Bull. Environ. Contam. Toxicol. (2004) 72:836–843

Bulletin of Environmental Contamination and Toxicology

Leaching Potential of Pesticides in a Vegetable Farm in the Cameron Highlands, Malaysia

B. S. Ismail,[1] C. K. Ngan,[1] U. B. Cheah,[2] W. Y. Wah Abdullah[3]

[1] School of Environmental and Natural Resource Sciences, Universiti Kebangsaan Malaysia, 43600 UKM, Bangi, Selangor, Malaysia
[2] Malaysian Agriculture Research and Development Institute (MARDI) Serdang, 43400 Selangor, Malaysia
[3] Malaysian Agriculture Research and Development Institute (MARDI) Cameron Highlands, 39200 Tanah Rata, Pahang, Malaysia

Received: 30 July 2003/Accepted: 5 January 2004

In modern agricultural practices, pesticides are used in order to reduce yield loss caused by pests although it is already known that excessive pesticide application could cause environmental problems. Bypass flow (overland and vertically through macropores) has been identified as an important mechanism for transporting pesticides to surface and groundwater (Foster et al. 1991; Williams et al. 1991). Pesticides can be transported by bypass flow either in solution or adsorbed on suspended or colloidal matter. Worrall et al. (1995) studied the properties of vertical bypass flow, which used a lysimeter to investigate suspended and colloidal matter in leachates. Vertical bypass flow can cause poor pest control, crop injury, and increased loss of pesticide or accumulation of pesticide in the soil (Kloppel et al. 1994).

The degree of damage suffered by crops varied with the aggregate stability and pore-size distribution of the topsoil (Hazelden 1991). The widespread use of pesticides has caused concerns about environmental pesticide contamination. Farmers tend to apply pesticides more frequently and sometimes at higher doses in order to control insect pests effectively. Continuous use of pesticides has been reported to cause contamination of surface and ground water as reported in several parts of the world (Kookana et al. 2001). Significant amounts of chlorpyrifos residues in ground water have been reported (Salama et al. 2001). The degree of pollution is exacerbated if it involves persistent pesticides. Preliminary studies have shown that chlorothalonil, a chlorinated fungicide, and chlorphyrifos and profenofos, organophosphate insecticides, are widely used in vegetable farms in the Cameron Highlands, Malaysia. However, studies on pesticide contamination in Malaysian agroecosystems are limited (Enoma et al. 2001). This study was conducted to examine the leaching potential of chlorothalonil, chlorpyrifos and profenofos in the vegetable agroecosystem of the Cameron Highlands, Malaysia.

MATERIALS AND METHODS

The field study was undertaken in the Cameron Highlands, which is situated in the north of the country and 1,830 m above sea level. It covers an area of 71,218 ha, of which about 7.2% is under cultivation.

Correspondence to: B. S. Ismail

The Highlands are characterized by rugged terrains and slopes that are often greater than 40^o in steepness. The soils are predominantly sandy loam in texture. Soil pH ranges between 4.5 and 5.5, but may be considerably higher in those areas previously treated with lime. The average monthly rainfall is between 105 and 317 mm with an average yearly rainfall of 2474 mm. The average daily relative humidity is 88%. The Cameron Highlands' dominant feature of high altitude gives it a cool sub-tropical climate with mean daily temperature ranging from 14^0 to 21^0C.

The experimental plot was established on a uniform slope of 2%. The plot consisted of a rectangular area of 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 surrounding drain was built around the plot to channel the runoff water and sediment to a collecting point where runoff water and sediment samples were collected. Sediments and surface water were collected using a bucket, which was installed under a shelter to prevent direct contribution to water volume by natural precipitation at the point of collection.

A lysimeter was installed in the plot to collect and measure leaching of the pesticides. 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) and gradually tapered at the front end to a height of 30 cm. The lysimeter was fabricated from stainless steel to withstand rusting throughout the duration of the experiment. 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 breather tube was connected to the opening. The lysimeter was partitioned into two parts by a PVC netting and a blanket of 25 μm glass fibre filter to keep soil particles from falling directly into the leachate. Leaching of water under the plot was collected from a lysimeter buried under the plot.

Sweet peas (*Pisum sativum*) were planted in the plots on January 4, 2000. 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 width. The pesticides used were chlorothalonil (Daconil®; containing 50% a.i w/w), chlorpyrifos (Dursban®; containing 30% a.i. v/v) and profenofos (Selecron®; containing 45% a.i. v/v). The treatments applied were chosen to be similar to the farmers' practices. The plot was sprayed using a knapsack sprayer at a spraying volume of 800 L ha^{-1}. The plot was first sprayed on January 19, 2000 (chlorothalonil and chlorpyrifos), then on February 2, 2000 (chlorothalonil and chlorpyrifos), on February 9, 2000 (chlorothalonil and profenofos), on February 16, 2000 (chlorothalonil and chlorpyrifos), on March 1, 2000 (chlorothalonil and chlorpyrifos) and finally on March 13, 2000 (chlorothalonil and chlorpyrifos and profenofos). The treatment rates for chlorothalonil, chlorpyrifos and profenofos were 0.12 kg a.i ha^{-1}, 0.67 kg a.i ha^{-1}

and 0.79 kg a.i ha^{-1}, respectively. Runoff water (2.5 L), leachate (2.5 L) and sediments (50 g) from the plot were sampled in the tipping bucket at 3 days before the first treatment and at intervals for 60 days after the last treatment.

The leachates collected from the lysimeter were sampled at day 3 before treatment and at intervals for 60 days after the last treatment. In order to determine the persistence of profenofos and chlorpyrifos under these field conditions, core soil samples were taken with an auger to depths of 10, 20, 30, 40 and 50 cm between 1 to 60 days after the last treatment. All samples were stored in the refrigerator at -5°C prior to analysis, which was carried out within 7 days after sampling.

Residues of the three pesticides in water samples were extracted in liquid-liquid extraction and the organic solvent was further concentrated and subjected to gas chromatography (GC) (Rand et al. 1976). However, for pesticide extraction from soil and sediment samples, different methods were employed for each pesticide. Chlorothalonil residue was extracted by shaking with acidic acetone. The solvent was then subjected to liquid-liquid extraction and the organic solvent was concentrated before subjecting it to GC. Chlorpyrifos residue was extracted with a hexane:acetone mixture (1:1) in Soxhlet extraction for 8 hr (USEPA 1977). The extract was concentrated and cleaned up with florisil. The extract then was concentrated again before subjecting it to GC. Profenofos residue was extracted with acetone in Soxhlet extraction for 4 hr. The extracted solvent was concentrated and extracted again in liquid-liquid extraction with dichloromethane. The extract was evaporated to dryness and redissolved in acetone before subjecting it to GC. A Hewlett-Packard model 6890 GC was used for residue detection. Chlorothalonil extracts were examined on GC equipped with electron capture detector (GC-ECD Hewlett-Packard G1530A). Temperature programming was also used, with an initial temperature of 100°C maintained for 1 min and raised to 250°C for 13.6 min. Injector and detector temperatures were kept adjusted to 250°C and 350°C, respectively. The capillary column employed was DB608, 30 m long, 0.32 mm i.d. and 0.25 µm film thickness. The carrier gas (helium) flow was maintained at 2 mL min^{-1}. Chlorpyrifos and profenofos extracts were detected on GC equipped with Nitrogen Phosphorus Detector (GC-NPD Hewlett-Packard 5890). Temperature programming was also used, with an initial temperature of 100°C maintained for 1 min and raised to 250°C for 4 min. Injector and detector temperatures were kept adjusted to 280°C and 300°C, respectively. The capillary column employed was UB3, 25 m long, 0.32 mm i.d. and 0.52 µm film thickness. The carrier gas (helium) flow was maintained at 2 mL min^{-1}. The recoveries of the three pesticides in water and soil samples were within the accepted value of >82% and >86%, respectively, when the samples were spiked at 0.01 mg kg^{-1}. The detection limit of the three pesticides in water samples was 0.01 ng mL^{-1} and in soil samples, 0.01 mg kg^{-1}.

RESULTS AND DISCUSSION

Table 1 shows the concentrations of chlorothalonil, chlorpyrifos and profenofos residues in bedload sediment. The range of concentrations found in bedload sediment for chlorothalonil, chlorpyrifos and profenofos were 0.008-0.111 mg kg^{-1}, 0.009-0.619 mg kg^{-1} and 0.009-0.350 mg kg^{-1}, respectively. Residues of chlorpyrifos and profenofos were not detected in the sediment on days 20 and 30, respectively. On the other hand, chlorothalonil residues could be detected in sediment up to day 60. Chlorpyrifos and profenofos concentrations in sediment were higher than chlorthalonil concentrations at day 2. This could be due to the wet sediment sample collected, which tends to have higher amounts of water-soluble pesticide. Profenofos has the highest water solubility (20 μg L^{-1}), followed by chlorpyrifos (2 μg mL^{-1}) and then chlorothalonil (0.2 μg mL^{-1}). Residues of these pesticides in the sediment showed a decrease in concentration with increasing sampling intervals. This decrease in concentration was probably due to various factors such as leaching, run-off, evaporation and degradation processes.

Table 2 shows the pesticide residues in leachate sampled from the lysimeter. The range of concentrations detected in leachate for chlorothalonil and chlorpyrifos were 0.005–0.014 ng mL^{-1} and 0.010-0.045 ng mL^{-1}, respectively. In general, a low concentration of the pesticides was detected in the water sampled from the lysimeter. This may be due to a large amount of the residues being adsorbed to the sediment. The residue of chlorothalonil and chlorpyrifos could be detected in the leachates up to 20 and 14 days, respectively. However, the residue of profenofos was detected only once on day 14 at approximately 0.018 ng mL^{-1}. These results indicate that the pesticides had a limited mobility in the soil studied as much of them were transported together with sediment.

Table 3 shows the residue concentrations of the three pesticides in runoff water samples. In runoff water samples, chlorothalonil, chlorpyrifos and profenofos were detected at levels ranging from 0.005 – 0.021 ng mL^{-1}, 0.016 – 0.083 ng mL^{-1} and 0.011 – 0.056 ng mL^{-1}, respectively. In general, the residue concentration of chlorothalonil decreased as the sampling intervals were lengthened, but, in contrast, the concentration of chlorpyrifos in runoff water increased. This may have been due to desorption of chlorpyrifos into water, as chlorpyrifos has high solubility. Residues of the chlorothalonil, chlorpyrifos and profenofos were not detected in surface runoff on day 30. It is well known that the leaching potentials of the pesticides are greatly influenced by the physico-chemical properties of the compounds, the soil components and environmental factors, such as amount of rainfall. In this case, the solubility of the compound and sorptive capacity may contribute at least in part in determining the leaching potential of the compounds. This may explain the low levels of chlorothalonil in the leachate and surface water. The residue of profenofos in surface water was found to be higher than chlorpyrifos, although it was applied only twice. However, the fluctuating concentration of profonefos in surface water and leachate could be attributed to rainfall variation in the area, and more residues were found in sediment.

Tables 4, 5 and 6 show the residues of chlorthalonil, chlorpyrifos and profenofos in the soil profiles, respectively. A high concentration of chlorothalonil was found in the top 20 cm of the soil core within 4 days after last treatment, but no residue was detected on day 6. Similarly, residues of chlropyrifos and profenofos

Table 1. Residue concentrations (mg kg^{-1}) in bedload sediment (± SD).

Days after treatment	Chlorothalonil	Chlorpyrifos	Profenofos
-3	ND	ND	ND
2	0.111± 0.002	0.619±0.001	0.350±0.020
3	0.065±0.025	0.184±0.010	0.127±0.036
4	0.051±0.005	0.158±0.010	0.087±0.050
6	0.046±0.003	0.120±0.050	0.055±0.002
10	0.012±0.001	0.081±0.009	0.013±0.002
14	0.011±0.006	0.009±0.001	0.013±0.004
20	0.009±0.005	ND	0.009±0.006
30	0.008±0.003	ND	ND
45	0.008±0.001	ND	ND
60	0.008±0.004	ND	ND

ND = not detected

Table 2. Residue concentrations (ng mL^{-1}) in leachates (± SD).

Days after treatment	Chlorothalonil	Chlorpyrifos	Profenofos
-3	ND	ND	ND
2	0.012± 0.002	0.015 ±0.004	ND
3	0.008±0.001	0.022 ±0.003	ND
4	0.014 ±0.001	0.045 ±0.002	ND
10	0.006 ±0.005	0.027 ±0.005	ND
14	0.006±0.001	0.010 ±0.001	0.018 ± 0.002
20	0.005±0.001	ND	ND
30	ND	ND	ND
45	ND	ND	ND
60	ND	ND	ND

ND = not detected

Table 3. Residue concentrations (ng mL^{-1}) in surface water runoff (± SD).

Days after treatment	Chlorothalonil	Chlorpyrifos	Profenofos
-3	ND	ND	ND
2	0.021±0.001	0.016±0.001	0.011±0.006
3	ND	0.031±0.009	ND
4	0.005±0.002	0.049±0.001	ND
6	0.006±0.005	0.056±0.001	ND
10	0.007±0.002	0.018±0.002	0.080±0.002
14	0.005±0.004	0.083±0.010	0.056±0.008
30	ND	ND	ND
45	ND	ND	ND
60	ND	ND	ND

ND = not detected

Table 4. Chlorothalonil residue (mg kg^{-1}) in different soil profiles (± SD).

Day after treatment	Depth (cm) 0-10	10-20	20-30	30-40	40-50
1	0.083±0.008	0.005±0.001	0.005±0.002	0.005±0.001	ND
2	0.078±0.006	0.007±0.005	ND	0.007±0.001	ND
3	0.044±0.004	0.042±0.007	ND	ND	ND
4	0.030±0.008	0.010±0.008	ND	ND	ND
6	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND
20	ND	ND	ND	ND	ND
30	ND	ND	ND	ND	ND
45	ND	ND	ND	ND	ND
60	ND	ND	ND	ND	ND

Table 5. Chlorpyrifos residue (mg kg^{-1}) in different soil profiles (± SD).

Day after treatment	Depth (cm) 0-10	10-20	20-30	30-40	40-50
1	0.065 ±0.003	0.029 ±0.003	0.019 ±0.002	0.019 ±0.240	0.019 ±0.002
2	0.005 ±0.001	ND	ND	ND	ND
3	0.007 ±0.002	ND	ND	ND	ND
4	0.005 ±0.002	ND	0.005 ±0.001	ND	ND
6	ND	ND	ND	ND	ND
10	ND	ND	ND	ND	ND
20	ND	ND	ND	ND	ND
30	ND	ND	ND	ND	ND
45	ND	ND	ND	ND	ND
60	ND	ND	ND	ND	ND

Table 6. Profenofos concentration (mg kg^{-1}) in different soil profiles (± SD).

Day after treatment	Depth (cm) 0-10	10-20	20-30	30-40	40-50
1	0.02±0.010	ND	ND	ND	ND
2	0.45±0.010	ND	0.27±0.01	0.14±0.020	0.22±0.023
3	0.26±0.007	ND	0.21±0.01	0.31±0.012	0.32±0.015
4	0.12±0.008	ND	ND	ND	ND
6	0.21±0.008	ND	0.29±0.01	0.25±0.006	ND
10	ND	ND	ND	ND	ND
20	ND	ND	ND	ND	ND
30	ND	ND	ND	ND	ND
45	ND	ND	ND	ND	ND
60	ND	ND	ND	ND	ND

ND = not detected

accumulated in the top 10 cm within 4 and 6 days, respectively, after the last application. Residues of chlorothalonil and chlorpyrifos were detected in the 30-40 cm and 40-50 cm depths, respectively, at day 1 after the last application. However, no residues were detected in the soil profile at depths greater than 10 cm at day 2. The residue of profenofos could be detected in soil at 40-50 cm depth at days 2 and 3 after the last application. This result clearly shows that the compounds did not persist in soil for more than 6 days, perhaps due to degradation processes (Singh-Kumar et al. 2002). Earlier reports had shown that the half-lives of chlorpyrifos, chlorothalonil and profenofos ranged from 10-120 days (Racke et al. 1992), 8.6 to 215 days (Singh-Kumar et al. 2002), and 8-10 days (Enoma et al. 2001), respectively. Our results seem to indicate that the dissipation rate we found was faster than those reported in earlier studies, which may be in part attributable to environmental factors such as higher rainfall in the tropics than under temperate conditions.

In conclusion, our results showed that the downward mobility of these pesticides is low and is unlikely to contaminate underground water in the study area. In soil, these pesticides seem less persistent, probably because of their high dissipation rates or because they are transported via sedimentation.

Acknowledgments. The death of Dr. UB Cheah was a great loss not only for our research team but also for the greater scientific community. His presence and contribution will be sorely missed. We thank Mrs. Jamiah Jaafar, Mr. Lim Teck Poi, Mrs. Siti Rahmah and Mr. Ma Choon Kwong for their assistance. This paper is part of the second author's Masters thesis submitted to the Faculty of Science and Technology, UKM. The authors express their sincere thanks to Mrs. Alena Sanusi for helpful comments on the manuscript. This work was funded by research grant IRPA 08-02-02-0011-EA185 from the Ministry of Science, Technology and Environment of Malaysia.

REFERENCES

Enoma AOS, Cheah UB, Lum KY, Ismail BS, Malik Z, Wan-Abdullah WY (2001) Fate of endosulfan and methamidophos in Cameron Highlands agroecosystems. In: Salama RB, Kookana RS (eds). Agrochemical pollution of water resources, Australian Centre for International Agricultural Research Proceedings No. 104. Australian Centre for International Agricultural Research, Canberra, p 45-51

Foster SSD, Chilton PJ, Stuart ME (1991) Mechanisms of groundwater pollution by pesticides. J Inst Water Environ Manag 5: 186-193

Hazelden J (1991) Soil properties affecting the carry-over of a herbicide. In Walker A (ed). Pesticides in soils and water: Current perspectives, British Crop Protection Council Monograph No. 47, British Crop Protection Council, Farham, p 93-100

Kloppel H, Haider J, Kordel W (1994) Herbicides in surface runoff: A rainfall simulation study on small plots in the field. Chemospere 28: 649-662

Kookana RS, Kerekes A, Oliver D, Salama RB, Byrne JD (2001) Sorption of selected pesticides and their metabolites in soil profiles of the Swan Costal Plain. In: Salama RB, Kookana RS (eds). Agrochemical pollution of water resources, Australian Centre for International Agricultural Research Proceedings No. 104. Australian Centre for International Agricultural Research, Canberra, p128-134

Racke KD (1992) The environmental fate of chlorpyrifos. Rev Environ Contam Toxicol 131: 1-151

Rand MC, Greenberg AE, Taras MJ (1976) Standard methods for the examination of water and wastewater. 17th Edn. Washington: American Public Health Association

Salama RB, Byrne JD, Pollock DW (2001) Nutrient and pesticide leaching in experimental sites in the Swan Coastal Plain. In: Salama RB, Kookana RS (eds). Agrochemical pollution of water resources, Australian Centre for International Agricultural Research Proceedings No. 104. Australian Centre for International Agricultural Research, Canberra, p 125-137

Singh-Kumar B, Walker A, Wright DJ (2002) Persistence of chlorpyrifos, fenamiphos, chlorothalonil and pendimethalin in soil and their effects on soil microbial characteristics. Bull Environ Contam Toxicol 69: 181-188

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

Williams RJ, Bird SC, Clare RW (1991) Simazine concentration in a stream of draining an agricultural catchment. J Inst Water Environ Manag 5: 80-84

Worrall F, Parker A, Rae JE, Johnson AC (1995) A study of suspended and colloidal matter in the leachate from lysimeters: Implications for pollution and lysimeter studies. In: Walker A, Allen R, Bailey SW, Blair AM, Brown CD, Gunter P, Leake CR, Nicholls PH (eds). Pesticide movement to water, British Crop Protection Council Monograph No.62. British Crop Protection Council, Farnham, p129-134