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Comparative Disappearance of Fonofos, Phorate and Terbufos Soil Residues under Similar South Dakota Field Conditions

N. Ahmad, D. D. Walgenbach, and G. R. Sutter

Entomology-Zoology Department, South Dakota State University and
Northern Grain Insects Research Laboratory, USDA-SEA-AR, Brookings, S. D. 57006

Granular formulations of fonofos, terbufos, and phorate are widely used soil insecticides for the control of corn rootworm larvae, Diabrotica spp. They are applied at the time of planting of corn at the rate of 1.1 kg AI/ha in or above seed furrows. Field performance of these compounds have been shown to differ significantly in different locations, owing perhaps to differential degradation rates and persistence in the soil. For effective control of corn rootworm larvae, insecticides must leave sufficient toxic residues in the soil for at least 10 wk after application. Several studies have been conducted on their persistence, degradation rates, and metabolism in soil and by soil microorganisms (LAVEGLIA & DAHM 1977). However, the data on their comparative degradation rates and persistence under similar field conditions is lacking which may help explain the inconsistency in field performance of these insecticides. Therefore, this investigation was conducted to compare degradation rates and persistence of these compounds under similar field conditions in South Dakota. Another objective was to study the effect of application rates and experimental location on insecticide persistence at various time intervals.

MATERIALS AND METHODS

On May 6, 1976, and May 12, 1977, we established, respectively, 9 and 7 insecticide plots of 2 x 3.5 m at 2 field locations, A (1976) and B (1977). Plots were located near Brookings, SD, and were ca. 6.5 km apart. Soil at the 2 locations consisted of silty clay loam with soil analyses showing 20% sand, 50% silt, 30% clay at field A and 30% sand, 20% silt, and 50% clay at field B. An organic matter content of 2.6 and 3.4% and pH 7.1 and 8, respectively, were found in soil samples of fields A and B. Plot areas were thoroughly rototilled and leveled, and PVC pipes 10-cm (diam) x 10 cm long were inserted vertically into the soil, ca. 30 cm apart, to a depth of ca. 9 cm. Each experimental plot (one plot for each sampling day) contained 12 PVC pipes for 4 treatments and 3 replicates. Granular formulations of fonofos 20 G (440 mg-field A and 26 mg-field B), terbufos (880 mg-field A and 34.6 mg-field B), and phorate 15 G (880 mg-field A and 34.6 mg-field B) were applied to the soil area enclosed within the PVC container, then covered with a 2-cm layer of soil. Plot areas outside the PVC container were devoid of any insecticide. Three insecticide treated and one untreated row of PVC pipes were randomly selected for each plot. The amount of insecticide granules applied at fields A and B was calculated to yield respectively 19 kg AI/ha

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and 1.1 kg AI/ha application rates. PVC pipes with or without insecticide treatments contained 800 to 1000 g of soil and were dug from the field plots at 0, 14, 28, 42, 49, 56, 70, 77, and 84 days post-treatment from field A and on identical days up to the 70th day from field B. The soil samples were wrapped with aluminum foil, enclosed in plastic bags, and stored at -20 C until needed for the determination of insecticide residues.

Prevailing weather conditions during the study period in 1976 and 1977 were recorded. Drought conditions existed in South Dakota, when the experiment was conducted at field A. Only 16 cm rainfall was recorded during the 84-day study period at field A, while 46 cm rainfall was recorded during the 1977 study period at field B.

At the time of residue determination each soil sample was thawed, weighed, and mixed on a sheet of aluminum foil. Soil moisture content was determined from duplicate 25 g soil subsamples of all the treatments by drying in an oven at 110 C for 24 h. Moisture content of the soil samples from field A varied between 9 to 17% while at field B it was between 14 to 23%. Residues were extracted from each replicate by taking 50 or 100 g triplicate soil subsamples.

Phorate, terbufos, and their oxidized products were extracted by slight modification of the procedure of BOYD (1972) using an extraction solvent mixture of chloroform and methanol (9:1 v/v). Soil samples were transferred to blender cups and homogenized for 10 min in the presence of 50 g sodium sulfate and 200 mL of extraction solvent. The solvent extract was then vacuum filtered through 2.5-cm layer of Celite 545 topped with a layer of sodium sulfate on a Whatman No. 2 filter paper. Remaining soil in the blender cup was reextracted twice with 150 and 100 mL extraction solvent and vacuum filtered in the same flask. An additional 100 mL extraction solvent was used to wash blender cups and the filtering funnel. The insecticide extract was concentrated to dryness. The concentrated insecticide residue was dissolved in 16 mL chloroform and oxidized with m-perchlorobenzoic acid as described by BOWMAN & BEROZA (1969) or dissolved in 10 mL benzene to separate parent phorate or terbufos by using silica gel column chromatography method of BOWMAN et al. (1969). The oxidation products, phoratoxon sulfone or terbufoxon sulfone, were further cleaned on a Florisil column prepared by the method of BECKMAN & GARBER (1969) and eluted with chloroform-acetone (9:1 v/v) mixture. Column elute was evaporated to dryness and the insecticide residue was redissolved in desired volume of acetone for GLC.

Fonofos residue from soil sample was extracted in benzene. Triplicate 50 g soil subsamples from each replicate were transferred to blender cups, homogenized with 200 mL benzene for 10 min and vacuum filtered through 2.5 cm Celite 545 and 1 cm layer of sodium sulfate on a Whatman No. 2 filter paper. Remaining soil in the blender cup was reextracted twice with additional 100 mL of benzene each time and vacuum filtered in the same flask. Fonofos extracts in benzene were concentrated to ca. 20 mL, decolorized with 80/100 mesh activated charcoal and drained through a glass wool-sodium sulfate plug into 100 or 150 ml volumetric flasks. Evaporating flasks and glass wool sodium sulfate plugs were washed with additional benzene and adjusted to desired volumes for GLC.

Extraction efficiencies of phorate, terbufos, and fonofos were determined by fortifying untreated field soils with 100, 50, and 6 ppm of the respective analytical standards in acetone (3 soil samples/fortification level). The fortified soil was extracted through the described procedure. These standards were used to calculate mean percent recoveries, retention times, and insecticide concentrations in the soil extracts.

Soil extracts were assayed with a gas chromatograph equipped with N-P-FID detector. All compounds were separated on a 1.8 m x 3.3 mm OD glass column prepacked with 10% DC 200 on 100/120 mesh Chromosorb W-HP-AW-DMCS Temperatures (C) of injection block, column, and detector were respectively 200, 210, and 300. Gas flow rates were: carrier gas helium 30 mL/min. Each extract was injected directly on the column 3 times using 1 µL syringe. Peak areas, retention times, and sample concentrations were recorded. Results were analyzed by two way analyses of variance and linear regression.

RESULTS AND DISCUSSION

Results presented in Tables 1 and 2 are based on mean residue levels from each replicate. Residue levels for all samples are expressed as units of ppm in oven dry soil. Phorate or terbufos residues were analyzed as a parent compound and also as a total oxidized product (phoratoxon or terbufoxon sulfone) for each sampling day and from each of the same replicate. Fonofos was determined only as a parent compound, and its oxygen analogue was not found in benzene extracts. The percentage recoveries of the insecticides from fortified soil samples were phorate 79 ± 4 phoratoxon sulfone 78 ± 2 terbufos 88 ± 3, terbufoxon sulfone 88 ± 4, and fonofos 98 ± 2. Retention time for each compound was determined by duplicate injections of 2, 4, 6, 8, and 10 ng/µL of insecticide standards; and they were for phorate 3.46 ± .03, phoratoxon sulfone 5.78 ± .03, terbufos 4.5 ± .04, terbufoxon sulfone 7.35 ± .02, and fonofos 4.75 ± .04 min. Sensitivity of the detector which yielded ca. 40 to 50% recorder response was 0.5, 1, and 2 ng respectively for phorate, terbufos and fonofos. It was observed that sensitivity of parent insecticides was better on this detector than their oxidized products (5 ng phoratoxon sulfone and 10 ng terbufoxon sulfone).

The data presented in Tables 1 and 2 indicated that fonofos was the most persistent insecticide under South Dakota field conditions. Fonofos dissipated from the soil at a very slow rate when compared to phorate or terbufos or their oxidized products. For example only 54% of the fonofos disappeared from field A on the 84th day post-treatement with 19 kg AI/ha, whereas 73% was lost on the 70th day post-treatment from field B at 1.1 kg AI/ha application rate. Unlike fonofos, phorate and terbufos dissipated very rapidly from the soil. More than 62 and 84% of the terbufos and 67 and 70% of the phorate were lost in 28 days respectively from fields A and B. Apparently, the parents of phorate and terbufos are rapidly metabolized in soil to their respective oxidation products as indicated in earlier studies (LAVEGLIA & DAHM 1977). The data shows that degradation of parental phorate or terbufos is followed by increasing residue levels of phoratoxon or terbufoxon sulfones. The oxidized products of phorate or terbufos appear to be more persistent in the soil and significant amounts could be detected for several weeks after their application. Two way analyses of variance yielded large F-values suggesting significant differences ($P<0.01$) within and among the residue levels of the insecticides. Therefore, the differential degradation rates of these insecticides under similar field conditions may be an important determinant for their field performance.

Table 1. Soil residues of insecticides after application of 19 kg AI/ha at field A in 1976 (Brookings, SD).[a]

	PPM insecticide residues ± standard deviation				
Days after application	Fonofos	Phorate	Phoratoxon sulfone	Terbufos	Terbufoxon sulfone
0	101±7	104±5	105±5	104±4	118±9
14	87±9	59±5	68±2	43±3	98±3
28	79±2	34±4	64±3	29±3	90±6
42	66±5	15±1	27±3	17±2	51±4
49	69±6	9±1	21±2	13±1	52±3
56	70±4	3±1	23±2	2±0.08	4±0.5
70	57±2	1±0.3	17±0.4	1±0.04	2±0.5
77	59±8	1±0.08	11±0.4	0.4±0.03	1±0.03
84	46±9	0.2±0.04	13±1	0.08±0.01	1±0.02

[a] Two way analysis of variance indicated highly significant differences ($P<0.01$) in the mean residue levels of each insecticide and days after application in the soil.

Table 2. Soil residues of insecticides after application of 1.1 kg AI/ha at field B in 1977 (Brookings, SD).[a]

	PPM insecticide residues ± standard deviation				
Days after application	Fonofos	Phorate	Phoratoxon sulfone	Terbufos	Terbufoxon sulfone
0	5.8±0.03	6.3±0.08	6.0±0.04	6.0±0.4	6.0±0.8
14	5.0±0.5	3.0±0.12	5.0±0.04	1.5±0.3	3.5±0.08
28	4.0±0.01	2.0±0.2	4.4±0.39	1.0±0.12	2.0±0.13
42	3.0±0.2	0.8±0.05	3.0±0.10	0.4±0.06	0.9±0.07
49	2.0±0.02	0.4±0.02	0.8±0.06	0.1±0.02	0.7±0.05
56	2.5±0.4	0.1±0.01	0.9±0.13	0.03±0.005	0.6±0.007
70	1.4±0.1	0.02±0.003	0.3±0.02	0.015±0.001	0.25±0.003

[a] Two way analysis of variance indicated highly significant differences ($P<0.01$) in the mean residue levels of each insecticide and days after application in the soil.

To facilitate comparisons and determinations of the residual half-lives, the mean ppm values of Tables 1 and 2 were converted to percent of insecticides recovered at each sampling day. Figures 1 and 2 graphically represent percent of remaining insecticides against the elapsed days. The half-lives of phorate, phoratoxon sulfone, terbufos, terbufoxon sulfone, and fonofos determined directly from Figure 1 were respectively 18, 32, 12, 39, and 82 days for field A; half-lives at field B were 14, 43, 11, 19, and 46 days respectively. These results indicated that half-life of phorate or terbufos or their oxidized products did not alter significantly due to higher or lower application rates under similar field conditions. However, fonofos half-life appears to change significantly with the rate of application at field A and B.

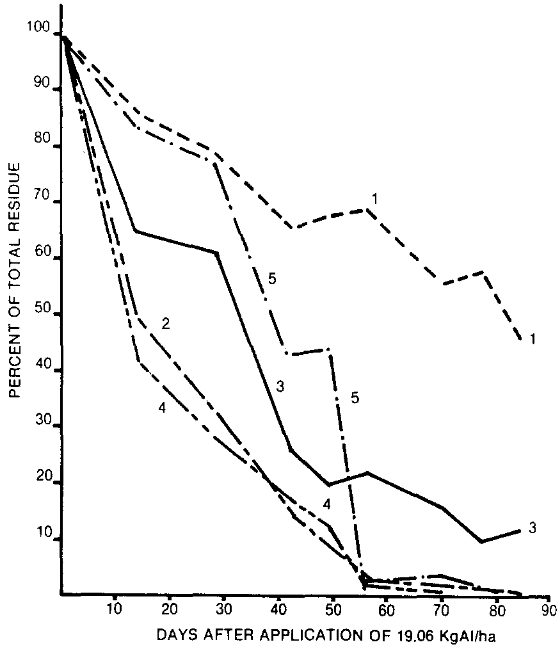

Figure 1. Disappearance of (1) fonofos (2) phorate (3) phoratoxon sulfone (4) terbufos, and (5) terbufoxon sulfone from field A soil in 1977.

Insecticide residue levels shown in Tables 1 and 2 were also subjected to linear regression analyses and ppm adjusted residue levels were plotted against respective sampling day. Slopes of the insecticides degradation calculated for the lines of regression were significantly different ($P<0.01$) from each other which indicated that each of the insecticides follows a different degradation pattern in the soil under similar field conditions. Also, highly significant negative correlation coefficients (-0.90 to -0.96) were found for all the insecticides, suggesting definite relationship between existing insecticide concentration and elapsed days after their field application. From our data in tables and the curvilinear parabolic type of degradation curves shown in Figures 1 and 2, it appears that dissipation rates of all the insecticides were dependent on and directly proportional to the concentration of remaining insecticides at any given sampling day, as would be the case for a first-order chemical reaction (GUNTHER & BLINN 1955).

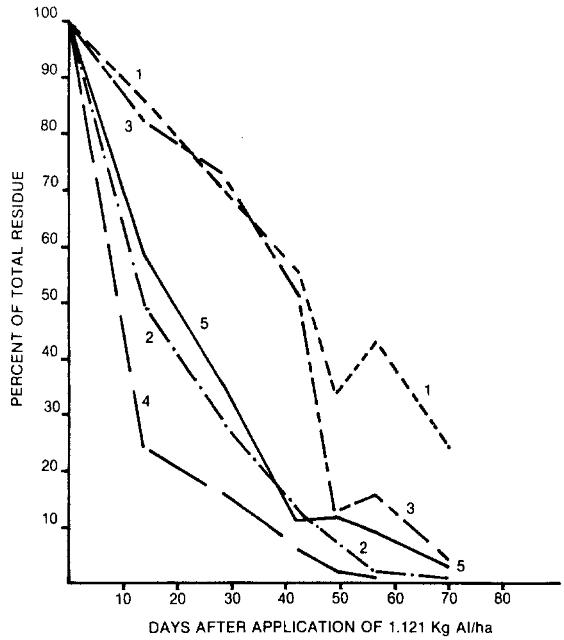

Figure 2. Disappearance of (1) fonofos, (2) phorate (3) phoratoxon sulfone, (4) terbufos and (5) terbufoxon sulfone from field B soil in 1977.

The studies presented in this report involving comparative degradation of insecticides may have been influenced by a variety of environmental forces such as drought conditions in 1976, soil pH, organic matter, moisture level, temperature, and photoperiod. Further work is needed to identify relevant effects of these variables on comparative degradation rates of the insecticides used in this study. The present study, however, demonstrates differential decay patterns for phorate, terbufos, and fonofos under similar field environmental conditions. These differences may be at least partially responsible for their varying effectiveness to control corn rootworm infestation.

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