Dissipation of Guthion, Sevin, Polyram, Phygon and Systox from Apple Orchard Soil[1]

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The development of resistance by certain insect species to the toxic action of organochlorine insecticides and the persistence of these chemicals in the environment has led to a decrease in their use over the last several years. In their place, numerous organophosphorous and carbamate insecticides have appeared; most of which are generally regarded to be much more biodegradable. However, to verify this claim for specific compounds under particular situations, more studies should be performed under actual use conditions where the compounds in question have been applied as part of a routine pesticide program.

In New York, 72,000 acres of commercial apple orchards are bombarded each season with an array of pesticide chemicals. A portion of each application invariably reaches the soil where it invades a relatively static environment subjected to minimum cultivation and protected from the weather by a vegetative cover and the shade of large trees. Since it is not unusual for an orchard to be treated with 6-8 different synthetic chemicals at a steady 10-14 day interval from late April to late August, it was felt that this situation represented an extreme case of potential soil pollution. In order to accurately assess this potential it would be necessary to follow the deposition, accumulation and dissipation of all of the materials entering the soil in one season. The data reported on the following pages are a result of a pilot project which was designed to examine some of the problems associated with such an environmental study. No attempts were made to develop the most sensitive detection methods or most efficient collection and extraction procedures. Rather, we hoped to get a semi-quantitative picture of the fate in soil of a total pesticide program as complex as that used in an apple orchard.

GENERAL METHODS

The primary sampling site was commercial orchard D located in the heart of upstate New York's apple region. Near the middle of the orchard is a block of 40-year old trees (MacIntosh variety) surrounded on three sides by a small stream, with a road bordering the fourth side. Every two weeks, beginning before the first spray of the season until well after

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the apples had been harvested, core soil samples were taken from this block at two different locations. The orchard owner kept careful records concerning the quantity of pesticide applied and the dates of application. His program was "typical" of most growers in the region and included the compounds shown in Table 1 together with one application of Amitrol-T (1 lb/acre) underneath the trees, one application of oil (5 gal/acre), one application of naphthylacetic acid (0.04 lb/acre) and several applications of sulfur (total 26 lbs/acre). However, for various reasons, only those compounds in Table 1 were studied.

TABLE 1

Insecticide-fungicide spray schedule for Orchard D, 1971.

Compound applied	Dates of application	Total amount of active ingredient applied (lb/acre)
Phygon (dichlone)	April 29	0.4
Polyram (metiram)	May 8,11,19,26; June 7	20
Systox (demeton)	May 19	0.6
Guthion (azinphos-methyl)	June 7,18,30; July 19	3
Sevin (carbaryl)	August 3,20	6

Soil samples were also removed from orchard 12A, an apple orchard maintained by the Experiment Station. Two replicate blocks were treated with 7 sprays of Guthion at the rate of 0.75 lb/acre each application (dates shown on Fig. 1), and two other blocks were treated with 3 cover sprays of Sevin at the rate of 3 lbs/acre each application (see Table 2). Sampling dates were chosen to give more detailed information than that obtained from orchard D.

At the two replicate locations in both orchards, 4 soil cores were removed from under 6 different trees in an area about half-way between the trunk and outer branches (KUHR et al. 1973). Each cylindrical core consisted of 3 soil plugs 1-5/8 inches in diameter and 2 inches long (only the top 2-inch plug was removed from orchard 12A). No attempt was made to scrape away surface vegetation or decaying plant debris before sampling. The 24 plugs from each depth were combined in a plastic bag, weighed and thoroughly mixed. Within 48 hours two subsamples were taken from each bag and extracted as described on the following pages (soil was held at 0-4°C until extracted). Results from the subsamples for the two replicates were averaged and are reported as ppm based on unscreened wet weight.

SPECIFIC ANALYTICAL PROCEDURES AND RESULTS

Guthion.-To 100 grams of soil in a 1-liter flask was added enough water to make a slurry plus 600 ml of 3:1 petroleum ether:isopropanol. The mixture was thoroughly agitated for 5 min on a wrist-action shaker and allowed to stand until the solvent layer separated. After decanting the solvent extract into a 1-liter separatory funnel, the alcohol was removed with three 150-ml washes of water. The remaining petroleum ether was dried over anhydrous sodium sulfate and a portion was concentrated 20X before analysis with a Tracor MT 220 gas chromatograph equipped with a flame-photometric detector maintained at 170°C, a 6'x1/4" column packed with 3% OV-1 on 60/80 Gas Chrom Q held at 210°C, and an inlet block set at 225°C. Using this procedure, the minimum detection level was 0.4 ppm Guthion. Recovery from spiked soil samples averaged 80% and reported results have been corrected to 100%.

The amounts of Guthion found in soil samples collected from orchard D during the summer of 1971 are shown in the lower portion of Fig. 1. No residues were detected in soil below the top 2-inch layer. Maximum contamination reached 1.6 ppm after the first application of Guthion in June, but then leveled off at about 0.7 ppm through the following 3 cover sprays. Within a month after the last application, residues of Guthion in the soil fell below detectable limits. Guthion levels were also below detectable limits before the first cover spray had been applied. A similar program was followed in 1972 and less extensive soil analyses indicated an almost identical dissipation rate. These results suggest that all of the Guthion reaching the soil in orchard D had disappeared before the season was over.

In orchard 12A, Guthion behaved somewhat differently, probably because the spray schedules, field conditions and application procedures were not the same (Fig. 1). Unfortunately, sampling did not begin until after Guthion had been applied 3 times. However, except for an unexplained build-up of residues near the end of August, soil contamination by this particular dithiophosphate remained at a fairly constant level through most of the summer. Then, after the last application on August 21, soil residues declined until they fell below detectable limits in October. Thus, in this instance it took about 2 months for most of the Guthion to disappear from the soil. Nevertheless, dissipation of Guthion from orchard 12A would appear to have been complete by the end of the year.

In general, these results are similar to those reported by SCHULZ et al. (1970). They found that over 90% of Guthion applied to the surface of soil had dissipated within 60 days. However, their detection methods were more sensitive indicating that the last few percentages of Guthion persisted for several more months.

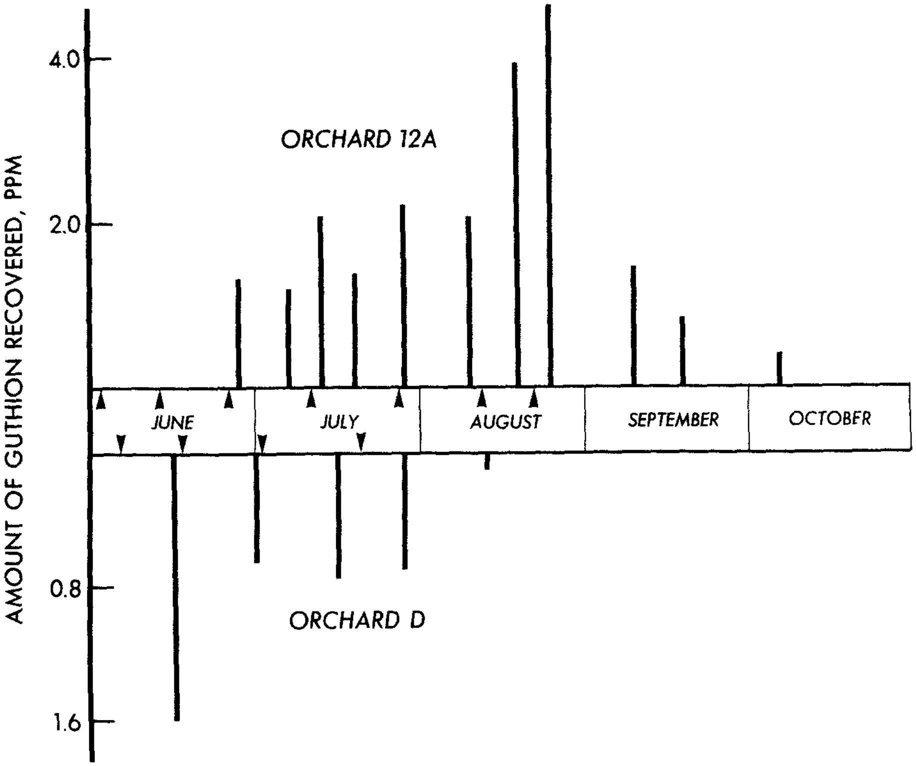

Fig. 1. Accumulation and dissipation of Guthion from orchard soil. Dates of application are indicated by arrows. Rate of application was 0.75 lb/acre each treatment.

Sevin.-A 100-gram soil sample was weighed into a 500-ml flask and agitated for 10 min with 250 ml of benzene. The extract was dried with anhydrous sodium sulfate, concentrated, cleaned up and analyzed by infrared spectroscopy as described by BRODERICK et al. (1966). Method sensitivity was 1 ppm and recovery from spiked soil averaged 96%.

Even though the two cover sprays applied to orchard D in August distributed 6 lbs of Sevin per acre, no Sevin was detected in any soil sample. This was not too surprising, however, since laboratory tests and previous experience have shown that this carbamate insecticide is very labile from certain soils. Since the nearest collection date following application of Sevin was 8 days, it is possible that almost all of the insecticide reaching the soil had been degraded before samples were taken.

More definite information was obtained from a study performed in orchard 12A (Table 2). Samples taken almost immediately after application on July 27 contained residues averaging 13.8 ppm. Within 1-2 days these levels had dropped to about 3 ppm, and after 2 weeks the amount of residue fell below detectable limits of 1 ppm. Thus, it is apparent that in only a matter of days Sevin soil residues had almost completely disappeared from orchard 12A, and probably also from orchard D. Rapid dissipation of Sevin from soil has also been reported by JOHNSON and STANSBURY (1965), although one other literature reference indicates that this compound may persist considerably longer in certain soil types (KAZAND et al. 1972).

TABLE 2

Distribution of Sevin residues in soil from orchard 12A, 1972.

Amount of active ingredient applied/acre	Date of application	Date of analysis	ppm recovered in top 2-inches of soil
3 lbs	June 27	June 28	3.18
		July 5	<1
3 lbs	July 27	July 27	13.8
		Aug. 10	<1
3 lbs	Aug. 21	Aug. 23	3.22
		Sep. 12	<1

Phygon.-The residue procedure used for detection of this fungicide was based on that of LANE (1958). To 50 grams of soil in a 250-ml flask was added 100 ml of benzene and the flask was agitated for 10 min. The resulting extract was dried over anhydrous sodium sulfate and Phygon was reacted with dry dimethylamine to give an orange color which was measured with a Coleman Junion Spectrophotometer at 495 mμ. Recovery from spiked soil averaged 97% with a sensitivity limit of 0.2 ppm.

Because of the low quantity of Phygon applied to the orchard and the limits of the detection procedure, recovery results were sporadic. No fungicide was found in soil collected before the spray schedule began. One week after the Phygon treatment, residues were observed in the top 2-inch soil layer. As the season progressed, residues appeared in lower soil depths but not with any regularity. This up-and-down appearance was also true for the top soil layer and a general decrease in contamination became evident only in late October. The average residue values for the 56 samples taken from May 5 to November 3 were 0.25 ppm Phygon at 0-2 inches, 0.08 ppm at 2-4 inches, and 0.07 ppm at 4-6 inches. However, the fact that Phygon was used the previous year but was not detectable in late

April of the test year, together with the general decline in residues near the end of October, imply that most of the fungicide had been altered within one year.

Polyram.-The procedure used for Polyram analysis was a modification of the methods of KEPPEL (1963) and CULLEN (1964). A 10-gram sample of soil slurried in 10 ml of acetonitrile was digested with 13 ml of 18N sulfuric acid for 20 min. During this time, the generated CS_2 was carried into 4 ml of Viles reagent through the aid of a stream of nitrogen. The colored copper chelate formed was measured with a Coleman Junior Spectrophotometer at 425 mμ. Recovery from Polyram-spiked soil ran 90% with a method sensitivity limit of 0.4 ppm.

Soil samples collected before the first Polyram application contained no detectable Polyram suggesting that all of the previous years' dosage had probably disappeared. During the Polyram spray period (May 8-June 7), residues accumulated in the top 2-inch soil layer up to a maximum of 6 ppm. For the following 4 months, residues, mostly below 1 ppm, were occasionally detected in the upper soil layer. In no case was any Polyram found in soil lower than 2-inches from the surface. Similar to Phygon studies, the results were very sporadic. Part of the reason may have been due to the small soil sample (10g) that was used for analysis and also due to the inherent instability of Polyram (CULLEN 1964). The very low maximum accumulation of 5-6 ppm in the soil compared with a total application of 20 lbs/acre within a month's time also speaks for the instability of this fungicide.

Systox.-A few specific Systox methods were briefly examined without success. Analyses using a total phosphorous procedure were inconclusive, partially because of the presence of Guthion later in the season, partially because of the low amount of Systox initially applied, and partially because of a number of interferring materials. However, the general indications were that this insecticide was unstable in orchard soil and failed to persist from one season to the next.

DISCUSSION

Although the sampling was not extensive and the analysis procedures were not the most sensitive, certain definite patterns appear evident. All five of the chemicals which were studied found their way into the orchard soil. Once there, they disappeared at different rates but all had almost completely dissipated by the end of the growing season, and certainly by the start of the following season. That is to say, all of the chemicals were biodegradable under the existing field conditions. The same 2-inch layer of soil under the trees of orchard D has been shown to contain DDT residues of approximately 235 ppm (KUHR et al. 1973). This is true even though DDT has not been applied to the orchard for over 10 years.

Of course, the results do not include any information about the metabolites or degradation products formed from these particular compounds. Whether or not they persist in the soil, or indeed are significant, requires a much more extensive evaluation. However, on the whole, it appears as though the newer organophosphorous and carbamate pesticides pose a much less serious threat as orchard soil pollutants than do the older standard compounds such as DDT and lead arsenate.

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