# Persistence of Azinphosmethyl in Soil

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Most of the research concerning degradation or disappearance of organophosphorus pesticide compounds from soil has involved relatively low initial levels of pesticide resulting from conventional applications of the compounds for insect control (CHISHOLM et al. 1955; STEWART et al. 1971). The finding at this laboratory (WOLFE and DURHAM 1966) 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 persistence of high concentrations of the pesticides, prompted additional investigation into the problem. More recently we reported on the persistence of parathion in soil following simulated spillage of emulsifiable concentrate and dilute formulations (WOLFE et al. 1973).

One of the main reasons for our concern about the problem is that applicators, when handling a pesticide they do not consider particularly hazardous, may tend to be more careless and produce more spillages. Azinphosmethyl has been considered very safe as far as hazard to the applicator is concerned. This is supported by the lack of reported illnesses due to occupational exposure to this compound. Such lack of illnesses may be partly due to the fact that dermally it is not particularly toxic, being only about one-tenth as toxic as parathion. In considering hazard from spillage of azinphosmethyl on soil, however, the main concern is that by the oral route it is approximately as toxic as parathion (GAINES 1969), a compound which applicators usually handle with great care because they consider it very hazardous.

The purpose of the present study was to determine the persistence of azinphosmethyl, O,O-dimethyl S(4-oxo-1,2,3-benzotriazin-3(4H)-ylmethyl) phosphorodithioate, residues in soil following topical applications of the compound. The results are intended to have application not only to the problem of hazard to children, pets and domestic farm animals who may come in contact with contaminated spillage areas, but also to problems related to waste pesticide disposal, leaching, and degradation or disappearance of the compound in the environment.

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## Materials and Methods

Treatments were made in field soil plots using three liquid azinphosmethyl concentrations and two different formulations. The treatments were: (a) undiluted commercial grade 18.1% liquid emulsifiable concentrate, (b) conventional dilute spray for orchard use prepared from water-wettable powder and containing 0.045% azinphosmethyl (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 semiconcentrate spray applications prepared from water-wettable powder and containing 0.36% azinphosmethyl (8X = 8 times the normal 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 pesticide concentrate 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 spray operation. The undiluted emulsifiable concentrate and 8X treatments were replicated 8 times in field plots and the 1X treatments were replicated 4 times.

The experimental plots were subjected to the natural elements such as rainfall (average approx. 25 cm per year), sunlight (over 275 days per year), and relatively high maximum temperatures (over 32°C for an average of 14 days each summer). The plots were covered with snow for approximately 2 months of each year. Soil assay of the plots used showed from 6.0 to 10.2% clay, 26.0 to 29.0% silt, 60.0 to 67.3% sand, and 1.0 to 3.4% organic matter. This assay classifies the soil type as sandy loam. The pH ranged from 6.6 to 7.8 with a mean of 7.2.

Square metal frames measuring 30 cm on each side 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 1.89 liters of liquid azinphosmethyl formulation was applied topically within the frame, a pool approximately 1.5 cm deep was formed before the material soaked into the soil. Samples of soil from two depths (0-2.5 and 2.5-7.5 cm) were taken 1 day following application and at regular intervals thereafter for 8 years. At the 8th year two test areas containing emulsifiable concentrate were sacrificed and four replicate samples were taken from each area at different depths in increments of 7.5 cm down to a 60 cm level.

Samples of soil to the 7.5 cm level in the 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 locations, especially after the 4th year of sampling. Cross contamination of samples below the 7.5 cm depth was negligible because samples in this area were taken only after the entire layer of soil had been carefully removed.

Azinphosmethyl content of soil samples was determined by the method of MEAGHER et al. (1960), a colorimetric procedure based on alkaline hydrolysis to anthranilic acid, followed by diazotization and coupling with N-(1-naphthyl)ethylenediamine dihydrochloride. Confirmation of samples, especially at the lower limits of detectability, was by gas chromatography. In order to obtain a workable retention time for the elution of azinphosmethyl a 1 m x 0.63 cm 4% SE-30/6% QF-1 column was employed. Detection was accomplished with a Melpar flame photometric detection system in the phosphorus mode of operation.

## Results and Discussion

The persistence of azinphosmethyl in sandy loam soil following gross topical contamination with 18.1% liquid emulsifiable concentrate formulation is shown in Table 1. The levels of pesticide in the soil, initially very high (25,570 to 70,944 ppm at the 0-2.5 cm level and 20,810 to 52,250 ppm at the 2.5-7.5 cm level), had decreased to between one-half and one-third of their original values by the end of the first year. From the second year and beyond, the rate of disappearance was considerably less but appreciable quantities still remained in both the top 2.5 cm and 2.5-7.5 cm levels through the end of the third year. From the 4th year through the 8th year the pesticide residue levels in the lower (2.5-7.5 cm) layer were consistently higher than in the top (0-2.5 cm) layer.

At the 8-year period where two test frame areas were sacrificed to determine whether any leaching of the azinphosmethyl beyond the 7.5 cm level had occurred, essentially no penetration was found beyond the 30 cm level (Table 2). Even though the exact rate of penetration is unknown it is important to note the lack of leaching in this soil type beyond 30 cm even when subjected to 8 years of normal weathering which included abundant snowfall and approximately 25 cm of rainfall per year.

## TABLE 1

### Disappearance of Azinphosmethyl from Sandy Loam Soil Following Gross Topical Contamination with 18.1% Liquid Emulsifiable Concentrate Formulation

| Sampling time (years) | Pesticide content of soil (ppm)[a] | |
|---|---|---|
| | Sample depth (cm) | |
| | 0 - 2.5 | 2.5 - 7.5 |
| 0[b] | 49,946 | 30,488 |
| 1/4 | 26,470 | 10,444 |
| 1/2 | 25,755 | 15,847 |
| 1 | 25,011 | 11,348 |
| 2 | 14,212 | 16,960 |
| 3 | 5,218 | 5,240 |
| 4 | 6,075 | 7,662 |
| 5 | 2,596 | 2,899 |
| 6 | 1,418 | 2,606 |
| 7 | 988 | 1,140 |
| 8 | 850 | 967 |

[a] Average of 8 replicates.

[b] Initial sampling 1 day after treatment.

## TABLE 2

### Leaching of 18.1% Liquid Emulsifiable Concentrate Azinphosmethyl Formulation in Sandy Loam Soil[a]

| Sample depth (cm) | Pesticide content of soil (ppm)[b] |
|---|---|
| 0 - 7.5 | 361.0 |
| 7.5 - 15 | 1054.0 |
| 15 - 22.5 | 62.3 |
| 22.5 - 30 | 3.7 |
| 30 - 37.5 | 0.5 |
| 37.5 - 45 | el[c] |
| 45 - 52.5 | el[c] |
| 52.5 - 60 | el[c] |

[a] Conducted at year 8 to study effect of leaching.

[b] Average of 8 replicates.

[c] Below lower limit of sensitivity of method ($<$ 0.05 ppm).

Persistence of azinphosmethyl at two depths in soil plots where the more dilute spray concentrations were applied topically are shown in Tables 3 and 4. As with the more concentrated applications discussed earlier, the levels of azinphosmethyl dropped off quite rapidly during the first year with relatively small amounts found thereafter. Where the 1X (0.045%) concentration was applied (Table 3) most of the pesticide had disappeared by one-fourth year with a leveling-off trend occurring at that point. There did not seem to be a noticeable difference between the emulsifiable concentrate formulation and the wettable-powder formulation. The amount for both types of formulations was not appreciably higher in the 0-2.5 cm level beyond the one-fourth year period. Where the 8X (0.36%) concentration was applied the disappearance for both the emulsifiable concentration and wettable-powder formulation seemed to be similar with most of the pesticide gone by four years. The amount found in the 0-2.5 cm level was generally higher than that found in the 2.5-7.5 cm level and it was not until later years that sampling showed some instances where there was slightly more at the lower level. The 8X concentration seemed to persist longer at the 0-2.5 cm level through the first year than did the wettable-powder formulation. After that the disappearance behavior of both types was essentially similar.

In the present studies the disappearance of azinphosmethyl from soil occurred at a slower rate than one might have expected considering exposure to natural elements in the field. This was especially evident where the emulsifiable concentrate dosage was involved.

Factors that probably affected the disappearance of azinphosmethyl from the soil are adsorption onto soil particles, photochemical decomposition, hydrolytic changes and volatilization. With the more dilute formulation applications, degradation by soil microorganisms may have also played a role, but where the emulsifiable concentrate material was applied the activity by microorganisms was probably reduced considerably by the formulation if the sterilizing effect was somewhat like that found for emulsifiable concentrate parathion (WOLFE et al. 1973). Adsorption of the azinphosmethyl on the soil particles undoubtedly played an important role. This was indicated in the leaching study where no pesticide was found past the 30 cm level. The fact that the pesticide disappeared more rapidly from the 0-2.5 cm level than from the 2.5-7.5 cm level may have been due to a greater exposure to the elements and degradation through photochemical and hydrolytic effects, as well as losses through increased volatilization. The lower level (2.5-7.5 cm) was "shielded" somewhat from photochemical effects and volatilization and losses were not as rapid, possibly because of this. However, the difference in losses was not extremely great.

TABLE 3

Disappearance of Azinphosmethyl from Sandy Loam Soil Following Gross Topical Contamination with 1X (0.045%) Spray Solution

| Sampling time (years) | Pesticide content of soil (ppm)[a] | | | |
|---|---|---|---|---|
| | Using EC formulation | | Using WP formulation | |
| | Soil depth (cm) | | Soil depth (cm) | |
| | 0 - 2.5 | 2.5 - 7.5 | 0 - 2.5 | 2.5 - 7.5 |
| 0[b] | 354.0 | 23.0 | 276.8 | 107.0 |
| 1/4 | 4.4 | 2.3 | 5.5 | 6.6 |
| 1/2 | 4.3 | 1.9 | 1.4 | 2.5 |
| 1 | 1.1 | 1.7 | 1.3 | 2.4 |
| 2 | 1.5 | 1.6 | 2.8 | 2.2 |
| 3 | 0.3 | 0.9 | 0.9 | 1.6 |
| 4 | 1.5 | 1.3 | 2.0 | 2.2 |
| 5 | el[c] | el[c] | el[c] | el[c] |
| 6 | el[c] | 0.1 | el[c] | 0.3 |
| 7 | el[c] | 0.3 | 0.4 | el[c] |
| 8 | el[c] | el[c] | el[c] | el[c] |

[a] Average of 4 replicates.
[b] Initial sampling 1 day after treatment.
[c] Below lower limit of sensitivity of method ($<$ 0.05 ppm).

Results of research reported in the present paper indicate that when a high concentration of azinphosmethyl is present as a result of spillage on soil, it may persist for a relatively long period of time. It is interesting to note that the 7,662 ppm soil content at the 4-year period where treatment was with emulsifiable concentrate is near the 8,634 ppm content of parathion in soil ingested by a child (QUINBY and CLAPPISON 1961), resulting in a near-fatal poisoning case. Considering that azinphosmethyl is as toxic orally as parathion, we feel that concern about the hazard of azinphosmethyl spillage should be equal to that of parathion. This emphasizes the importance of digging up contaminated soil areas and disposing the material where it will not be a hazard to small children or animals, and will not be available on the surface to contaminate the general environment.

TABLE 4

Disappearance of Azinphosmethyl from Sandy Loam Soil Following Gross Topical Contamination with 8X (0.36%) Spray Concentration

| Sampling time (years) | Pesticide content of soil (ppm)[a] | | | |
|---|---|---|---|---|
| | Using EC formulation | | Using WP formulation | |
| | Soil depth (cm) | | Soil depth (cm) | |
| | 0 - 2.5 | 2.5 - 7.5 | 0 - 2.5 | 2.5 - 7.5 |
| 0[b] | 2436.0 | 207.4 | 2764.0 | 159.1 |
| 1/4 | 507.5 | 90.8 | 432.0 | 53.2 |
| 1/2 | 1062.0 | 54.6 | 70.1 | 52.7 |
| 1 | 773.8 | 90.2 | 36.5 | 32.1 |
| 2 | 35.5 | 14.1 | 55.5 | 37.7 |
| 3 | 3.1 | 3.4 | 3.4 | 5.7 |
| 4 | 14.5 | 7.4 | 23.9 | 11.4 |
| 5 | 3.9 | 0.1 | 0.7 | 0.2 |
| 6 | 2.3 | 4.9 | 1.1 | 5.4 |
| 7 | 1.7 | 5.4 | 0.7 | 1.0 |

[a] Average of 8 replicates.
[b] Initial sampling 1 day after treatment.

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