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PERSISTENCE OF CHLORPYRIFOS AND FENPROPATHRIN ALONE AND IN COMBINATION WITH FERTILIZERS IN SOIL AND THEIR EFFECT ON SOIL MICROBES

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Abstract

The study was designed to determine the persistence of chlorpyrifos (an organophosphate) and fenpropathrin (pyrethroid) pesticide alone and in combination with synthetic fertilizers viz., Urea, DAP, SOP and Foliar fertilizer Polydol with tap/hard water. All the fertilizers were added @ 1% to the soil collected from vegetable growing area of Memon Goth, Karachi and insecticide fortification was done @ 100 ppm and 1000 ppm. Results indicated that the addition of fertilizers had no effect on the persistence of OP and pyrethroid pesticides. Similarly, the changes observed in the pH both with tap and hard water had no effect on the persistence. The 2-months study showed 100% persistence of both the pesticides.

Introduction

Pesticide formulations, mostly organic in nature, are likely to be degraded after application to plant/soil. The degradation/persistence of pesticide formulations depends upon a number of variables like temperature, moisture, acidity, adjuvants and structure of the compounds etc. Due to the introduction of high yielding varieties and new technologies, the soil is continuously being depleted in major nutrients as well as trace elements. To overcome this deficiency, chemical fertilizers are applied along with pesticide formulations if they are compatible and advantageous. Widespread use of pesticides over the past 30 years has resulted in the imbalance of the natural biological system, (Agnihotri *et al*., 1981).

Soil microorganisms play an important role in the soil ecosystem as they consume and degrade certain pesticides. These microorganisms degrade pesticides to artificial chemicals and use them as growth substances, consequently decreasing the persistence of the pesticides in the environment. This microbial activity depends upon many factors like temperature, pH, moisture and oxygen content, type of soil, nature of pesticide, tillage and vegetation. Pesticide may have the potential of disturbing microbial events in the environment, polluted by these chemicals by reduction of species number, alteration of habitat with species reduction, changes in behaviour, growth changes altered reproduction, changes in food quality and quantity, resistance, susceptibility and biological magnification as reported by Pimental (1971).

According to the report of Sakata *et al*., (1990) the half-life of fenpropathrin was 11-17 days in aerobic upland soils collected from different locations in Japan and negligible in sterilized soil. Chlorpyrifos is a slowly degradable pesticide and non-systemic in nature whereas fenpropathrin is degraded quickly when exposed to light and air. Chlorpyrifos was found persistent at low concentration, in the surface soil (0-25 mm)

(Haigreaves *et al.*, 1999). The degradation of the chlorpyrifos studied in Australia under standard laboratory conditions (25°C, 60% field moisture capacity and darkness for 24 months) showed 75-90% loss of residues during the 24 month incubation period (Sundaram *et al.*, 1999).

Appreciable difference in degradation rate has been observed in soils with different pH values. A faster rate was observed in soil with higher pH and cation exchange capacity, under laboratory conditions (Huang *et al.*, 2000). Repeated application of chlorpyrifos did not modify its degradation rate whereas others suppressed their own rate of degradation. When applied in combination with fenamiphos and chlorothalonil, the degradation rate of chlorpyrifos was decreased. The effects of chlorpyrifos on the soil microbial characteristics were insignificant (Singh *et al.*, 2002a). The half-life of chlorpyrifos was 36-46 days with negligible effects on microbial characteristics (Sing *et al.*, 2002b). Chlorpyrifos degradation increases with soil temperature. A positive correlation between the pesticide degradation rate and soil water content has been reported by Castro *et al*., (2002).

The objective of the present investigation was to estimate the degradation of chlorpyrifos and fenpropathrin in combination with fertilizers DAP, SOP, Urea and foliar fertilizer Polydol in agricultural soil at recommended and 10 times higher than the recommended dose (RD) under laboratory conditions using hard and tap water.

Materials and Methods

Collection of soil: Soil used for the study was collected from vegetable growing fields of Memon Goth, Karachi in polythene bags from 0-25 cm depth randomly and carried to the laboratory. Soil was stored in the refrigerator at 5-6^{o}C and kept moist to maintain the biological activity between the time of collection and preparation of the inoculum.

Soil treatment, incubation: The treatments were done by mixing fertilizers @ 1% and each of the organophosphorus and pyrethroid pesticides separately @ 100 ppm and 1000 ppm with 25 gm of dried sterilized soil in glass tubes. Pesticides used were Kurifast 40% EC (chlorpyrifos) and Dathrin 20% EC (fenpropathrin) whereas the fertilizers used were Polydol (foliar fertilizer) received from M/s. Pak Agro Chemicals and DAP, SOP and Urea purchased from local market.

Treatments used for the experiment were as follows:

T1 -	Soil + Pesticide.	T2 -	Soil + Pesticide + Culture
T3 -	Soil + Pesticide + Culture + DAP.	T4 -	Soil + Pesticide + Culture + SOP.
T5 -	Soil + Pesticide + Culture + Urea.	T6 -	Soil + Pesticide + Culture +Polydol.

Soil culture was prepared by adding 1 gm of soil in 100 ml of sterilized water.

After preparing each treatment the soil was flooded with water (tap/hard water separately) to cover the surface. All the treatments were kept at room temperature (28-30^{o}C) under darkness for 1, 7, 14, 30 and 60 days. Tubes were randomly selected for extraction and analysis at the day of application (0 day) and after 1,7,15,30 and 60 days of incubation. All treatments were run in triplicate.

Extraction and analysis of pyrethroids and organophosphate: For extraction of both organophosphates and pyrethroids, the treated 25 gm soil samples were air dried, homogenized with 0.5 gm charcoal activated for 4 hr at 120°C, 1.0 gm Florisil activated for 4 hours at 650°C and 5 drops of 25% NH_4OH solution, placed over a 2.5 cm layer of anhydrous sodium sulphate (analytical grade) in a glass column with 34 cm length and 2.5 cm diam. Extraction was done by using a solution of n-hexane (distilled) and acetone (distilled) in a ratio of 2:1 as per Mumtaz *et al.*, (1983).

Eluted material was collected in a 250 ml conical flask (Pyrex) and later evaporated on rotary evaporator to almost dryness taken-up in 2-5 ml quantity n-hexane in small glass vials for GLC determination.

Gas chromatographic determination: The extract was analyzed on Shimadzu GC-14-B (Japan) model (equipped with flame ionization detector) for OP and pyrethroid pesticides with the parameters as follows: Column temperature 240°C, injector temperature 270°C and detector temperature 300°C where as hydrogen gas flow was 0.7 kg/cm^2, air flow and nitrogen gas flow was 0.5 kg/cm^2. The length of glass column was 1m with 0.3 mm internal diam., packed with 3% OV-101 on 100-120 mesh chrom WAW, DMCS treated.

The retention time, detection limits and % recovery of chlorpyrifos and fenpropathrin are as follows:

Retention time of chlorpyrifos:	1.6 min.
Retention time of fenpropathrin:	5.2 min.
Detection limit:	1 μg
Recovery percentage:	100%

Microbial growth activity: Aliquot samples of approximately 1 gm of soil from each treatment were also taken to monitor the microbial activity by the standard dilution pour plate technique (using nutrient agar medium). The plates were incubated at room temperature for 24 hours. Colonies were counted and observed. Later on the colonies were picked up and transferred to nutrient broth tubes for further identification.

pH observation: The change in pH with (tap/hard water) fertilizer and pesticide individually with soil was observed and recorded after 0, 24 and 48 hours. Similarly the pH changes in tap and hard water after adding soil, fertilizers and pesticides in combination was also observed after 0,7,15,30 and 60 days.

Results and Discussion

Results of the study showed that chlorpyrifos belonging to organophosphorus group and fenpropathrin pyrethroid group were stable upto 2 months incubation in soil i.e. degradation was not observed in the parent compounds of both the pesticides. Upto 100% recovery of the active ingredients of the parent insecticide was obtained for both the pesticides after 2 months in all the six treatments. Chromatogram of the formulated pesticides at 0 day and after 1 month and 2 months extracted samples from treated soils are presented in Fig. 1. In all the six treatments (T_1-T_6), pH was noted at different time intervals for both the pesticides with tap water and hard water treatments, individually

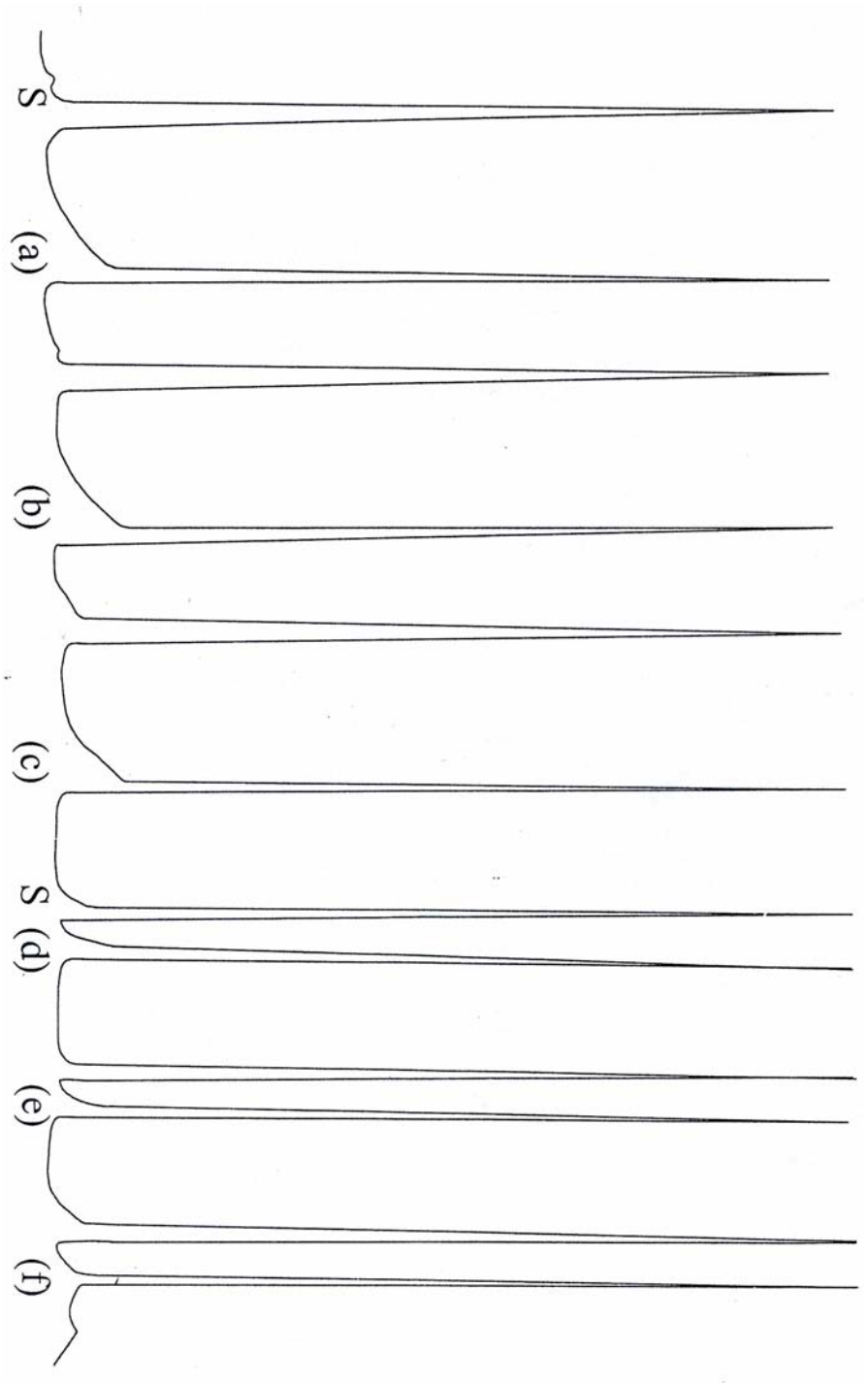

Fig. 1. Gas chromatograms of fenpropathrin (a-c), chlorpyriphos (d-f), extracted from treated soil. a&d (0 day), b&e (1 month), c&f (2 months) and S (solvent).

and in combination (Table 1 and 2). The soil pH measured without treatment was considered as control, and the changes in pH occurred were measured by the addition of pesticides and fertilizers individually. The pesticides and fertilizers pH was also monitored separately to note the difference in change of pH when combined. One month incubation observations reflect, pH change with chlorpyrifos and fenpropathrin after adding fertilizer and pesticides in combination, but the change in pH had no effect on the degradation of active ingredients of both the pesticides i.e., chlorpyrifos and fenpropathrin which shows that the pH has no relation to pesticides persistence, whereas it has been reported by *Gold et al.,* (1996) that soil pH and clay content greatly affect the persistence of pesticides. Racke *et al.,* (1994) and Cink & Coats, (1993) found that the applied concentration has a significant effect on the degradation of chlorpyriphos in urban soil (pH 7.8). Similarly it is reported by Huang *et al.,* (2000) that degradation of chlorpyrifos was enhanced with higher pH due to addition of animal derived lagoon effluent, a good source of inorganic nutrients. It was also noted that a single microbial community became dominant. Therefore with this background 0% degradation was observed in our study of 2 months incubation as the high dose applied was near to the termite control rate (1000 $\mu g\ g^{-1}$) whose degradation rate is much slower and may be concentration dependent in the soil environment. Due to the high dose, the microbial fauna is disturbed and degrading bacterial population is lowered, therefore the pesticide persist for a longer time. Pesticide adsorption and desorption are important processes that influence the amount of pesticide retained by the soil matrix and its susceptibility to movement in the soil profile (Zku & Selim, 2002).

Table 1. pH changes in tap and hard water after adding soil, fertilizers and pesticides individually.

Treatments	TAP WATER			HARD WATER		
	0 hour	24 hours	48 hours	0 hour	24 hours	48 hours
Control (only water)	7	9	9	7	8	8
Soil + water	7	9	9	7	8	8
SOP + water	8	10	10	7	8	9
DAP + water	7	7	7	7	6	5
Urea + water	7	9	9	7	8	8
Polydol + water	7	7	7	7	6	6
Dathrin + water	8	9	9	6	6	9
Kurifast + water	8	9	9	6	8	7

Tap water: Water supplied by the University of Karachi.
Hard water: Hardness = 342 ppm.

Note: The value of 342 calcium carbonate has been chosen to simulate average hard (irrigation) water conditions or average untreated hard water, which is established by the WHO in requirements for public health and agricultural pesticides (A.C. Hill, 1964).

The studies of the effect of both the pesticides (chlorpyrifos and fenpropathrin) on microbial growth showed that 100 ppm fortification had no adverse effect whereas 1000-ppm showed certain changes, few colonies were suppressed whereas count of some of the bacterial colonies was increased. Two months incubation showed that the *Bacillus* sp., was found sensitive in the soil fortified with chlorpyrifos whereas fenpropathrin did not

Table 2. Observation of ph changes in tap and hard water after adding soil, fertilizers and pesticides in combination

Treatments	Tap water										Hard water									
	0 Day		7 Days		15 Days		30 Days		60 Days		0 Day		7 Days		15 Days		30 Days		60 Days	
	K	D	K	D	K	D	K	D	K	D	K	D	K	D	K	D	K	D	K	D
T_1 S (Autoclaved) + P	7	8	7	7	8	7	8	7	8	7	7	8	7	7	7	7	7	7	7	7
T_2 (S + P + C)	7	8	7	7	7	7	8	7	8	7	7	7	7	7	7	7	7	7	7	7
T_3 (S + P + C + DAP)	7	8	5	7	7	7	7	6	7	6	7	8	7	7	7	7	7	7	7	7
T_4 (S + P + C + SOP)	8	8	8	7	8	6	9	9	9	9	7	6	7	8	7	8	7	8	7	8
T_5 (S + P + C + UREA)	7	8	8	9	9	9	9	9	9	9	7	7	7	7	7	7	7	9	7	9
T_6 (S + P + C + POLYDOL)	7	6	8	6	9	9	8	9	8	9	7	6	7	7	7	8	7	8	7	8

Key:
K = Kurifast (Chlorpyriphos)
D = Dathrin (Fenpropathrin)
S = Soil
P = Pesticide.
C = Culture (Un-autoclaved Soil+Water).
DAP = Diamonium Phosphate.
SOP = Salt of Potash

have adverse effect on *Bacillus* sp. One type of colony, small size and pin pointed identified as *Klebsiella* spp., was enhanced in all the treatments except T_1 (Soil autoclaved + pesticide). The *Klebsiella* was again the most abundant nitrogen-fixing bacteria. Its enhancement was positive from soil fertility aspects. The information so far obtained reflects that research is further needed for 6 months to 2 years observation, especially when chlorpyrifos is used for termite control.

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