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Research article

COMPARISON OF THE MOBILITY OF THE HERBICIDES 2,4-D AND ^{14}C-PARAQUAT IN SELECTED MALAYSIAN AGRICULTURAL SOILS

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ABSTRACT: The increased use of agricultural chemicals has raised questions about the adverse effects of pesticides, consequences of leaching of toxic residues into water bodies. In the current study, the leaching behavior of 2,4-D (2,4-Dichlorophenoxyacetic acid) and paraquat (1,1'-dimethyl-4,4'-bipyridylium dichloride) was investigated under laboratory conditions. The residue levels of 2,4-D and ^{14}C-paraquat in the soil profile was determined using the High Performance Liquid Chromatography (HPLC) and the Liquid Scintillation Counter (LSC), respectively. The mobility of 2,4-D and ^{14}C-paraquat in two soil types (clay and clay loam) of the Kerian ricefields was determined using laboratory column experiments. The study showed that the mobility of 2,4-D is greater than paraquat in both soil types. The greater mobility of 2,4-D and its deeper penetration into the soil column probably due to its lower adsorption relative to that of paraquat. The difference in the 2,4-D mobility in the two soil types appears to be related to the organic carbon distribution in the soil profile, whereas, results showed that the total amount of ^{14}C-paraquat moving downward in both soil types was not affected significantly by the soil structure. The mobility of 2,4-D was found to be sensitive to the amount and duration of the percolated rainfall. The total amount of ^{14}C-paraquat that leached into the soil was not significantly affected by increase in the amount and duration of rain. Comparison of the mobility of 2,4-D and ^{14}C-paraquat in the intact-core and packed columns revealed that the extent of mobility was less in the intact soil core.
Keywords: Mobility, 2,4-D, ^{14}C-labeled paraquat, tropical agricultural soils, soil core

INTRODUCTION

Malaysia is a tropical country in which large areas of its land have been used for agriculture. The hot and humid climate of this tropical country has resulted in the exposure of agricultural crops to various pests and diseases. Therefore, the use of pesticides in Malaysia is a prerequisite for successful cultivation and agriculture production. However, the over use of pesticides has caused a series of environmental problems [1, 2, 3, 4, 5, 6, 7]. There are numerous factors that influence leaching, but the most important are the duration and amount of precipitation. Pesticide leaching generally increases with increased amount of precipitation [8, 9, 10, 11]. The effects of the amount and duration of rainfall on pesticide leaching depend also on soil texture and the chemical structure of the pesticides [12, 10]. Leaching, as reported by Chopra et al. [13], is the main cause of groundwater contamination by pesticides. In the present study, 2,4-D and paraquat were selected as model compounds, which are regularly being used for rice cultivation in Kerian, Perak. Research on the leaching of 2,4-D and paraquat in soils could be a good reference for understanding the mobility mechanism of ionisable herbicides in soils because 2,4-D is an anionic herbicide that is moderately adsorbed to soil [14] while paraquat is a cationic herbicide that is very strongly adsorbed to the clay fraction of soils and is quite immobile [15]. The objective of the study was to monitor the leaching behavior of 2,4-D and ^{14}C-paraquat through soil columns of the two selected soil types and also, to evaluate the effects of duration and amount of simulated rain on the mobility of 2,4-D and ^{14}C-paraquat. Figure 1 shows the chemical structures of 2,4-D and paraquat.

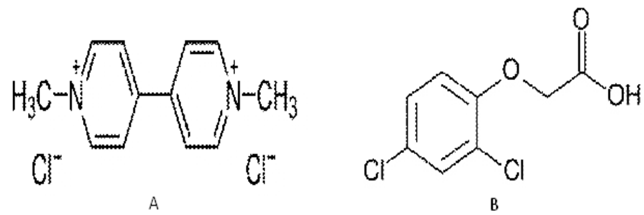

Fig. 1 Chemical structures of paraquat (A) and 2,4-D (B)

MATERIALS AND METHODS

All reagents used in the present study were of analytical grade. The HPLC-UV (Agilent 1100 series) and LSC (Model TR 2550 AB) were used to detect 2,4-D and ^{14}C-paraquat residues in the supernatant, respectively. The soils used in the study were clay and clay loam obtained from the Kerian rice fields**.** The 2,4-D of 99.7% purity was purchased from the laboratories of Dr. Ehrenstorfer, Germany. The Radio-labelled paraquat [Methyl-1-^{14}C] was obtained from the Institute of Isotopes, Budapest. The concentration of the radio-labelled paraquat was 100 µCi with a specific activity 32.3 mCi/mmol. Details of the chemicals and reagents, analytical instruments, standard solution preparation and ^{14}C-paraquat, 2,4-D extraction from soil samples are described in the extension of a previously published paper based on the kinetics of microbial degradation of 2,4-D and ^{14}C-paraquat [16].

In the current research, to evaluate the effect of simulated rainfall and soil texture on the mobility of 2,4-D and ^{14}C-paraquat, the method developed by Cox et al. [17] was adapted. The polyvinyl chloride (PVC) cylinders for the mobility study of 2,4-D were cut beginning at the top from 5.0 cm to 30.0 cm, at 5.0 cm intervals so as to produce six smaller tubes, which were re-assembled to create the whole column. However, because of strong adsorption of paraquat to all types of soil, the PVC cylinders for the mobility study of ^{14}C-paraquat were cut beginning at the top from 2.0 cm to 20.0 cm, at intervals of 2.0 cm, thus producing ten smaller tubes, which were re-assembled to create the whole column. The PVC columns were carefully hand-packed with both soil types, and the soil columns were maintained at 50% field capacity. The aqueous solution of each herbicide, corresponding to the maximum application rates in the agricultural areas (2 and 1.2 kgha^{-1} for 2,4-D and paraquat respectively) was applied to the top soil segments of the appropriate columns at concentrations appropriate for the two compounds. One hour after treatment, 25 mL of distilled water, simulating 5 mm rainfall per day was introduced into the columns. The PVC columns, carefully packed with clay loam soil, were then subjected to treatments similar to those described above. One hour after treatment with the herbicide, the soil columns were simulated with 5.0 or 10.0 mm rainfall and the procedure repeated daily for 10 days. In a different set of experiments, the PVC columns were prepared in the same way as described above, packed with clay loam soil and subjected to treatments similar to those described above. One hour after treatment, the columns were simulated with 5 mm rainfall and this was followed daily for 10, 15 and 20 days. At the end of each above treatment the columns were sectioned to analyze the distribution of 2,4-D and ^{14}C-paraquat in every soil segment. The treatments were replicated thrice (for the two herbicides) and two untreated control columns. To this end, a trial for comparison of the mobility of 2,4-D and ^{14}C-paraquat in the intact-core and packed columns revealing the extent of mobility was evaluated. Packed and intact core clay soil samples were prepared in a mini-lysimeter system. This comprised PVC tubes (8.5 cm diameter, 30 cm long; 8.5 cm diameter, 20 cm long; for 2,4-D and ^{14}C-paraquat respectively) containing disturbed and undisturbed soil from the Kerian rice field site. The intact core columns of soil were collected from the field by driving the tubes upside down into the soil until the soil surface was about 1 cm below the bottom of the tube. The intact core soil columns were removed by excavating the PVC tubes and carefully cutting across the soil at the base. The packed columns were prepared in the same way as described previously using clay soil. The amount of herbicide corresponding to the maximum application rate was applied to the top soil segments of the appropriate columns, as an aqueous solution at concentrations appropriate for the studied compounds. One hour after treatment, 5 mm of simulated rainfall was added, followed by the same amount daily for ten days. At the end of the ten days, the distribution of 2,4-D and ^{14}C-paraquat in each soil segment was analyzed as described previously. Two replicate columns for each treatment and two untreated control columns were maintained concurrently.

Statistical analysis

All data was subjected to analysis of variance and means were compared by the LSD test at the 5% level of significance.

RESULTS AND DISCUSSION

Effect of Daily Application of Simulated Rain on the Mobility of 2,4-D and ^{14}C-paraquat

In tropical developing countries, the leaching of pesticides through the soil has been the subject of much attention recently. However, evaluation of pesticide leaching under field conditions is difficult due to high variability caused by soil and climatic factors within and between years. On the other hand, the use of soil columns under laboratory conditions is a more economical and faster way of assessing pesticide leaching in the field. In the present study, evaluation of 2,4-D and ^{14}C-paraquat leaching under laboratory conditions could be a good reference for understanding and comparing the mobility mechanism of an anionic and cationic herbicide in Malaysian agricultural soils. Figure 2 and 3 show the 2,4-D and ^{14}C-paraquat residue detected in the soil column segments of both types of soil, respectively. It appeared that the structure of the soil and the total organic matter content influenced the mobility of 2,4-D in the soil column. From Figure 2, it can be seen that the mobility of 2,4-D significantly decreased in soil with higher content of organic matter. In the clay soil, the 2,4-D moved downward to 20 cm and no residue was observed below that depth. Meanwhile, in the clay loam soil, the 2,4-D moved only to the depth of 15 cm and was not detected below that depth. The average 2,4-D residue concentration (mg/kg) in the first 5 cm of the soil layer was 1.062 (±0.090) and 0.516 (±0.002) for the clay loam and clay soil, respectively. This data is in agreement with observations from other column studies, whereby the presence of organic matter decreased the movement of pesticides in the soil due to increased pesticide adsorption [18, 19, 20].
Figure 3 show that ^{14}C-paraquat residue was only detected at the surface layers (0- 4 cm) of both types of soil. The average ^{14}C-paraquat residue concentration (mg/kg) in the first 2 cm of the soil layer was 2.67 (±0.040) and 2.76 (±0.001) for clay loam and clay soil, respectively. The depth of distribution of ^{14}C-paraquat showed that there was little or no vertical movement of ^{14}C-paraquat in the soils. Results showed that vertical movement of dissolved paraquat was limited to the time of water percolation through the soil profile. However, the vertical movement of such a highly adsorbed pesticide may be significant if the pesticide is complex or adsorbed onto mobile colloids or dissolved organic matter. Paraquat residues at the soil surface could potentially pose some environmental risk through soil erosion that could cause the pesticide to enter the aquatic environment [21]. There was no evidence of the leaching of paraquat in the two types of soil tested as no trace of paraquat was detected below the depth of 4 cm. Thus, under selected conditions, paraquat would not be able to enter water bodies. The low mobility of paraquat in the soil column study was undoubtedly due to strong adsorption to the soil. It appeared that the structure of the soil and the total organic matter content did not have any influence on the mobility of paraquat in the soil column. Paraquat is strongly adsorbed to soil and is inactivated rapidly and completely by soil particles. It may be inactivated almost immediately on contact with the soil, precluding a build-up of active residues. The paraquat ions' positive charge is strongly attracted to the negative charge of soil clay particles and the soil's natural capacity for this herbicide is several hundred times more than the normally recommended application rate [22].

Effects of the Amount and Duration of Simulated Rain on the Mobility of 2,4-D and ^{14}C-paraquat in soil

In the current study, the importance of the amount and duration of rainfall with regards to the distribution of both herbicides throughout the packed soil columns of the clay loam soil was investigated. The 2,4-D content at the (0-30) cm soil depth in the clay loam soil for the two different amounts of simulated rainfall (5 and 10 mm) is presented in Table 1.

Table 1. Average 2,4-D residue concentrations (mg kg^{-1}) in packed clay loam columns for 5 and 10 mm of simulated rainfall.

	Soil layers (cm)					
Rainfall (mm)	0-5	5-10	10-15	15-20	20-25	25-30
5 mm	0.988 (±0.073)	0.596 (±0.041)	0.537 (±0.002)	ND	ND	ND
10 mm	0.373 (±0.012)	0.555 (±0.010)	0.382 (±0.002)	0.531 (±0.002)	0.201 (±0.001)	0.106 (±0.001)

ND=Not detected
Standard deviation (±)

Ten days after application of the herbicide, 2,4-D was detected mainly in the (0-15) cm zones. However, 10 mm of rainfall caused greater movement of 2,4-D than did 5 mm of rainfall (Table 1). The highest concentration of 2,4-D residues was observed in the (0–5) and (5-10) cm depth in the clay loam soil for simulated rainfall of 5 and 10 mm respectively. Consequently, 2,4-D mobility in the soil increased with increasing amount of rainfall. Aquino et al. [14] reported that 2,4-D may be quite mobile in aqueous systems because of its acidic carboxyl group ($pK_a = 2.8$) with high water solubility. The average 2,4-D residue concentrations in clay loam for 5 and 10 mm of simulated rainfall are summarized in Table 1. The concentration of 2,4-D residues in the first 5 cm of the clay loam soil layer was 0.988 (±0.073) and 0.373 (±0.012) mg/kg for 5 and 10 mm of simulated rainfall, respectively. These findings indicated that 2,4-D is more mobile with 10 mm of simulated rainfall than with 5mm. 2,4-D herbicides dissolve easily in water and in the present study it was found that 2,4-D moved almost at the same pace as the water down soil profile. The results reported are in line with those of Blenkinsop [8] and Lewan. [9] where it was suggested that pesticide leaching generally increases with increased amount of annual precipitation. The same continuous flow conditions used for the 2,4-D experiment was applied using ^{14}C-paraquat. The leaching behavior of ^{14}C-paraquat was studied in packed soil columns for two levels of simulated rainfall (5 and 10 mm). Table 2 represents the leaching profile of ^{14}C-paraquat in the packed soil columns after percolation of water equivalent to 5 and 10 mm rainfall. The results indicated that the ^{14}C-paraquat was fairly immobile in clay loam soil columns and mobility did not increase with increased volume of water. However, under both conditions of simulated rainfall, the ^{14}C-paraquat did not leach out of the column and was not detected below the depth of 6 cm. After percolation of water equivalent to 5mm of simulated rainfall, the ^{14}C-paraquat leached down to the (2-4) cm depth and approximately 96% of the applied herbicide was retained in the top (0-4) cm layer. Increasing the amount of water (by percolation) did not result in a significant increase in downward mobility and ^{14}C-paraquat continued to remain in the plough layer of the soil (0–6 cm) profile. These results are in agreement with those of Hartley and Kidd [23] where it was reported that paraquat was immobile in silty loam and silty clay loam soils, slightly mobile in sandy loam soils, and potentially mobile in sandy soils containing extremely low amounts of organic matter and clay. Paraquat is quickly and strongly adsorbed by soil particles and was shown to be very immobile in soil [24, 25, 26].

Table 2. Average ^{14}C-paraquat residue concentrations (mg kg^{-1}) in packed clay loam soil columns for 5 and 10 mm of simulated rainfall

	Soil layers (cm)							
Rainfall (mm)	0-2	2-4	4-8	8-10	10-12	12-14	16-18	18-20
5	2.391 (±0.020)	1.712 (±0.001)	ND	ND	ND	ND	ND	ND
10	1.706 (±0.002)	2.365 (±0.003)	0.159 (±0.003)	ND	ND	ND	ND	ND

ND=Not detected
Standard deviation (±)

The average ^{14}C-paraquat residue concentrations in clay loam soils for 5 and 10 mm of simulated rainfall are summarized in Table 2. The average ^{14}C-paraquat residue concentration (mg/kg) in the first 2 cm of the soil layer was 2.391 (±0.020) and 1.706 (±0.002) for 5 and 10 mm simulated rainfall, respectively.

In the following experiment, the influence of the duration of rain on the mobility of 2,4-D and ^{14}C-paraquat herbicides were investigated. The importance of the duration of rainfall in causing the movement of 2,4-D down the soil profile was evident in the experiment (Fig. 4). Provision of 5 mm simulated rainfall for ten days, following the application of 2,4-D to the soil surface, caused the chemical to be leached into the (0 to 15) cm zone of the column. Simulation of rain for 15 days caused more of the chemical to be leached to the (0 to 20) cm zone. As the time of exposure to simulated rainfall was prolonged to 20 days, the herbicide leached deeper and accumulated at the (0 to 30) cm zone in the packed clay loam soil columns (Figure 4). The results of the study are consistent with those of other studies carried out in Malaysia. Ismail and Ooi [27] demonstrated that Metsulfuron-methyl was leached to about 24.65 and 39.88% of the applied radioactive pesticide for rainfall simulations of 100 and 200 mm, respectively. Similar observations have also been reported by other researchers [28, 29].

The effect of the duration of rain on the mobility of ^{14}C- paraquat in packed clay loam soil columns was also studied. Figure 5 shows the ^{14}C-paraquat residue detected at the (0–6) cm soil depth in the clay loam soil for different durations of simulated rainfall. The influence of the duration of rain in the column leaching studies confirmed that paraquat is immobile in clay loam soil. Simulation of rain for 10, 15 and 20 days caused more of the ^{14}C-paraquat to be leached only to the (0 to 6) cm zone. No residue of ^{14}C-paraquat was observed below the depth of 6 cm. The results showed that the total amount of ^{14}C-paraquat that leached in the clay loam soil was not affected significantly by increase in the duration of rain from 10 days to 20 days. The insignificant mobility of paraquat in the soil suggests strong binding of paraquat to the soil adsorption sites. The duration of rainfall had little significance on the movement of ^{14}C-paraquat in the soil. A similar observation by Amondham et al. [15] on paraquat mobility studies conducted using both field and laboratory (soil column) experiments with clay soil showed low leaching of paraquat with accumulation only in the surface (0-5) cm segment under field conditions and in the (0-1) cm segment in the laboratory soil column experiment. Paraquat is not readily desorbed from soil binding and thus is unlikely to contaminate ground water beneath agricultural soils [30]. Furthermore, the USEPA [31] reported that paraquat did not leach below 9 cm in loamy sand soil in field studies conducted, although in one of the plots paraquat was found in the soil segment of (11.4 to 25.4) cm after 296 days. Consequently, paraquat is tightly bound onto soil particles and hence leaching is not considered to be a problem.

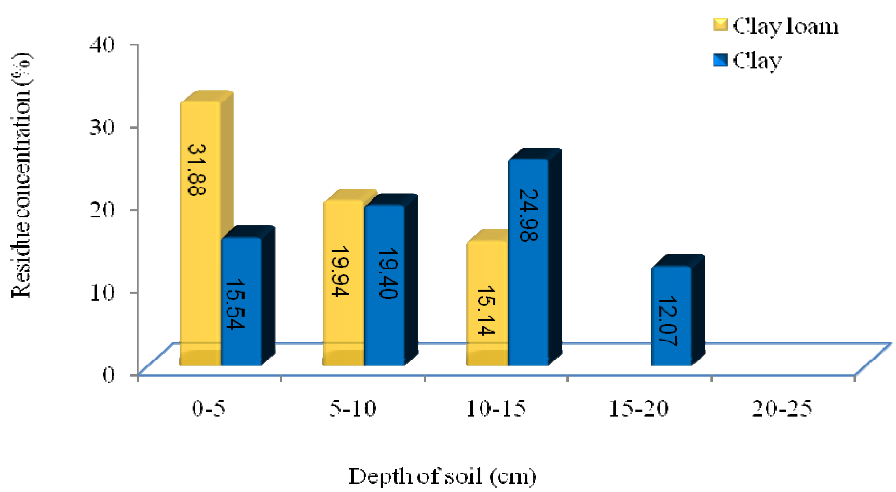

Fig. 2 Effect of daily application of simulated rain on the mobility of 2,4-D in clay and clay loam soil

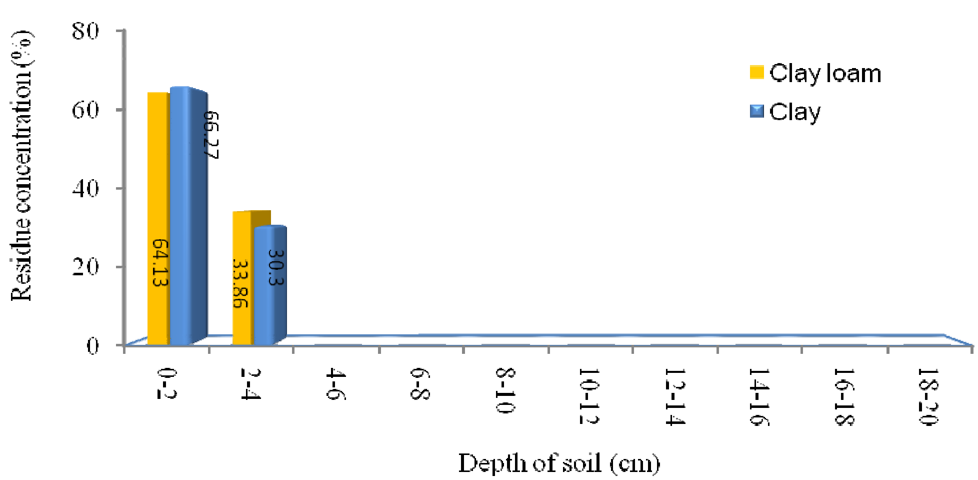

Fig. 3 Effect of daily application of simulated rain on the mobility of ^{14}C-paraquat in clay and clay loam soils

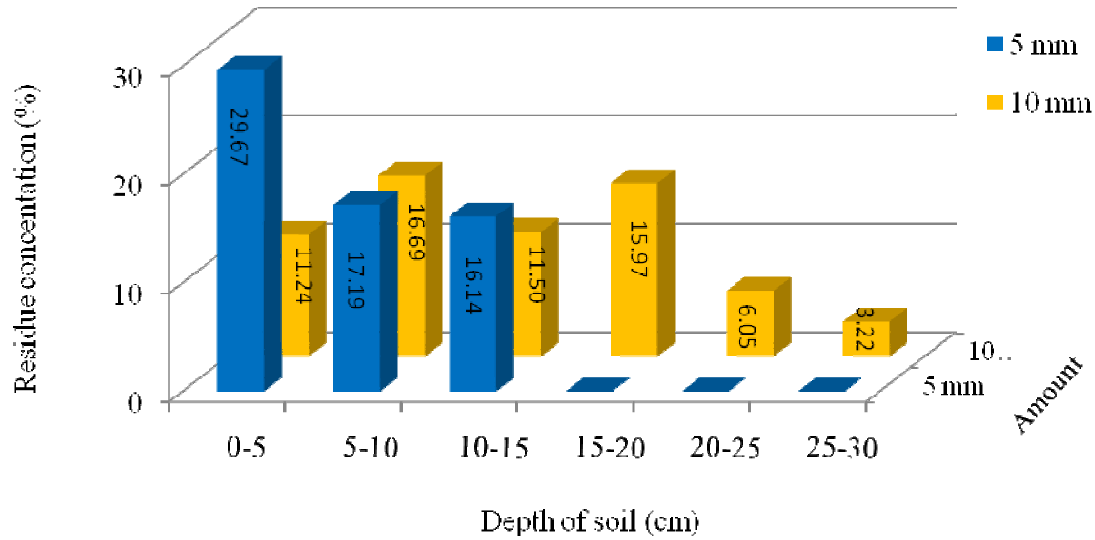

Fig. 4 Effect of the amount of rainfall on the leaching of 2,4-D in packed clay loam soil columns

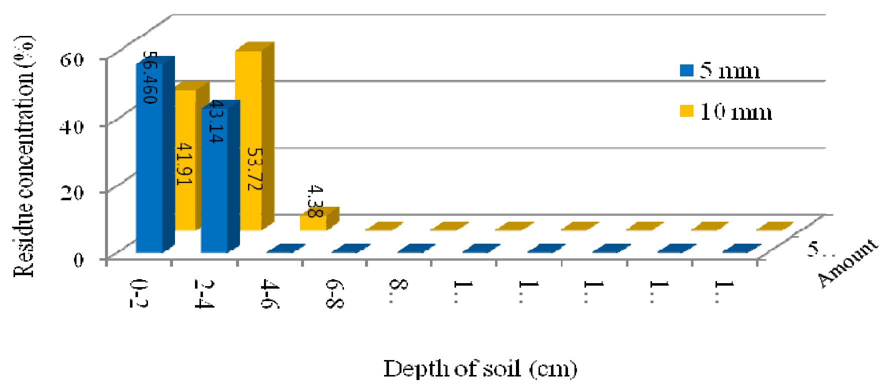

Fig. 5 Effect of the amount of rainfall on the leaching of ^{14}C-paraquat in packed clay loam soil columns

Mobility of 2,4-D and ^{14}C-paraquat under packed and intact core columns

The intact soil cores better simulate the conditions observed in the field and therefore 2,4-D and ^{14}C-paraquat leaching was also studied in these columns. Ghosh and Sing [32] reported that intact columns better approximate field movement of water and solute than columns with repacked soils, as preferential flow, which very much affects chemical movement in the field, may predominate in intact columns. Figure 6 and 7 illustrate the comparison between the distribution of 2,4-D and ^{14}C-paraquat in packed and intact core clay soil columns under similar simulated conditions, respectively. In intact clay soil columns, at simulation of 5 mm rainfall over a ten-day period, 2,4-D leached down to the (0-20) cm layer and was evenly distributed in the (0-15) cm soil profile. A comparison of the leaching behavior of 2,4-D in the packed and the intact columns following similar rainfall conditions showed that the leaching pattern was quite different (Figure 6). In packed columns, more 2,4-D leached to the lower layers of the soil and the maximum amount was obtained in the second (5-10 cm) and third (10-15 cm) column sections of the clay soil (Figure 6). Certainly, 2,4-D is more mobile in the packed soil columns than in the intact soil columns. Comparing the mobility of 2,4-D in intact-core and packed columns (where soil is under disturbed conditions) revealed that the extent of mobility is less in the intact core.

Singh et al. [33] reported that the loose structure of the packed soil facilitated downward flow of the compound. Preferential flow through macropores, which are likely to be maintained in the intact columns, could greatly reduce the retention of the solute in the soil profile and thus may increase the hazards of groundwater contamination, whereas, in the packed columns, water, along with the applied pesticide, pass through the soil matrix and considerable retardation of the pesticide is observed. This was further evident from the leachate parameters observed in the packed and the intact columns (Figure 6).

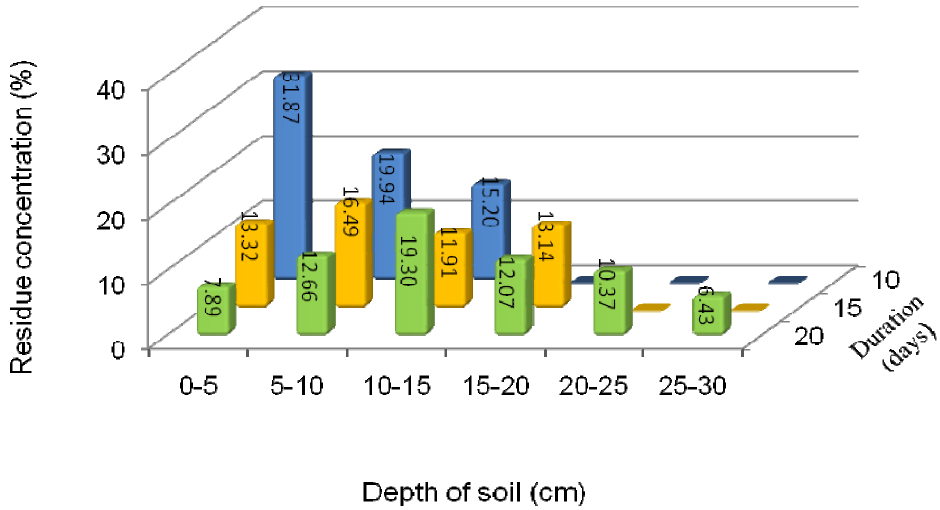

Fig. 6 Distribution of 2,4-D in packed and the intact soil columns

The results for paraquat under the same procedures as 2,4-D were as follows: In the packed columns with percolating water equivalent to 5 mm rainfall over a 10 day period, ^{14}C-paraquat leached down to (0-4) cm depth and the major portion of the ^{14}C-paraquat (66.27%) was retained at the top (0-2) cm layer. Nearly the same results were obtained for the ^{14}C-paraquat leaching in the packed clay soil column (Figure 7), suggesting that, after an average rainfall (5 mm) over a ten-day period, paraquat was practically immobile in the clay soil, as >97% still remained at the application zone itself (0-4 cm). In the intact columns, at simulation of 5 mm rainfall, maximum amounts of ^{14}C-paraquat (70.53%) were recovered from the top layer (0-2 cm), contrary to the results of 2,4-D movement in intact core columns under similar conditions. Certainly, 2,4-D is more mobile in the intact soil columns than paraquat because of different physical and chemical properties of its constituents.

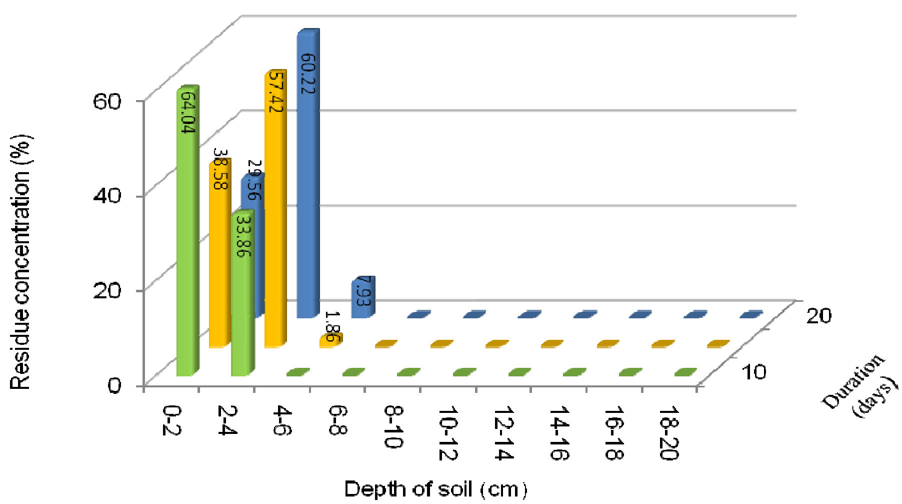

Fig. 7 Distribution of ^{14}C-paraquat in packed and intact soil columns

CONCLUSION

The finding of this study emphasizes the necessity for carful use pesticides in controlling of weeds in tropical agricultural soils. The results indicate that the cationic herbicide paraquat is fairly immobile in clay and clay loam soil, but 2,4-D, an anionic herbicide, is quite mobile and may pose a threat to soil and groundwater contamination.

REFERENCES

[1] Erdogrul, O., Covaci, A. and Schepens, P. 2005. Levels of organochlorine pesticides, polychlorinated biphenyls and polybrominated diphenyl ethers in fish species from Kahramanmaras, Turkey. Environ. Int., 31: 703-711.

[2] Fava, L., Orru, M. A., Crobe, A., Caracciolo, A. B., Bottoni, P. and Funari, E. 2005. Pesticide metabolites as contaminants of groundwater resources: Assessment of the leaching potential of endosulfan sulfate, 2,6-dichlorobenzoic acid, 3,4-dichloroaniline, 2,4-dichlorophenol and 4-chloro-2-methylphenol. Microchem. J., 79: 207-211.

[3] Tariq, M. I, Afzal, S. and Hussain, I. 2004. Pesticides in Shallow Groundwater of Bahawalnagar, Muzafargarh, D.G. Khan and RajanPur Districts of Punjab, Pakistan. Environ. Int., 30: 471-479.

[4] Majumdar, K. and Singh, N. 2007. Effect of soil amendments on sorption and mobility of metribuzin in soils. Chemosphere, 66: 630–637.

[5] Shukla, G., Kumar, A., Bhanti, M., Joseph, P. and Taneja, A. 2006. Organochlorine pesticide contamination of ground water in the city of Hyderabad. Environ. Int., 32: 244-247.

[6] Song, N.H., X.L. Yin, G.F. Chen and H. Yang. 2007. Biological responses of wheat (Triticum aestivum) plants to the herbicide chlorotoluron in soils. Chemosphere, 68: 1779-1787.

[7] Sudaryanto, A., Kunisue, T., Kajiwara, N., Iwata, H., Adibroto, T. A., Hartono, P. and Tanabe, S. 2006. Specific accumulation of organochlorines in human breast milk from Indonesia: Levels, distribution, accumulation kinetics and infant health risk. Environ. Pollut., 139: 107-117.

[8] Blenkinsop, S., Fowler, H. J., Dubus, I. G., Nolan, B. T. and Hollis, J. M. 2008. Developing climatic scenarios for pesticide fate modelling in Europe. Environ. Pollut., 154: 219-223.

[9] Lewan, E., Kreugerand, J. and Jarvis, N. 2009. Implications of precipitation patterns and antecedent soil water content for leaching of pesticides from arable land. Agr. Water Manag., 96: 1633-1640.

[10] Nolan, B. T., Dubus, I. G., Surdyk, N., Fowler, H. J. and Burton, A. 2008. Identification of key climatic factors regulating the transport of pesticides in leaching and to tile drains. Pest Manag. Sci., 64: 933-944.

[11] Tiktak, A., De Nie, D. S., Garcet, J. D. P., Jones, A. and Vanclooster, M. 2004. Assessment of the pesticide leaching risk at the pan-European level: The EuroPEARL approach. J. Hydrol., 289: 222-238.

[12] McGrath, G. S., Hinz, V. and Sivapalan, M. 2008. Modelling the impact of within-storm variability of rainfall on the loading of solutes to preferential flow pathways. Eur. J. Soil Sci., 59: 24-33.

[13] Chopra, B., Kumari, S. and Sharma, K. S. 2010. Evaluation of leaching behavior of pendimethalin in sandy loam soil. Environ. Monit. Assess., 160: 123-126.

[14] Aquino, A. J. A., Tunega, D., Haberhauer, G., Gerzabek, M. H. and Lischka, H. 2007. Interaction of the 2,4-dichlorophenoxyacetic acid herbicide with soil organic matter moieties: a theoretical study. Eur. J. Soil Sci., 58: 889-899.

[15] Amondham, W., Parkpian, P., Polprasert, C., Delauneand, R. D. and Jugsujinda, A. 2006. Paraquat adsorption, degradation and remobilization in tropical soils of Thailand. J. Environ. Sci. Health Part B, 41(5): 485-507.

[16] Ismail, B. S., Sameni, M. and Halimah, M. 2011. Kinetics of the microbial degradation of 2,4-D and ^{14}C-labeled paraquat in two types of tropical agricultural soil. World Appl. Sci. J., 14(2): 324-333.

[17] Cox, L., Walker, A., Hermosin, M. C. and Cornejo, J. 1996. Measurement and simulation of the movement of thiazafuon, clopyralid and metamitorn in soil column. Weed Res., 36: 419-429.

[18] Ismail, B. S. and Kalithasan, K. 1997. Mobility of metasulfuron-methyl in tropical soils. Aust. J. Soil Res., 35: 1291-1300.

[19] Oppong, F. K. and Sagar, G. R. 1992. Degradation of triasulfuron in soil under laboratory conditions. Weed Res., 32: 167–173.

[20] Abdullah, A. R., Sinnakkann S. and Tahir, N. M. 2001. Adsorption, desorption and mobility of metsulfuron methyl in Malaysian agricultural soils. Bull. Environ. Contam. Tox.,, 66: 762-769.

[21] Roberts, T. R., Dyson, J. S. and Lane, M. C. 2002. Deactivation of the biological activity of paraquat in the soil environment: a review of long-term environmental fate. J. Agr. Food Chem., 50: 3623-3631.

[22] Dinis-Oliveira, R. J., Duarte, J. A., Sanchez-Navarro, A., Remiao, F., Bastos, M. L. and Carvalho, F. 2008. Paraquat poisonings: mechanisms of lung toxicity, clinical features and treatment. Crit. Rev. Toxicol., 38: 13-71.

[23] Hartley, D. and Kidd, H. 1990. The Agrochemicals Handbook, 2nd edition. Royal Society of Chemistry, Cambridge CB4 4WF, England.

[24] Bromilow, R. H. 2004. Paraquat and sustainable agriculture. Pest Manag. Sci., 60: 340-349.
[25] Cheah, U. B., Kirkwood, R. C. and Lum, K. Y. 1997. Adsorption-desorption and mobility of four commonly used pesticides in Malaysian agricultural soil. Pestic. Sci., 50: 53-63.
[26] Halimah, M., Ismail, B. S., Sameni, M. and Nashriyah, M. 2011. Adsorption study of ^{14}C-paraquat in two Malaysian agricultural soils. Environ. Monit. Assess., 176(1): 43-51
[27] Ismail, B. S. and Ooi, K. E. 2012. Adsorption, desorption and mobility of metsulfuron-methyl in soils of the oil palm agroecosystem in Malaysia. J. Environ. Biol., 33: 573-577.
[28] Ismail, B. S., Ngan, C. K., Cheah, U. B. and Abdullah, W. Y. 2004. Leaching potential of pesticides in a vegetable farm in the Cameron Highlands, Malaysia. Bull. Environ. Contam. Tox., 72: 836-843.
[29] Rahman, A., Baki, B. B. and James, T. K. 1997. Mobility of four sulfonylurea herbicides in some New Zealand and Malaysian soils. (in) Proceedings of the 16th Asian-Pacific Weed Science Society Conference, held on September 8-12, 1997, Kuala Lumpur, Malaysia, 139-143.
[30] Mehdi, S., Halimah, M., Nashriyah, M. and Ismail, B. S. 2009. Adsorption and Desorption of Paraquat in Two Malaysian Agricultural Soils. Am.-Eurasian J. Sustain. Agr., 3(3): 555-560.
[31] USEPA. 1997. Paraquat dichloride. EPA 738-F-96-018, Registration Eligibility Decision (RED), Office of Prevention, Pesticides and Toxic Substances, U.S. Environmental Protection Agency, Washington, DC., USA. http://www.epa.gov/oppsrrd1/REDs/0262red.pdf
[32] Ghosh, K. R. and Sing, N. 2009. Leaching behaviour of azoxystrobin and metabolites in soil columns. Pest Manag. Sci., 65: 1009-1014.
[33] Singh, N., Kloeppel, H. and Klein, W. 2002. Movement of metolachlor and terbuthylazine in core and packed soil columns. Chemosphere, 47: 409-415.