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Effect of Manuring on the Persistence and Degradation of Soil Insecticides

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The use of soil-applied insecticides is a widely adopted management strategy to control insect pests in corn. A recent problem that has developed with continued use of an insecticide is the phenomenon of enhanced degradation by soil microorganisms (Felsot et al. 1981). Enhanced degradation occurs when a soil-applied pesticide is more rapidly degraded by soil microorganisms that have previously been exposed to the same pesticide or class of pesticides. Several factors such as microorganisms present, soil texture, moisture, and pH govern the enhanced degradation of soil insecticides. One factor of unknown importance is the application of manures to agricultural soils.

Manuring is a commonly adopted agronomic practice in crop production. It influences a number of factors, including microbial activity, microbial diversity, and physical, chemical, and biological characteristics of soil. Because soil characteristics such as organic matter content and pH affect the rate of pesticide degradation (Anderson 1981; Stevenson 1972), manure application may alter the rate and (or) mechanism of pesticide degradation. Previous research on the effect of manures on pesticide degradation has been mainly from the waste-disposal point of view, focusing on the fate of persistent pesticides as affected by laboratory amendments at extremely high loading rates (Doyle et al. 1978, 1981). This study was initiated to determine the short-and long-term effects of recommended field loading rates of hog manure on the persistence and degradation of seven soil insecticides in comparison with nonmanured soil.

MATERIALS AND METHODS

Four treatments were considered. The first two used field-collected soil with and without manuring history. The second two used soil with no manuring history but to which two loading rates of fresh dried manure were added in the laboratory. Two field-collected Tama silt loam soils, one with 7 continuous years

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of hog manuring (pH 5.8; organic matter 5.6%) and the second with no history of manuring for the 7-year period (pH 7.3; organic matter 4.2%), were collected at the beginning of the 1986 growing season from the same field near Stanwood, Iowa. The soil with a history of manuring received hog manure equivalent to 180 lb of nitrogen/acre/year. The soils were sieved to remove debris, and stored at 4°C until used.

For the fresh manure additions, hog manure was collected from the Swine Nutrition farm at Iowa State University. The manure was oven-dried at 65°C to facilitate uniform mixing with the soil. The quantity of manure used in the laboratory amendments was based on the nitrogen requirements of the corn crop (N=185 lb/A) and the nitrogen content of the dry hog manure (N=3.1%). This gave a recommended loading rate of 3 English tons of dry hog manure per acre (1x); a rate 10 times higher (10x) was also included. The manure was uniformly mixed with the field-collected soil, which had no history of manuring and incubated aerobically at 25°C for a 2-week period. Additionally, soils with a history and no history of manuring were also incubated under similar conditions.

After a 2-week incubation, a 50-g dry-weight portion of each soil was separately treated with each of the seven ^{14}C insecticides in acetone at 5 ppm as described by Lichtenstein and Schultz (1959). The following radiolabelled insecticides were obtained from the respective manufacturers: ^{14}C-U ring-carbofuran (FMC Corporation, Princeton, NJ), ^{14}C-2,6-phenyl-chlorpyrifos (Dow Chemical Company, Midland, MI), ^{14}C-ethyl-1-ethoprop (Rhone-Poulenc Inc., Monmouth Junction, NJ), ^{14}C-U ring-fonofos (Stauffer Chemical Company, Mountain View, CA), ^{14}C-methylene-terbufos and ^{14}C-methylene-phorate (American Cyanamid Corporation, Princeton, NJ), and ^{14}C-U ring-isofenphos (Mobay Chemical Company, Kansas City, MO). The radiopurity of each chemical was greater than 98%.

After insecticidal additions, aliquots of treated soils were taken for incubation and also for analysis of initial insecticide concentration. Each treatment was replicated four times, and the treated soils were placed in 8-oz French square bottles. Soils were moistened to field capacity (1/3 bar soil moisture tension) with distilled water, and glass vials containing 0.1N NaOH were placed in each bottle to trap the $^{14}CO_2$ evolved. The bottles were closed tightly and incubated at 25°C for 3 weeks. The CO_2 traps were replaced daily for the first week and on alternate days for the subsequent 2 weeks and then analyzed for $^{14}CO_2$ by liquid scintillation counting.

At the end of the incubation period, ^{14}C-insecticide residues in the soil were extracted twice with acetone-methanol (1:1) and once with acetone-methanol-dichloromethane (1:1:1) and partitioned into dichloromethane as described by Lichtenstein et al. (1973). Thin-layer chromatography and autoradiography techniques, as described by Hsin and Coats (1986), were used to characterize carbofuran (Koeppe and Lichtenstein, 1984), chlorpyrifos, ethoprop, fonofos, phorate, terbufos, isofenphos (Racke and Coats 1987b), and their respective metabolites.

The influence of manuring on the total microbial numbers was determined by using soil dilution plate counts. Nutrient agar was used for culturing soil bacteria, and rose bengal agar was used for culturing soil fungi. Final plate counts were taken after 1 week, and each dilution was replicated thrice.

RESULTS AND DISCUSSION

Virtually no carbofuran was recovered in the soils with no manure-history and laboratory amendments (Table 1). However, 21% of the applied ^{14}C-carbofuran persisted in manure-history soil. The field in which the soils were collected had had a carbofuran failure (rootworm control had been ineffective), and the increased persistence in the manure-history soil suggested that manuring inhibited the development or expression of enhanced degradation. In all the treatments, a large portion of the applied ^{14}C-carbofuran was converted to soil-bound residues. Although the bound residues are subject to further degradation and release by soil microorganisms (Racke and Lichtenstein 1985), their insecticidal activity is drastically reduced (Lichtenstein et al. 1977). Less binding was observed in manure-history soil, and, in general, the proportion of soil-bound residues formed was inversely related to the insecticide degradation in soil.

A twofold increase in the persistence of chlorpyrifos was observed in soil with manure history as compared with nonmanured soil. The hydrolysis product of chlorpyrifos (3,5,6-trichloropyridinol) was present at a concentration four times higher in nonmanured soil than in soil with a history of manuring. The persistence of the parent compound in laboratory amendments was greater than that in nonmanured soil but significantly less than that in soil with a manure history. Relative binding of ^{14}C-chlorpyrifos was relatively less in manure-history soil.

Fonofos was more persistent in soil with a history of manuring. Laboratory amendments resulted in lesser persistence of the parent fonofos as compared with nonmanured soil. The increased fonofos degradation in these treatments resulted in a greater production of $^{14}CO_2$ and soil-bound residues. The short-term effect of manuring on fonofos degradation observed in the current investigation was similar to the results of Lichtenstein et al. (1982).

At the end of the 3-week incubation, nearly all the terbufos applied was metabolized to its primary and secondary oxidative products, terbufos sulfoxide and terbufos sulfone. Soil with a history of manuring had increased levels of sulfoxide and decreased levels of sulfone as compared with the other treatments. Addition of manure at the rate of 30 tons per acre resulted in increased levels of sulfone and decreased levels of sulfoxide. In soil with manure history, 72% of the applied ^{14}C-terbufos was recovered as sulfoxide and sulfone, and a lower concentration of bound residues was recovered.

Table 1. Effect of manuring on the persistence and degradation of soil insecticides during a 3-week incubation.

	^{14}C recovered, % of applied ^{14}C insecticide				
	No manure	3 Tons/A	30 Tons/A	7 years	LSD
			Carbofuran		
Carbofuran	0.25^{a}	0.71^{a}	0.18^{a}	21.44^{b}	0.75
3-ketocarbofuran phenol	1.09^{a}	0.15^{b}	0.91^{c}	2.95^{d}	0.17
Soil-bound	74.07^{a}	75.20^{a}	78.94^{b}	60.76^{c}	3.67
$^{14}CO_2$	13.85^{a}	12.11^{b}	11.74^{bc}	11.21^{c}	0.62
Others^{e}	1.82^{a}	1.22^{b}	1.59^{ab}	2.65^{c}	0.45
Total	91.08^{a}	89.39^{a}	93.36^{b}	99.01^{c}	2.06
			Chlorpyrifos		
Chlorpyrifos	34.66^{a}	36.63^{a}	47.93^{b}	70.83^{c}	5.21
3,5,6-t Pyridinol	28.95^{a}	23.06^{b}	14.15^{c}	7.07^{d}	4.04
Soil-bound	17.12^{a}	17.73^{a}	17.16^{a}	7.23^{b}	0.63
$^{14}CO_2$	12.64^{a}	11.75^{b}	7.25^{c}	10.26^{d}	0.47
Others^{e}	6.06^{a}	9.23^{b}	10.98^{b}	3.31^{c}	2.60
Total	99.43	98.40	97.47	98.70	NS
			Fonofos		
Fonofos	46.15^{a}	37.33^{b}	28.74^{c}	52.76^{d}	4.56
Methylphenyl sulfone	4.53^{a}	5.68^{ab}	7.48^{bc}	9.78^{c}	2.84
Soil-bound	23.88^{a}	25.43^{b}	30.67^{c}	18.21^{d}	0.99
$^{14}CO_2$	19.44^{a}	19.86^{a}	23.27^{b}	10.44^{c}	0.56
Others^{e}	1.58^{a}	1.57^{a}	2.35^{ab}	3.00^{b}	1.30
Total	95.58^{a}	89.87^{b}	92.51^{ab}	94.19^{a}	3.72
			Terbufos		
Terbufos	0.58^{a}	0.45^{a}	0.99^{b}	0.45^{a}	0.19
Terbufos sulfoxide	45.99^{a}	42.52^{b}	20.02^{c}	56.20^{d}	2.62
Terbufos sulfone	18.22^{a}	21.04^{b}	32.54^{c}	14.71^{d}	1.95
Soil-bound	13.24^{a}	15.96^{b}	23.42^{c}	9.93^{d}	0.91
$^{14}CO_2$	12.04^{a}	13.35^{b}	12.78^{ab}	13.24^{b}	1.01
Others^{e}	5.02^{a}	5.75^{b}	7.07^{c}	4.07^{d}	0.59
Total	95.09^{a}	99.07^{b}	96.82^{ab}	98.60^{b}	2.45
			Ethoprop		
Ethoprop	25.15^{a}	20.39^{b}	15.07^{c}	62.78^{d}	4.12
Soil-bound	26.93^{a}	27.94^{a}	27.12^{a}	16.02^{b}	1.41
$^{14}CO_2$	47.76^{a}	51.97^{b}	50.57^{ab}	20.83^{c}	3.22
Total	99.84^{a}	100.30^{a}	92.76^{b}	99.63^{a}	2.03

Table 1 (Continued)

	No manure	3 Tons/A	30 Tons/A	7 years	LSD
			Phorate		
Phorate	0.07^a	0.14^{ab}	0.10^a	0.18^b	0.07
Phorate sulfoxide	5.43^a	7.05^a	7.94^a	16.02^b	4.49
Phorate sulfone	45.50^a	43.27^a	33.10^b	54.71^c	5.27
Soil-bound	18.69^a	18.89^a	28.76^b	11.64^c	1.17
$^{14}CO_2$	19.70^a	20.85^b	21.37^b	14.90^c	0.83
Others^e	8.16^{ab}	8.88^a	7.64^b	2.53^c	0.91
Total	97.55^a	99.06^{ab}	98.91^{ab}	99.98^b	1.62
			Isofenphos		
Isofenphos	70.43^a	73.72^b	66.92^c	70.31^a	3.25
Isofenphos oxon	7.97^a	9.62^b	6.49^c	10.19^b	1.02
Soil-bound	6.79^a	7.73^b	9.33^c	4.94^d	0.39
$^{14}CO_2$	4.46^a	6.20^b	7.53^c	3.96^d	0.12
Others^e	0.39	0.40	0.22	0.24	NS
Total	90.04^a	97.67^b	90.49^a	89.64^a	3.37

a-d:Means in each row with the same letter are not significantly different at 5% level; e:includes volatile products other than $^{14}CO_2$ as well as polar, water soluble products; NS:Not significant; LSD:Least significant difference

Table 2. Influence of manuring on total microbial numbers

Treatment	Numbers per gram dry weight soil	
	Bacteria (10^6)	Fungi (10^4)
No manure	6.6^a	5.0^a
3 Tons/A	101.0^b	32.0^b
30 Tons/A	291.0^c	47.0^c
7 Years	10.0^a	8.3^a
LSD	15.8	5.4

a-c:Means in each column with the same letter are not significantly different at the 5% level; LSD:Least significant difference

Phorate was rapidly oxidized to its metabolites, phorate sulfoxide and phorate sulfone. The level of sulfone was greater than that of sulfoxide in all the treatments. As in terbufos, soil with a history of manuring had greater persistence of the metabolites resulting in significantly less recovery of $^{14}CO_2$ and bound residues. The relatively shorter persistence of parent terbufos and phorate in soil and the role played by their oxidative metabolites towards target-pest activity has been previously reported (Harris and Chapman 1980).

Sixty-two percent of the applied ^{14}C-ethoprop was persistent in manure-history soil, which was 2.5-to 4.2-fold higher than in the other three treatments. The increased persistence was also indicated by low levels of $^{14}CO_2$ and bound residues. Ethoprop degradation was rapid in nonmanured and laboratory-amended soils, with about 50% of the applied insecticide being mineralized to $^{14}CO_2$.

The degradation of isofenphos was not greatly influenced by manuring. Although enhanced microbial degradation of isofenphos because of repeated use has been reported (Chapman et al. 1986; Racke and Coats 1987a), isofenphos is highly persistent in the first year of application. More than 65% of the applied parent insecticide persisted in all the treatments at the end of the 3-week incubation. Significantly lesser amounts of bound residues and $^{14}CO_2$ were recovered in soil with a manure history.

Application of manure for 7 continuous years in the field did not significantly increase the total number of bacteria and fungi as compared with nonmanured soils (Table 2). Bacteria have been reported to be the most important group of microorganisms in enhanced biodegradation of pesticides (Racke and Coats 1987a). Manure may serve as a readily available energy source for the existing bacterial population, reducing the probability of a selective advantage developing for a bacteria that can utilize a pesticide as a nutrient source.

Laboratory manure treatments of soil resulted in 15-and 44-fold increases in bacterial numbers at 3 and 30 tons loading rate per acre, respectively, as compared with nonmanured soil. The fungal population also increased by 6-and 9-fold at the two loading rates over that of non-manured soil. This stimulation of microbial activity in laboratory-amended soils may be responsible for the increased breakdown of fonofos, terbufos, and phorate in these soils. Increased degradation of permethrin (Doyle et al. 1981) and carbofuran (Koeppe and Lichtenstein 1984) in dairy manure-amended soils has been reported. However, these researchers used extremely high loading rates (15-fold higher than the recommended rate) and focused mainly on the short-term effects of manuring on pesticide degradation.

Organic matter is a major adsorbent in the soil, and persistence of soil insecticides may be positively correlated with the organic matter content. Soil that received manure for 7 years had a higher organic matter content of 5.6%, as compared with 4.2% in nonmanured soil. This increase in organic matter content may be an additional reason for the increased persistence in manure-history soils.

Continued history of manuring lowered the soil pH from 7.3 in nonmanured soil to 5.8 in soil with manure history. The pH of laboratory-amended soils was not significantly lowered, and it remained at 6.9 and 7.2 for the two loading rates used. Soil pH may directly or indirectly influence the degradation of insecticides by affecting the ionic or molecular character of the chemical, the cation exchange capacity, or the ability of the microbial population to respond to a given chemical. Getzin (1973) reported that carbofuran broke down much faster in alkaline than in acid soil and also observed that microbial action was involved. The increased rate of carbofuran degradation was inhibited by lowering the pH to below 6.0 (Read 1983). Walker et al. (1986) found slow degradation of two fungicides (Iprodione and Vinclozolin) in soils with a pH below 5.5. Strong adsorptive bonds between the insecticides and soil colloids, coupled with a low activity of degrading bacterial populations, may contribute to the increased persistence in acidic soils. Isofenphos, a phosphoramidate, is more acid-labile than the other insecticides studied, yet also persisted in the lower-pH soil.

In summary, the three possible explanations for greater persistence of the organophosphorus and carbamate insecticides in a soil with a 7-year history of manuring include (1) less selection pressure for pesticides inasmuch as nutrients may forestall development of adapted species of microbes, (2) higher organic matter may contribute to greater binding of the insecticides making them less available for microbial degradation, (3) lower pH may reduce rates of chemical and biological degradation. It is possible that all three factors contributed to the increased persistence. This study found no evidence that amending soil with manure encourages the development of enhanced microbial degradation of pesticides.

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