

A STUDY OF THE EFFECT OF HYDROGEN-ION CONCENTRATION ON THE TOXICITY OF CERTAIN INSECTICIDAL SPRAYS

> Thesis for the Degree of M. S. MICHIGAN STATE COLLEGE Geary Masami Sone 1951

#### This is to certify that the

thesis entitled

A STUDY OF THE EFFECT OF HYDROGEN-ION CONCENTRATION ON THE TOXICITY OF CERTAIN INSECTICIDAL SPRAYS presented by

Geary Masami Sone

has been accepted towards fulfillment of the requirements for

M.S. degree in Entomology

Ray Hutson

Date\_\_\_November 9, 1951

**O**-169

1 1 1 • •

١

## A STUDY OF THE EFFECT OF HYDROGEN-ION CONCENTRATION ON THE TOXICITY OF CERTAIN INSECTICIDAL SPRAYS

•

BY

GEARY MASAMI SONE

4

### A THESIS

Submitted to the School of Graduate Studies of Michigan State College of Agriculture and Applied Science in partial fulfillment of the requirements for the degree of

MASTER OF SCIENCE

Department of Entomology

1951

, ,

#### ACKNOWLEDGMENTS

The writer wishes to express his thanks to Professor Ray Hutson and Associate Professor Herman L. King of the Michigan State College Entomology Department for their suggestions and guidance in the preparation of this thesis, and to his wife, Monica Sone, for the preliminary typing of the manuscript.

## TABLE OF CONTENTS

I.	INTRODUCTION	•	•	•	•	•	•	•	•	Page 1
II.	REVIEW OF LITERATURE .	•	•	•	•	•	•	•	٠	4
III.	METHODS AND PROCEDURES	•	•	•	٠	•	•	•	•	11
IV.	DISCUSSION	٠	•	•	•	•	•	•	•	15
۷.	SUMMARY	•	•	•	٠	•	•	•	•	20
VI.	EXPERIMENTAL DATA	٠	•	٠	•	٠	٠	•	•	25
VII.	LITERATURE CITED	•	•	•	•	•	•	•	•	34

#### I. INTRODUCTION

The fact that various diluents of an insecticidal composition have an effect upon insect toxicity has long been known to chemists and entomologists.

In general, the components of a composition may affect each other physically or chemically. There are many factors which govern the physical and chemical properties of an insecticidal composition. Physical properties may be altered by wetting ability, emulsifying characteristics, penetration power, sticking properties, dispersing characteristics, specific gravity, electrical charge and volatility.

Examples of chemical properties altered by the components of the composition are factors such as pH (a measure of the acidity or alkalinity of a dispersion or a composition), ability to combine or polymerize with one or more components, oxidizing and reducing characteristics, and buffering ability.

Chemical and physical changes in the composition are brought about by additional factors such as temperature, humidity, presence or absence of water, nature of container (iron, paper, glass), character of the surface upon which the composition is applied (whether treated with other noncompatible pesticides), pH of leaf surface, and pH of water used for spray.

It is known that many insecticides are less effective under certain alkaline conditions than neutral or slightly acidic condition. The spray water in Michigan is obtained from such sources as ponds, rivers, reservoirs, lakes and, to a limited extent, from municipal water supplies. The waters from these sources have varying pH ranges.

Records<sup>1</sup> show the pH of the surface water in this state to be alkaline in reaction. The Institute for Fisheries Research of the Michigan Department of Conservation gave records on the alkalinity of 111 lakes in 24 counties. Of these, only six gave an acid reaction, ranging from pH 5.9 to 6.8. The remaining 105 lakes ranged from pH 7.2 to 9.2.

Few data were available for the streams of Michigan, but they too indicate that waters are predominantly alkaline. One study on Michigan streams, that of Creaser and Brown<sup>2</sup> (1927) on the streams in the upper portion of the Lower Peninsula, reported a range of pH 7.1 to 8.2, all alkaline.

The pH of the municipal water supplies ranges from 7.1 to 7.7. This range of pH fluctuates daily depending upon the condition of the raw water.

<sup>&</sup>lt;sup>1</sup>Institute for Fisheries Research, Michigan Department of Conservation.

<sup>&</sup>lt;sup>2</sup>Hydrogen-ion Concentration of Brook Trout Water of Northern Lower Michigan, Ecology 8:98-105.

The writer took ten samples from spray water sources in various parts of the agricultural area of this State. The pH ranged from 7.8 to 8.1, all alkaline.

With alkalinity of Michigan surface water as high as pH 9.2, it seemed possible that water used for spraying purposes might have detrimental effects on the toxicity of insecticides. This possibility led to an inquiry into the effects of pH on the toxicity of insecticides.

#### II. REVIEW OF LITERATURE

Richardson and Shepard (1930) studied the toxicity of nicotine to the house mosquito Culex pipiens L. in aqueous solutions at various pH values. A few similar experiments were also made with pyridine and methylpyrrolidine. Solutions of 0.03 M concentration, adjusted to pH values of 2.4, 3.6, 5.0, and 7.0 with sulphuric acid, and at pH 9.7 (the free base) showed a toxic action that increased with increasing pH value. Solutions adjusted to pH 3.6 and 5.0 with hydrochloric acid gave similar results to those adjusted with sulphuric acid. Solutions of 0.1 M, 0.03 M, 0.01 M and 0.001 M concentrations were adjusted to pH 5.0 with sulphuric acid and compared in toxicity with solutions of the base of the same molar concentrations. At each nicotine concentration, the free base was about 5 to 7 times more toxic than was the nicotine sulphate solution at pH 5.0. The addition of an inorganic hydroxide (0.05 to 0.001 N) to an aqueous solution in nicotine had no apparent effect on the toxicity of that solution. Pyridine solutions (0.03 M and 0.12 M) were about twice as toxic as solutions of the same molar concentration titrated to pH 5.0 to 4.9 respectively, with sulphuric acid. Methylpyrrolidine solution (0.03 M) was about 19 times more toxic than methylpyrrolidine hydrochloride solution of pH 3.0. It was discovered that the speed of toxic action to the larva of <u>Gulex pipiens</u> of nicotine, pyridine, and methylpyrrolidine in aqueous solution was directly related to the concentration of the undissociated molecules. It was believed that the toxicity resulted largely from the penetration of the molecules into the body through the wall of the alimentary tract. Nicotine ions were somewhat toxic but much less so than nicotine molecules. It was believed that the change in toxicity of a nicotine solution with change in pH resulted largely from the dissociation of pyrrolidine nitrogen. In this study it was also shown that the free base in solution was much more toxic than nicotine sulphate.

Brown and Hoskins (1939) found that pH not only affected the toxicity of insecticides but that it had an important relation to the amount of oil deposited by petroleum oil emulsions emulsified with sodium oleate triethanolamine and hemoglobin. Oil deposit increased when the pH was increased from 2.5 to 10.0.

Carter (1940) demonstrated the relationship of pH values of cryolite to its phytotoxicity. He took eight samples of natural cryolite and reported that pH values ranged from 6.00 to 7.10. The pH value of the domestic synthetic cryolite ranged from 7.45 to 8.10. He found that the foreign synthetic cryolite varied considerably in pH. Carter believed the titratable acidity and low pH values of some of the samples might have been partially responsible for the burning that sometimes

followed the applications of cryolite insecticides. Two samples of cryolite were reported to have caused excessive burning when used on vegetations such as beans, peas, corn, cotton and peanuts. However, other samples having a greater titratable acidity have not been reported as causing burning.

Baker and Questal (1939) reported that corn appeared to be susceptible to injury when treated with domestic synthetic cryolite. In an effort to reduce this injury, colloidal bentonite clay was added to these nicotines to act as a possible buffer.

Hoskins (1940) stated that stomach poisons are nearly always swallowed along with the food to which they have been added and hence are subjected to the conditions prevailing during the digestive process. It is to be expected then that the manner and severity of the toxic action will be dependent upon the chemical substances which occur in the fluids of the digestive tract. Hoskins observed definitely that the pH of the digestive tract affected the toxicity of certain types of insecticides.

Wigglesworth (1935) demonstrated that the digestive juices of most insects were weakly acid or weakly alkaline. The pH of the mid-gut contents in the cockroach averaged 6.2, in <u>Disippus</u> 7.0-7.5, in <u>Chironomus</u> larvae 7.2-7.8, in <u>Glossina</u> 6.5-6.6, in <u>Apis</u> 5.6-6.3, and in <u>Apis</u> larva 6.8. Wigglesworth observed that more acid conditions sometimes resulted in bacterial fermentation notably in the crop of Orthoptera, in which the pH commonly ranged from 5.0 to 5.9. This effect naturally varied with the diet. In the cockroach Blatella the pH in the crop fell to 4.4 after feeding with glucose which is readily broken down to lactic acid, 4.8 after lactose and 6.3 after protein. Wigglesworth demonstrated that it was characteristic of larvae of Trichoptera and Lepidoptera that mid-gut contents were always strongly alkaline (pH 9.0-9.4). Similar conditions were met with in some herbiverous Coleoptera, but in the case of Lepidoptera, alkalinity was not confined to phytophagous species. Wigglesworth also observed that in a few insects, there were localized differences within the mid-gut. In Tenebrio larvae the anterior two-thirds of the mid-gut turns litmus red while the posterior third turns it blue. In Lucilia larvae the short middle segment of the mid-gut was strongly acid, with a pH of 3.0 to 3.5, while the segments anterior and posterior to it were about pH 7.5, except toward the hind end, where the contents were strongly alkaline as the result of ammonia production. A similar region, with a pH of 3.0, occurred near the junction of mid-gut and hind gut in the wood-feeding termite. The nature of the acid in these cases was not known with certainty, but it was thought to be phosphoric acid.

H. S. Swingle (1938) made a study on the pH of insect

digestive tracts and the effect on various arsenicals. He found phosphate as a component of the digestive secretions from nine species of insects. He found that the formation of soluble arsenic from acid lead arsenate, calcium arsenate and magnesium arsenate was largely dependent on the hydrogen-ion concentration of the solution. It was influenced to a lesser extent by the concentration of acids, bases, and salts in the The presence of phosphates greatly increased the solution. amount of soluble arsenic formed from acid lead arsenate in alkaline solutions. This was apparently due to precipitation of part of the lead as lead phosphate, as this compound was found to be very insoluble in alkaline solutions. Phosphates influenced the solubility of the arsenic in calcium and magnesium arsenates to only a slight extent. It was discovered that the relative toxicity of acid lead arsenate, calcium arsenate and magnesium arsenate to nine species of phytophagous insects was correlated with the relative amounts of soluble arsenic formed from the arsenates in phosphate solutions having the same pH was was found in the mid-guts of these insects. For insects having alkaline reaction in their mid-gut, acid lead arsenate was least toxic; for insects having an acid reaction of pH 6.0 in their mid-gut, magnesium arsenate was most toxic and acid lead arsenate least toxic. It appeared possible to predict the relative order of toxicity of acid lead arsenate, calcium lead arsenate and magnesium arsenate to chewing

insects, if the hydrogen-ion concentrations in the insects' mid-guts were known.

Kenaga (1950) studied the effects of pH on several organic toxicants. He showed that certain alkaline conditions were detrimental to the insecticidal properties of lindane, parathion, and the dicyclohexylamine salt of 2-cyclo-hexyl-4, 6 dinitrophenol. In tests with lindane at pH 10.25, 80% mortality was observed on southern army worm. With the same toxicant, but with pH 6.5, mortality dropped to 70%. He also found that the alkaline dispersions of dicyclohexylamine salts of 2-cyclohexyl-4, 6 dinitrophenol were inferior to neutral dispersions in contact action against the two-spotted mite adults. With a pH of 10.25, only 15% mortality was attained. However, with a pH of 6.7, 100% mortality was observed. It was also found that alkaline compositions of parathion were significantly less effective than neutral dispersions in residual action. Against the two-spotted spider mite 100% mortality was attained with a pH of 10.2, but the residual action dropped markedly. With a pH of 7.0, a mortality of 100% was observed, but there was no marked drop in the residual action.

Ginsburg (1937) studied the relationship of  $CO_2$  to the solubility of arsenates. He discovered that  $CO_2$  did not increase the solubility of lead arsenate. However,  $CO_2$  did increase the solubility of calcium arsenate. Since calcium arsenate contains  $CO_2$ , this was considered one of the factors

## in considering the solubility of arsenic.

#### III. METHODS AND PROCEDURES

The experiment was carried out under laboratory conditions. Mexican bean beetle larvae <u>Epilachna varivestus</u> Muls. were used in testing the effects of pH levels on the toxicity of four groups of insecticides. Only the third instar larvae were used for this purpose. This insect was chosen since it is relatively easy to rear under greenhouse conditions and is a pest of economic importance. The insects were reared in the greenhouse on cranberry beans. Before each test, the required number of third instar larvae were collected in a glass container with cranberry leaves

Cranberry bean plants were used as host plants for spraying. This variety was very appropriate since the plant maintained its rigidity throughout its growth. In addition to the above quality, this variety of beans was readily attacked by the insects. The test plants were grown individually in 4-inch flower pots. These plants developed mature primary leaves only and attained the height of six inches when used. In order to encourage large primary leaves, potassium nitrate fertilizer was used.

Alkaline and acid conditions of the spray water were obtained by adding magnesium carbonate and glacial acetic acid, respectively, to distilled water with a pH level of 7.0. The acid water was buffered with magnesium carbonate to stabilize the hydrogen-ion concentration. Alkalinity was maintained at a pH level of 8. Acidity was stabilized at the pH level of 6. Since the distilled water indicated pH 7.0, it was used without any chemical alteration. The pH levels were measured by a Hellige pH colorimeter and were corrected with a Beckman glass electrode pH meter. There was a difference of .4 in the pH reading between two types of pH indicators. Each solution was checked with both pH meters before being used as a spray diluent.

The pH levels of 6, 7, and 8 were chosen since the surface and the ground waters of the state vary in pH levels from 6 to 8.1. The writer also took ten samples from various parts of the agricultural area of the state. These samples showed a range in pH from 7.8 to 8.1.

In order to study the effects of pH on sprays, four insecticides were used. These represented such groups as botanical, chlorinated hydrocarbon, inorganic, and organic phosphate insecticides. Rotenone was used as a botanical insecticide, DDT for a chlorinated hydrocarbon, lead arsenate for an inorganic material and parathion for the organic phosphate group. All formulations used in this study were wettable powders containing 4%, 15% or 50% toxicant, an inert diluent and small amounts of surface active ingredients (See Table V).

Two different methods of applying toxicants to the host plants were attempted before a suitable method was chosen. At first, cranberry bean plants containing mature primary leaves were dipped in each insecticidal dispersion of various concentrations. This method was abandoned since there was an excessive amount of spray run-off and there were no possible means of controlling the amount of spray deposits on the plants. Furthermore, this method of dipping did not simulate the natural spraying conditions. These factors necessitated the use of another method.

The second method was the spraying of the insecticide with a De Vilbiss atomizer sprayer, type LXG, No. 5021. This proved to be an excellent choise. All sprays were applied under a pressure of ten pounds. The turntable in the spray chamber rotated at the speed of fourteen revolutions per minute. Each plant was placed on the turntable until nine revolutions were completed. At this time there was an indication of run-off and the spraying was considered complete.

Preliminary spray tests were made before the actual experiment was started to determine the range of concentrations in which the dosage mortality curve occurred. Rotenone, parathion, lead arsenate, and DDT were used. Individual insecticides were tested at five different concentrations. All four insecticides were dispersed in distilled water at pH 7.0.

For the final test each material was tested at three pH levels, using five concentrations of insecticides and a blank at each pH level. The test was replicated five times. Each replicate plant was infested with five third-instar larvae

immediately after the spray application. The plants were covered with screen cylinders after the infestation.

The mortality counts were made at varying lengths of time since the insecticides used varied in toxicity. All comparable replicates were checked at identical length of time.

#### IV. DISCUSSION

Whether an arsenical is quickly toxic to either animal or plant life depends largely upon the solubility of the compound. Particle size, the minerals which occur in water supplies, the other insecticides, fungicides and additives which are mixed with arsenical suspensions, the carbon dioxide present in the air or produced by plant respiration, the hydrogen-ion concentration of the liquid medium, whether it be in the spray tank or in the digestive tract of the insect, all have decided relation to solubility and ultimate effectiveness. This experiment has been limited to the effect of hydrogen-ion concentration on the toxicity of the insecticide.

Volck (1911) pointed out that acid lead arsenate is stable under acid condition, but is changed to basic lead arsenate under neutral or alkaline conditions with liberation of excess arsenic oxide. This liberation of arsenic oxide is necessary in the change from acid to basic arsenates, for acid lead arsenate contains 33% As<sub>2</sub>)<sub>5</sub> and basic lead arsenate only 23%.

Results obtained in the study of the effect of hydrogenion concentration on lead arsenate are given in Table I, in which the data are given, and in Fig. 1, which presents the data graphically. At pH 8, the toxicity of lead arsenate was less than at pH levels of 6 and 7. This difference in toxicity was greatest at the median lethal concentration, which is considered to be a critical point. At this point the sensitivity of such tests is the greatest. Since lead arsenate is stable under acid condition and unstable under alkaline conditions, there is contradiction in the experimental data. Since the solubility of acid lead arsenate is enhanced by the alkalinity of the water, it is possible that some soluble arsenic, which is the toxic component, was lost by run-off from the test plant, leaving the insoluble residue reduced in Quantity of total arsenic. At pH 6 and pH 7, the loss of soluble arsenic through run-off was slight since at these pH levels, lead arsenate is stable and only a small amount of soluble arsenic is produced. Therefore, the stable form adhered to the plant without reduction of total arsenic. At a high concentration of lead arsenate, the hydrogen-ion concentration had no significant effect on toxicity. High concentration probably compensated for the loss of toxicity through hydrolysis.

٠.

Parathion (0,0-diethyl-0-p-nitrophenyl thiophosphate, C<sub>10</sub>H<sub>14</sub>NO<sub>5</sub>PS) is an organic phosphate produced by German research laboratories. It was made available in the United States in 1946. It is only slightly soluble in water, slightly soluble or insoluble in petroleum ether, kerosene, or refined spray oil, and completely miscible in acetone, ethyl ether, cyclohexanone, alcohols, esters, and animal or vegetable oils. It is hydrolyzed in the presence of alkaline material such as lime, lime-sulfur, and bordeaux mixture.

The effects of hydrogen-ion concentration upon a parathion spray solution are shown in Fig. 2 and Table II. There appeared to be no significant difference in toxicity of the parathion at pH 6 and pH 7. Slight acidity of the spray diluent did not cause any appreciable change in toxicity in comparison to neutral water. There was a significant difference in the toxicity at pH 8 up to the median lethal concentration. The experiment indicated that slight alkalinity hydrolyzed parathion to the point which reduced the kill of third instar larvae approximately 12%. This reduction of kill was consistent at varying concentrations up to the median lethal concentration. The median lethal dosage was 2 lbs. per 100 gallons of water. Above this critical area of the toxicity curve, the curve approached closer to the toxicity curve of pH 6 and pH 7. This was probably due to increased concentration of toxicant which overcame the reduction in toxicity from hydrolysis of parathion. There is also some possibility of fumigant effect with an increase in concentration of parathion. However, it is believed that the Mexican bean beetles are not affected by fumigants as much as small organisms such as mites and aphids.

In studying the effects of hydrogen-ion concentration on various insecticides, rotenone was used as a representative of the group of botanical insecticides. Plants belonging to the genera <u>Derris</u>, <u>Lonchocarpus</u>, <u>Tephrosia</u>, and <u>Milletia</u> are re-

presented by the largest number of species known to contain rotenone and rotenoids. Rotenone is not a stable insecticide. It decomposes in various organic solvents. The rate of this decomposition depends on the solvent, temperature, access of air and other factors.

Experimental data shown in Fig. 3 and Table III indicate that there are no significant changes in the toxicity of rotenone at the pH level of 6 in comparison to neutral water. The toxicity of rotenone at the pH level of 8 was consistently lower than at pH 6 and 7.

Rotenone is unstable in alkaline media. This experiment has shown that alkalinity can reduce toxicity significantly. The greatest reduction in toxicity appeared at median lethal concentration. At low and high concentrations of rotenone, the toxicity was almost uniformly reduced. At a pH level of 8, the hydrogen-ion concentration reduced the toxicity of rotenone even at high concentration. It is believed that alkalinity splits the molecule at the central pyrone ring or, when dilute, racemizes the compound and promotes oxidation. The first stage in decomposition results in the formation of a hydroxyl group, the second, in the production of dehydrorotenone, and the third, in a split molecule.

Dichlorodi phenyltrichloroethane, C<sub>14</sub>H<sub>9</sub>Cl<sub>5</sub> (commonly known as DDT) was tested at three hydrogen-ion levels, pH 6, pH 7 and pH 8. It is commonly understood that DDT should not

be compounded with strong alkalies. This experiment showed no significant reduction in toxicity by using water at pH 8 as indicated in Fig. 4 and Table IV. At the concentration of 12 lbs. of DDT per 100 gallons of water, there was some difference in mortality at the three pH levels. However, it was concluded that the difference was not significant. The conclusion was derived by using Wilcoxon's rapid approximate statistical procedures. It was evident that the hydrogen-ion concentration must be higher than pH 8 to have any significant reduction in the toxicity of DDT.

#### V. SUMMARY

One of the factors which may alter the effectiveness of insecticidal sprays is the pH, which is a measure of the acidity or alkalinity of the mixture. It is known that many insecticides are less effective under alkaline conditions than under neutral or slightly acidic condition.

It has been found that the formation of soluble arsenic from acid lead arsenate, calcium arsenate and magnesium arsenate is largely dependent on the hydrogen-ion concentration of the solution. It is influenced to a lesser extent by the acids, bases, or salt in the solution. It has been shown that certain alkaline conditions are detrimental to the insecticidal properties of lindane, parathion, and DDT.

The writer undertook a study of the effect of hydrogenion concentration on the toxicity of certain insecticidal sprays in relation to the pH of spray water in the state of Michigan.

Ten samples of spray water were collected from various parts of the agricultural area of the state. The pH ranged from 7.8 to 8.1, all alkaline. With ten samples of spray water having pH values as high as 8.1, it seemed probable that water used for spraying purposes might have detrimental effects on the toxicity of the insecticides. The effects of pH levels on the toxicity of four insecticides were tested under laboratory conditions, using third instar Mexican bean beetle larvae <u>Epilachna varivestis</u> Muls. as a test insect. The insects were reared in the greenhouse on cranberry beans.

Alkaline and acid conditions of spray water were obtained by adding magnesium carbonate and glacial acetic acid, respectively, to distilled water. The acid water was buffered with magnesium carbonate to stabilize the hydrogen-ion concentration. The three pH levels used for spray formulation were 6, 7, and 8. These levels were chosen since the samples collected at various water sources fell approximately in this range. The pH levels were measured by a Hellige pH colorimeter and were checked with a Beckman glass electrode pH meter.

Four insecticides were used in this experiment, namely, rotenone, DDT, lead arsenate, and parathion. (See Table V for insecticide formulations).

Two different methods of spray applications were used. First, plants were dipped in various insecticidal disperions. Later this method was abandoned since there was an excessive amount of spray run-off and there were no possible means of controlling the amount of spray deposit. This method did not simulate the natural spraying conditions. The second method of spray application was with the De Vilbiss atomizer sprayer. All plants were sprayed to the point when there was indication of run-off. At this point the spraying was considered complete. Preliminary tests were made to determine the range of concentrations in which dosage mortality curve would occur. For the final test each material was tested at three pH levels using five concentrations of each insecticides and a blank at each pH level. The test was replicated five times. Each replicate (one plant) was infested with five third-instar larvae immediately after the spray application.

For each type of spray, different time intervals were used in making mortality counts since the insecticides used varied in toxicity. All comparable replicates were checked at identical lengths of time.

The results of the experiment have shown that at pH 8, the relative toxicity of lead arsenate was less than at pH levels of 6 and 7. The difference in toxicity was greatest at the median lethal concentration which was considered to be a critical point. It was concluded that since the solubility of acid lead arsenate is enhanced by the alkalinity of the water, it was possible that soluble arsenic was lost by run-off which caused the reduction in toxicity of lead arsenate.

There was no significant change in the toxicity of the parathion at pH 6 or pH 7. Slight acidity of the spray diluent did not cause appreciable change in toxicity. There was significant difference in toxicity at pH 8 up to the median lethal concentration. The experiment indicated that slight alkalinity hydrolyzed parathion at the lower concentration to the point which reduced the kill approximately twelve percent. The amount of parathion above the median lethal concentration was not affected significantly by the variation in hydrogenion concentration.

Experimental data indicated that there was no significant differences in the toxicity of rotenone at the pH levels of 6 and 7. The toxicity of this insecticide at the pH level of 8 was consistently lower. The experiment showed that weak alkali can significantly lower the toxicity of rotenone. The greatest reduction in toxicity appeared at the median lethal concentration.

It is generally understood that DDT should not be compounded with strongly alkaline media. However, this experiment indicated that there were no significant differences in toxicity caused by using water at pH 8. It was evident that hydrogenion concentration must be higher than pH 8 to have any reduction in the toxicity of DDT.

The final conclusion derived from this study of the hydrogen-ion concentration on the toxicity of lead arsenate, parathion, rotenone, and DDT is that these insecticides were affected only slightly by using water in which the pH ranged from 6 to 8.1. These were the pH levels found in the ten samples of water collected from the agricultural area. The greatest reduction in toxicity at pH 8 was found at the median lethal concentration and there were no significant changes above this concentration. Since the grower strives for a kill of 95 percent or

more and at that level the experiments indicated that there were no appreciable reductions in toxicity at pH 8, it could be concluded that alkalinity at pH level of 8 has little or no detrimental effect at concentrations where most of the insects are killed.

The entire experiment was limited to the study of the effects of hydrogen-ion concentration on the toxicity of lead arsenate, parathion, rotenone, and DDT. No discussion was made of possible reactions of magnesium salts. However, it should be recognized that magnesium carbonate, or other salts, might cause variation in toxicity.

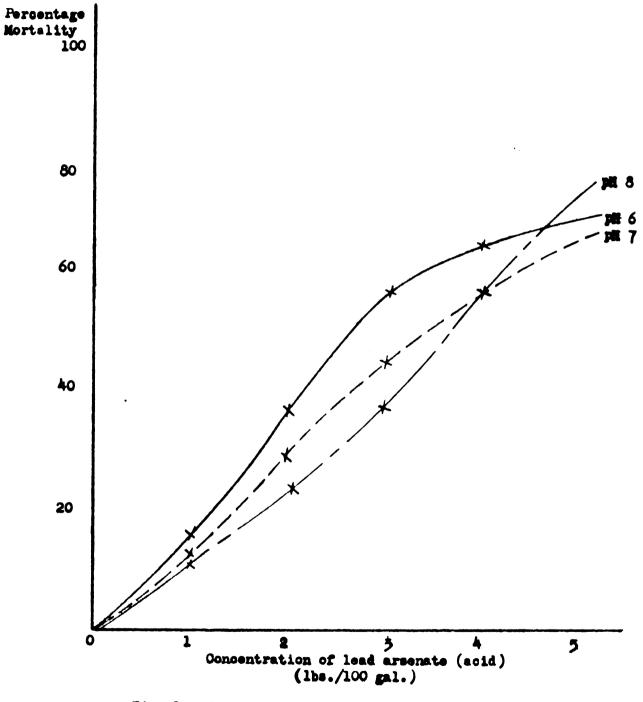


Fig. 1. Nortality of Mexican Bean Beetles following treatment with lead arsonate. Mortality observed 60 hours after treatment.

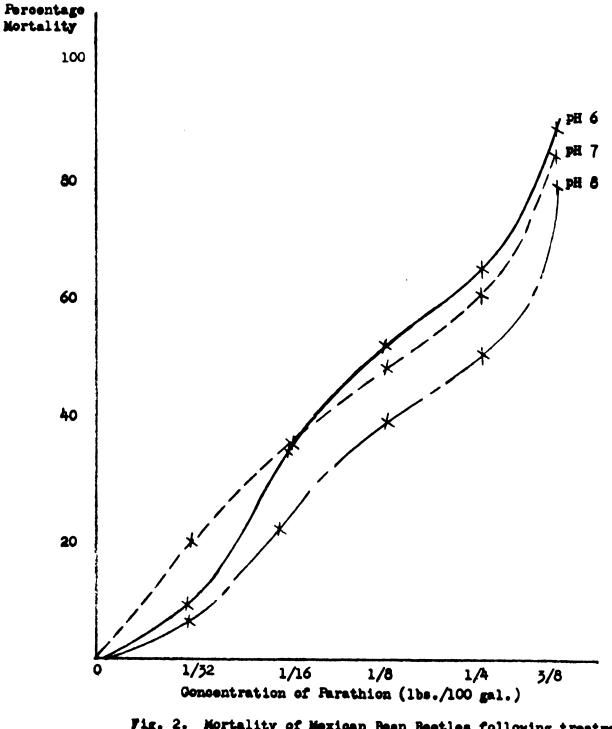


Fig. 2. Mortality of Mexican Bean Beetles following treatment with parathion. Mortality observed 6 hours after treatment.

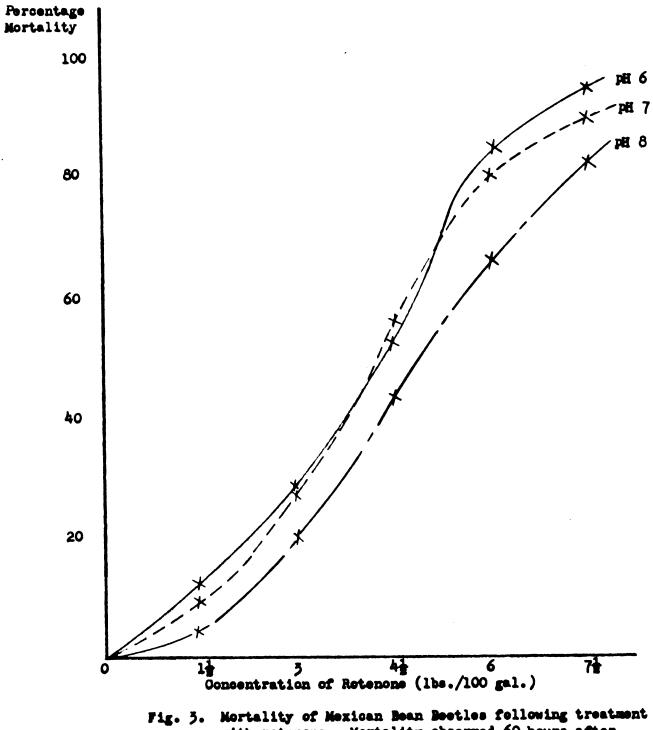
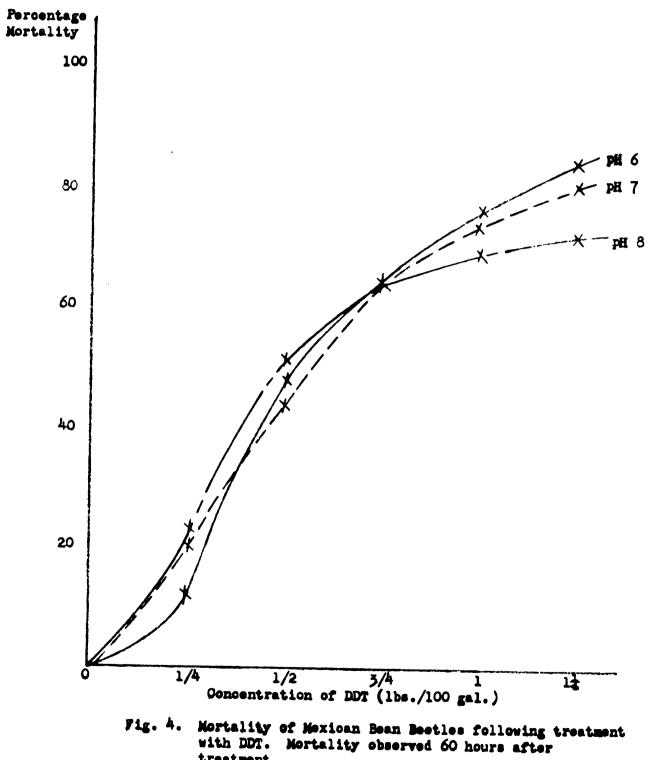


Fig. 3. Mortality of Mexican Bean Beetles following treatment with rotenome. Mortality observed 60 hours after treatment.



treatment.

## TABLE I

# MORTALITY OF MEXICAN BEAN BEETLES FOLLOWING TREATMENT WITH LEAD ARSENATE AT THREE PH LEVELS

(Each replicate consisted of five 3rd instar larvae. Counts were made 60 hours after treatment).

-				pH6			
			R	eplicate	8		
0	on <b>c.</b> Ibs.	I	II	III	IV	<b>V</b>	Avgs.
0	lbs.	0	0	0	0	0	0
1	#	1	1	1	2	0	1.0
2		1	2	2	3	1	1.8
3	Ħ	2	2	3	4	3	2.8
4		2	3	4	4	3	3.2
5	<b>U</b>	3	3	3	4	4	3.4

			рнү			
		R	eplicate	8		
Conc.	I	II	ĪII	IV	<b>V</b>	Avgs.
0 lbs.	0	0	0	0	0	0
1 "	0	0	1	0	1	0.4
2 •	0	2	2	2	2	1.8
3 •	4	1	2	3	1	2.2
4	3	1	4	4	2	2.8
5 •	<b>4</b>	4	2	4	2	3.2

		R	.eplicate	8		
Conc.	I	II	III	IV	<b>.</b>	Avgs.
lbs.	1	1	Q	0	0	0.4
H		1	1	0	0	0.6
<u> </u>	1	1	1	2	l	1.2
5 1	4	1	2	3	1	2.0
L 8	4	4	4	1	1	2.8
j <b>I</b>	3	3	3	3	5	3.4

## TABLE II

MORTALITY OF MEXICAN BEAN BEETLES FOLLOWING TREATMENT WITH PARATHION AT THREE PH LEVELS

(Each replicate consisted of five 3rd instar larvae. Counts were made 6 hours after treatment).

			pH6			
Conc.	<b>T</b>	R	eplicat	es TV	V	Avea
0 lbs.	0	0	0	0	0	Avgs. O
1/32 •	0	1	1	0	0	0.4
1/16 •	2	1	2	1	3	1.8
1/8	4	3	2	3	1	2.6
1/4 •	4	3	4	4	0	3.0
3/16 #	5	5	5	3	4	4.4

pH7

•

_	_		eplicat	88		
Conc.	<u> </u>	II	III	IV	<b>V</b>	Avgs.
0 lbs.	0	0	0	0	0	0
1/32 •	1	1	2	0	1	1.0
1/16 *	2	2	1	2	1	1.8
1/8 *	3	3	2	2	2	2.4
1/4 •	4	2	0	4	4	2.8
3/16 "	4	4	4	4	5	4.2

pH8

			рно			
		R	eplicate	98		
Conc.	<u> </u>	II	III	IV	<u> </u>	Avgs.
0 lbs.	0	0	0	0	0	0
1/32 *	0	0	1	0	0	0.2
1/16 •	2	1	2	0	1	1.2
1/8 •	3	2	1	2	2	2.0
1/4 •	4	4	3	2	2	3.0
3/16 •	3	4	4	4	5	4.0

## TABLE III

MORTALITY OF MEXICAN BEAN BEETLES FOLLOWING TREATMENT WITH ROTENONE AT THREE PH LEVELS

(Each replicate consisted of five 3rd instar larvae. Counts were made 60 hours after treatment).

			pH6			
Conc.	Ŧ	F	leplicate	s IV	V	Avgs.
0 lbs.	0	0	0	0	0	0
1 1 1	l	1	1	0	0	0.6
3 🕷	0	0	2	2	4	1.6
41 1	2	2	3	1	3	2.2
6 *	4	5	4	4	3	4.0
7늪 비	4	4	5	5	5	4.6

pH7

		F	leplicate	8		
Conc.	<u> </u>	II	III	IV	<u> </u>	Avgs.
O lbs.	0	0	0	0	0	0
1월 *	0	1	0	0	1	0.4
3 "	2	1	2	1	1	1.4
41 *	3	2	2	1	4	2.4
6 •	4	3	5	4	3	3.8
7 *	4	3	5	5	5	4.4

Uno	

	-		рно			
		F	eplicate	8		
Conc.	I	II	III	IV	<u> </u>	Avgs.
O lbs.	0	0	0	0	0	0
11/2 *	1	0	0	0	0	0.2
3 *	2	θ	2	1	0	1.0
4 <sup>1</sup> / <sub>2</sub> •	2	1	2	2	2	1.8
6 •	3	3	3	4	3	3.2
7 <del>1</del> •	4	5	4	3	4	4.0

## TABLE IV

### MORTALITY OF MEXICAN BEAN BEETLES FOLLOWING TREATMENT WITH DDT AT THREE PH LEVELS

(Each replicate consisted of five 3rd instar larvae. Counts were made 60 hours after treatment).

			pH6			
Conc.	I	R II	eplicate III	s IV	V	Avgs.
0 lbs.	0	0	0	0	0	0
1/4 •	l	0	0	1	0	0.4
1/2 "	3	1	4	2	2	2.4
3/4 *	3	2	4	3	4	3.2
1 *	5	4	4	3	3	3.8
1 *	4	4	4	4	5	4.2

Replicates						
Conc.	I	II	III	IV	<b>V</b>	Avgs.
0 lbs.	0	0	0	0	0	0
1/4 "	0	2	1	1	1	1.0
1/2 •	3	2	2	3	1	2.2
3/4 #	2	2	4	4	4	3.2
1 "	3	5	2	3	4	3.4
14 "	4	5	4	4	3	4.0

nH8	
DITO	

			рна			
Conc.	т	R	eplicate	S TV	V	Avgs.
0 lbs.	0	0	0	0	0	0
1/4 "	1	1	1	2	0	1.0
1/2 •	2	3	3	3	2	2.6
3/4 *	2	3	4	3	4	3.2
1 *	3	4	4	3	3	3.4
12 "	4	4	4	. 3	3	3.6

#### TABLE V

## CONCENTRATION AND KIND OF INSECTICIDE APPLIED STUDY OF THE EFFECT OF HYDROGEN-ION CONCENTRATION ON ITS TOXICITY

Insecticides	Pounds per 100 Gellons of Water
Arsenate of lead <sup>3</sup>	1 2 3 4 5
Parathion (15%) <sup>4</sup>	1/32 1/16 1/8 1/4 3/8
Rotenone (4%) <sup>5</sup>	1 <del>호</del> 3 4호 6 7호
DD <b>T (50%)<sup>6</sup></b>	1/4 1/2 3/4 1 1

<sup>3</sup>Ortho Arsenate of Lead, California Spray and Chemical Company, Richmond, California.

<sup>4</sup>Dow Chemical Company, Midland, Michigan.

<sup>5</sup>E-Z-Flo Rotenone Spray Dust No. 44, Michigan Fertilizer Company, Lansing, Michigan.

<sup>6</sup>Deenate, E. I. DuPont de Nemour and Company, In., Wilmington, Delaware. Baker, W. A. and D. D. Questal

1939 Investigations of Insecticides for Control of European Corn Borer at Toledo, Ohio, 1937-38. Journ. Econ. Ento., 32:526-530.

Carter, R. H.

1940 The Titratable Acidities and pH Values of Gryolite Insecticides. Jour. Econ. Ent., 33:699.

Fleck, E. E., and Haller, H. L.

1946 Stability of DDT and Related Compounds. J. Am. Chem. Soc., 68:142-143.

Frear, D. E. H.

1948 Chemistry of Insecticides, Fungicides, and Herbicides. D. Van Nostrand Company, Inc., 2:11-39.

Hoskins, W. M.

1939 Recent Contribution of Insect Physiology to Insect Toxicology and Control. Hilgardia 13, No. 6, 338-353.

- Kenaga, Eugene E.
  - 1949 Insecticidal Activity of Various Formulations of Several Organic Toxicants with Special Reference to pH. Proceedings of the Fifth Annual Meeting of the North Central State Branch of the American Association of Economic Entomologist, 8-10.

Jones, H. A., and Haller, H. L.

1931 The "Yellow Compounds" Resulting from the Decomposition of Rotenone in Solution. J. Am. Chem. Soc., 53:2320-2324.

1951 Agricultural Entomologist, Dow Chemical Company, Midland, Michigan. (oral communication).

Richardson, C. H.

1942 Inorganic Stomach Poisons. Chem. and Chemical Engineering News., 20:241.

Richardson, C. H. and H. H. Shepard

1930 Hydrogen-ion Effect on Nicotine. Jour. Agri. Res., 41:337-348. Shepard, H. H.

1939 The Chemistry and Toxicology of Insecticides. Burgess Publishing Co., Minneapolis, Minnesota. 79-90.

.

Shepard, H. H.

1951 The Chemistry and Action of Insecticides. Burgess Publishing Co., Minneapolis, Minnesota. 326-327.

Swingle, H. S.

1938 Relative Toxicities to Insects of Acid Lead Arsenate, Calcium Arsenate and Magnesium Arsenate. Jour. Econ. Ent., 31:430-441.

Volck, W. H.

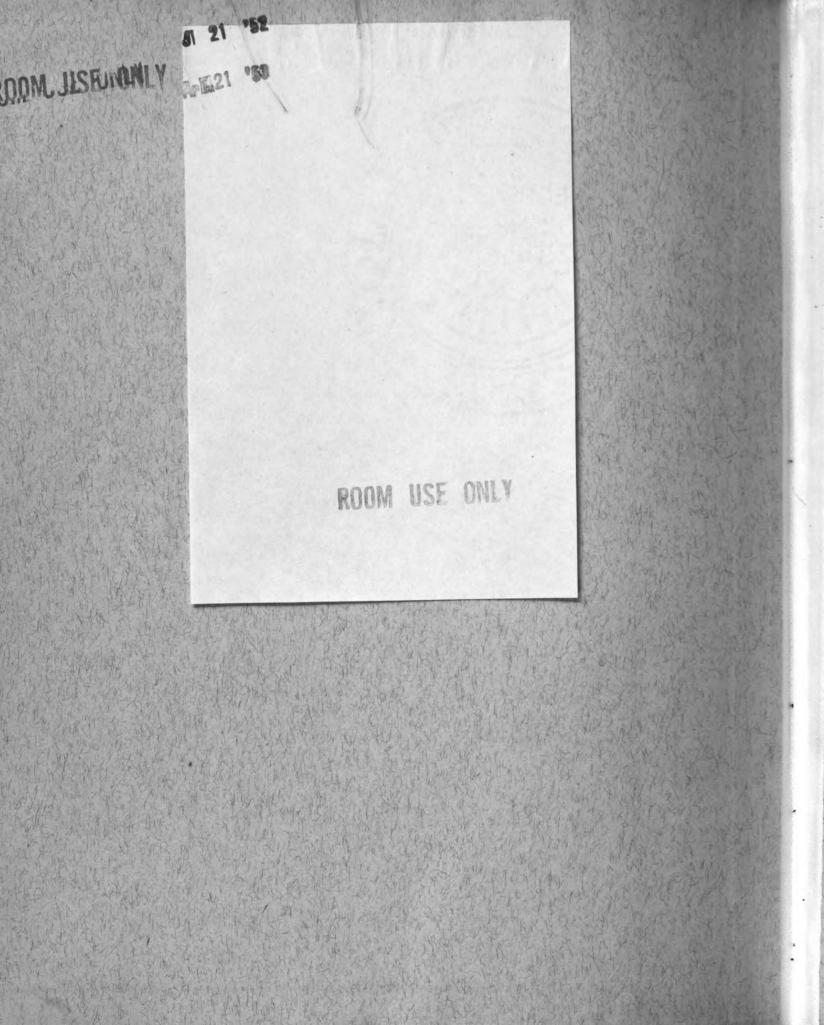
1911 The Significance of Lead Arsenate Composition. Science., 866-870.

Wigglesworth, V. B.

1937. The Principles of Insect Physiology. E. P. Dutton & Company, Inc., New York, New York. 272-277.

Wilcoxon, F.

1949 Some Rapid Approximate Statistical Procedures. American Cyanamid Co., New York, New York. 4-5.



• '. . • • • • / -

