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Losses of Organophosphorus Insecticides during Application to the Soil^a

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In a study of the soil persistence of the organophosphorus insecticide, Zinophos, we found by analysis a short time after application, that only 54% of the insecticide which we intended to apply was actually present (1). Since the application had been made with attention to accuracy, and since similar discrepancies were noted in a parallel study at another location, we concluded that the losses were real and not due to application error. Such losses are undesirable, not only because they reduce the effectiveness of the pesticide, but also because they may result in environmental contamination.

An examination of the more recent literature on the use and persistence of soil insecticides has indicated that apparently other workers have not investigated this problem. Edwards (2) refers to losses during application but does not cite any investigations. Only a few reports contain data which permit an estimate of these losses. Bohn (3) indicates a 16% loss of dimethoate during application, while Menzer *et al* (4) recovered an average of 82% of disulfoton and 103% of phorate immediately after application.

It might be assumed that when such losses occur they are due to evaporation from the soil surface prior to incorporation, and to drift or evaporation of spray particles during the moment of application. However, since machinery designed for the application of pesticides to soil surfaces operates at low pressures and with nozzles close to the soil surface, the losses during application would seem to be minor. We have made a two year study of this problem using the insecticides Zinophos (0,0-diethyl 0-2-pyrazinyl phosphorothioate) and Dyfonate (0-ethyl S-phenyl ethylphosphonodithioate). Our experiments were designed to

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account for the pesticide from the spray tank to the soil and for the first 24 hours after reaching the soil. The results show that losses of 13 to 40% of such pesticides can occur and that most of the loss is due to evaporation or drift during the act of spraying.

EXPERIMENTAL

Field plots:

In the 1969 tests emulsible formulations (4 lb/gal) of Dyfonate and Zinophos were applied to 20 x 100 foot plots at 3.87 and 3.54 lb. a. i. per acre, respectively, based on the volume of spray used. The plots were replicated three times, one being double-disked immediately after spraying, another double-disked two hours later, and a third left untilled. The weather was calm and overcast during the application and the soil and the air temperatures were 71°F. The soil type was Chehalis silt loam, pH 6.0.

Duplicate samples of the spray mixture in the tank were removed before and after application for the determination of the concentration of the pesticides. The volume of spray applied to the plots was read from the gauge on the tank, and with the concentration provided by analysis and the plot size, was used to calculate the treatment rate. The application equipment has been described in a previous report (1, Dyfonate, 1970).

The amount of insecticide reaching the soil surface was determined in two ways; by analysis of soil samples collected with a soil auger, and by collecting the spray in shallow 7-inch aluminum pans, each containing 200 g of soil, which were uniformly distributed at 10 per plot. Immediately after the sprayer had passed over the plots, the contents of the pans from each plot were placed in a jar containing 200 ml of acetone and capped with an air tight lid. The soil was sampled, according to the time schedules shown in Table II, by random collection of 30 3/4 x 6-inch cores from each plot. The cores were placed in acetone at once as above. All samples were stored under refrigeration until extraction.

Only Dyfonate was studied in the 1970 experiment. The 20 x 50 foot plots were replicated 6 times and were treated with an emulsible formulation (4 lb./gal) at 4.78 lb. a. i. per acre based on the volume of spray

applied. This volume was determined more accurately than before by volumetrically measuring the amount of liquid in the tank before and after spraying. Samples of the spray mixture were collected as before to determine the actual concentration of Dyfonate. The aluminum pans were used to monitor the amount of spray reaching the soil by placing 4 pans on each plot. The contents of two pans from the opposite sides of each plot were combined in jars containing acetone so as to provide two samples from each plot. Soil samples were taken as previously described, 20 cores per plot.

The soil type in the 1970 test was Newberry sandy loam, pH 5.6 - 5.8. The weather was calm and partly cloudy during the application with an air temperature of 61°F and a soil temperature of 66°F.

Analysis:

The spray mixture samples were extracted, after saturating the spray mixture with sodium chloride, by shaking with three portions of hexane at the rate of 1/2 ml hexane per gram of spray. The hexane extract was dried and stored under refrigeration until analysis. The soil samples were extracted as previously described (1). Analysis was by gas liquid chromatography using an electron capture detector.

The reliability of the analytical method was confirmed by analyzing samples of untreated soil fortified with known amounts of the insecticides. Average recoveries were 88 and 91%, for Dyfonate and Zinophos, respectively.

RESULTS AND DISCUSSION

The losses of the two insecticides are illustrated in Table I. The data from the 1969 experiments are from the plots tilled immediately after application and are based on analyses of single composite samples consisting of the contents of 10 pans or of 30 6-inch cores as previously described. The averages shown for Dyfonate in the 1970 experiment are based on 12 pan composites (2 for each of the 6 plots) and 6 soil core composites (20 from each plot) and are thus statistically more reliable. We believe that the sampling error in the case of the 1969 plots is low, however, because of the demonstration in Table III of a low inter-plot and inter-sample variation. Since application, sampling and analytical techniques were unchanged between the 1969 and 1970 experiments, the

error encountered in the earlier tests should be no larger. A greater source of error in the 1969 tests might have been our reliance on the spray tank gauge for determining the volume of spray used in the applications. This might account for the larger loss of Dyfonate in 1969 than in 1970 although, as we point out later, other factors could also explain this difference.

TABLE I

Loss of Pesticides During Application

	<u>Zinophos^{a/}</u>		<u>Dyfonate^{a/}</u>		<u>Dyfonate^{b/}</u>	
	<u>lb/A</u>	<u>% loss</u>	<u>lb/A</u>	<u>% loss</u>	<u>lb/A</u>	<u>% loss</u>
Rate of application	3.54		3.87		4.78	
Deposit based on pan analysis ^{c/}	2.14	39.5	3.19	17.6	4.18	12.6
Deposit based on soil analysis ^{c/}	2.22	37.3	2.94	24.1	3.98	16.7

- a/ 1969 experiment, data based on one 10 pan sample and one 30-core sample.
- b/ 1970 experiment, data based on twelve 2-pan samples and six 20-core samples.
- c/ Pan samples collected immediately after application. Soil samples collected after tilling, within 30 minutes of application.

The insecticide concentrations were expressed in pounds per acre, those based on pan analysis calculated from the area of the pans, and those based on soil analysis calculated from the estimated weight of a 6-inch acre, $1.933 \times 10^6 \pm 0.049 \times 10^6$ pounds. This value was calculated from dry weight of the samples collected in the 1970 experiment and from the volume of the sampling device. It was assumed that no pesticide was present at depth greater than 6 inches. The agreement between the two calculations indicates that this assumption and the weight and area estimates are valid.

It is evident that a major loss occurred during the act of spraying. Nearly 40% of the Zinophos and up to 24% of the Dyfonate failed to reach the soil surface (Table I). This difference between the two insecticides may be due to differences in vapor pressure, 3×10^{-3} and 0.38×10^{-3} mm Hg at 30°C, for Zinophos and Dyfonate, respectively. The higher temperature in 1969 (71°F) than in 1970 (61°F) may explain the greater loss of Dyfonate in the earlier test.

The analyses of the treated soil in the period immediately after application are shown in Table II. Although the values are somewhat erratic, it is evident that neither pesticide suffered significant losses during the 24 hour period following application, regardless whether the plot was tilled. This is a surprising result since it is generally assumed that these pesticides evaporate rapidly from untilled soil surfaces. The results with Dyfonate confirm those presented earlier (1) which showed that losses are negligible during the first 72 hours.

TABLE II
Loss of Pesticides from Soil During
the First Day after Application

Plot	Time of sampling, hours ^{a/}	Zinophos, ppm	Dyfonate, ppm
Plot 1, disced immediately	1/2	1.15	1.52
" " " "	4	1.24	1.58
" " " "	22	1.23	1.27
Plot 2, disced 2 hrs. later	1/2	1.50	2.06
" " " " " "	2	1.41	1.67
" " " " " "	4	1.26	1.41
" " " " " "	22	1.10	1.42
Plot 3, not disced	22	1.34	1.51

a/ Time recorded from completion of application.

The 1970 experiment with Dyfonate provided an opportunity to assess the uniformity of application obtained by the equipment used. The 2-pan composite samples, which were collected immediately after the sprayer had passed over the plots, are in close agreement in Dyfonate content, Table III.

TABLE III
Uniformity of Application of Dyfonate
in 1970 Experiment^{a/}

Replicate	Dyfonate deposit, grams/m ² ^{b/}	
	Sample 1	Sample 2
I	0.417	0.510
II	0.505	0.503
III	0.513	0.483
IV	0.478	0.463
V	0.441	0.431
VI	0.440	0.437

a/ Based on analysis of Dyfonate collected in pans.

b/ Least significant difference (0.05) = 0.072.

These experiments show that losses of pesticide occurred during application to soil even though the distance between spray nozzle and target is short. Such losses must be considerably higher when pesticides are applied to plants, especially trees. These losses can probably be reduced in some cases by the use of granular formulations or the ultra low volume (ULV) method of application.

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