Persistence of Parathion in Soil

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Concern about persistence of synthetic pesticides in soil and the environment in general has been greater where chlorinated hydrocarbon compounds have been involved than where organophosphorus pesticides have been used. This is understandable, inasmuch as organophosphorus compounds generally degrade more rapidly in the environment. Most of the research concerning degradation or disappearance of organophosphorus compounds from soil has involved relatively low initial levels of pesticide resulting from conventional applications of the compounds for insect control. At these levels the degradation of organophosphorus compounds has generally been much more rapid than with chlorinated hydrocarbon compounds (1,2). Recently Stewart et al. (3) found traces of parathion in soil 16 years after the last application. The finding at this laboratory (4) that spillage of emulsifiable concentrate parathion and azinphosmethyl on soil at spray machine fill sites, air application flight strips, and other locations may be a hazard to children because of the presence of persistently high concentrations of the pesticides, has prompted our further investigation into the problem of persistence of organophosphorus compounds in soil. The purpose of the present study was to determine the disappearance of parathion residues in soil following topical applications of the compound. The results are intended to have application to problems related to waste pesticide disposal, of leaching, and of degradation or disappearance of parathion in the environment, as well as to the problem of hazard to children who may come in contact with contaminated spillage areas.

Materials and Methods

The experiment involved treatments of field soil plots using three liquid parathion concentrations and two different formulations. Treatments were: (a) undiluted commercial grade 45.6% liquid emulsifiable concentrate, (b) conventional dilute spray for orchard use prepared from water-wettable powder and containing 0.03% parathion (referred to as 1X concentration), (c) a dilute spray similar to (b) except prepared from emulsifiable concentrate, (d) a spray mixture of the type commonly used for semi-concentrate spray applications prepared from water-wettable powder and containing 0.24% parathion (8X--eight times the normal 1X

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concentration), and (e) a spray mixture similar to (d) except prepared from emulsifiable concentrate. The undiluted emulsifiable concentrate treatment was included in order to simulate spillage of concentrate pesticide and the more dilute concentrations were used because of the occasional practice of dumping various quantities of unused liquid spray formulation from spray machines onto the ground after finishing a particular spray operation. The undiluted emulsifiable concentrate and 8X treatments were replicated four times in each of three field plots. The 1X treatments were replicated four times in two field plots.

All experimental plots were subjected to the natural elements such as rainfall (average approximately 10 inches per year), sunlight (over 275 days during each year), and relatively high maximum temperatures (over 90^{o}F for an average of 14 days each summer). The plots were covered with snow for approximately 2 months of each year. All three plots were sandy loam soil; however, plot 3 was on the verge of being classed as loamy sand. Plot 1 soil contained 11.2% clay, 34.2% silt, 54.6% sand, and 2.5% organic matter. The pH ranged from 4.4 to 5.4 with a mean of 4.7. This plot was subjected to sprinkler irrigation for a 24-hour period each 2 weeks during the summer season. The other two plots were not irrigated. Plot 2 soil contained 10.2% clay, 29.0% silt, 60.8% sand, and 3.4% organic matter. The pH ranged from 6.7 to 7.4 with a mean of 7.1. Plot 3 soil contained 6.0% clay, 26.0% silt, 67.3% sand, and 1.0% organic matter. The pH ranged from 6.6 to 7.8 with a mean of 7.3.

Metal frames 12-inches square were used to outline the individual soil test areas within each experimental plot. These were left in place for the duration of the experiment. The frames were pressed into the soil so that when 2 quarts of liquid parathion formulation were applied topically within the frame, a pool approximately 3/4-inch deep was formed before the material soaked into the soil. Samples of soil from two depths (0-1 in. and 1-3 in.) were taken 1 day following application and at intervals thereafter up to 5 years. At the 6th-year period two soil test areas were sacrificed and four replicate samples taken from each area at different depths in increments of 3 inches down to the 24-inch level.

Soil samples to the 3-inch level in all plots were taken by use of a cork borer tube which was cleaned after collection of each sample. Care was taken to minimize cross contamination between soil samples at different depths. However, it was difficult to avoid some cross contamination, due to limited surface area of test plots, especially after the 3rd year of sampling. It was felt that cross contamination of samples below the 3-inch depth was negligible because samples in this area were taken by removal of entire layers of soil.

Parathion content of soil samples was determined in most cases by the method of Averell and Norris (5). In later years gas liquid chromatography was occasionally utilized as a check for accuracy and was used for analysis of deep soil samples where pesticide might be expected to be present in very low levels, if at all. This system was also used for analysis of paraoxon and other closely related alteration or breakdown products. Analysis for aminoparathion was by a modification of the Averell-Norris method and analysis for p-nitrophenol was by the method of Elliott et al. (6).

The effect of parathion on soil microorganisms was determined using number of colonies developed on nutrient yeast dextrose agar as an indicator. Soil innoculations at four different dilutions were made in 100 mm petri dishes containing the media. Because of the difficulty of accurately classifying the many different organisms found in soil they were divided into only two categories: filamentous and nonfilamentous.

Results and Discussion

As can be seen in Fig. 1, parathion persisted at relatively high levels for 5 years following gross topical contamination with the 45.6% emulsifiable concentrate formulation. The levels of pesticide in the soil, initially very high (30,000 to 95,000 ppm), were considerably lower by the end of the first year. By the second year the rate of disappearance was much less, with appreciable quantities remaining in both the top 1 inch and the 1- to 3-inch levels at the end of the 5th year. The lowest level found in a single sample at that time was 13,800 ppm (approximately 1.4%) parathion in the top 1 inch of soil. This level is higher than that involved in a near-fatal poisoning case where a child ingested soil from a contaminated area in a driveway near his home (7). In that incident the soil contained 8,634 ppm of parathion and was a result of spillage which had occurred at least 6 months prior to the incident.

There was no great difference in rate of disappearance of parathion among the three emulsifiable concentrate experimental plots. In individual plots more parathion was present in the top 1 inch of soil than in the 1- to 3-inch level for approximately 2 years; however, after that period the difference became much less. At 5 years some of the 3-inch depth samples contained more parathion than those from the 1-inch depth. At the 6-year period where soil was checked in increments of 3 inches down to the 24-inch level, very little parathion was found below the 9-inch level (see Table 1).

At the 4th-year period following application two emulsifiable concentrate plots were checked for presence of parathion alteration products in the top 3 inches of soil. Where parathion content of soil ranged from 16,662 to 26,746 ppm the amount of p-nitrophenol found ranged from 11.2 to 41.0 ppm. No aminoparathion, paraoxon or S-ethyl parathion could be detected. The inability to find aminoparathion was expected because of the great instability of the compound. Instrumentation available at the time the samples were analyzed was not adequate to properly identify and quantitate paraoxon and S-ethyl parathion. However, a recent recheck of the sample extracts by improved methods has indicated the presence of small amounts of paraoxon and S-ethyl parathion. Improved instrumental capability in recent years has allowed additional studies at this laboratory on parathion alteration products in soil which will be reported at a later date.

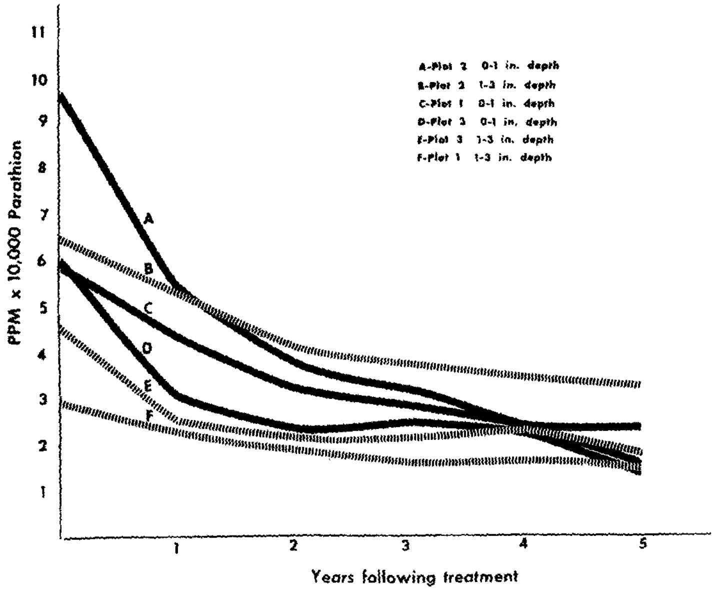

Figure 1. Disappearance of parathion from sandy loam soil, following gross topical contamination with emulsifiable concentrate formulation (45.6%), at two depths in three experimental plots. Each value average of 4 replicates.

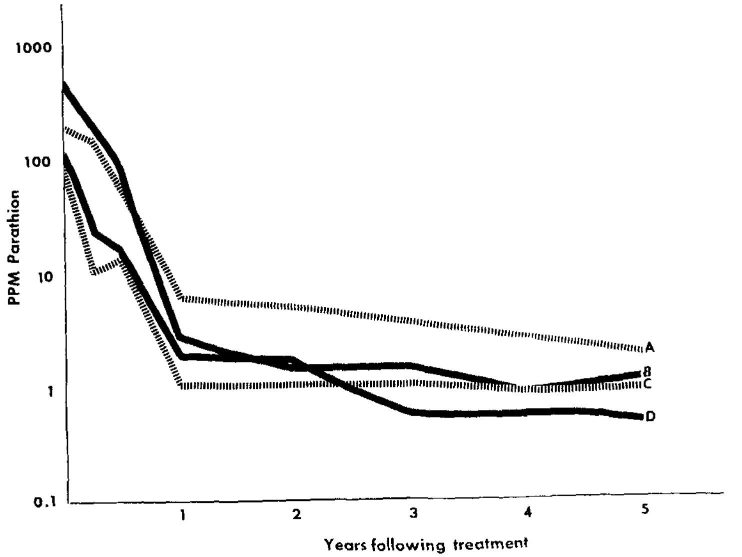

Figure 2. Disappearance of parathion from top 1 inch of sandy loam soil following topical applications of two concentrations using two formulations. A = 8X (0.24%) and C = 1X (0.03%) sprays using water-wettable powder formulation. B = 8X (0.24%) and D = 1X (0.03%) sprays using emulsifiable concentrate formulation. A and B average of 12 replicates and C and D average of 8 replicates.

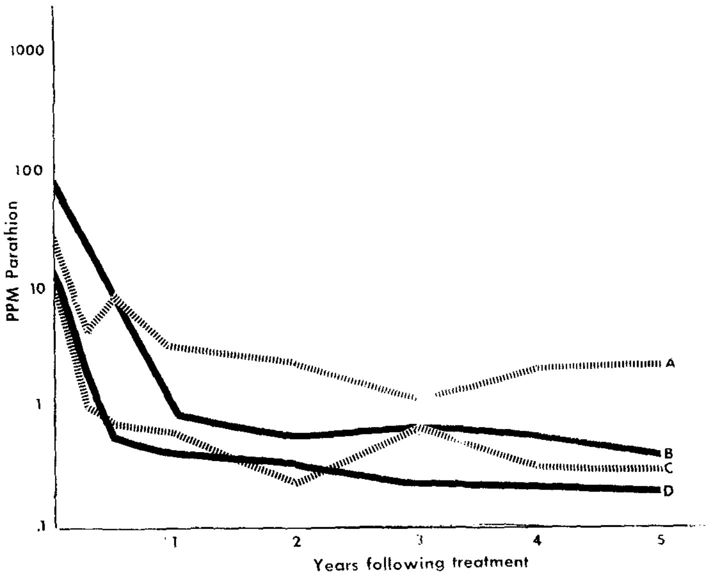

Figure 3. Disappearance of parathion from 1- to 3-inch depth of sandy loam soil following topical applications of two concentrations, using two formulations. A = 8X (0.24%) and C = 1X (0.03%) sprays using water-wettable powder formulation. B = 8X (0.24%) and D = 1X (0.03%) sprays using emulsifiable concentrate formulation. A and B average of 12 replicates and C and D average of 8 replicates.

TABLE 1

Parathion in Soil at Different Depths Six Years After Topical Application of Emulsifiable Concentrate Formulation (45.6%).

Depth (inches)	PPM Parathion*	
	Plot 1	Plot 2
0-1	14,500	15,370
1-3	14,900	9,330
3-6	9,900	9.65
6-9	149.4	9.48
9-12	0.004	0.097
12-15	0.048	0.008
15-18	0.004	0.017
18-21	0.011	el**
21-24	el**	el**

*Average of 4 replicates.

**Below lower limit of sensitivity of method (< 0.002 ppm)

Figures 2 and 3 show persistence of parathion at two depths in soil plots where the more dilute liquid spray concentrations were applied topically. There was very little difference in values obtained among these experimental plots; therefore, average values for replicates in the three plots were used in plotting the curves. As with the more concentrate applications discussed above, the levels of parathion in soil dropped off quite rapidly during the first year with a trend toward leveling off thereafter. Where the 1X (0.03%) concentration was applied, average levels after 5 years were from 0.6 to 1.2 ppm in the top 1 inch of soil and from 0.2 to 0.3 ppm in the 1- to 3-inch depth. Where the 8X (0.24%) concentration was applied, average levels after 5 years were 0.4 to 1.5 ppm in the top 1 inch of soil and from 1.2 to 3.6 ppm in the 1- to 3-inch level. It appears that slightly higher levels of pesticide remained in the soil after 5 years where water-wettable formulation was used than where the emulsifiable was used. Two sets of the experimental plots will be retained so that samples can be analyzed after much longer periods of time than 5 years. By using more sensitive methods, perhaps any differences at low levels can then be more clearly defined.

On finding relatively high levels of parathion in the top 3 inches of soil in the concentrate plots at the end of the 2-year period, we decided to determine if soil microorganisms were being appreciably affected. Soil isolations at four different dilutions were made on yeast-dextrose agar. Counts of the number of colonies that had developed in 6 days at 70°F were used as an indicator. As can be seen in Table 2, under the conditions of our experiment, fewer colonies were isolated from the concentrate parathion soil plot than from untreated control soil nearby. Also, when untreated control soil inoculum was placed in media containing 0.5% parathion the counts were considerably lower, and where the media contained 5.0% parathion the microorganism colony development was almost completely inhibited. Where the inoculum was from a plot treated with parathion 2 years earlier, and containing approximately 3.4% parathion, there was also similar reduction in the media containing 0.5% parathion, indicating that there had been no appreciable development of resistance to the pesticide by the organisms as indicated by the methods used in the test.

Table 3 shows results of inoculations of soil taken from another concentrate parathion plot at the 5th year following topical application with the pesticide. This is compared with untreated control soil inoculum taken nearby. In this experimental plot area the counts for the untreated control area were

TABLE 3

Effect of Parathion on Soil Microorganisms Expressed as Colony Numbers on Nutrient Yeast-Dextrose Agar Following Soil Isolations.

Sample	Culture Dilution in H_2O	Number of Colonies Developed in 6 Days at 70°F[a/]	
		Nonfilamentous	Filamentous
1[b/]	1-1000	2500.0	1000.0
	1-10,000	817.3	477.0
	1-100,000	181.0	100.3
	1-1,000,000	57.0	24.3
2[c/]	1-1000	89.0	18.6
	1-10,000	21.3	4.6
	1-100,000	5.6	0.6
	1-1,000,000	2.6	1.0

[a/] Each value is average of counts observed on three 100 mm petri dishes. Sampled from top 1 inch of soil.

[b/] Untreated control soil near treated plots.

[c/] Soil 5 years after topical application with 45.5% emulsifiable concentrate. Approximately 2.9% parathion at time of sampling.

TABLE 2

Effect of Parathion on Soil Microorganisms Expressed as Colony Numbers on Nutrient Yeast-Dextrose Agar Containing Different Levels of Parathion as an Indicator.

Media	Culture Dilution in H_2O	Number of Colonies Developed in 6 Days at 70°F[a]			
		Soil from Control Plot Containing no Parathion		Soil from Test Plot Containing approx. 3.4% Parathion[b]	
		Nonfilamentous	Filamentous	Nonfilamentous	Filamentous
A:					
Contained	1-1000	$<$ 200.0	10.0	106.0	0.0
no	1-10,000	83.0	6.7	26.7	0.0
Parathion	1-100,000	61.7	9.0	3.7	0.0
	1-1,000,000	24.7	4.7	4.3	0.3
B:					
Contained	1-1000	40.3	2.3	6.3	0.0
0.5%	1-10,000	2.3	0.7	4.7	0.0
Parathion	1-100,000	0.7	0.0	0.0	0.0
	1-1,000,000	0.7	0.0	0.0	0.0
C:					
Contained	1-1000	0.0	2.0	0.0	0.0
5.0%	1-10,000	0.0	0.0	0.0	0.0
Parathion	1-100,000	0.0	0.0	0.0	0.0
	1-1,000,000	0.0	0.0	0.0	0.0

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[a] Each value is average of counts observed on three 100 mm petri dishes. Sampled from top one inch of soil.

[b] Topical application of 45.5% emulsifiable concentrate parathion 2 years earlier. Innoculum from this plot included to determine if any microorganisms subjected to parathion in soil for a two-year period had developed a detectable resistance to the pesticide.

also considerably higher than those for the treated plot. Counts for the plot treated with parathion 5 years earlier were much lower than the control, indicating that growth of microorganisms was still being inhibited to some extent after this period of time.

It should be pointed out that the counts shown in Tables 2 and 3 are not comparable since isolations were made in different years and at different times of the year.

In the above studies disappearance of parathion from soil occurred at a much slower rate than one might have expected, considering the year-around exposure to the natural elements. This was especially true in the experimental plots where the highly concentrated formulation was involved.

Many factors undoubtedly affected the disappearance of parathion from the soil, such as adsorption onto soil particles, volatilization, leaching, photochemical decomposition, chemical decomposition, and microbiological degradation, to name a few. Under conditions of this study adsorption undoubtedly played an important role. Leaching apparently was minimal. We did not attempt to determine loss from volatilization.

Findings reported in the present paper emphasize that when a high concentration of parathion is present as a result of spillage on soil it may persist for a long period of time and thus should be dug up and disposed where it will not be a hazard to small children or animals, and will not be available on the surface to contaminate the environment.

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