LOSS OF TRIAZOPHOS AND MEVINPHOS IN SOIL[1]

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The loss of triazophos and mevinphos in soils under laboratory and semi-field conditions was determined by gas chromatography. Mevinphos was less persistent than triazophos. Degradation rates were rapid and varied with the kind of insecticide as well as soil type. Loam soil with higher organic matter content retained triazophos longer than the clay-loam soil. Microbial activity did not show a marked influence in the degradation of the insecticides. Except for the first-order reaction of triazophos in loam soil, insecticide degradation followed second-order kinetics.

The recoveries and the minimum detection limits of the method used were: triazophos, 98 percent and 0.01 mg/kg: mevinphos; 78 percent and 0.005 mg/kg.

Pesticides are introduced into the environment in a variety of ways, mainly through directed applications in agriculture, in forest pest control and for control of pests affecting human health. In all these operations, the soil is the main matrix of deposition either by direct or indirect routes. Pesticides are subsequently transferred to other components of the biosphere by a variety of mechanisms.

At present, the organophosphate compounds comprise the single most-used insecticide group. They are generally less persistent than the organochlorines because they are readily oxidized, volatilized and hydrolyzed. Triazophos [Hostathion: 1-phenyl-3(0,0)-diethyl-thionophosphoryl)-1,2,4-triazole] and mavinphos [Phosdrin: 60% w/w of the E-isomer of dimethyl-2-methoxy carbonyl-1-methylvinyl phosphate) are among those widely used in vegetable production.

Triazophos has a rat acute oral LD_{50} of 82 mg/kg and an acute dermal LD_{50} of 1100 mg/kg. It is currently one of the effective insecticides for the control of the diamondback moth, *Plutella xylostella* in cabbage especially in high elevation areas.

Mevinphos is a systemic compound with a rat acute oral LD_{50} of 3.7-12 mg/kg and an acute dermal LD_{50} of 16.0-33.8 mg/kg. It is among the few "older" compounds still effective against the diamondback moth in some vegetable producing areas.

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Both insecticides have a wide spectrum of activity, are relatively non-persistent on plants and in soils, but are highly toxic to non-target organisms especially fish. Their widespread use on crops and soil could therefore possibly affect soil microorganisms and non-target soil invertebrates which play essential roles in maintaining soil fertility and in controlling pests. Also, their fate as influenced by soil properties and other environmental factors is still poorly understood especially under Philippine conditions. It is therefore necessary that their degradation characteristics in soils be studied.

MATERIALS AND METHODS

I. Degradation Rates in Enamel Tray

Fortification. Oven-dried and air-dried clay loam soils were fortified at 100 ppm. Another set of air-dried samples were further fortified at 50 ppm. Fortification was done by adding a quantity of the pesticide dissolved in acetone (1.0 mg/ml) to 300 g of soil. The soil was thoroughly mixed and the solvent was allowed to evaporate. To this was added a sufficient amount of unfortified soil to yield a total weight of one kg of soil. About three g of sieved freshly collected non-agrarian soil was added to air-dried samples to ensure the presence of microorganisms. The entire sample was mixed for one h in a mechanical shaker, placed in a 9-3/4 x 14-1/3 x 2-1/8 in. enamel tray and the moisture content was adjusted to 40 percent of saturation.

Storage. Each tray was covered with a glass plate and exposed to sunlight. Samples were hand-mixed every other day and evaporation losses were replaced with distilled water at least three times a week to maintain the soils at a constant moisture level.

Soil Extraction. Twenty g of soil from each tray was placed in a screw-cap bottle and shaken for one h with 40 ml of 1: 1 petroleum ether-acetone (for triazophos) or 1:1 hexane-acetone (for mevinphos) in a wrist-action shaker. The supernatant was decanted and filtered through anhydrous sodium sulfate into a 250-ml Erlenmeyer flask. The soil was then washed twice with 40 ml of the solvent mixture by shaking for 10 min. The soil, bottle, and sodium sulfate were further rinsed with 40 ml of solvent mixture. The extract was concentrated to near dryness in a rotary evaporator and the residue was dissolved in five to ten ml of methanol prior to gas chromatography.

II. Comparative Behavior in Enamel Trays and Clay Pots

A comparative study on the behavior of the pesticides in enamel trays and clay pots was conducted at the 100 ppm fortification level using air-dried loam soil. Two sets of samples were placed separately on each holder. In one set of samples, the condensed moisture on the underside of the glass cover was returned to the soil by washing with distilled water. In another

set, the condensate was collected and the plate was washed with 1:1 methylene chloride-hexane solution. The condensate was extracted with the methylene chloride-hexane solution, the extract was combined with the wash solution, and the combined organic phase was analyzed. Soil analysis was done as in the preceeding.

Water Analysis. To a 50 ml sample in a 250-ml separatory funnel was added 80 ml of 1:1 methylene chloride-hexane solution, the mixture was shaken for two min and allowed to stand. The aqueous layer was drawn into a second 250-ml separatory funnel and the remaining extract in the first funnel was filtered through a column of anhydrous sodium sulfate into the second flask. Another 80 ml portion of 1:1 methylene chloride-hexane solution was added to the aqueous phase in the second separatory funnel and shaken vigorously for two min. The aqueous layer was drawn off into the empty separatory funnel and the methylene chloride extract was filtered through the previously used column of anhydrous sodium sulfate. The aqueous layer was finally washed with 80 ml of hexane. The filter tube was rinsed with three-10 ml portions of hexane. The combined extracts were concentrated in a rotary evaporator and the pesticide was dissolved in five to 10 ml of methanol for gas chromatography.

III. Degradation in Soil Following Application by Spraying

KK hybrid cabbage were grown on clay soil in the screenhouse. They were sprayed weekly starting two weeks after transplanting with triazophos and mevinphos at recomended rates (0.1 kg a.i/ha.). Random soil samples were collected from each plot immediately after spraying and at definite intervals thereafter. The samples were mixed, quartered, partitioned and analyzed as before.

Gas Chromatography. A Varian 1400 gas chromatograph equipped with an alkali flame thermionic detector was used for the analysis with the following parameters:

Column	:	3' x 1/8" stainless steel with 3% OV-1 on 80/100 Gas Chrom Q	
Temperatures (°C)	:	Column	170
		Detector	220 for mevinphos
		Detector	225 for triazophos
		Injector	230
Flow rates (ml/min)	:	Nitrogen	21
		Hydrogen	38
		Compressed Air	to 200
Retention Time (min)	:	Mevinphos	2.5
		Triazophos	3.5

Quantitation was based on peak height. To correct for changes in detector sensitivity with time, a standard solution was injected after very two injections of samples.

Figures 1 and 2 show the gas chromatograms of mevinphos and triazophos, respectively. The recoveries and the minimum detection limits of the method used were: triazophos, 98 percent and 0.01 mg/kg; mevinphos, 78 percent and 0.005 mg/kg.

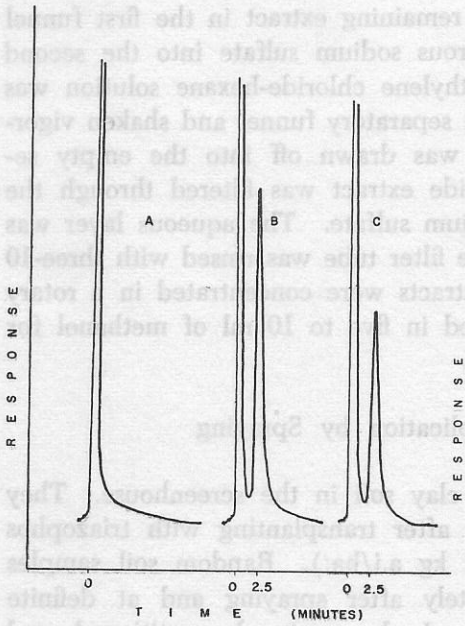

Fig. 1. Typical gas chromatograms of A) control, B) mevinphos standard and C) soil treated with mevinphos

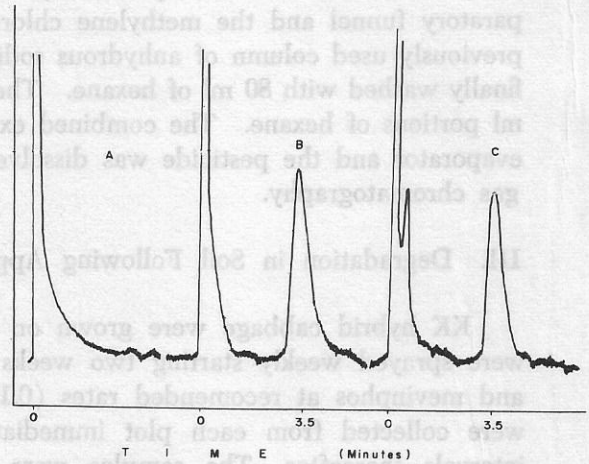

Fig. 2. Typical gas chromatograms of A) control B) triazophos standard and C) soil treated with triazophos

RESULTS AND DISCUSSIONS

Once the insecticides are on or in the soil, they are exposed to a variety of biological, physical, and chemical factors. The mechanisms responsible for their disappearance from the soil are still incompletely understood but volatilization, leaching, oxidation, hydrolysis, photodecomposition, and microbial activity all play a part. On the other hand, adsorption on the soil matrix could be responsible for inactivation or loss of activity as well as "prolonged" degradaton.

The chemical and physical characteristics of the soils tested are shown in Table 1 while in Table 2 is shown the meteorological conditions for the duration of the experiments.

TABLE 1. **Chemical and Physical data of soils used in tests.**

Property	Soil Type Clay-loam	loam	Clay
% moisture	11.8	7.2	11.8
pH	6.2	5.4	6.2
Organic Matter	3.4	4.9	2.32
CEC	38.9	19.6	37.79
% Silt	20.4	36.6	
% Sand	41.9	40.1	
% Clay	27.7	23.3	

I. Degradation Rates in Enamel Tray

As shown in Table 3 and Figure 3, triazophos appeared to be more persistent in loam ($t_{1/2}$ = 3.5 days) than in clayloam soil ($t_{1/2}$ = 0.6 days). This could be due to greater organic matter content in the former which immobilizes the insecticide thus making it unavailable for degradative reactions or volatilization (Stevenson, 1975; Stewart et al., 1977; Heuer et al., 1976; Saltzman et al., 1972). Lichtenstein et al., 1977 and Katan et al., 1976 have demonstrated that this binding by soil components depends on the pesticide itself and may vary even with such closely related compounds as parathion and methyl parathion. This observation on the relationship between organic matter content and degradation rate is in agreement with the report by Bock et al., (1975) that 50 percent loss of triazophos was observed after about 18 days in sandy soil while this same percent loss was extrapolated to occur only after about 87 days in sandy loam soil.

The effect of soil microorganisms on the persistence of the pesticide was studied by comparing degradation rates in both the oven-dried and air-dried soil samples; a quantity of freshly collected non-agrarian soil was added to the air-dried sample to ensure the presence of microorganisms (Iwata et al., 1973; Lichtenstein and Schulz, 1964). No noticeable difference was observed between air drying and oven-drying, suggesting that the level or kind of microorganisms present in the experiment may not have significantly affected triazophos degradation.

Two unidentified GLC peaks were observed in both soil types with triazophos; the first peak with retention time of 0.5 min appeared in soil sampled one hour after treatment while that with retention time of 13.2 min appeared after seven days. These metabolites increased with the disappearance of the parent compound and persisted even after 28 days. Furthermore, triazophos degradation in loam soil followed first-order kinetics (Figure 4) while second-order kinetics was observed in clay-loam soil (Figure 5).

TABLE 2. **Meteorological data for the experimental period, September 6 to October 4, 1976 and September 14 to December 8, 1977 (UPLB Meteorological Station)**

Experimental period	Temperature	Relative Humidity	Sunshine	Solar Radiation
	(°C)	(%)	(Hrs. & Min)	(g-cal-cm^2 day^{-1})
Sept. 6- Oct. 4, 1976	26.8	87.0	4.7	345.5
Sept. 15- Dec. 8, 1977	26.9	86.7	6.7	382.3

TABLE 3. **Decline of triazophos residues from clay-loam and loam soil. UPLB, 1977**

Soil Type	Days After Fortification									
	0[1]	1	2	3	5	7	9	14	21	28
A. Clay-Loam										
Air-dried										
(50 ppm)	25.7[2]	9.8	7.2	7.9	[3]	—	4.2	—	ND[4]	ND
(100 ppm)	57.0	18.9	13.4	10.3	5.5	5.5	4.4	2.9	0.7	ND
Oven-dried										
(100 ppm)	50.8	28.3	17.9	17.2	11.6	12.2	5.4	3.4	0.8	ND
B. Loam										
Air-dried										
(50 ppm)	32.2	24.8	23.2	23.0	12.4	11.8	—	5.4	2.1	ND
(100 ppm)	59.1	41.0	39.2	28.8						
Oven-dried										
(100 ppm)	54.2	42.9	34.3	29.8	20.8	19.6	15.6	9.2	6.2	ND

[1] Samples taken one-hour after fortification
[2] Figures given are averages of three replicates, one analysis per replicate.
[3] No result
[4] Non-detectable (< 0.005 mg/kg)

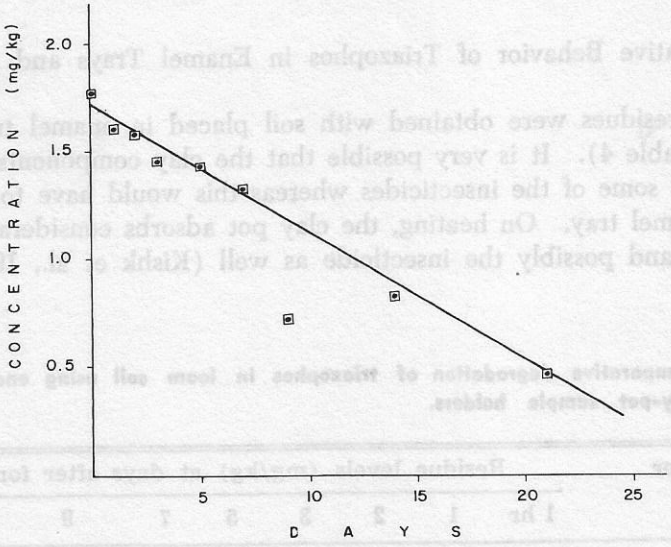

Fig. 3. Comparative degradation curves of triazophos in loam and clay-loam soil

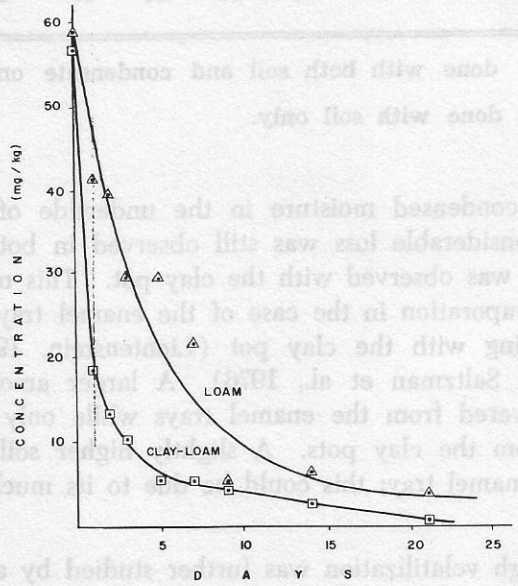

Fig. 4. Degradation of triazophos in loam soil showing first-order kinetics

As expected, mevinphos did not persist and no residues can be detected after two days.

II. Comparative Behavior of Triazophos in Enamel Trays and Clay Pots

Higher residues were obtained with soil placed in enamel trays than in clay pots (Table 4). It is very possible that the clay components of the clay pot adsorbed some of the insecticides whereas this would have to be minimal with the enamel tray. On heating, the clay pot adsorbs considerable amounts of moisture and possibly the insecticide as well (Kishk et al., 1976).

TABLE 4. **Comparative degradation of triazophos in loam soil using enamel tray and clay-pot sample holders.**

Sample Holder	Residue levels (mg/kg) at days after fortification								
	1 hr	1	2	3	5	7	9	14	28
A. Enamel Tray[a]	55	54	37	23	23	20	9.4	4.8	1.83
Clay Pot	42	24	30	19	19	13	4.5	2.9	ND
B. Enamel Tray[b]	73	56	28	19	32	19	12	6.7	ND
Clay Pot	46	27	28	26	24	15	6.0	6.3	ND

[a] Sampling was done with both soil and condensate on the underside of the glass cover.
[b] Sampling was done with soil only.

Although the condensed moisture in the underside of the glass covers was returned, a considerable loss was still observed in both sample holders; more moisture loss was observed with the clay pot. This moisture loss could be due to rapid evaporation in the case of the enamel tray but more of adsorption and binding with the clay pot (Lichtenstein, 1969; Yaron et al., 1974; Yaron, 1975; Saltzman et al., 1976). A larger amount of condensed moisture was recovered from the enamel trays while only minimal amounts were recovered from the clay pots. A slightly higher soil temperature was also noted in the enamel tray; this could be due to its much lower capability to radiate heat.

The loss through vclatilization was further studied by analyzing the condensed moisture in the underside of the glass cover. No triazophos was detected with water extracts but two unidentified metabolites were observed which gave retention times of 1.6 and 2.1 min respectively at 170°C column temperature. Soil extracts likewise showed the same peaks at the same

column temperature in addition to the one previously detected with retention time of 13.2 min at the operating temperature for soil (Fig. 6). The peaks were assumed to be triazophos metabolites inasmuch as they did not appear in the gas chromatograms obtained for the control and triazophos standards. This will be confirmed subsequently.

III. Loss in Soil Following Repeated Application by Spraying

Based on the half-lives obtained after the last spray application, triazophos also appeared to be more persistent ($t_{1/2}$ = 2.7 days) than mevinphos ($t_{1/2}$ = 0.8 days).

An accumulation of triazophos residues resulting from repeated spray application was observed especially after the fifth treatment while mevinphos residues remained at low levels even after the last treatment (Figure 7).

Reports have been made on the pseudo-first order kinetics of pesticides (Beynon et al., 1973; Yaron et al., 1974). In this experiment, however, degradation of triazophos and mevinphos were observed to follow second-order kinetics (Figures 8 and 9) although triazophos was earlier shown to degrade by first order kinetics in loam soil (Figure 4).

The rapid loss of mevinphos is in agreement with the report by Getzin and Chapman (1959), Burns (1971), and Beynon et al., (1973). A greater binding between the soil components and mevinphos than with triazophos may have taken place such that the insecticide became unextractable. The water solubility of the insecticides may have played a role also; there were heavy rains during the trial period and this could nave been responsible for the rapid loss of mevinphos although it did not appear to alter triazophos persistence. This could be explained by the water-solubility of the two compounds. Mevinphos was water-miscible while triazophos is soluble to only 39 ppm at 23°C. Likewise, mevinphos has a higher vapor pressure 1.24 x 10^{-4} mm Hg at 20°C) than triazophos (2.9 x 6^{-6} mm Hg at 30°C) so that the former could have volatilized faster than the latter.

The possible degradation scheme of triazophos as proposed by Bock et al., (1975) is shown in Figure 10. On the other hand, the products of degardation and the major route for the loss of mevinnphos in soil have not been established but it is unlikely that it would differ significantly from that shown on plants (Figure 11) by Beynon et al., (1973).

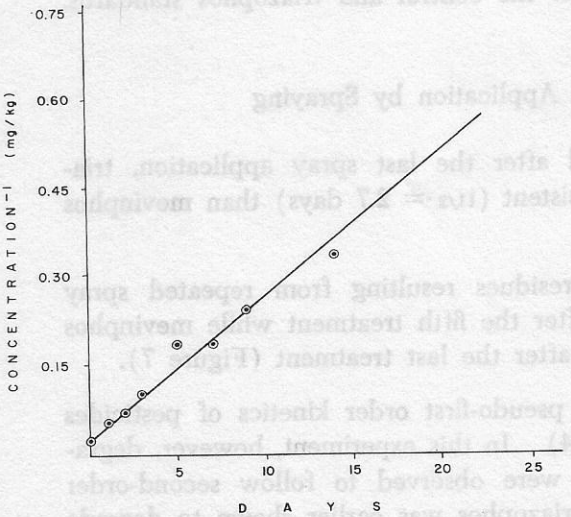

Fig. 5. Degradation of triazophos in clay-loam soil showing second-order kinetics.

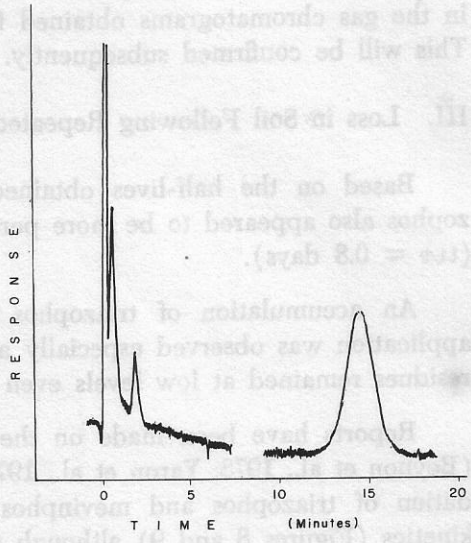

Fig. 6. Typical gas chromatograms at 170°C showing possible triazophos metabolites

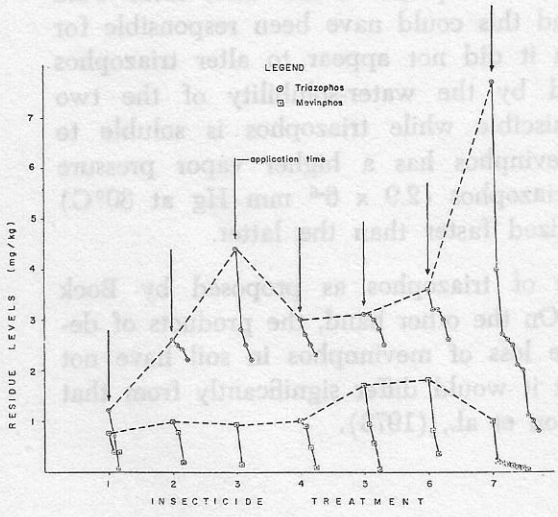

Fig. 7. Residue levels of triazophos and mevinphos in soil after repeated spray applications.

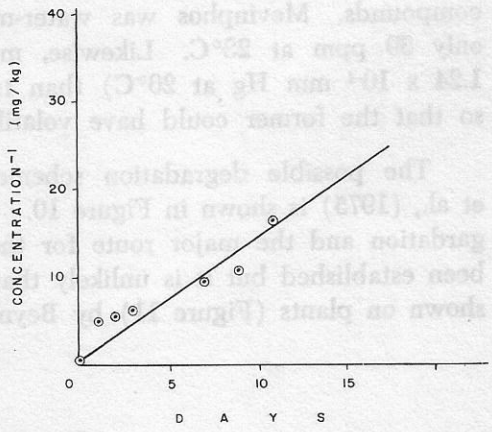

Fig. 8. Degradation of mevinphos in clay soil by second-order kinetics

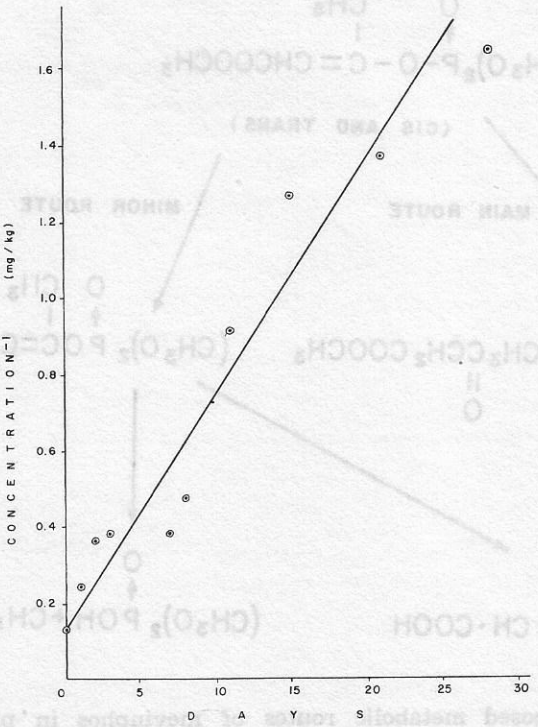

Fig. 9. Degradation of triazophos in clay soil showing second order kinetics.

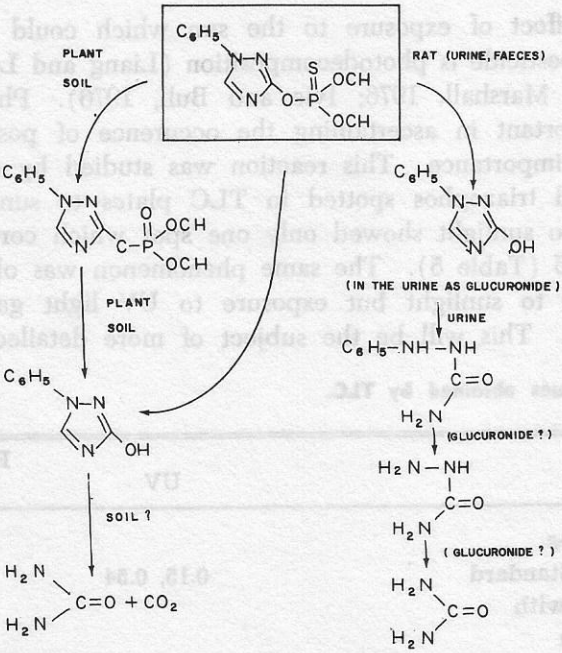

Fig. 10. Degradation scheme of triazophos (Bock et al. 1975)

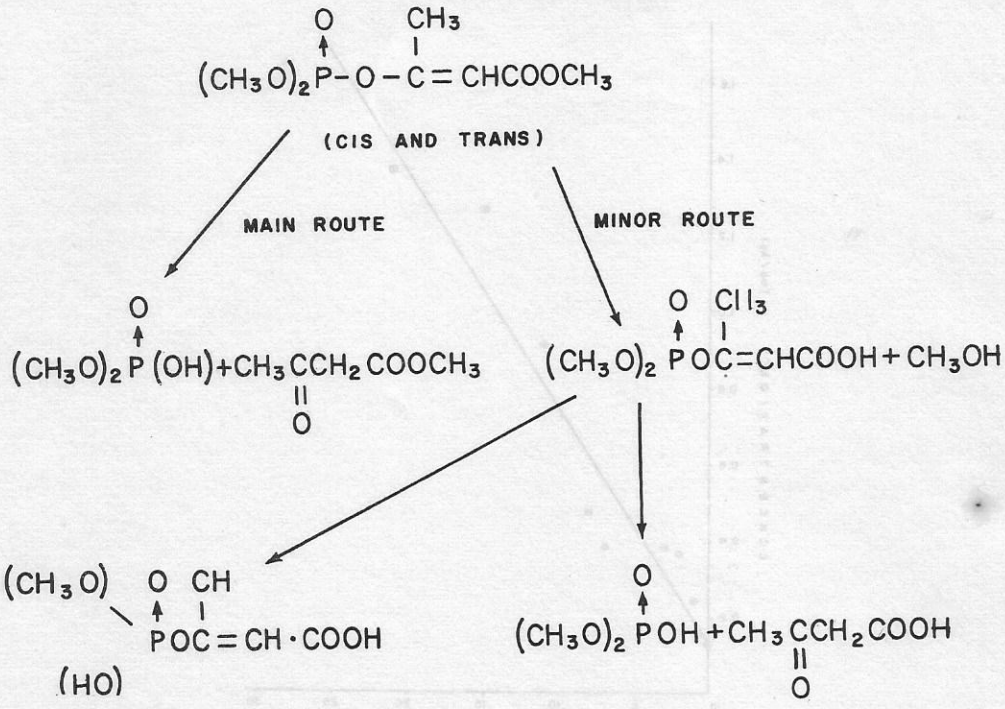

Fig. 11. Proposed metabolic routes of mevinphos in plants (Beynon et al., 1973)

IV. Photodecomposition.

A related effect of exposure to the sun which could account for the rapid loss of a pesticide is photodecomposition (Liang and Lichtenstein, 1976; Greenhalgh and Marshall, 1976; Ivie and Bull, 1976). Photodecomposition studies are important in ascertaining the occurence of possible metabolites of toxicological importance. This reaction was studied by exposing fortified soil samples and triazophos spotted in TLC plates to sunlight. The TLC plates exposed to sunlight showed only one spot which corresponds to triazophos, Rf = 0.5 (Table 5). The same phenomenon was observed with soil extracts exposed to sunlight but exposure to UV light gave a faint spot with Rf of 0.15. This will be the subject of more detailed studies.

TABLE 5. **Rf values obtained by TLC.**

	Rf	
	UV	Sunlight
Triazophos		
Triazophos Standard	0.15, 0.54	0.53
Soil extract with		
Clay-loam		0.54
Loam		0.53

Rf of unexposed triazophos standard = 0.53 to 0.54.

SUMMARY AND CONCLUSION

In laboratory and semi-field experiments, the loss of triazophos and mevinphos in soil were relatively rapid. It was affected by soil type with mevinphos being less persistent than triazophos. Loam soil with higher organic matter content retained triazophos longer than the clay-loam soil. This could be due to greater organic matter content in the former which immobilizes the insecticide, thus making it unavailable for degradation reactions or volatilization. Microbial activity did not show a marked influence in the degradation of the two insecticides indicating that the level or kind of microorganisms present in the experiment may not have significantly altered pesticide degradation. Enamel trays appear to be superior to clay pots in conducting laboratory study of this type inasmuch as the clay appears to absorb some of the pesticide thus resulting in lower recovery values. Except for the first-order kinetics for triazophos in loam soil, degradation of both insecticides followed second-order kinetics.

Triazophos-treated soil exposed to sunlight gave only one spot on TLC which corresponded to the standard while that exposed to more intense UV radiation gave an additional faint spot.

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