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Persistence and Degradation of PP993 Pyrethroid, Fonofos, and Chlorpyrifos in a Quebec Cornfield's Soil

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Chemical control has been considered the main management strategy for corn rootworms (CRW) since the successful use of chlorinated hydrocarbons in the late 1940s (Fulton 1946; Hill *et al.* 1948). However, both northern corn rootworm (NCR) *Diabrotica barberi* (Smith and Lawrence) and western corn rootworm (WCR) *Diabrotica virgifera virgifera* (Le Conte), developed resistance to the cyclodiene soil insecticides in the late 1959s and early 1960s (Bigger 1963; Patel and Apple 1966), and to organophosphorus and carbamate soil insecticides in the early 1970s (Caro *et al.* 1973; Williams *et al.* 1976; Ball 1981). With the development of integrated pest management strategies, research has begun to focus on factors such as selectivity, reduction of application rates and environmental fate of chemicals.

In this experiment, residue levels of PP993 (a new pyrethroid insecticide), fonofos and chlorpyrifos, were studied to determine if chemicals, applied to Quebec cornfields at recommmended rates at seeding time, persisted through the period when NCR larvae were active and up to the end of the growing season. The study field at Ormstown had been in continuous corn production since 1972, during which time no insecticide had been used. The soil was a clay loam type and had an average pH of 5.8.

MATERIALS AND METHODS

PP993 as Force® 1G, (2,3,5,6-tetrafluoro-4-methylbenzyl *cis*-3-[Z-2-chloro-3,3,3-trifluoroprop-1-enyl]-2,2-dimethylcyclopropanecarboxylate), fonofos (O-ethyl S-phenyl ethylphosphorodithioate) as Dyfonate® 20G, and chlorpyrifos (O,O-Diethyl-O-(3,5,6-trichloro-2-pyridyl) phosphorothioate) as Lorsban® 15G, were mixed into the soil at planting time with a hand applicator. The application was made in an 18 cm wide band at 3 cm deep and at a rate of 11.2, 5.6 and 7.5 g/10m of row, respectively. The experimental area consisted of two blocks, with each block divided into three subplots. The treatment insecticides were randomized within each block. Each subplot consisted of a 10m row planted with Pioneer® 3994 corn hybrid on 10 May, 1985. Two untreated rows were planted to corn between each subplot.

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Six randomly-selected soil cores, 10cm deep and 5cm in diameter, were removed with a golf cup cutter from each treatment plot and mixed together in groups. Sampling was performed immediately after application, then at 4,8,12 and 23 week intervals. Composite samples from each treatment were brought to the laboratory in plastic bags and stored in a deep freeze at -20°C pending analysis. Samples were then thawed and mixed thoroughly in a home cement mixer and passed through a No. 15 sieve for chemical analysis and moisture determination.

A slight modification to the procedure of Belanger and Hamilton (1979) for extracting insecticides from soils was used in this experiment. Three moist subsamples equivalent to 10g of oven-dry soil from each insecticide treatment, taken at each sampling date, were weighed into 50mL flasks fitted with a teflon-lined stopper. Thirty mL of a mixture of 1:1 acetone:hexane (v/v) of high purity chromatography grade were added to the soil sample, which was then agitated vigorously on a mechanical shaker for two hours. The flask contents were then transferred to a 40X150mm centrifuge tube fitted with a teflon-lined screw cap, then centrifuged (Sorvall® laboratory centrifuge) at 2000 rpm for 5 min. to separate the organic solution from the soil. Each soil sample was re-extracted three more times with 25 mL aliquots of the same solvent mixture. The combined supernatants were washed with 250mL distilled water in a 500mL separatory funnel to remove the acetone. The remaining hexane solution was dried over sodium sulfate in a 22mm i.d. X 400mm long (234mL) Chromaflex® column. The dried solution was diluted to 50mL with fresh hexane.

A Varian® model 3700 gas chromatograph fitted with a Ni^{63} electron capture detector, and a Hewlett Packard® recording integrator (model 3390A) were used for analyzing insecticide residues. A glass column, 1.22m long X 3mm i.d., was packed with Chromosorb W, 100-120 mesh, coated with three per cent OV-17. Operating conditions were: column temperature, 250°C for PP993 and fonofos, 270°C for chlorpyrifos; injector temperature, 250°C; detector temperature, 300°C; nitrogen carrier gas flow rate 50mL/min.; injecting volume 1µL. Recoveries were measured by adding 10 ppm of each insecticide (granular formulation) to an untreated soil sample from the same field and allowing it to stand at room temperature for one hour before extraction. The samples were then processed and analyzed as described above. Quantitation was performed by the method of external standards. Three replicated determinations of each sample were performed and reported values were calculated on an oven-dry basis.

RESULTS AND DISCUSSION

Average recoveries of 89.6 $\pm$ 0.43, 91.0 $\pm$ 0.36, and 89.5 $\pm$ 0.71 per cent were obtained with PP993, fonofos and chlorpyrifos respectively. The concentrations of insecticide remaining in the soil and percentage of the initial concentration of insecticide at each sampling date are given in Table 1 and Figure 1, respectively. The initial concentrations of PP993, fonofos and chlorpyrifos detected in the top 10cm layer of the soil were 0.62, 7.16

and 5.44 ppm respectively (Table 1). Fig. 1 shows that chlorpyrifos decreased to *ca.* 65 percent by four weeks after application, whereas both PP993 and fonofos decreased to *ca.* 75 per cent in that time. Residue levels of all insecticides dissipated at a faster rate during the first four weeks, followed by a slower rate during the rest of the growing season. Fig. 1 shows that 50 per cent of the parent PP993, fonofos and chlorpyrifos in the soil had dissipated in *ca.* 9,12 and 11 weeks respectively. Residues of both fonofos and chlorpyrifos were greater than 2.65 ppm during the critical 4 to 12 week period which coincided with the presence of the NCR larvae in the field, whereas PP993 remained above the 0.27 level. Approximately 30 per cent of the applied fonofos remained at the and of the growing season, whereas *ca.* 20 per cent of PP993 or chlorpyrifos remained.

Table 1. Persistence of PP993, fonofos, and chlorpyrifos in Ormstown, Quebec, cornfield soil.

Weeks after insecticide application	PP993 (1G) 11.2g/10m of row (*)	fonofos[1] 5.6 g/10m of row (*)	chlorpyrifos[2] 7.5g/10m of row (*)
0	0.62 ± 0.05	7.16 ± 1.07	5.44 ± 0.42
4	0.46 ± 0.06	5.41 ± 0.25	3.53 ± 0.61
8	0.34 ± 0.03	4.32 ± 0.23	3.22 ± 0.79
12	0.27 ± 0.02	3.43 ± 0.41	2.65 ± 0.10
23	0.13 ± 0.01	2.21 ± 0.03	1.30 ± 0.14

[1]As Dyfonate 20 G
[2]As Lorsban 15 G
*Values in ppm ± S.D.

The relatively substantial amounts of PP993, fonofos and chlorpyrifos (Table 1) detected from 4 to 12 weeks after application allows an estimate to be made of their likely effectiveness against NCR larvae. In this study, residues of 0.27, 3.43 and 2.65 ppm were detected for PP993, fonofos and chlorpyrifos at 12 weeks after application. These amounts are far in excess of the LD50 values of 0.197, 0.883 and 0.661 ppm resepctively, observed by Elhag (1987) for PP993, fonofos and chlorpyrifos in soil bioassays. In this experiment 50 per cent of the applied chemicals had dissipated from 9 to 12 weeks after application. Whereas Suett (1971) and Mathur *et al.* (1976) found that 50 and 60 per cent of fonofos applied to mineral soil had disappeared in 11 and 18 weeks,

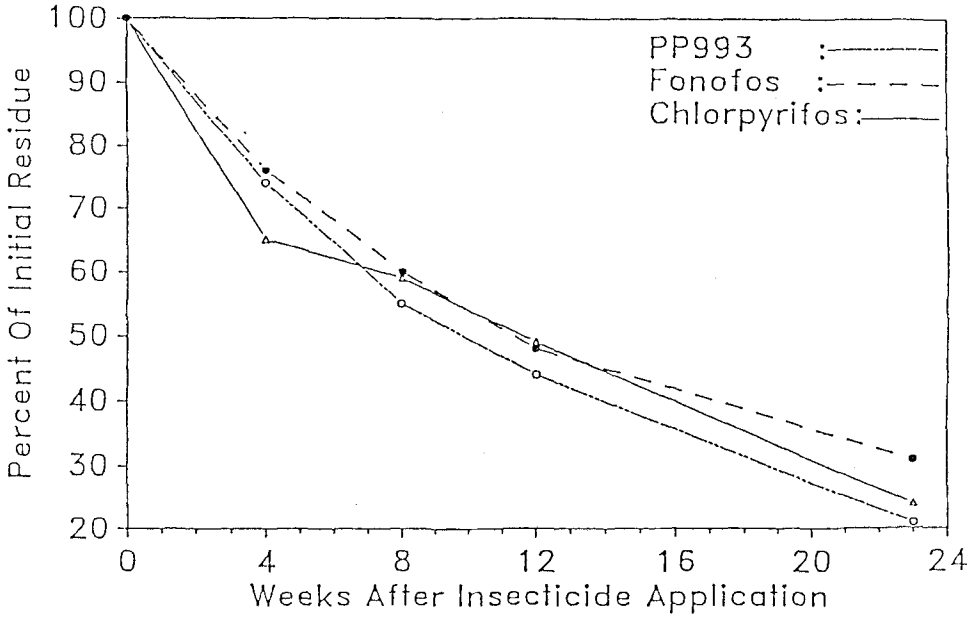

Figure 1. Comparative decline rate of PP993, fonofos and chlorpyrifos as percentage of the initial amount measured at application time.

respectively, Ahmad *et al.* (1979) reported 46 days as the "half life" for fonofos in their particular soil. The data in Fig. 1 demonstrate that 20-30 per cent of the applied chemicals was still present in the soil at the end of the growing season. Due to the effect of winter cold, one would anticipate no appreciable change in residues from the end of the growing season through to the following spring. However, as the spring soil temperature exceeds the critical level of 6-7°C, as reported by Suett (1971, 1975), the residues should start to decline again. Suett (1975) reported that the primary breakdown mehcanisms of parent organophosphorus and carbamate insecticides in soil were mainly microbiological and were inhibited while soil temperatures remained below 6-7°C. Presumably then, under Quebec weather conditions, a small amount of fonofos would be present the following season; Saha *et al.* (1974) found that 3-10 per cent of fonofos was retained by the soil for 29 months in Saskatchewan.

Prolonged persistence of insecticides, particularly if they remain biologically active, may encourage the development of resistant strains of organisms. Moreover, micro-organisms could become adapted for rapid breakdown of insecticides, as reported by Belanger *et al.* (1982). Harris (1972) and Harris *et al.* (1981) noted that many organophosphorus and carbamate insecticides have positive temperature coefficients and that their toxicity decreases as temperatures decline. However, Harris *et al.* (1981) also reported that permethrin, fenvalerate, and cypermethrin are 1.4 to 1.9 times more toxic at 15°C than at 32°C. It seems likely that the low soil temperatures prevailing during winter and early spring in Quebec would reduce substantially the potential toxicity of any insecticide residues persisiting into spring.

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