Bull Environ Contam Toxicol (2008) 81:294–298
DOI 10.1007/s00128-008-9468-8

Study on the Downward Movement of Carbofuran in Two Malaysian Soils

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Received: 6 December 2007 / Accepted: 12 May 2008 / Published online: 28 June 2008

Abstract The downward movement of carbofuran in two Malaysian soil types was studied using soil columns. The columns were filled with disturbed and undisturbed soils of either the Bagan Datoh soil (clay) or the Labu soil (sandy clay). The average total percentage of carbofuran in the leachate of the undisturbed Labu soil after 14 days of watering (80.8%) was approximately similar to that of the total amount from the disturbed soil (81.4%). However, carbofuran leaching was observed in the disturbed soil after the fourth day of watering whereas for the undisturbed soil, leaching occurred after the first watering. A similar trend was observed in the Bagan Datoh soil where the residue of carbofuran was detected after the first day of watering in the undisturbed soil column but only at the eighth day of watering in the disturbed soil column. The total percentage carbofuran in the leachate of disturbed and undisturbed soil columns from Bagan Datoh after 14 days of watering was 3.6% and 41.7%, respectively. The study showed that less leaching occurred in soil columns with high organic content such as the Bagan Datoh soil and especially so in disturbed soils where the organic matter was homogeneously mixed in all layers.

Keywords Carbofuran · Leaching · Clay · Sandy clay · Soil

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The adsorption and desorption characteristics which determine the movement of pesticides through the soil profile, their bioavailability, microbial degradability and persistence depend upon soil properties such as organic matter content, clay content and the physico-chemical properties of the pesticide, i.e., size, shape, solubility in water, p*K* values and polarity (Calderbank 1989). The potential for leaching is the greatest when highly soluble chemicals are used in well-drained sandy soils with low organic matter content (Reddy and Singh 1993).

Carbofuran (2,3-dihydro-2,2-dimethylbenzofuran-7-yl-*N*-methyl carbamate) is a broad spectrum systemic acaricide, insecticide and nematicide included in the general group of the carbamate derivative pesticides (Javier-Benitez et al. 2002). It is widely used for the control of soil dwelling and foliar-feeding insects including wireworms, white grubs, weevils, stem borers, aphids and several other insects (Kale et al. 2001). In Malaysia, the usage of carbofuran in oil palm plantations has declined but it is used extensively for control of rice pests in paddy fields and also for vegetable and fruit pests. As a result of its widespread use, air, food, surface water and underground water are contaminated with carbofuran residue and its metabolites (Tariq et al. 2006), which may affect human health.

Carbofuran is highly toxic to animals and humans both by oral and inhalation routes and therefore, may pose a serious threat to those in contact with it in manufacturing and formulation plants or in crop fields (Gupta 1994; Lalah and Wandiga 1996). Due to its acute toxicity, the fate of its residue in terms of persistence and mobility is of great concern. Carbofuran is known to be a more persistent insecticide than other carbamate or organophosphorus insecticides (Jui-Hung et al. 1997).

The use of soil columns to simulate pesticide movement in soil for mobility studies are well documented (Abdullah et al. 2001). Two types of disturbed and undisturbed (intact) soil namely clay (Bagan Datoh soil) and sandy clay (Labu soil) soils were used in the investigation on the leaching behavior of carbofuran in soils. The use of disturbed soil in the experiment could be correlated to soil in fields which were rotavated prior to planting. The using of intact soil columns would show the mobility of carbofuran in natural soil profile conditions. Reports on the mobility of carbofuran in soil from oil palm plantations is limited. Therefore, understanding the mobility pattern in oil palm soils is important in order to understand its behavior and possibility of contamination of underground soil water.

The purpose of this study is to investigate the downward movement of carbofuran in disturbed and intact soil columns of two selected soils, namely the Bagan Datoh (clay) and Labu (sandy clay) soils.

Materials and Methods

The carbofuran-free soils were collected from oil palm plantations, near Labu, in the State of Negeri Sembilan and classified as sandy clay soil (clay 41.9%, silt 2.07%, sand 50%, pH 4.42, CEC (cmol/mg) 3.92), and from Bagan Datoh, in the State of Perak, and classified as clay soil (clay 42.7%, silt 32.2%, sand 25.2%, pH 3.68, CEC (cmol/mg) 20.0); the two locations are situated 60 km southeast and 130 km north-west of Kuala Lumpur, respectively. The soils were then kept at 4°C until use.

A weighed amount of 0.05 g of analytical grade carbofuran was dissolved in acetonitrile and diluted to 50 mL to prepare a stock standard solution of 1,000 μg/mL. The high performance liquid chromatograph (HPLC) was calibrated using five working standard solutions of carbofuran at concentration levels of 0.1, 0.25, 0.5, 1 and 2.5 μg/mL, which were prepared by appropriate dilution of 1,000 μg/mL stock standard solution with acetonitrile, prior to injection into the HPLC. Each concentration of the standard solution was injected twice.

The EPA method (EPA 8318A) with slight modifications was used for the extraction and analyses of carbofuran residue in the soils (EPA 2007). Five grams of each type of soil sample were weighed into 30 mL centrifuge tubes individually, prior to fortification with 0.1 mL of 50 μg/mL analytical grade carbofuran (purity 99.9%) to give a final concentration of 1 μg/g soil. After spiking, the soil was then mixed thoroughly and a total of 12 mL acetonitrile (analytical grade 99%) was added 1 h later, followed by shaking on a reciprocative shaker at 250 rpm for 2 h. The extraction was repeated twice with 10 mL acetonitrile followed by shaking for 1 h and centrifuging at 2,700 rpm for 10 min. All extracts from each sample were transferred to a round bottomed flask to evaporate the solvent using a rotary evaporator, followed by redissolving in 5 mL acetonitrile prior to analysis with the HPLC.

Extracted residues were determined by a HPLC (H/P Agilent 1100) fitted with a LC Column ZORBAX 300SB-C_{18} (4.6 × 250 mm), 5 μm thickness. The injection volume was 20 μL. The mobile phase used was acetonitrile:water (50:50 v/v) with a flow rate of 1 mL/min; detection was at 280 nm and the peak area was used for quantification.

Columns for the leaching studies were constructed from six 5 cm sections of the PVC tubing (5 cm internal diameter) reassembled using parafilm and plastic tape to recreate the whole column of 30 cm. Aluminum foil was used to cover the end of the columns in order to keep the soil inside the columns. Small pores were made with a tiny needle in order to allow the water to pass through the column. A beaker was placed at the bottom of each column to collect the leachate. The columns were placed in the laboratory throughout the study period. For the first set of experiments the disturbed and undisturbed soil samples were collected from up to a depth of 25 cm for the Labu and Bagan Datoh soils from oil palm plantations, respectively.

For the mobility study of the disturbed soil, the soil was collected from 0 to 25 cm depth, mixed thoroughly and each column was packed carefully with each soil type individually. Columns were shaken during filling and saturated with calcium chloride solution (0.01 M) which was passed through to aid in soil compaction. Soil-filled columns were kept in the upright position during the insecticide mobility test. The soil, saturated with calcium chloride solution (0.01 M) was allowed to drain overnight prior to the application of the insecticide treated soil sample to the soil surface.

For the mobility study in the intact soils, the soil was collected using an auger (5 cm diameter) from up to a depth of 30 cm. The soil column was repacked into a PVC column to simulate the soil profile as in the field. The intact soil-filled columns were similarly saturated as above with calcium chloride and allowed to drain overnight. The top of the columns were filled up with the carbofuran-treated soil as described earlier. Control for the two soil types was also prepared as described earlier except that no carbofuran-treated soil was placed on top of the soil columns.

A 50 g air-dried and sieved soil sample spiked with 100 μg/g carbofuran was added to the top of each column of both the disturbed and undisturbed soil columns except for the control soil column. A piece of filter paper was placed on the soil surface inside the column, to provide uniform distribution of water over the soil surface. Soil columns were watered for 14 days with 50 mL/day of deionised water which is equivalent to a 25.5 mm rainfall (as 14 days rainfall). A total of 50 mL leachate was collected after each watering and the leachate was then analysed directly by the HPLC fitted with a UV detector as described above. All the experiments were carried out in triplicate.

On completion of the leaching experiment, soil from each column was cut into six 5 cm sections each. Eighty-four soil samples (including experiment replications and control columns) were allowed to dry completely at room temperature (27°C) for 72 h before extraction was done. One subsample from each of the above mentioned soil samples was used for carbofuran determination. The residue of carbofuran in the soil subsamples was determined by the method described above.

Table 1 Average percentage of carbofuran residue in disturbed and undisturbed soil columns from Labu

Watering (number of days)	Undisturbed soil		Disturbed soil	
	Average residue in leachate (%)	SD[a]	Average residue in leachate (%)	SD[a]
1	5.6	3.41	ND[b]	ND
2	12.4	1.40	ND	ND
3	12.3	1.79	ND	ND
4	10.9	2.45	0.2	0.07
5	8.4	2.01	2.3	0.06
6	6.2	0.70	10.1	0.57
7	5.2	0.61	14.5	0.88
8	4.2	0.56	14.2	0.16
9	3.6	0.50	11.8	0.05
10	2.9	0.40	8.4	0.12
11	2.6	0.45	6.0	0.14
12	2.2	0.37	4.2	0.11
13	2.0	0.30	3.5	0.36
14	1.7	0.21	2.3	0.25
Total	80.8	6.92	81.4	6.44

[a] Standard deviation

[b] Not detected

Results and Discussion

A HPLC was calibrated by standard solutions. The calibration curve showed a correlation coefficient (r^2) of 0.9998. The EPA method (EPA 8318A) with slight modifications was used for extraction and analysis of carbofuran in soil samples and the detection limits reported were 2 μg/L and 22 μg/kg for water matrix and soil, respectively.

The percentage recovery carbofuran from the two soil types studied namely, Labu and Bagan Datoh soils were 98.7% and 76.1% with the standard deviation of ±1.78, ±3.35, respectively. The recovery of carbofuran in the water solution was 104.7 ± 1.78%. Higher recovery (98.7%) was obtained in the Labu soil and this may be due to the high content of sand (56%), which did not strongly adsorb or retain carbofuran molecules. The recovery of carbofuran in the Bagan Datoh soil was lower (76.1%), and this may be due to higher organic carbon content which may cause stronger adsorb ion of the carbofuran as compared to that in Labu soil. The retention time of carbofuran was 4.05 min. The control soils, which were not treated with carbofuran, did not show any carbofuran residue.

Table 1 shows the percentage carbofuran residue in the Labu soil during the 14 days of watering. After 14 days of watering the total percentage carbofuran in the leachate from the disturbed soil and undisturbed sandy clay soil was 81.4% and 80.1%, respectively (Table 1). The total percentage carbofuran in the leachate from the undisturbed soil was slightly higher as compared to that from the disturbed soil. It is worth noting that all the results are expressed as percentage of the initial amount of carbofuran in the treated soil placed at the top of the columns. In the Labu soil, detectable amounts of carbofuran in the leachate was observed on day-4 after watering from the columns containing disturbed soil, whereas the residue was detected as early as the first day of watering from the undisturbed soil columns.

Table 2 shows the percentage carbofuran residue in the leachate of disturbed and undisturbed Bagan Datoh soils during the 14 days of watering. A similar trend was observed in the column containing the disturbed Bagan Datoh soil, as it showed detectable amounts of carbofuran in the leachate after 8 days of watering, whereas it was observed that the residue was detected in the leachate of the undisturbed soil on day-1 of watering. After 14 days of watering the total percentage carbofuran in the leachate of the undisturbed and disturbed Bagan Datoh soil was 41.7% and 3.6%, respectively.

It was observed that the total percentage carbofuran in the leachate of the disturbed soil of Bagan Datoh was approximately 11-times more than that in the undisturbed soil after 14 days of watering. These results are in contrast to those of the Labu soil, whereby the total percentage residue in the leachate was almost the same for both the disturbed and undisturbed soils. In the Bagan Datoh soil it was shown that the maximum amount of carbofuran in the leachate of the undisturbed soil was obtained during the

Table 2 Average percentage of carbofuran residue in disturbed and undisturbed soil columns from Bagan Datoh

Watering (number of days)	Undisturbed soil		Disturbed soil	
	Residue in leachate (%)	SD[a]	Average residue in leachate (%)	SD[b]
1	3.4	0.39	ND[c]	ND
2	5.4	0.00	ND	ND
3	4.3	0.16	ND	ND
4	4.5	0.00	ND	ND
5	3.0	0.25	ND	ND
6	3.6	0.17	ND	ND
7	2.8	0.20	ND	ND
8	3.1	0.00	0.1	0.02
9	2.3	0.52	0.1	0.01
10	2.2	0.07	0.2	0.01
11	1.9	0.18	0.3	0.002
12	1.9	0.08	0.7	0.04
13	1.4	0.06	0.8	0.06
14	1.4	0.16	1.3	0.06
Total	41.7	0.39	3.7	0.06

[a] Standard deviation for analysis of two subsamples

[b] Standard deviation

[c] Not detected

2nd and 3rd day of watering. On the contrary, no residue was found in the leachate of the disturbed soil during the first 7 days of watering. However, in Labu soil columns, the maximum amount of carbofuran residue in the leachate of the undisturbed soil was obtained on day-2 and day-3 whereas no residue in the leachate of the disturbed soil was detected during the first 3 days of watering.

Table 3 shows the percentage residues of carbofuran in each soil segment of the disturbed and undisturbed soil columns of Labu and Bagan Datoh after 14 days of watering. It was observed that in the disturbed Labu soil, the residue of carbofuran was higher in the lower profile of the soil column. Approximately 3.6% carbofuran was found in the 25–30 cm soil layer. However on the other hand, it was observed that the residue of carbofuran decreased with increasing depth of the disturbed and undisturbed soils. More residues were accumulated at the top layers of the soil column.

Table 3 Percentage carbofuran residue in soil profiles from Labu and Bagan Datoh soils (±standard deviation)

Depth (cm)	Labu soil		Bagan Datoh soil	
	Undisturbed	Disturbed	Undisturbed[a]	Disturbed
0–5	3.5 (±2.23)	0.5 (±0.04)	26.1 (±6.66)	33.4 (±2.88)
5–10	2.8 (±1.12)	0.3 (±0.10)	5.3 (±3.41)	12.3 (±1.00)
10–15	2.5 (±0.89)	0.9 (±0.06)	2.9 (±5.39)	13.0 (±0.64)
15–20	2.4 (±0.76)	1.4 (±0.10)	2.5 (±2.17)	12.4 (±0.78)
20–25	1.7 (±0.09)	1.9 (±0.10)	1.8 (±0.88)	9.8 (±0.99)
25–30	2.0 (±0.41)	3.6 (±0.06)	1.6 (±2.31)	3.1 (±0.14)

[a] Standard deviation for analysis of two subsamples

The current results clearly show that carbofuran is more mobile in the Labu soil as compared to the Bagan Datoh soil. More carbofuran residue was observed in the leachate of the Labu soil. Soil composition such as organic matter and sand content plays an important role in influencing the mobility of carbofuran. The Labu soil contained more sand than the Bagan Datoh soil and less organic matter. Higher sand content contributes to better porosity, while less adsorption occurs due to less organic matter content, consequently causing more downward movement of carbofuran through the column. The effect of organic matter content on the adsorption of pesticide molecules have been shown by Oppong and Sagar (1992).

It is interesting to note that the mobility of carbofuran is higher in undisturbed soil columns than in disturbed soil columns. The difference in mobility is more apparent in the Bagan Datoh soil than in the Labu soil. It could be that in the disturbed soil column, the soil was mixed thoroughly before placement into the column. Therefore, the top layer which contained higher organic carbon was distributed evenly in the column, and this increased adsorption and hence reduced mobility.

The results of this study are consistent with previous studies on adsorption/desorption of this compound on soils from Labu and Bagan Datoh. For the Labu soil, the range of the K_d values was 0.9–1.2 whereas it was 2.7–2.9 for the Bagan Datoh soil, so adsorption of carbofuran in the Bagan Datoh soil is higher than that in the Labu soil. High adsorption may reduce the mobility of carbofuran through the soil column. It could therefore be concluded that organic matter content in the soil may increase adsorption, consequently reducing the leaching of carbofuran as shown from the results of the Bagan Datoh soil. More intensive studies need to be carried out to measure the mobility of carbofuran in different soil types in order to prevent contamination of underground water especially in areas where the chemical is used intensively.

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