The Persistence of Zinophos and Dyfonate in Soil[a]

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Knowledge of the fate of pesticides applied to the soil for the control of soil pests is useful not only because of the potential for environmental contamination but also in the development of more efficient usage of these materials. Biological evidence, such as the re-infestation of the pest, is testimony that the pesticide has disappeared, but it does not indicate how the pesticide was lost and is only a crude measure of when it was lost. More precise information about the role of the soil type, weather, and the chemical and physical properties of the pesticide itself can be obtained by direct analysis of the soil.

The insecticides Zinophos (O,O-diethyl O-2-pyrazinyl phosphorothioate) and Dyfonate (O-ethyl S-phenyl ethylphosphonodithioate) promise to become replacements for the more persistent insecticides such as DDT and dieldrin in the control of soil insect pests. Previous studies by Onsager and Rusk (1) have shown the half life of granular Zinophos to be 14 days and that of granular Dyfonate, 47 days under summer conditions of Eastern Washington. A granular formulation of Zinophos had a half life of about 4 weeks under Western Washington summer conditions (2). The half life of Dyfonate EC was shown to be 28 days in Wisconsin by Schulz and Lichtenstein (3).

We have had several occasions since the introduction of Zinophos in 1960 to study its behavior in soil and, more recently, we have made similar studies of Dyfonate. The results of some of these experiments are presented here. Temperature is the most important climatic factor in the loss of these materials from soil with rainfall having very little influence.

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EXPERIMENTAL

Field Plots - Dyfonate:

Replicated 20 x 50 foot plots near Corvallis, Oregon were treated June 10, 1970 with a 4 lb/gal EC formulation of Dyfonate at 4.78 lb. a. i. per acre. The soil type was Newberry sandy loam, pH 5.6 to 5.8. The ground sprayer was equipped with a 20-foot boom 16 inches above the ground. The 24 nozzles (Spraying Systems Tee Jet 8002) were arranged to provide sufficient overlap for double coverage of the soil and were calibrated to deliver 75 gallons per acre. The plots were double disced and rolled immediately after application. The weather was calm and partly cloudy with an air temperature of 61°F and a soil temperature of 66°F.

The soil was sampled on a schedule shown in Table I with a 3/4-inch soil auger taking twenty 6-inch cores at random from each plot. The soil cores were placed immediately in jars containing 200 ml of acetone.

Field Plots - Zinophos:

The first Zinophos experiments were performed June 5, 1961, at Corvallis. The replicated plots (60 x 106 feet) were treated with a 4 lb/gal EC formulation at 2.5, 5 and 10 lb. a. i. per acre, using a boom equipped weed sprayer. The plots were rototilled immediately after treatment. The soil type was Chehalis silt loam, pH 6.0. The plots were sampled at random as above taking fifty cores per plot according to the schedule in Table II.

Two 10 x 20-foot plots near Corvallis were treated September 12, 1964 with Zinophos 4 lb/gal EC at 2 and 10 lb. a. i. per acre. The sprayer had a 10-foot boom with 12 nozzles (Spraying Systems Tee Jet 8003) 20 inches above the soil. The soil type was Woodburn clay loam, pH 5.7. The sprayer was calibrated to deliver 50 gallons per acre. The plots were rototilled immediately after application. The weather was calm and sunny with an air temperature of 82°F and a soil temperature of 78°F. Forty soil cores were taken at 0 - 3, 4 - 6, and 7 - 12-inch depth on the schedule shown in Table III.

Plots at Prosser, Washington were treated September 10, 1964 using the same rates and formulation. The pesticide was applied with a 3-gallon hand sprayer, each plot covered 3 times. The pesticide was immediately incorporated into the soil by hand raking. Samples were collected as described above. The air temperature during application was 72°F and the soil type was Sagemore sandy loam, pH 7.5.

Analysis:

The samples were extracted by shaking with hexane or chloroform on a reciprocal shaker for one hour. Dyfonate samples were analyzed by gas liquid chromatography using an electron capture detector and the Zinophos samples by the spectrophotofluorometric method of Kiigemagi and Terriere (4).

The reliability of the analytical methods was confirmed by analysis of samples of untreated soil fortified with known amounts of the insecticides. Average recoveries were 88 and 86%, for Dyfonate and Zinophos, respectively.

RESULTS AND DISCUSSION

The mean air temperature during the Dyfonate plot sampling period was 61°F, the maximum temperature 97°F, and the rainfall 5.60 inches. The estimated half life of Dyfonate under these Western Oregon summer conditions was about 40 days (Table I). A value of 47 days has been estimated for a granular formulation under Eastern Washington summer conditions (1). Twenty seven percent of applied Dyfonate was still recovered 4 months after treatment as compared to 24% recovered by Schulz and Lichtenstein (3) in Wisconsin. The rate of decline of the residue slowed to an average of 0.004 ug per gram of soil per day after 84 days, as compared to a rate of 0.062 ug/gram/day during the first 14 days. Records show that 91% of the rainfall occurred after the 84th day indicating that leaching was not an important avenue of loss. The loss was probably accelerated by the soil temperatures, which in summer are usually higher than the air temperatures. In this case, the mean soil temperature at the 2-inch level for the entire sampling period was 76°F, with a maximum of 103°F.

TABLE I

The Persistence of Dyfonate in Soil under Summer Conditions [a/]

Days After Application	Dyfonate[b/] Residue, ppm	% of Initial Concentration	Accumulated Rainfall, Inches[c/]
0	2.05±0.13	100	----
1	1.92±0.12	94	0.05
3	1.81±0.12	88	0.09
7	1.52±0.09	74	0.07
14	1.18±0.04	58	0.00
28	1.11±0.04	54	0.29
56	0.95±0.06	46	0.00
84	0.79±0.06	39	0.00
120	0.55±0.06	27	5.10

a/ Plots near Corvallis, Oregon treated with 4 lb/gal EC formulation at 4.78 lb/acre.

b/ Average and standard deviation of 6 replicates.

c/ During the sampling interval.

A semilog plot of the persistence data (Figure 1) shows an essentially bimodal curve similar to those reported by Lichtenstein and Schulz for aldrin and lindane (5), and for parathion (6), and by Menn et al (7) for Imidan. It can be postulated that these bimodal curves represent two degradation mechanisms. It is suggested that in the early stages (in the first two weeks in this case) mostly physical factors, such as volatalization, are operating, and that at the latter stages the disappearance of the insecticide is mostly due to chemical and biological factors such as hydrolysis and metabolism.

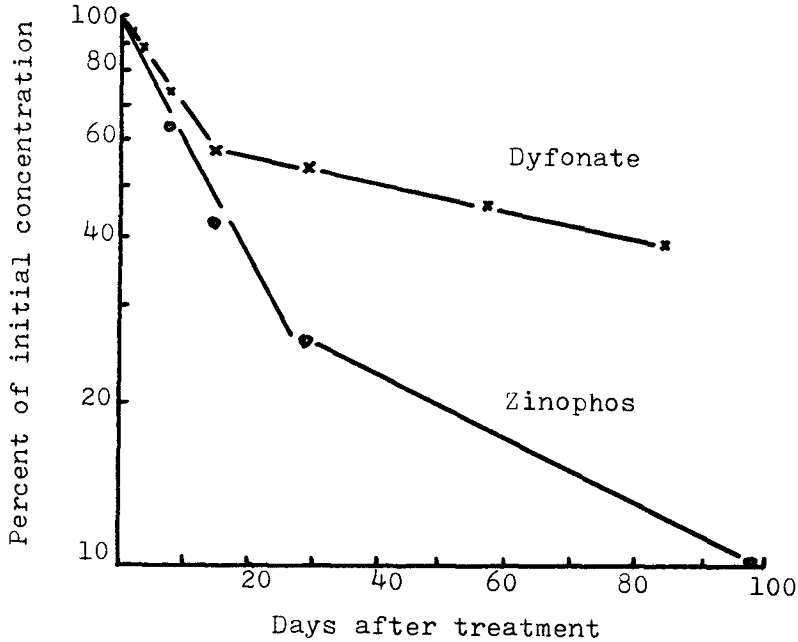

Figure 1. Disappearance of Dyfonate and Zinophos from Soil under Oregon Summer Conditions.

The half life of Zinophos under summer conditions was about 13 to 17 days, depending on the application rate (Table II). When plotted, these data also display a bimodal curve with the change in slope occurring after 28 days.

TABLE II

The Persistence of Zinophos in Soil under Summer Conditions [a/]

Days After Application	Zinophos Residue, ppm 2.5 lb/A	5 lb/A	10 lb/A
0	0.95	2.96	4.99
7	0.61	2.25	4.98
14	0.41	1.88	2.75
28	0.25	0.74	0.93
97	<0.10	0.18	0.22

a/ Plots near Corvallis, Oregon treated with 4 lb/gal EC formulation.

The data in Table III show that the half life of Zinophos is much longer under winter conditions. In Western Oregon it was about 14 to 18 weeks and in Eastern Washington about 17 to 22 weeks. At both locations the decline of the residue was quite slow for the first two months, then becoming more rapid so that 80% of the initial dose was lost in about six months. The mean winter temperature at Corvallis was 46°F and at Prosser 42°F. It may be noted also that soil temperatures in winter are generally lower than air temperatures. These results support the contention that the major losses of Zinophos are by volatilization and metabolism, both processes being temperature dependent.

TABLE III

The Persistence of Zinophos in Soil under Winter Conditions [a/]

Days After Application	Zinophos Residue, ppm [b/] Oregon 2 lb/A	Oregon 10 lb/A	Washington 2 lb/A	Washington 10 lb/A
0	0.48	2.40	0.48	3.53
7	0.50	1.90	0.44	1.63
14	0.49	1.88	0.35	1.50
27	0.51	2.08	0.52	2.08
56	0.50	2.07	0.64	2.14
124	0.16	1.20	0.43	1.70
192	0.11	0.54	0.11	0.50

a/ Plots near Corvallis, Oregon and Prosser, Washington treated with a 4 lb/gal EC formulation.

b/ Calculated to 6-inch depth.

The lesser importance of rainfall in the decline of Zinophos is illustrated by the fact that, although the precipitation in Corvallis during the experiment was 37.4 inches and in Prosser 6.14 inches, its rate of loss at the two locations was quite similar (Table III). Analysis of the soil from both locations at 0 - 3, 4 - 6, and 7 - 12-inch levels indicated no pronounced downward movement despite the fact that the water solubility of Zinophos is about 1000 ppm.

The analysis of the soil samples from the different depths also showed that the mixing of the insecticide with the soil was poor at both locations. Immediately after incorporation over 90% of the insecticide was in the upper three inches.

The conversion of Zinophos to its oxygen analog must occur to a small extent in soil, or if it is formed it must disappear rapidly for only traces of this compound were found during the analyses. Laboratory tests showed that Zinophos is stable for at least 13 days in solutions of pH 1 to 10. It is unlikely, therefore, that hydrolysis is a major avenue of breakdown. This view is supported by Getzin (8) who found that microbial action accounted for 70% of Zinophos degradation in soil.

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