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Persistence of Pesticide Formulations Alone and in Combination with Fertilizers in Soil

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Experiments were designed to investigate the persistence of the active ingredients in commercial pesticide formulations *viz*; cypermethrin 10% EC, fenvalerate 20% EC, deltamethrin 25% EC, malathion 25% EC, profenofos 40% EC and chlorfenvinphos 25% EC alone and with various commercial fertilizers *viz*; urea, DAP (Diammonium phosphate) & SOP (Sulphate of potash) in soil. All fertilizers were added @ 1% to soil collected from vegetable growing areas near Karachi with insecticide fortifications @ 100 ppm and 400 ppm. Results indicate that the application of fertilizers with insecticides does affect the persistence of the insecticides to some extent although each insecticide behaved differently. Malathion was most affected by all fertilizers and deltamethrin least affected.

Key words: Persistence, Fertilizer, Insecticide, Soil.

Introduction

Pesticide formulations, mostly organic in nature, are liable to degrade after application to plant/soil. The degradation/ presistence of pesticide formulations is an important factor and depends upon a number of variables like temperature, moisture, acidity, adjuvants and structure of the compound etc. Due to the introduction of high yielding varieties and new technology, the soil is continuously being depleted in major nutrients as well as trace elements. To replace these nutrients, chemical fertilizers are being applied along with pesticide formulations if they are compatible and advantageous.

Some work has been done on the compatibility of pesticides and fertilizers this aspect such as the study of carbofuran coated fertilizer which proved to be stable with low toxicity (Zhou ZuCheng 1995). High levels of effectiveness were demonstrated in field trials in Poland with a wide range of pesticides applied along with the foliar fertilizers Basfoliar and Solubur DF (Mrowczynski *et al* 1997). A study of the effect of foliar fertilizer on residues of profenofos showed that the difference between residues of profenophos alone and profenophos that had been applied in combination with fertilizer, reduced with time (Shahin and El Atlal 1990). A recent study conducted in Belgium indicated increased pesticide persistence by a mechanism of slow release of insecticides (aldicarb, thiofanox, imidacloprid, chlorpyrifos and chlor fenvinphos) in soil related to presence of organic matter (Rouchaud *et al* 1996).

In a study conducted on persistence of pesticide formulation malathion 25 WP, the degradation was only 1% from the day of treatment upto 6-months with urea @ 2% combination (Singh and Prasad 1982). Under practical field conditions, it has been found that chlorfenvinphos depletes only slowly on peat but on other soils in United Kingdom, the initial half-life was usually within the range of 4-30 weeks (Beynon and Stoydin 1966; Suett 1971).

This study was undertaken to examine the persistence and compatability of pyrethroid and organophosphate insecticides most commonly used now-a-days for crop protection in Pakistan, *viz*; cypermethrin, deltamethrin, fenvalerate, profenofos, chlorfenvinphos and malathion alone and in combination with the fertilizers urea, ADP (diammonium phosphate) and SOP (sulphate of potash) in soil.

Materials and Methods

Chemicals and glasswares. Glass column 34cm length with 2.5 cm dia, microsyringe 100 µl, glass tubes, conical flask, volumetric flasks, petri dishes (dia 3.5"), commercial formulations of both pyrethroids (Cypermethrin, Deltamethrin and Fenvalerate) and organophosphorus compounds (Profenofos, Chlorfenvinphos and Malathion) were used for the study. All other reagents (*n*-hexane and actone) were of analytical grade or equivalent, charcoal activated for 4 h at 120°C, florisil 60-100 mesh activated for 4 h at 650°C, amonium hydroxide solution 25% in distilled water, and anhydrous sodium sulphate. Commercially available fertilizers urea, DAP (diammonium phosphate) and SOP (sulphate of potash) were procured from the market.

Soil. Soil used for the study was collected from a vegetable growing fields near Karachi, brought to the laboratory and

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stored in the refrigerator (approximately 5-6°C) to maintain biological activity between the time of collection and its use to prepare an inoculum. Soil was dried and passed through a 2 mm sieve prior to pesticide/fertilizer treatment.

Soil treatment, incubation and sampling. The treatments were prepared by mixing fertilizers @ 1% and each of the three organophosphorus or pyrethroid insecticides @ 400 ppm with 25 g of dried soil (1 ml = 10 mg) from a 1% stock solution in *n*-hexane. Treatments were designated as follows:

Soil + Pesticides.....T1
Soil + Pesticides + Urea.....T2
Soil + Pesticides + DAP T3
Soil + Pesticides + SOP T4

Soil inoculum (15 ml-suspension) prepared as 20% soil in distilled water was uniformly sprinkled on each treatment. After pesticide/fertilizer and soil inoculum application, the soil was flooded with water to the extent as to cover the surface and moisture maintained during the incubation period. The treated soil in petridishes were kept at room temperature (28-30°C) in the laboratory. Dishes were randomly selected for extraction and analysis on the day of application (0 day) and after 1, 5, 10, 15 days and 1 month of incubation. All treatments were run in triplicate.

Extraction and analysis of pyrethroids & organophosphates. For extraction of both organophosphates and pyrethroids from soil, the soil samples (25 g) were air dried, homogenized with charcoal (0.5 gm) and florisil (1.0 gm) and 5 drops of NH_4OH solution, placed above a 2.5 cm layer of sodium sulphate in a glass column and extracted by the method of Mumtaz *et al* (1983) with a slight modification in the eluting solvent ratio of *n*-hexane-acetone (2:1 instead of 4:1).

After extraction, the eluate was evaporated to almost dryness and taken-up in 2 ml *n*-hexane for GLC determination.

Gas chromatographic determination. A Pye-Unicam series-204 gas liquid chromatograph, equipped with a Flame Ionization detector was employed with the following operating parameters.

Organophosphorus pesticides. Glass column 1 meter long x 4 mm i.d. packed with 3% OV-101 on 100-120 mesh chrom WAW, DMCS treated.

Temperature. Injector 250°C. Column oven 200°C, detector 250°CC, attenuation 128. Nirogen carrier gas 40 ml min^{-1}, hydrogen 40 ml min^{-1} and air 300 ml min^{-1}, chart speed 120 sec cm^{-1}.

Pyrethroids. Similar to organophosphorus pesticides except for the column oven temperature. It was 220°C.

GLC retention time, detection limits and percent recovery of mixtures of studied organophosphorus and synthetic pyrethroid pesticides are separately given in Table 1. The chromatograms of 0 day and 1 month study are presented in Fig 1-2.

Results and Discussion

Effect of fertilizers on organophosphates. Average results of 400 ppm fortification presented in Table 2 showed that malathion, profenofos and chlorfenvinphos alone and in combination with urea, SOP and DAP behaved differently. Malathion alone in soil did not degrade during the 1 month of incubation, whereas in the presence of all the chemical fertilizers little degradation was observed on 1, 5, 10 and 15 days, but nearly 65-67% degradation of the insecticide was observed at 1 month. All treatments were stabile up to 5-days. Profenofos alone in soil gradually degraded from the 5th day after treatment (24%)degraded to the end of the experiment (77% degraded). The profenofos and urea treatment was stabile but upto 10 days, 24% and 77% degradation was observed at 15 and 30 days respectively. The profenofos, DAP and SOP treatments were stabile upto 5

Table 1
Percent recovery, minimum limit of detection and GC retention times of studied compounds

Pesticide group	Quantity injected (μg)	Percent recovery	Min. limit detection (μg)	Rt. time (min)
Pyrethroids				
Cypermethrin	1.00	95.00	0.10	14.00
Fenvalerate	1.00	95.00	0.10	20.60
Deltamethrin	1.00	90.00	0.25	30.80
Organophosphates				
Malathion	1.00	99.00	0.05	2.00
Profenofos	1.00	99.00	0.10	4.00
Chlorfenvinphos	1.00	99.00	0.05	3.00

days but the amount degraded gradually increased to 85% within one month. Chlorfenvinphos alone and with urea, was stabile upto 15 days but was degraded (upto 62%) without fertilizer and 33% degraded with ureas. Treatment with DAP and SOP were stabile for 5 days. At day 10 decrease of (15%-17%) of the chlorfenvinphos has been degraded and 73% deterioration was observed at 1 month in both treatments.

Effect of fertilizer on pyrethroid. Results presented in Table 3 show that 50% degradation occurred by the 5th day for all cypermethrin treatments. The amount degraded in-

Table 2
Persistence of organophosphates in soil alone and in combination with fertilizers

(Fertilizers	Active ingredient % (days)					
Treatments*)	0	1	5	10	15	30
Malathion 25% EC						
T1	25.0	25.0	25.0	24.9	24.9	24.9
T2	25.0	25.0	25.0	25.0	24.9	8.25
T3	25.0	25.0	25.0	24.9	22.5	8.75
T4	25.0	25.0	25.0	25.0	24.9	8.25
Profenofos 40% EC						
T1	40.0	40.0	30.4	21.17	14.11	9.4
T2	40.0	40.0	40.0	40.0	30.4	9.4
T3	40.0	40.0	40.0	20.9	14.11	6.0
T4	40.0	40.0	40.0	32.9	24.0	6.0
Chlorfenvinphos 24% EC						
T1	24.0	24.0	24.0	24.0	24.0	9.3
T2	24.0	24.0	24.0	24.0	24.0	15.9
T3	24.0	24.0	24.0	19.2	16.8	6.5
T4	24.0	24.0	24.0	20.0	18.6	6.6

*Treatments: T1, Soil + Pesticides; T2, Soil + Pesticide + Urea; T3, Soil + Pesticide + DAP; T4, Soil + Pesticide + SOP.

Table 3
Persistence of pyrethroids in soil alone and in combination with fertilizers

(Fertilizers	Active ingredient % (days)					
Treatments*)	0	1	5	10	15	30
Cypermethrin 10% EC						
T1	10.0	10.0	5.40	4.50	2.16	0.00
T2	10.0	10.0	5.31	3.75	3.12	3.12
T3	10.0	10.0	5.0	2.50	2.25	2.25
T4	10.0	10.0	4.79	4.79	4.37	0.79
Fenvalerate 20% EC						
T1	20.0	20.0	20.0	20.28	14.60	10.50
T2	20.0	20.0	20.0	14.60	12.0	3.32
T3	20.0	20.0	10.0	9.0	7.0	3.5
T4	20.0	20.0	13.0	8.6	7.38	2.63
Deltamethrin 25% EC						
T1	25.0	25.0	24.9	24.0	12.5	12.5
T2	25.0	25.0	23.8	16.65	16.65	12.5
T3	25.0	25.0	24.0	17.5	16.65	12.5
T4	25.0	25.0	25.0	17.5	16.5	10.0

*Treatments: T1, Soil + Pesticides; T2, Soil + Pesticide + Urea; T3, Soil + Pesticide + DAP; T4, Soil + Pesticide + SOP.

creased near 100% at 1 month for cypermethrin alone and with SOP but for the urea and DAP treatments, only 70% and 80% degradation respectively occurred. Fenvalerate alone, was stabile for 10 days and 50% degradation occurred after 1 month. Fenvalerate treatments with Urea, SOP and DAP was less stabile with a maximum of 85-90% deterioration after 1 month. A similar pattern of deterioration was observed for all fertilizer treatments.

Deltamethrin alone and in all combination with fertilizers was 50% degraded after 1 month. In soil alone it was stabile upto 10 days whereas with urea, SOP and DAP, deterioration started after 5 days of treatment.

Conclusion

It is evident from the results that the six insecticides studied responded differently. According to literature (Pesticide Manual 1998), 50% deterioration (DT50) occurs within 1-3 weeks for most of the organophosphates and for pyrethroids some have half-life in soil upto 75-80 days. For malathion, as reported the persistence is 2-years (Farm Chemical Hand Book 1990). In our study, malathion showed stability in the treatment without fertilizer but with urea, SOP and DAP combination, degradation occurred within 1 month incubation in contrast to the finding by Kalyan Singh where only 1% degradation is reported upto 6 months with urea @ 2% combination in the absence of soil which may be due to the fertilizers increasing the population of certain bacteria responsible for degradation of this insecticide. As reported in a recent study (Rouchaud 1996), the persistence of chlorfenvinphos increased in the presence of organic matter and our urea treatment responded similarly with 67% of the insecticide remaining after 1 month compared to 38% for chlorfenvinphos alone. Amongst the six insecticides, the persistence of malathion in combination with all the three fertilizers was the most affected while deltamethrin and profenofos were the least affected. In case of chlorfenvinphos, only urea showed positive response in persistence, and for cypermethrin, urea and DAP, whereas for fenvalerate neither of the three fertilizers showed positive response in persistence. Generally, it is noted that there is no harm in applying the fertilizer alongwith the insecticide.

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