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Residues and Decay of Some Insecticides in Different Types of Water

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Abstract: Residues and decay of four insecticides; pirimiphos-methyl, chlorpyrifos-ethyl, cypermethrin and fenvalerate, were determined in three types of water; distilled water (pH 6.4), well water (pH 7.6) and standard hard water (SHW, pH 7.8). These insecticides were added to the three types of water at recommended rates that used to control the insect pests on crops. Samples of water were taken from treated types of water after zero, 7, 14, 21 and 75 days. Water samples were extracted and cleaned-up then analyzed by using gas chromatography for determining the insecticide residues. The data showed that the decay of pirimiphos-methyl after one week was (49.9%) in well water compared with that of distilled and SHW (29.4 and 44.5%). Decay of chlorpyrifos-ethyl in distilled water after one week was 11.7% then increased afterwards and reached 29.5, 40.8 and 99.5% of the amount determined at zero (initial deposit) after 14, 21 and 75 days. Same trend of chlorpyrifos-ethyl decay was observed in well and SHW. Pirimiphos-methyl was vastly degraded when compared with chlorpyrifos-ethyl in the three different types of water. The data also showed that the decay of cypermethrin was high after one week in the three types of water where it exceeded 75%. On the other hand, the decay of fenvalerate after one week was high in well and SHW water (67.8 and 67.7%) compared with that of distilled water (48.8%). Further, decay of synthetic pyrethroid insecticides (cypermethrin and fenvalerate) was relatively high after one week when compared with organophosphorus insecticides (pirimiphos-methyl and chlorpyrifos-ethyl) in the three types of water.

Key words: Pirimiphos-methyl, synthetic pyrethroid insecticides, chlorpyrifos-ethyl, cypermethrin, organophosphorus insecticides, fenvalerate

INTRODUCTION

Insecticides are synthetic biologically active compounds which introduced into environment deliberately to control insects, weeds and disease. They are divided into many classes, of which the most important are Organochlorine, organophosphorus, carbamate and pyrethroid compounds. Despite of their benefits many of them may produce a range of toxic side effect that poses potential hazards to the environment. In fact, some of these chemicals are non-biodegradable and remain dangerous for a long time (Ioannis *et al.*, 2001; Troiano *et al.*, 2001). For example, organochlorine pesticides are known to resist biodegradation and therefore they can be recycled through food chains and produce a significant magnification of the original concentration at the end of the chain (Milidas, 1994). Also, the existence remaining residues of organophosphorus and synthetic pyrethroid

insecticides in vegetables, fruits, soil, drainage and ground water have been recorded (Sullivan, 1980; Galera *et al.*, 1997; Zidan *et al.*, 1996). The residues of these compounds could reach the aquatic environment through direct run off, leaching, careless disposal of empty containers, equipment washings (Milidas, 1994). Therefore, it's well known that the applications of insecticides are a contaminate source for the aquatic environment (Shukla *et al.*, 2006). This kind of contamination of natural water may have ecotoxicological effects for aquatic flora and fauna as well as for humane health (Witter *et al.*, 1999; Jergentz *et al.*, 2005; Sereda and Meinhardt, 2005). Contamination of ground water resources by pesticides has become more prominent in countries where ground water aquifers constitute is main drinking water resources (Schiavon *et al.*, 1995; Mohorjy and Grigg, 1995). This problem is severe in arid land such as Saudi Arabia (Al Alawi and Abdulrazzak, 1994). So, our long term objective is focused on determination the

residue and decay of commonly used insecticides such as pirimiphos-methyl, chlorpyrifos-ethyl, cypermethrin and fenvalerate in Saudi Arabia as a source of water pollution whether, in well water or in distilled water compared to standard hard water. Accordingly, the purpose of the present study was to determine certain insecticide residues in the aquatic system as a module for insecticides contaminating natural sources of ground water in Saudi Arabia. Furthermore, a better understanding of environmental impact of pesticides pollution on this area would be useful tool for the effective management and control of the natural area with respect to the pesticides residues.

MATERIALS AND METHODS

Chemicals: Four insecticides were purchased locally in Saudi Arabia and used for this experiment. Two of them belongs to organophosphates; Actellic (pirimiphos-methyl) O-(2-diethylamino-6-methylpyrimidin-4-yl) O,O-dimethyl phosphoro-thioate, 50% EC and Dursban (chlorpyrifos-ethyl) O,O-diethyl O-(3,5,6-trichloro-2-pyridinyl) phosphorothioate, 48% EC, were applied at rates of 2.0 ml L⁻¹. The other two belongs to synthetic pyrethroid; Cypermethrin { α -cyano-3-phenoxybenzyl (\pm)-cis, trans-3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate}, 10% EC was applied at a rate of 0.5 ml L⁻¹ and Sunicidin (fenvalerate) RS)- α -Cyano-3-phenoxybenzyl (RS)-2-(4-Chlorophenyl)-3-methylbutyrate, 20% EC at rate of 0.75 ml L⁻¹.

Residue analysis

Sampling: Three types of water were used; distilled water (pH 6.4), well water (pH 7.6) and Standard Hard Water (SHW) (pH 7.8). Well water was obtained from a well at King Faisal Research Station at Al-Hassa, Saudi Arabia. Standard hard water was prepared by adding 0.304 g of CaCl₂ and 0.139 g of MgCl₂ to a liter of distilled water. Distilled water was obtained from the laboratory. Recommended rates of each insecticide were added to ten liters of different types of water. Treated water was stored at room temperature (20-25°C.) for three months. Three samples of water each 50 mL were taken at the following intervals (zero, 7, 14, 21 and 75 days) from each treatment for extraction.

Extraction: Samples (50 mL/each) were extracted according to the method adopted by Bullock (1984) and Al-Sarar (1996) by shaking vigorously with 50 mL acetonitrile for 3 min. Then transferred to separator funnel and 50 mL of petroleum ether was added and shaken for 2 min. The organic layer was separated and the aqueous

layer was taken and another 30 mL of petroleum ether was added to it and shaken again for 2 min. The two organic layers were taken and concentrated using rotary evaporator to about 5-10 mL.

Clean up: Extracted samples were cleaned up based on the method of Abo-El-Saad (2001). Therefore, activated florisil 60-100 mesh (10 g activated at 130°C for 16 h) was added to 300×25 mm chromatographic column in small portions, while tapping the column. A layer of anhydrous sodium sulfate was placed at the top of florisil. The column, pre wet by allowing 20-25 mL of petroleum ether. Extracted samples were transferred to the column. A total of 40 mL of the eluting mixtures (15 and 50% diethyl ether in petroleum ether (20 mL/each) for pirimiphos-methyl or chlorpyrifos-ethyl) and 80% benzene in petroleum ether for cypermethrin or fenvalerate were used. The eluent was concentrated to 5 mL.

Determination: Determination of insecticides was carried out by gas liquid chromatography (GC-14 Shmiadzo) equipped with FPD and ECD detectors. The conditions for pirimiphos-methyl and chlorpyrifos-ethyl were: column (4% OV-210 on chromosorb WHP80-100 mesh), 220°C, injector 250°C and detector 250°C. Same conditions were used for cypermethrin and fenvalerate except for column temperature was 230°C. Nitrogen was used as carrier gas (99.99% purity) at flow rate of 60 mL/min⁻¹. The residue was calculated according to the method of Goodspeed and Chestnut (1991). The average rates of recovery of each insecticide were determined and the quantification of the residues was corrected according to the rate of recovery. The data were subjected to statistical analysis (Snedecor and Cochran, 1967).

RESULTS AND DISCUSSION

Residues and decay of pirimiphos-methyl: Results of Table 1 revealed that the maximum amount of residues was at zero (813.5, 735.3 and 855.7 mg kg⁻¹) in distilled, well and SHW, respectively. By increasing time from treatment the residues reduced where it reached 574.1, 246.3, 208.4 and 9.5 mg kg⁻¹ after 7, 14, 21 and 75 days, respectively in distilled water. Same trend of residue reduction was observed in both well and SHW where it reached 368.1, 61.3, 45.5 and 25.3 mg kg⁻¹ in well water and 475.3, 359.1, 239.2 and 6.7 mg kg⁻¹ in SHW after 7, 14, 21 and 75 days, respectively. The data also showed that the decay of pirimiphos-methyl after one week was high in well water (49.9%) compared with that of distilled and SHW (29.4 and 44.5%). Moreover, the mean amount of residues revealed that along 75 days, well water had the

Table 1: Residues and decay of Pirimiphos-methyl in different types of water under laboratory conditions

Time (day)	Distilled water residues (mg kg ⁻¹)	Decay (%)	Well water residues (mg kg ⁻¹)	Decay (%)	Standard hard water residues (mg kg ⁻¹)	Decay (%)
0	813.5±9.6	0.0	735.3±10.4	0.0	855.7±1.3	0.0
7	574.1±3.8	29.4	368.1±19.0	49.9	475.3±11.1	44.5
14	246.3±1.2	69.7	61.3±3.1	91.7	359.1±7.2	58.0
21	208.4±5.2	74.4	45.5±1.4	93.8	239.2±3.2	72.0
75	9.5±5.9	98.8	25.3±2.1	96.6	6.7±0.1	99.2
Mean	368.5		251.9		429.4	
LSD _{0.05}	72.6		40.7		60.4	

Table 2: Residues and decay of chlorpyrifos in different types of water under laboratory conditions

Time (day)	Distilled water residues (mg kg ⁻¹)	Decay (%)	Well water residues (mg kg ⁻¹)	Decay (%)	Standard hard water residues (mg kg ⁻¹)	Decay (%)
0	544.8±9.8	0.0	584.1±4.8	0.0	794.3±7.9	0.0
7	480.8±7.8	11.7	550.1±19.0	5.8	479.3±7.9	39.7
14	383.8±4.2	29.5	441.9±9.6	24.2	438.2±1.2	44.8
21	322.6±9.3	40.8	343.1±8.5	41.2	367.4±8.1	53.7
75	2.6±0.2	99.5	8.9±0.1	98.5	9.9±0.1	98.7
Mean	336.9		385.5		417.8	
LSD _{0.05}	125.8		157.3		37.1	

Table 3: Residues and decay of cypermethrin in different types of water under laboratory conditions

Time (day)	Distilled water residues (mg kg ⁻¹)	Decay (%)	Well water residues (mg kg ⁻¹)	Decay (%)	Standard hard water residues (mg kg ⁻¹)	Decay (%)
0	27.2±0.2	0.0	27.3±0.9	0.0	40.6±1.6	0.0
7	5.6±0.1	79.4	5.9±0.9	78.4	7.1±1.1	82.5
14	3.6±1.3	86.8	4.3±0.4	84.2	5.9±0.6	85.5
21	3.0±0.3	88.9	1.9±0.2	93.0	3.1±0.2	92.4
75	2.1±0.1	92.2	1.5±0.1	94.5	1.1±0.3	97.3
Mean	8.3		8.1		11.6	
LSD _{0.05}	6.6		1.1		11.6	

Table 4: Residues and decay of fenvalerate in different types of water under laboratory conditions

Time (day)	Distilled water residues (mg kg ⁻¹)	Decay (%)	Well water residues (mg kg ⁻¹)	Decay (%)	Standard hard water residues (mg kg ⁻¹)	Decay (%)
0	67.7±9.4	0.0	47.9±1.6	0.0	82.7±3.9	0.0
7	10.3±0.8	48.8	15.4±4.4	67.8	19.3±3.8	67.7
14	7.7±0.5	88.6	9.4±1.9	80.4	11.9±2.1	85.6
21	6.1±1.3	91.0	5.8±0.4	87.9	9.1±0.3	89.0
75	2.4±0.1	96.5	3.2±0.6	93.3	4.1±0.3	95.0
Mean	18.6		16.3		25.5	
LSD _{0.05}	32.8		3.6		4.7	

less residues or more decay followed with distilled and SHW. The statistical analysis showed significant differences between the determined amount of residues at zero (initial deposit) and that after 7 days.

Residues and decay of chlorpyrifos-ethyl: Data of Table 2 revealed that the maximum amount of residues was at zero (544.8, 584.1 and 794.3 mg kg⁻¹) in distilled, well and SHW, respectively. By increasing time from treatment the residues reduced where it reached 480.8, 383.8, 322.6 and 2.6 mg kg⁻¹ after 7, 14, 21 and 75 days, respectively in distilled water. Same trend of residue reduction was observed in both well and SHW where it reached 550.1, 441.9, 343.1 and 8.9 mg kg⁻¹ in well water and 479.3, 438.2, 367.4 and 9.9 mg kg⁻¹ in SHW after 7, 14, 21 and 75 days, respectively. Decay of chlorpyrifos-ethyl in distilled water after one week was 11.7% then increased afterwards and reached 29.5, 40.8 and 99.5% of the amount determined at zero (initial deposit) after 14, 21 and 75 days.

Same trend of decay was observed in both well water and SHW where it reached 98.5 and 98.7% after 75 days. However, the decay was rapid after one week in distilled and well water compared with that of SHW.

Residues and decay of cypermethrin: Data revealed that the maximum amount of residues was at zero (27.2, 27.3 and 40.6 mg kg⁻¹) in distilled, well and SHW, respectively (Table 3). Then residues reduced to 5.6, 3.6, 3.0 and 2.1 mg kg⁻¹ after 7, 14, 21 and 75 days, respectively in distilled water. Same trend of residue reduction was observed in both well and SHW where it reached 5.9, 4.3, 1.9 and 1.5 mg kg⁻¹ in well water and 7.1, 5.9, 3.1 and 1.1 mg kg⁻¹ in SHW after 7, 14, 21 and 75 days, respectively. The data also showed that the decay of cypermethrin was high after one week in the three types of water where it exceeded 75%. The statistical analysis revealed significant differences between the amount of residues determined at zero and that at one week while no

significant differences between the amount of residues after one week and that after 14, 21 and/or 75 days. From the previous data it is apparent that the rate of cypermethrin was relatively high in the three types of water after one week then reduced afterwards.

Residues and decay of fenvalerate: Results of Table 4 showed that the maximum amount of residues was at zero (67.7, 47.9 and 82.7 mg kg⁻¹) in distilled, well and SHW, respectively. By increasing time from treatment the residues reduced where it reached 10.3, 7.7, 6.1 and 2.4 mg kg⁻¹ after 7, 14, 21 and 75 days, respectively in distilled water. Same trend of residue reduction was observed in both well and SHW where it reached 15.4, 9.4, 5.8 and 3.2 mg kg⁻¹ in well water and 19.3, 11.9, 9.1 and 4.1 mg kg⁻¹ in SHW after 7, 14, 21 and 75 days, respectively. The data also showed that the decay of fenvalerate after one week was high in well and SHW water (67.8 and 67.7%) compared with that of distilled (48.8%). Further, the decay of fenvalerate was relatively high after one week in the three types of water. The statistical analysis revealed significant differences between the amount of residues determined at zero and that at one week while no significant differences between the amount of residues after one week and that after 14, 21 and/or 75 days in both well and SHW.

From the results it is apparent that the rate of decay of pirimiphos-methyl was more compared with that of chlorpyrifos-ethyl in the three different types of water where the rate of decay of chlorpyrifos-ethyl was relatively low during the first two weeks then the rate increased significantly afterwards. Moreover, the decay of synthetic pyrethroid insecticides (cypermethrin and fenvalerate) was relatively high after one week when compared with organophosphorus insecticides (pirimiphos-methyl and chlorpyrifos-ethyl) in the three types of water. The persistent of chlorpyrifos-ethyl point to the expected risk on the environment when extensively used for controlling insect pests on crops and leached to ground water. Further, the variation of decay in the three types of water might due to the difference in pH's or the presence or absence of ions, cations, micro flora and/or micro fauna in water. The results in line with Ioannis *et al.* (2001) who reported that the presence of humic substances in lake, river marine water reduces degradation rate of pesticides in comparison with distilled water and ground water. However, the photo degradation process in soil is faster than in water.

DISCUSSION

The above results given in Table 1 revealed that the residue of pirimiphos-methyl in the three types of water was considered high after 75 days especially in ground

well water in which the residue of this insecticide was 25 mg kg⁻¹ even though percent of decay of such insecticides was reached in well water to 96.6%. This level has ecotoxicological effects for aquatic flora and fauna as well for human health if used for public consumption (Witter *et al.*, 1999; Jergentz *et al.*, 2005; Sereda and Meinhardt, 2005).

Table 2 showed that residue of chlorpyrifos-ethyl was 8.9 and 9.9 mg kg⁻¹ after 75 days in well water and SHW, respectively. These data indicated that the residue of this insecticide in both well water and SHW was not acceptable range for drinking water since this insecticide could be highly effective on human health. This data were in consistent with those reported by Abo-El-Saad (2001) who found that chlorpyrifos-ethyl residue was significantly higher on vegetable than acceptable range in Saudi Arabia. This is could be due to slow degrading of this insecticide by microbial action (WHO, 2004).

In contrast, cypermethrin and fenvalerate residues in the three types of water were found to reach less level after 75 days compared to organophosphorus compound. However, we observed that residue of cypermethrin in the three types of water were less than fenvalerate that may be due to the absence of acid moiety in fenvalerate which could played a fundamental role in its degradation.

It would be fairly concluded that increasing water consumption for domestic use is leading to potential water shortage in Saudi Arabia as well as, water pollution by pesticides make us attention to focus on many studies related to water management program. This study was considered essential because on such investigation had been undertaken previously in Saudi Arabia and its will provide an important information for alarming on the health of humane beings in this region and to develop strategies for minimizing the impact of agricultural on water resources. This data can be used to design an integrated management program to control the concentration of pesticides in drinking water. More detailed monitoring studies have to be carried out on different seasons with a wider spectrum of pesticides to get a clear baseline data for the entire location.

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