

THE PERSISTENCE OF PARATHION, TOXAPHENE AND METHOXYCHLOR  
IN SOILS

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By

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G. P. C.

## PREFACE

With the introduction of D.D.T. during World War II, a new era started in the field of insecticides. Prior to that time, insecticides were of inorganic nature with the exception of rotenone, pyrethrum, nicotine and a few other toxicants of plant origin. The new synthetic organic compounds gained rapid popularity because of their exceedingly high toxicity against most pests, greater stability and long lasting residual action.

It was this property of stability and persistent action which immediately raised many problems for the research worker. It was soon found that D.D.T. and other chlorinated compounds were stored in the adipous tissues of animals and that the toxicants were excreted unchanged in the milk of animals sprayed, dipped or otherwise coming in contact with these insecticides. (3) (30) Additional studies showed that this phenomenon was not limited to the animal kingdom but that plants sprayed with these compounds would absorb and translocate the poison throughout their whole system. (20)

Again, because of their apparent stability and unusual potency as insecticides, the question immediately arose as to whether prolonged and repeated spraying of crops might result in the accumulation of harmful residues in the soil. In the case of D.D.T. extensive studies have been made concerning the interaction between soil and toxicant and the subsequent effects on plants and soil micro-organisms. It appears to be well established that deposits of this compound on the soil are exceptionally stable, resist bacterial action, are

insoluble in water and therefore do not leach appreciably. (9)

Hence, indiscriminate use of this and similar insecticides may lead to a more or less permanent poisoning of the soil. The harmful effects of arsenical residues in the soils of certain orchards in Washington (13) after many years' use of lead and calcium arsenates suggests that similar troubles might be encountered with the newer insecticides.

At the present time adequate data are not available to indicate the permanence and stability of the more recently developed insecticides under all soil and climatic conditions. Soil type and character, especially the quantity of organic and colloidal clay, are important in determining the persistence of insecticidal residues.

It was thought desirable to conduct a series of experiments dealing with the stability of some of these insecticides, parathion, toxaphene, and methoxychlor, when mixed with soil and incubated under known conditions. It is hoped that the findings of this study, together with others, will be of benefit to the farmers of this region in determining crop and soil management practices.

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## INTRODUCTION

A review of the literature shows that studies on soil residues of the synthetic organic insecticides, their decomposition and phytotoxicity centers almost exclusively on D.D.T. (p, p' dichlorodiphenyl-trichloroethane). Even in this case, there is some disagreement in the results obtained by different workers. For example, Foster (9) claimed that D.D.T. mixed in muck soil and exposed to outdoor weathering has remained stable and persisted without detectable changes in toxicity for a period of four years. Likewise Fleming (8) found that the effectiveness of D.D.T. residues in some types of soils did not change in 5 years but in others the toxicity decreased considerably. On the other hand, Sakimura (22) reported that the residual toxicity of D.D.T. dropped by two-thirds after 26 months of application. It appears, therefore, that the decomposition of this insecticide in soil varies with different types of soil and even with similar types of soil in different localities.

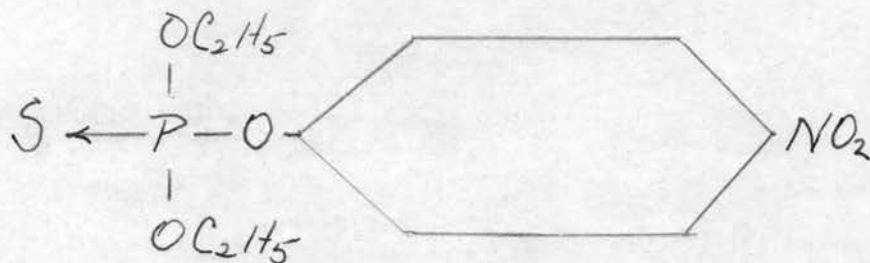
From the very nature of the problem it is hardly possible to obtain a complete answer in any single experiment.

For each new chemical having established value as an insecticide, fungicide, herbicide or other agricultural use it is important to know whether or not they are toxic to plants, either when applied to the plant or when incorporated into the soil. It is also important to know whether or not they persist in the soil, whether they are broken down chemically by organisms and whether they are leached from the soil. For the experiments described in this paper the insecticides parathion,

toxaphene and methoxychlor were chosen for investigation; and are described in the order mentioned.

The development of the organic phosphates as insecticides apparently resulted from the discoveries of Schrader of Germany, immediately prior to 1941. Since the facts regarding these materials were intimately connected with chemical warfare research, they were not published until after the defeat of Germany. Of these materials three have reached commercial status as insecticides; viz., hexaethyl tetraphosphate, tetraethyl phrophosphate, and parathion.

Parathion or O, O-diethyl-O-para-nitrophenylthiophosphate,



was apparently first prepared by Schrader by treating phosphorus trichloride with sodium ethoxide and the resulting product with sodium paranitrophenate. The compound is a dark brown to yellow liquid, with a theoretical boiling point of  $375^{\circ}$ , a specific gravity of 1.26 at  $25^{\circ}$  and a vapor pressure of about 0.0006 m.m. Hg. at  $24^{\circ}$  (12) It is water soluble to the extent of 20 p.p.m. and hydrolyzes in alkaline solution but not in water forming para-nitrophenol and diethylortho-thiophosphoric acid.

Parathion shares with some other insecticides the remarkable property of being absorbed by plants and dispersed throughout their whole system. Thus, parathion has been shown to be translocated throughout the plant when applied to the leaves in the form of spray.

(24) Likewise, it has been shown that this insecticide is absorbed through the roots of plants (20), through the fruit (16), and that some plants grown in treated soil produced tissue lethal to insects. (21)

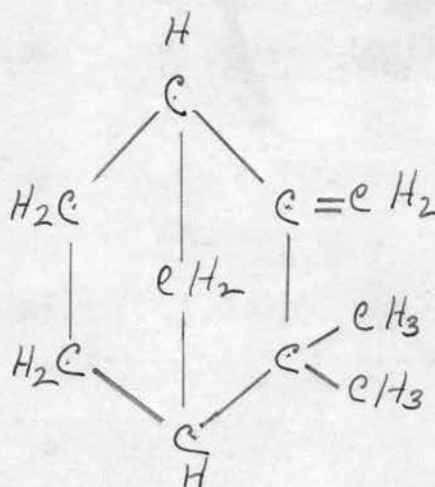
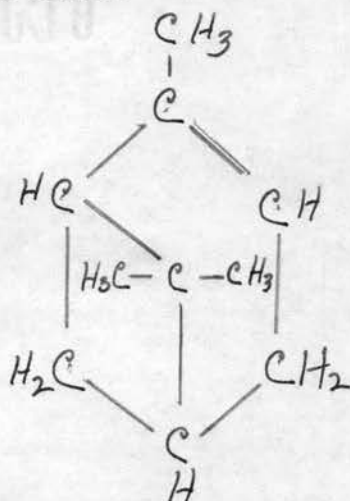
Parathion decomposes rapidly loses its insecticidal activity according to Ginsburg et al. (11) They found virtually no residues on crops harvested 12 or more days after application of dusts or sprays. Furthermore, parathion seems to disappear rapidly on exposure on an inert glass surface. Among the possible explanations are volatilization, mechanical dissipation and decomposition. The general consensus is that the disappearance of parathion residues is due predominantly to direct volatilization. This is based on the fact that parathion in its pure state exhibits a slight vapor pressure.

Zimmerman (32) has postulated that organic phosphates in the soil may decompose producing ethylene vapors. He based this hypothesis in his observations that plants grown in treated soil showed typical symptoms of ethylene poisoning. However, McIlrath (16) produced similar malformations in cotton plants by direct application of commercial formulations of parathion on the leaves. This suggests that the results observed by Zimmerman might have been due to absorption of parathion through the roots and its translocation to the leaves. There seems to be, therefore, some disagreement as to the stability of parathion residues and to the possible causes of its deterioration.

Toxaphene is a yellow waxy solid with a mild piney odor, it melts in the range of 65 to 90° C. and its density is 1.6, it is insoluble



in water but readily soluble in organic solvents. Toxaphene is made by chlorinating camphene to a chlorine content of from 67 to 69 per cent which results in a material with the approximate formula  $C_{10}H_7Cl_8$ . Camphene, in turn, is made by isomerizing alpha pinene, a major constituent of turpentine. The structural formulas of pinene and camphene are shown below:



It is apparent from the structural formula of camphene that when chlorine is added to it the reaction may be substitution, addition, rearrangement or a combination of these. It is not surprising therefore that the structural formula of toxaphene is not known.

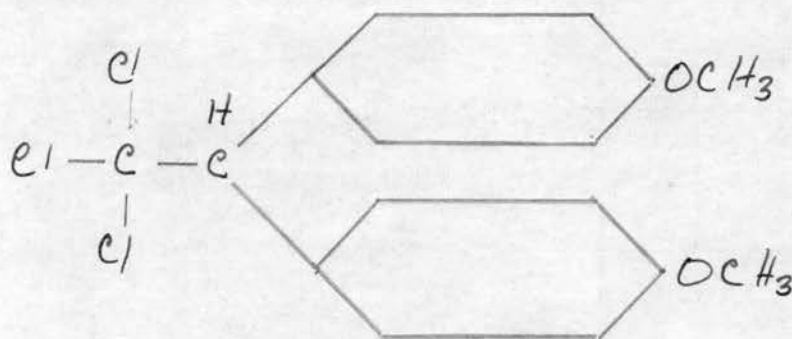
Since its introduction, toxaphene has steadily increased in importance due to its selective toxicity to insects unaffected by D.D.T. Unfortunately, like the other synthetic insecticides, toxaphene is highly toxic to certain plants. This has been shown by Cullinan (4), and Kelsheimer (14). The latter reported the almost complete destruction of a crop of cucumber and squash in Florida. In contrast to these reports toxaphene appeared to be harmless to other plant species. (18) (26)

The toxicity of soil residues of this insecticide is also a

controversial subject in the literature. Cullinan (5) reported that toxaphene depressed plant growth when applied to the soil at low levels, whereas Watts (29) could not detect any damage to cotton planted in soil containing the equivalent of 2,000 pounds toxaphene per acre. Woodbury (2) mentions that toxaphene deposits in soil might be transitory, on the other hand, Foster (10) reported that large amounts of toxaphene in the soil will remain toxic to crops for several months.

Since toxaphene has attained an important place among the insecticides in general use, information on the persistence of its residues and factors influencing its deterioration in the soil, should be welcomed by workers in this field and farmers in general.

Methoxychlor is the approved common name for the residual-effect, chlorinated-hydrocarbon insecticide known chemically as 2,2 bis (p-methoxyphenyl) 1,1,1, trichloroethane.



This compound is a white solid, soluble in many of the common organic solvents but insoluble in water. Methoxychlor was developed in an attempt to correct some of the disadvantages of D.D.T., yet keeping most of its insecticidal qualities. D.D.T. is known to penetrate the skin and to appear in the milk of animals sprayed with normal amounts of toxicant. Thus, a potential hazard exists for

consumers of milk and milk products.

Experiments conducted by entomologists of the U.S.D.A. have shown that in contrast to D.D.T., methoxychlor has less tendency to be stored in the body fat and to be excreted in the milk of treated animals. (28) Other desirable properties such as low phytotoxicity and low toxicity to warm-blooded animals makes this insecticide specially attractive to farmers.

It has already been mentioned that parathion is highly unstable in alkaline solutions. In the same manner, toxaphene and methoxychlor are so unstable in basic solutions that their determination is based on the alkaline dehydrohalogenation of the insecticides. Presumably, the three insecticides should be stable in mildly acid media, however, no specific mention to this effect has been found in the literature.

To our best knowledge, no work has been reported on the possible effects of soil pH on residues of parathion, toxaphene and methoxychlor. Research on this problem is important not only for these insecticides but with all chemicals applied to crops.

The purpose of the investigations reported herein was three-fold in nature:

(A) To obtain information as to the persistence of known amounts of parathion, toxaphene and methoxychlor when mixed with the soil.

(B) To study the effect of soil pH on the rate of decomposition of these compounds.

(C) In the case of parathion, to determine if volatilization is the main cause of the disappearance of this insecticide when mixed with soil.



## MATERIALS AND METHODS

The soil chosen for these experiments was a stephensville fine sandy loam, rich in organic matter, which had not been previously sprayed or treated in any way for the control of insects or weeds. In preparation for sampling the soil was sieved through a 1/4-inch mesh screen and mixed thoroughly to insure uniformity.

Three soil treatments were included in these experiments: a control or untreated soil, an acid soil, and a basic soil. The pH of samples of these soils was determined as follows: a portion of soil was wetted in a beaker with distilled water until a thin paste was formed. The pH of the mixture was ascertained using a Beckman pH meter. The average of five determinations showed a pH of 6.5 for the untreated soil. To prepare an alkaline soil one gram of calcium hydroxide was added to five hundred grams of the soil and completely mixed; a pH of 7.8 was obtained. Likewise, one half gram of aluminum sulphate added to five hundred grams of the raw soil produced a pH of 4.7. In this way three pH levels were obtained; viz., acid (pH 4.7), near neutral (pH 6.5), and basic (pH 7.8). Individual five hundred gram samples of soil were weighed into two quart-size glass jars, and the pH was adjusted as described above and the soil treated with the insecticide dispersed in water.

The experiments were carried through a period of six months, each experiment lasting 8 weeks. Four sets of samples were prepared with each insecticide; one set was analyzed at the end of 1, 2, 4 and 8 weeks. The jars were kept open and the soil moisture was maintained by daily additions of water. Moreover, the jars were shaken

periodically so as to expose a fresh portion of the soil to the air; hence, actual field conditions were simulated. In the case of parathion duplicate sets of samples were prepared for each of the sampling intervals. In one set the jars were sealed airtight to prevent possible volatilization of the insecticide while in the other set the jars were kept open. In all cases the sets consisted of duplicate soil samples for each of the three pH levels. Additional samples were prepared with each insecticide and analyzed immediately in order to determine the recovery of the poison under experimental conditions. The three experiments, one with each insecticide, were carried under greenhouse cover so as to keep the soil at optimum conditions to temperature and humidity.

The parathion solution was prepared from a concentrate containing twenty-five per cent technical parathion in an inert organic solvent ("Thiophos," American Cyanamide Co.). A portion of forty milliliters of the concentrate was measured into a 2,000 cc. volumetric flask and diluted to volume with distilled water. An aliquot containing twenty milliliters of this emulsion, equivalent to one hundred milligrams of parathion, was pipetted evenly over the soil in each jar. The jars were then shaken vigorously to insure complete mixing of the insecticide with the soil.

The aqueous dispersion of toxaphene was prepared from a 40 per cent wettable powder (Hercules Powder Co.). Twenty grams of this powder were weighed into a 2,000 cc. flask and made to volume with distilled water. The emulsion was stirred constantly while 25 cc. aliquots were measured. These aliquots, containing one hundred milligrams of toxaphene were pipetted into individual jars as previously described.

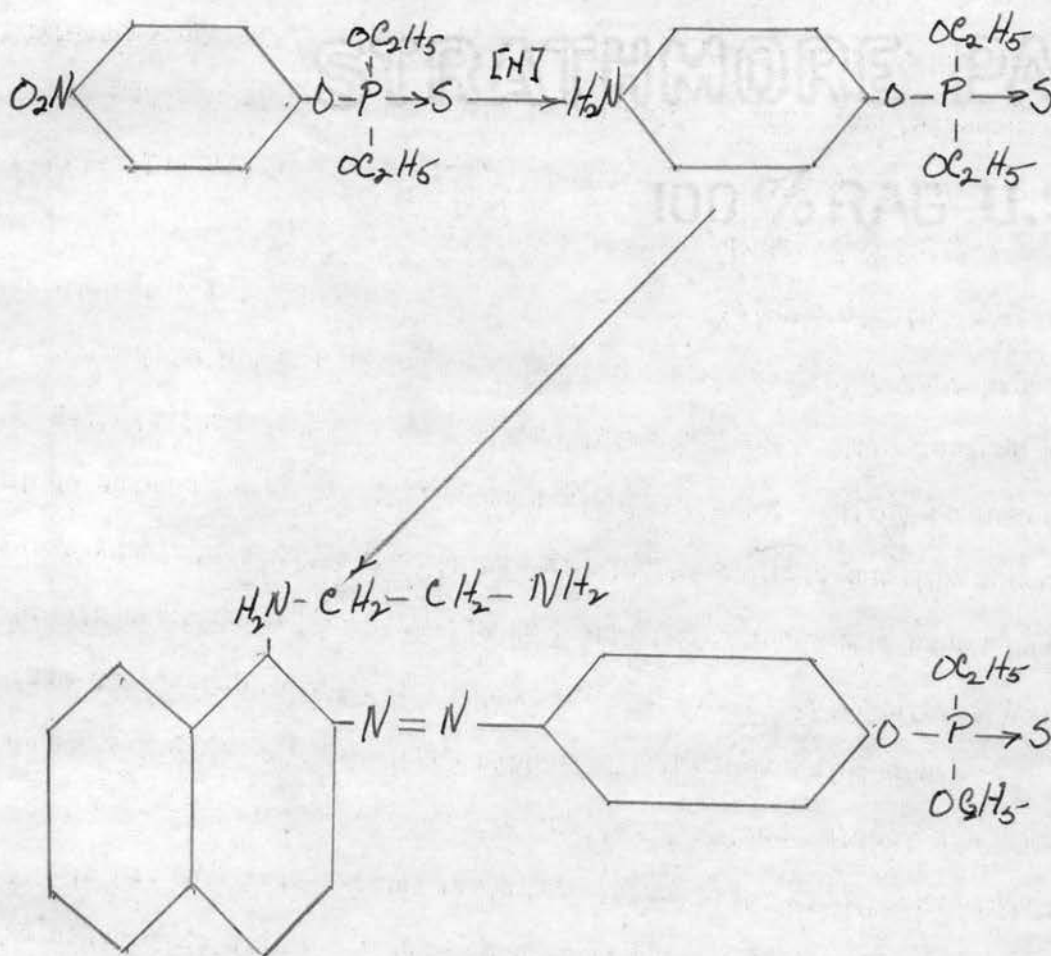


The solution of methoxychlor was prepared from a concentrate contained 25 per cent technical methoxychlor ("Marlate," DuPont). A twenty milliliter portion of this concentrate was made to 1,000 milliliter volume with distilled water. Aliquots of twenty milliliters of this emulsion, containing one hundred milligrams of methoxychlor, were pipetted into each jar and thoroughly mixed with the soil.

At the time of analysis the soil samples were extracted with six hundred milliliters of solvent in closed mason jars. Six jars at a time were tumbled end over end in a shaking machine at approximately 50 r.p.m. for sixty minutes. Benzene was used to extract parathion and methoxychlor from the soil while a mixture of two parts benzene and one part of isopropanol was used for toxaphene; the extract was filtered and a suitable aliquot measured into a beaker. The benzene was evaporated at low temperature under a current of air to reduce decomposition of the insecticide and the dried residue carried through the regular procedure of analysis as described for each insecticide. A discussion of the methods of determination for parathion, toxaphene and methoxychlor follows.

Two methods have been proposed for the determination of parathion. One method has been devised for the assay of technical grades of parathion and its formulations by means of the polarograph. (2) The electrolysis is carried out in an acetone-water solution with potassium chloride as the electrolyte and gelatine as the suppressor. For spray residues Averrel and Norris (1) have developed a method that is sensitive to about 20 micrograms of parathion. The method is based on the reduction of the nitro group of parathion to the amine, diazotization and coupling with N-(1-naphthyl) ethylenediamine

hydrochloride which gives an intense magenta color with an absorption peak at 555 mμ. The presumed gross chemistry of the analytical procedure is shown below:



The resultant color is remarkably intense per unit of parathion which makes it readily adaptable for the quantitative estimation of the insecticide residues in soils. This method has the additional advantage that aniline hydrochloride may be substituted for pure parathion in the preparation of the standard since the former gives a color of the same shade an intensity as parathion.

There is no specific qualitative or quantitative test for

toxaphene. The total chlorine content for toxaphene was determined by refluxing the compound in an isopropanol solution with metallic sodium. The chlorides formed were then estimated by the titration method of McLean.(17) This last method was used in these investigations because of its relative simplicity and the absence of interfering colors in the soil extract. In this method the chlorides obtained by dehydrohalogenating toxaphene are precipitated by the addition of a known volume of 0.03 N silver nitrate. The precipitate is filtered and the filtrate acidified with nitric acid. The excess silver nitrate is titrated, in the presence of a starch-nitrite buffer, with a 0.012 N potassium iodide solution until a permanent blue color appears. The factor used to convert the chlorides to toxaphene is 1.46. This factor is based on a chlorine content of 68.54 in toxaphene, the theoretical amount required by the formula  $C_{10}H_{10}Cl_8$ .

Methoxychlor is usually estimated by the methods originally devised for the determination of D.D.T. The Schechter-Haller method (28) may be applied to methoxychlor using the absorption maximum at 535 mu. The final pink color is due to a complex formed between sodium methylate and the dehydrohalo-genated-nitrated methoxychlor, but the method is less sensitive than would be desired. The Stiff-Castillo method (27) for D.D.T. is also applicable to the determination of small amounts of methoxychlor although it is only about one fifth as sensitive as for D.D.T.

A recent method determines methoxychlor specifically and with a greater degree of sensitivity. The method of Fairing and Warrington (7) involves the quantitative dehydrohalogenation of methoxychlor

with alcoholic potassium hydroxide and treatment of the produce with 85 per cent sulfuric acid to produce a red complex with an absorption maximum at 555 mμ. The procedure is sensitive to about 5 micrograms of methoxychlor and has been used successfully in the determination of residues in a number of crops. The method as originally published was intended for the determination of residues on milk and other products in which fat and oils would interfere. For this investigation the method was modified by eliminating the steps involved in the destruction of fatty substances, besides a few other minor adaptations in technique were used which made the procedure more suitable for the estimation of methoxychlor in soil.



## RESULTS AND DISCUSSION

The results obtained in the experiments with parathion, toxaphene and methoxychlor are presented in Tables I, II and III respectively. It should be noticed that analysis of the soil, immediately after mixing with the insecticide, showed essentially complete recoveries of the amounts added in the case of parathion and toxaphene. About 90 per cent of added methoxychlor could be demonstrated by analysis immediately after mixing with the soil.

The decomposition of parathion proceeded gradually but consistently and at the end of two months only about one-third of the insecticide remained in the soil. The disintegration of the toxicant was most rapid during the first two weeks when 40 mg. of the insecticide were lost. This amount of parathion is much larger than would be expected to accumulate in the soil from spray run-off. It follows that there is very little probability of poisoning the soil with parathion with normal usage for insect control since its rate of decomposition is very high in the first few days after application.

As mentioned in the introduction, it has been postulated that parathion residues in crops and soil are lost mainly through volatilization. The data obtained from this experiment show that there is no significant difference between the insecticide recovered from the soil in the closed and open jars. Since the closed jars were sealed air-tight and handled the same as the open jars, the data seem to indicate that the deterioration of parathion is mainly, if not entirely, a chemical process.

TABLE I  
CONCENTRATIONS OF PARATHION RECOVERED AT STATED INTERVALS AFTER APPLICATION  
IN THE SOIL

Time Interval*		Acid (pH 4.7)		Untreated (pH 6.5)		Basic (pH 7.8)	
		Open	Close	Open	Close	Open	Close
		mg.	mg.	mg.	mg.	mg.	mg.
1st. Week	(a)	82.8	73.2	76.2	71.4	68.4	63.0
	(b)	70.2	75.6	68.4	72.6	66.0	80.4
	Ave.	76.5	74.4	72.3	72.0	67.2	71.7
2nd. Week	(a)	43.2	67.2	67.6	54.8	42.0	38.0
	(b)	67.2	56.8	63.6	68.0	44.0	53.2
	Ave.	55.2	62.0	65.6	61.4	43.0	45.6
4th. Week	(a)	45.4	53.3	48.0	57.6	49.2	47.3
	(b)	57.1	49.2	50.4	50.4	32.2	44.4
	Ave.	51.3	51.3	49.2	54.0	40.7	45.8
8th Week	(a)	34.8	35.3	34.1	36.0	28.3	28.3
	(b)	35.5	36.5	35.5	35.0	27.4	26.4
	Ave.	35.2	35.9	34.8	35.5	27.9	27.3

\*Analysis in triplicate of the soil immediately after mixing with the insecticide showed a concentration of 104.5 mg. parathion.

TABLE II

CONCENTRATIONS OF CHLORINATED CAMPHENE RECOVERED AT STATED INTERVALS AFTER APPLICATION TO THE SOIL

Time Interval*		Acid (pH 4.7)	Untreated (pH 6.5)	Basic (pH 7.8)
		mg.	mg.	mg.
1st. Week	(a)	82.7	84.6	83.8
	(b)	80.8	82.8	85.1
	Ave.	81.8	83.7	84.5
2nd. Week	(a)	73.1	80.4	80.4
	(b)	75.9	78.7	77.9
	Ave.	74.5	79.5	79.2
4th. Week	(a)	70.4	72.2	51.3
	(b)	72.6	66.4	53.0
	Ave.	71.6	69.3	52.2
8th. Week	(a)	70.3	69.3	48.3
	(b)	72.9	67.1	49.5
	Ave.	71.6	68.2	48.9

\*Analysis in triplicate of the soil immediately after mixing with the insecticide showed a concentration of 96.2 mg. chlorinated camphenes.

TABLE III

CONCENTRATIONS OF METHOXYCHLOR RECOVERED FROM THE SOIL AT STATED INTERVALS  
AFTER APPLICATION

Time Interval*		Acid (pH 4.7)	Untreated (pH 6.5)	Basic (pH 7.8)
		mg.	mg.	mg.
1st. Week	(a)	48.3	53.7	40.0
	(b)	54.4	55.0	39.5
	Ave.	51.4	54.4	39.8
2nd. Week	(a)	29.8	30.8	22.5
	(b)	31.8	34.3	24.3
	Ave.	30.8	32.5	23.4
4th. Week	(a)	27.3	27.5	15.3
	(b)	29.0	31.1	19.5
	Ave.	28.2	29.3	17.4
8th. Week	(a)	23.7	22.5	17.7
	(b)	23.1	23.7	16.6
	Ave.	23.4	23.1	17.2

\*Analysis in triplicate of the soil immediately after mixing with the insecticide showed a concentration of 89.6 mg. methoxychlor.



There was no apparent difference in the stability of parathion, as measured by its recovery, in the acid soil and in the control. However, the alkaline soil definitely increased the rate of decomposition of the insecticide. The action of the lime was rather constant throughout the experiment, the recovery of parathion from basic soil being around 20 to 30 per cent less than from the acid or neutral soil.

The results obtained with toxaphene followed a somewhat different pattern. On the first two weeks of the experiment about 30 per cent of the toxaphene was lost presumably through decomposition; from then on the residue remained practically constant throughout a period of six weeks. Toxaphene is a mixture of chlorinated camphenes and it may well be that some of the isomers are less stable than others, and this may account for the initial decrease in the apparent concentration of the insecticide.

Liming of the soil had a pronounced effect on the stability of toxaphene residues. As will be seen from the data, at the end of eight weeks about 50 per cent of the insecticide had disappeared from the basic soil as compared to 30 per cent for the acid and neutral soils. The relative stability of this insecticide in acid and near neutral soils may constitute a serious hazard since toxaphene has been proposed for the control of the corn root worm and other soil pests. (15) (19) For this purpose the insecticide is mixed with the soil in rather high concentrations.

The effect of liming in enhancing the rate of decomposition might have some practical applications in decontaminating soils poisoned with this insecticide.

According to Smith and Wenzell (25), toxaphene is attacked by the soil bacteria. They further postulate that the insecticide is a source of food for soil microorganisms. The results presented by these workers are not too conclusive since by their own admission adequate controls were not kept in their experiments. The data presented in Table II are not in entire agreement with the conclusions of Smith and Wenzell and additional work along these lines would be highly desirable.

Contrary to all expectations, methoxyehlor was found to be the least stable of the three insecticides studied. Close to 75 per cent of the insecticide deteriorated in the first two weeks. Like toxaphene, the remaining deposit of methoxyehlor persisted relatively constant for the duration of the experiment. It is evident from the data that the chances of building up a toxic residue in soil, through repeated spraying, are very small.

As in the case of parathion and toxaphene, the liming of the soil significantly accelerated the destruction of methoxyehlor. This effect of the alkaline soil in enhancing the degradation of parathion, toxaphene and methoxyehlor is to be expected since the three insecticides are known to be unstable in basic media.

## CONCLUSIONS

Parathion, toxaphene and methoxychlor were mixed with soil at three pH levels. Analyses were made at stated intervals and the results showed that, under the conditions of these experiments:

- (1) Toxaphene was found to be the most persistent of the three insecticides studied, parathion was somewhat less stable, and methoxychlor was the least permanent.
- (2) The three insecticides showed rapid disappearance during the first two weeks after application; this precludes the possibility of a permanent poisoning of the soil by repeated spraying with the toxicants.
- (3) Increasing soil pH by adding lime greatly enhanced the decomposition of the insecticides, the effect being more pronounced in the case of toxaphene.
- (4) Parathion was not lost from the soil by volatilization to any appreciable extent; rather the insecticide disappeared slowly, presumably by chemical degradation.
- (5) In all cases the insecticides were detected in the soil at the end of two months; therefore, these chemicals should be used cautiously when applied in high concentration directly to the soil for the control of worms and other soil pests.

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