphate, the Erlenmeyer flask containing the eluate was replaced with a fresh one and the column was eluted with 15% diethyl ether in the petroleum ether. The process was repeated with 200 mL of 50% diethyl ether in the petroleum ether. The eluates were separately concentrated almost to dryness

using a rotary evaporator and transferred to a graduated glass tube with hexane and concentrated to a final volume of 1 mL using a gentle stream of purified nitrogen gas prior to chromatographic analysis.

The multi-residue technique (EPA 1977) was also used in the analysis of methamidophos residues in runoff water and leachate. The sample (500 mL) was extracted with 200 mL methylene chloride/hexane mixture (15:85 v/v) in a 2-L separating funnel. The aqueous phase was drained and the extraction process repeated two more times. The solvent mixture was added together and dried over a column of anhydrous sodium sulphate, then concentrated to about 5 mL using a rotary evaporator in a water bath at a temperature of 40°C. A stream of nitrogen was used to evaporate hexane to about 0.5 mL. Hexane (3 mL) was subsequently added and evaporated to 0.5 mL. This process was repeated two times to ensure the removal of traces of methylene chloride. As no interference in the gas chromatography determination occurred, the clean-up process was not necessary.

For the determination of methamidophos residues, the extracts of soil, runoff water and leachates were investigated on a gas chromatograph (Hewlett Packard Model 5890) equipped with a nitrogen-phosphorous detector (NPD). Temperature programming was also used, with an initial temperature of 50°C maintained for 3 min and raised to 200°C for 16 min. Injector and detector temperatures were kept adjusted at 250°C and 280°C, respectively. The capillary column employed was Carbowax, 25 m long, 0.32 mm i. d. and 0.3 μm film thickness. The carrier gas (helium) flow was maintained at 2 mL min^{-1}. Under the conditions described, the minimum detection limits of methamidophos in water and soil were 0.01 ng mL^{-1} and 0.002 mg kg^{-1}, respectively.

Recovery studies on spiked samples of methamidophos were carried out to evaluate the efficiency of the method. Methamidophos was spiked onto sandy loam soil from the same location at 0.01 mg kg^{-1} and 0.1 mg kg^{-1}. The residues were extracted and analyzed as described. Recoveries obtained for the methamidophos were between 79.5% to 86.5%.

The insecticide was also spiked into distilled water to provide concentrations of 0.01, 0.1 and 1.0 ng ml^{-1} and extraction was carried as described previously. Recoveries of methamidophos were between 78.3% to 89.6%.

RESULTS AND DISCUSSION

Leaching of methamidophos was not detected on the day of treatment. Residues of the insecticide were, however, detected at 2, 3, and 4 DAT with residue levels ranging from 0.03 ng mL^{-1} to 0.2 ng mL^{-1} (Table 1). The highest and lowest residue levels were detected at 3 DAT and 4 DAT, respectively.

Leaching of methamidophos was not observed at 0 DAT and 1 DAT. That

Table 1. Methamidophos residues in the leachate

Days after treatment	Concentration (ng mL^{-1})
-1	ND
0	ND
1	ND
2	0.068
3	0.203
4	0.028
5	ND
7	ND

ND: not detected

Table 2. Methamidophos residues in the runoff water

Days after treatment	Concentration (ng mL^{-1})
0	ND
7	0.643
21	ND
24	ND

ND: not detected

methamidophos residue was not detected within the first DAT may be due to the fact that the input of water to the soil was not sufficient to initiate substantial movement of the pesticide to the depth of 40 cm where the lysimeter was situated. But as the soil became more saturated, there was sufficient leaching beyond the root zone to enable the detection of methamidophos residues at 2, 3 and 4 DAT.

The relatively short time it took for methamidophos to be detected in the lysimeter demonstrated the high mobility of the pesticide in the sandy loam soil. This is in conformity with earlier findings on the mobility of the insecticide in laboratory experiments. A K_{oc} of 20.83 was observed for methamidophos in the sandy loam soil, which implies very high mobility. Soil thin-layer chromatography and soil column studies also point to the high mobility of methamidophos. A high R_f of 0.92 in the soil thin layer chromatography study has been obtained for methamidophos (Enoma 1999). Soil column studies showed increasing amounts of methamidophos residues in the leachate with increasing simulated rainfall, suggesting that the movement of methamidophos would be more severe under intensive precipitation.

Leachates collected at 5 and 7 DAT were devoid of methamidophos residues. This showed that although methamidophos is highly mobile in the sandy loam soil, it is not persistent. It also demonstrated that the half-life of a pesticide in soil is one of the important factors that determine its potential to leach. The half-life of

Table 3. Methamidophos residues in the sediment

Days after treatment	Concentration (mg kg^{-1})
-1	ND
4	0.095
5	0.261
7	0.327
21	0.095
24	0.077

ND: not detected

Table 4. Methamidophos residues at different soil depths

DAT	Concentration at different depths of soil (mg kg^{-1})				
	0-10 cm	10-20 cm	20-30 cm	30-40 cm	40-50 cm
3	0.034	0.010	0.009	0.006	0.004
5	0.020	0.009	0.008	0.004	0.003
7	0.014	0.005	0.004	0.002	ND

ND: not detected

methamidophos in the sandy loam soil has been evaluated under laboratory studies to be about 5 days (Enoma 1999).

A runoff sample collected at 7 DAT showed the presence of 0.643 ng mL^{-1} of methamidophos residues (Table 2). The pesticide was not detected in subsequent runoff samples collected at 21 and 24 DAT. The absence of the insecticide residues in runoff at the latter sampling intervals suggests rapid dissipation of methamidophos in the sandy loam soil. It is, therefore, not surprising that Cheah (1996) did not find methamidophos residues in his broadscale survey of water sources in the Cameron Highlands and Johore agroecosystems. Sethunathan et al. (1977) reported that most organophosphates such as parathion have a short half-life in water with little indication of residue build-up. This observation is in line with that reported by Goebel et al. (1982) who observed that the organophosphorous pesticides are hydrolyzed rapidly and demonstrate short half-lives in water due to their high solubility in that medium.

Methamidophos residues in sediment were detected at every interval of the sampling period, with concentrations ranging from 0.077 mg kg^{-1} to 0.327 mg kg^{-1} (Table 3). A fluctuation in the level of methamidophos within the sampling interval was observed. This may be attributed to differences in rainfall, temperature, and agronomic practices among other factors between sampling intervals. The lowest levels of 0.095 mg kg^{-1} and 0.077 mg kg^{-1} were detected at 21 and 24 DAT, respectively. These results indicated the non-persistent nature of methamidophos.

Methamidophos was detected at different depths of the soil profile throughout the sampling period. Residue levels ranged from <0.002 mg kg^{-1} at 7 DAT to 0.034 mg kg^{-1} at 3 DAT (Table 4).

Residue levels at 3, 5 and 7 DAT ranged from 0.004 mg kg^{-1} to 0.034 mg kg^{-1}, 0.003 mg kg^{-1} to 0.020 mg kg^{-1} and 0.002 mg kg^{-1} to 0.014 mg kg^{-1} respectively. Decreasing residue levels of 0.034 mg kg^{-1} (0 - 10 cm), 0.010 mg kg^{-1} (10 - 20 cm), 0.009 mg kg^{-1} (20 - 30 cm) 0.006 mg kg^{-1} (30 - 40 cm) and 0.004 mg kg^{-1} (40 - 50 cm) were detected with increasing depths at 3 DAT. This trend was also observed for sampling conducted at 5 DAT and 7 DAT. Residues were consistently higher at the 0 - 10 cm depth. This may be due to higher organic matter content at this depth arising from the application of organic manure such as chicken dung and deposits of crop residues. It has been observed, however, that some organophosphates behave like the chlorinated organics with higher adsorption in the surface soil (Whitney 1967; Swoboda and Thomas 1968).

Methamidophos residues decreased rapidly with increasing sampling intervals. The insecticide level reduced by 41% (5 DAT) and 58.82% (7 DAT) at the 0-10 cm layer from an initial concentration of 0.034 mg kg^{-1} (3 DAT). This is a reflection of the short half-life of methamidophos in the sandy loam soil. Previous studies by Cheah (1996) did not indicate the presence of methamidophos residues in the sandy loam soils of the Cameron Highlands and Johore agroecosystems. The results of this study are in agreement with previous findings.

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REFERENCES

Ahuja LR (1986) Characterization and modelling of chemical transfer to runoff. Adv Soil Sci 4:149-188

Cheah UB (1996) The environmental fate of selected pesticides in Malaysian agroecosystems. Ph D Thesis. University of Strathclyde, Glasgow

Cheah UB, Sharma ML, Aminuddin BY, Mohammud CH, Zain-Mohd M (1994) Agricultural impacts on groundwater quality. Australian Centre for International Agricultural Research Proceedings 61:22-28

Enoma ASO (1999) The environmental fate of selected pesticides in Malaysian agricultural soils. Ph D Thesis. Universiti Kebangsaan Malaysia, Bangi.

EPA (1977) Manual of analytical methods for the analysis of pesticide residues in human and environmental samples. United States Environmental Protection Agency, Washington DC.

Goebel H, Gorbach S, Knauf W, Rimpau RH, Huttenbach H (1982) Properties, effects, residues and analytics of the insecticide endosulfan. Residue Rev 83:1-165

Ismail BS, Kalithasan K (1997) Effects of repeated application on persistence and

downward movement of four herbicides in soil. Australian J Soil Res 35:503-513
Klöppel H, Haider J, Kördel W (1994) Herbicides in surface runoff: A rainfall simulation study on small plots in the field. Chemosphere 28:649-662
Main DS (1995) The fate of selected herbicides in agricultural soils. Ph D Thesis. University of Strathclyde, Glasgow
Oppong K F, Sagar GR (1992) The activity and mobility of triasulfuron in soil as influenced by organic matter, duration, amount and frequency of rain. Weed Res 32:157- 165
Riley MB, Keese RJ, Camper ND, Whitwell T, Wilson PC (1994) Pendimethalin and oxyfluorfen residues in pond water and sediment from container plant nurseries. Weed Tech 8:299-303
Sethunathan N, Siddaramappa R, Rajaram KP, Barik S, Wahid PA (1977) Parathion: residues in soil and water. Residue Rev 68:9-122
Swoboda AR, Thomas GW (1968) Movement of parathion in soil columns. J Agric Food Chem 16:923-927
Talekar NS, Lee EM, Chen JS, Sun TL (1978) Insecticide residues in subtropical soil: Their degradation, persistence and absorption into root crops. Pesticide Manag, Biotrop Spec Publ 7:105-115
Vereecken H, Doring U (1995) The fate and mobility of pesticides at laboratory, lysimeter and field scale: A European project. In: Walker A, Allen R, Bailey SW, Blair AM, Brown CD, Gunther P, Leake CR, Nicholls PH (eds). Pesticide movement to water, British Crop Protection Council, London. p 147-154
Wauchope RD (1978) The pesticide content of surface water draining from agricultural fields – A review. J Environ Qual 7:459-472
Whitney WK (1967) Laboratory tests with dursban and other insecticides in soil. J Econ Entomol 60:68-74