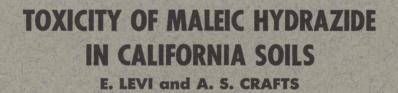
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TOXICITY OF PENTACHLOROPHENOL AND ITS SODIUM SALT IN THREE YOLO SOILS¹

W. A. HARVEY² and A. S. CRAFTS³

INTRODUCTION

IN 1940, HANCE⁴ discovered a notable activation of herbicidal solution by using a water soluble chlorinated phenate. He found that the addition of $\frac{1}{4}$ to $\frac{1}{5}$ of 1 per cent by weight of this activator and of an oxidizing substance to a herbicide solution reduced the concentration of weed killing chemical by from one half to one eighth that ordinarily used (depending on the toxic substance employed and the weeds) with equally satisfactory or even superior results. This activator has since been known as pentachlorophenol or PCP; it is available as the oil soluble parent phenol and as the water soluble sodium salt (Na PCP).

Crafts (1944) described studies where PCP was added to petroleum oils in order to fortify them so that the oil even when diluted or emulsified with water would remain effective. Good results were obtained by adding 0.5 per cent PCP to a 6 per cent diesel oil emulsion. Barley seems to be the only plant surviving two sprayings of this mixture. Hance (1948) mentions a mixture of sodium chlorate (NaClO₃) (20 pounds) and water soluble Na PCP (4 pounds) in 100 gallons of water as a good contact herbicide. Aldrich and Willard (1949) obtained good preëmergence weed control in corn by using 8 and 12 pounds Na PCP per acre. Heavy rain fell within 30 minutes after the application.

Many other workers (Barrons, 1948; Hance, 1948; Shafer, 1948; and Wilson and Hall, 1948) report encouraging results with PCP or with its Na salt, mostly as preëmergence treatments. This chemical is now being widely used, principally as a fortifying agent and in preëmergence applications. Sugar cane and pineapple are quite resistant to PCP; when the chemical is correctly applied, good results are obtained in preëmergence treatments.

According to Barrons (1948), selectivity is based on depth protection. The top growth pushing through the surface layer of soil containing the active chemical toxicant apparently does not absorb lethal amounts because the waxy stems or leaf surfaces do not permit the entry of such ionic materials as the phenolic salts. Roots that lack a waxy covering do absorb such salts, and germinating seeds are thus killed. These chemicals apparently have only an acute and local toxicity. The occasional injury resulting to top growth is, according to Barrons, noticeable only on cotyledons and primary leaves and does not affect subsequent growth.

The increasingly widespread use of PCP and its Na salt has created a need to determine their toxicity and their rate of breakdown in some California soils.

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^{*} See "Literature Cited" for citations referred to in text by author and date.

MATERIALS AND METHODS

The soils used in the study were of the Yolo series, an agronomically important California soil of neutral reaction and of recent alluvial origin. Air dried and screened samples of fine sandy loam, clay loam, and adobe clay types were employed. The method followed in determining the initial residual toxicity of these herbicides was described in detail by Crafts (1944). PCP was added to the soil in dry, powdered form and thoroughly mixed on a revolving mixer. The soil was wetted to field capacity and seeded.

The Na salt (water soluble) was taken from a stock solution diluted to the desired volume to bring the soil to field capacity, added in three increments to obtain a more even distribution of the chemical, and then seeded.

The indicator plants used in both tests were Kanota oats. Thirty days after planting, plant heights and crop yields were recorded and the plant matter was returned to the cans. After 30 days of drying, the soil was pulverized and poured into the cans on top of the dried plant material; the cans were watered to bring the soil back to field capacity, reseeded, and run for 30 days as before. Five such runs were made and five replicates were used throughout. The concentrations used were: 0.0, 5.12, 10.24, 20.48, 41.0, 82.0, 164.0, 328.0, 656.0, and 1,213.0 p.p.m. pentachlorophenol on an air dry soil basis.

Figures 1 to 6 clearly show the slow decomposition of these compounds and the narrow range within which they remain quite effective in the soils. Little difference can be observed between the parent phenol and its sodium salt. Tables 1 and 2 indicate the actual experimental values obtained.

Examination of the results obtained, particularly the data for the second cropping, proves that whenever the chemical had decomposed, crop yields of treated soils were higher than the checks. The differences in yields between crops probably are due more to seasonal environmental conditions prevailing in the greenhouse than to any other cause.

DISCUSSION AND CONCLUSIONS

Several points of interest in the use of organic herbicides are shown by these experiments. It is important to note that there are no significant differences in toxicity between the straight pentachlorophenol and its sodium salt. Probably when the latter is added to the soil in solution the alkaline reaction is reduced by the soil buffer resulting in precipitation of PCP in a finely divided state. This is essentially the same condition that exists in the soils treated directly with PCP. Hence, from the standpoint of soil effects, it makes no difference whether the parent compound or its sodium salt is used; the end result is a soil toxicity related only to soil type and dosage. This may explain some of the disastrous results of using oil emulsions containing PCP as preëmergence sprays on sugar beets and other susceptible crops. Apparently the water solubility of the phenate is of little consequence once the chemical comes into intimate contact with the soil. It should be noted that in these tests both the PCP and the Na PCP were thoroughly mixed with the soil, not just sprayed on the surface where differential water solubility might affect movement into the soil.

It seems evident that under greenhouse conditions which could be described

as warm and moist, the PCP compounds tested did not break down appreciably in the soil over a period of 12 months. This is in decided contrast to other organic chemicals studied. Because PCP is a potent fungicide this failure of decomposition in warm moist soils may relate to an inhibition of microbiological activity in the treated soils.

This notable stability coupled with the fact that PCP compounds are not fixed on the clay fraction of the soil, thus moving freely with percolating water, indicate that residual toxicity may be a problem in regions of acid soils. Only leaching could be relied upon to rid the soil of this toxicant. Once the material is added and leached down into the soil, it retains its effectiveness for a long time regardless of soil type or fertility level. Because soils from the Yolo series only were tested, any generalizations concerning soils with different characteristics are hazardous.

However, previous experience with Yolo clay loam indicates that it might be expected to alter the toxicity of a chemical as much as almost any other California soil. Consequently, the build-up of residues of PCP in a great many soils might become a real problem.

As mentioned above, no fixation of PCP on the clay fraction could be detected in these experiments. Since such fixation might be expected to liberate minerals in an ionic form, thus making them available to plants, it is interesting to note that the second cropping data show marked increases in yields in almost all instances. Evidently some other mechanism is effective here. Possibly the same degree of toxicity that destroys microörganisms in the cultures showing continued inhibition of plant growth may, in the lower dosages, prevent microbial activity and, hence, bring about partial sterilization, a phenomenon that long has been known to stimulate growth of higher plants. Many soil microörganisms may be killed by these phenol compounds and their subsequent decomposition, or the absence of microbial activity may make available to the indicator plants the total supply of mineral elements in the soil. Such response would be particularly notable in the Yolo clay loam.

This difference in yields for particular values, which had caused severe growth inhibition in the first run, may, to a minor degree, be influenced by available minerals still not utilized. They therefore should be considered apart from general yield increases for different croppings that are probably due mostly to environmental conditions.

Preëmergence treatments with PCP compounds can be quite successful if sufficient moisture follows the application. For preëmergence treatments the Na PCP would appear to be the desirable form. Where weeds have already emerged but the crop has not, the use of PCP in oil as a contact spray has proved useful. Even with the parent phenol in oil, immediate rainfall may produce crop injury.

The results obtained in this experiment show that relatively large quantities of PCP are necessary to inhibit growth to any great extent. In this experiment the 164.0 and 328.0 p.p.m. used would be equivalent to more than 574 and 1,148 pounds of PCP per acre added in the field, and distributed in one acre foot of soil. Most workers report successful results with less than 40 pounds of PCP per acre, indicating that the chemical is active in a relatively shallow soil layer.

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No reports of persistent residual toxicity in soils in which such quantities were used have been noted, and the amounts required to produce toxicity in these tests indicate little need to be fearful. In general, 164.0 p.p.m.—corresponding to 574 pounds per acre foot, at least 14 times that ordinarily used—produced no injury. If PCP toxicity should occur, leaching could be practiced or a different cropping system not requiring its use could be followed.

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TABLE 1

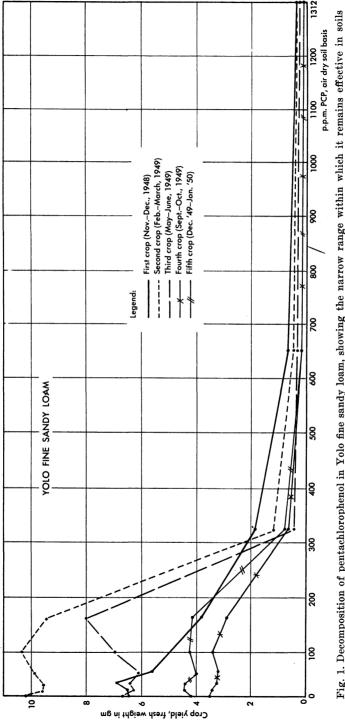
FRESH WEIGHTS OF KANOTA OAT PLANTS GROWN IN THREE CALIFORNIA (YOLO) SOILS CONTAINING INCREASING CONCENTRATIONS OF PENTACHLOROPHENOL (Values are averages of five replicates)

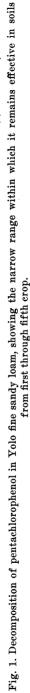
PCP concentration in p.p.m. (air dry soil basis)	Soils		
	Yolo fine sandy loam	Yolo clay loam	Yolo adobe clay
	(wt, gm)	(wt, gm)	(wt, gm)
	First cropping (November-December, 1948)		
0.00	6.5 6.6 6.5 6.8 5.6 5.2 3.8 1.8 0.6 0.4	8.3 10.1 9.6 9.4 9.0 7.7 6.9 3.8 1.6 0.6	4.9 4.2 5.2 4.7 4.0 3.0 0.9 0.4 0.4
	Second cropping (February-March, 1949)		
0.00. 5.12. 10.24. 20.48. 41.00. 82.00. 164.00. 228.00. 566.00. 312.00.	10.1 9.1 9.6 9.9 10.3 9.5 1.2 0.5 0.4	15.3 17.0 16.7 17.0 17.4 17.5 18.5 2.4 0.6 0.4	6.9 5.6 6.1 7.2 8.1 9.3 8.0 0.6 0.4 0.3
	Third cropping (May-June, 1949)		
0.00. 5.12. 10.24. 20.48. 41.00. 82.00. 164.00. 328.00. 556.00. 1312.00.	6.6 6.3 6.4 6.1 7.0 8.0 0.4 0.3 0.2	11.0 13.3 11.8 12.0 12.2 12.8 12.5 1.7 0.4 0.3	$\begin{array}{c} 4.9\\ 4.3\\ 4.0\\ 4.7\\ 4.7\\ 4.4\\ 5.1\\ 7.5\\ 0.6\\ 0.3\\ 0.2\\ \end{array}$
	Fourth cropping (September-October, 1949)		
0.00. 5.12. 10.24. 20.48. 41.00. 82.00. 164.00. 328.00. 656.00. 312.00.	3.5 3.4 3.3 3.2 3.3 2.9 0.5 0.2 0.1	5.16.16.66.77.26.46.01.70.30.2	3.2 3.7 3.5 3.0 3.2 3.3 2.9 0.8 0.4 0.2
	Fifth cropping (December, 1949-January, 1950)		
0.00. 5.12. 10.24. 20.48. 41.00. 82.00. 164.00. 328.00. 656.00. 312.00. 556.00. 312.00. 557.00. 55	4.2 4.1 4.4 4.4 4.0 4.2 4.1 0.7 0.2 0.3	$5.9 \\ 6.8 \\ 6.6 \\ 6.1 \\ 6.1 \\ 6.2 \\ 6.1 \\ 4.1 \\ 0.4 \\ 0.3$	3.7 3.6 4.2 3.5 3.6 3.8 4.1 0.4 0.3 0.2

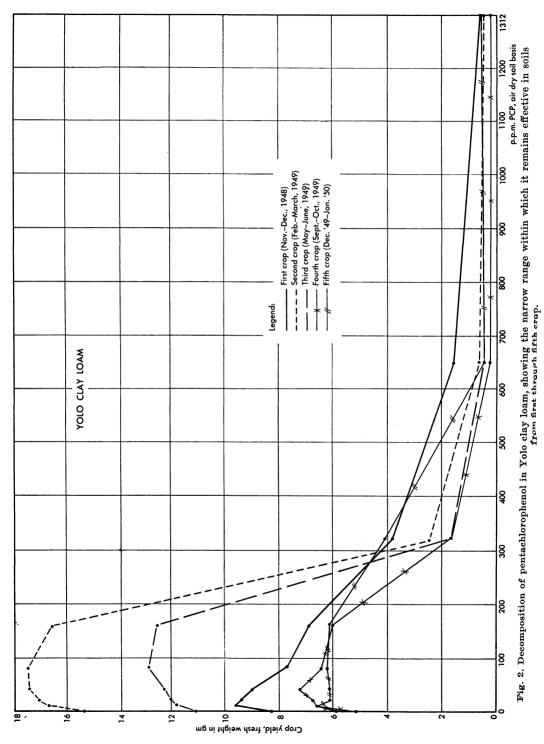
TABLE 2

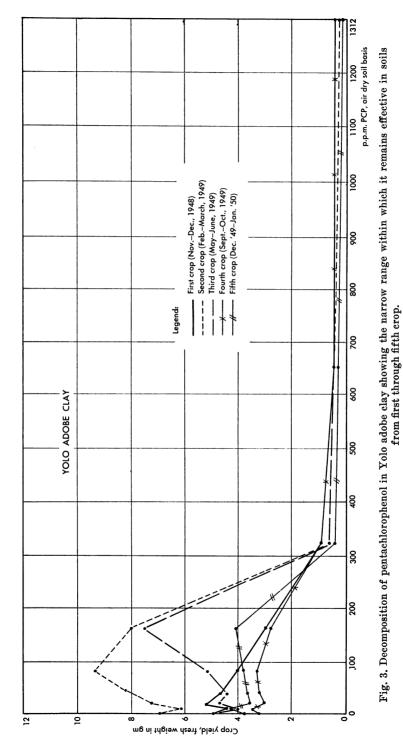
FRESH WEIGHTS OF KANOTA OAT PLANTS GROWN IN THREE CALIFORNIA (YOLO) SOILS WITH VARIOUS CONCENTRATIONS OF SODIUM PENTACHLOROPHENATE (Values are averages of five replicates)

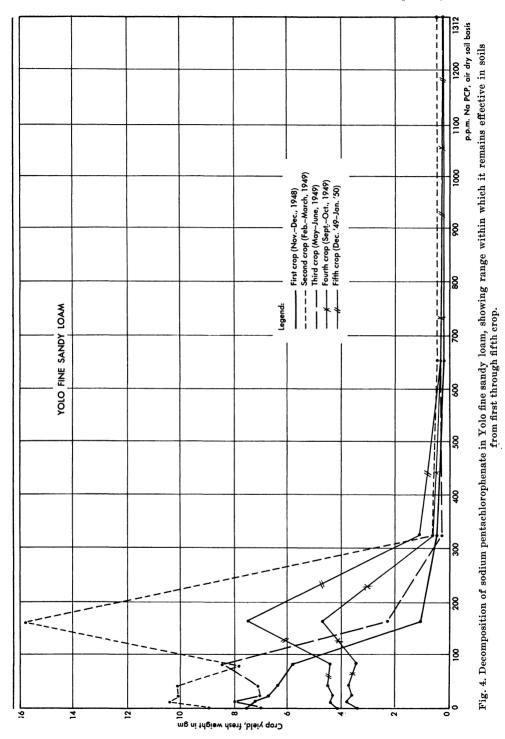
PCP concentrations in p.p.m. (air dry soil basis)	Soils		
	Yolo fine sandy loam	Yolo clay loam	Yolo adobe clay
	(wt, gm)	(wt, gm)	(wt, gm)
	First cropping (November-December, 1948)		
0.00	7.4 7.5 7.2 6.7 6.4 5.8 1.1 0.5 0.2 0.2	$\begin{array}{c} 6.5\\ 6.1\\ 7.1\\ 6.9\\ 6.5\\ 5.8\\ 3.1\\ 3.0\\ 1.6\\ 0.7 \end{array}$	$\begin{array}{c} 6.9 \\ 5.8 \\ 5.4 \\ 5.5 \\ 4.7 \\ 2.4 \\ 0.8 \\ 0.3 \\ 0.2 \\ 0.2 \end{array}$
	Second cropping (February-March, 1949)		
0.00	9.0 9.5 10.4 10.1 10.1 7.8 15.8 0.6 0.4 0.3	8.0 7.3 8.0 8.4 9.1 15.1 4.4 1.4 0.5 0.4	$\begin{array}{c} 6.2 \\ 5.9 \\ 6.3 \\ 7.0 \\ 8.6 \\ 4.2 \\ 0.8 \\ 0.4 \\ 0.6 \\ 0.3 \end{array}$
	Third cropping (May-June, 1949)		
0.00	7.0 7.4 8.0 7.0 7.1 8.4 2.3 0.3 0.3 0.2	7.7 7.9 7.1 7.1 8.0 10.0 8.4 0.3 0.2	5.1 5.4 6.3 7.3 8.4 1.8 0.3 0.2 0.2
	Fourth cropping (September-October, 1949)		
0.00	3.4 3.8 3.6 3.7 3.4 4.7 0.6 0.3 0.2	5.0 5.5 5.2 5.0 4.5 4.4 1.3 0.3 0.2	$\begin{array}{c} 3.4\\ 3.5\\ 3.8\\ 3.4\\ 3.5\\ 3.6\\ 1.9\\ 0.5\\ 0.4\\ 0.2\\ \end{array}$
	Fifth cropping (December, 1949–January, 1950)		
0.00	4.1 4.4 4.3 4.5 4.4 7.5 1.1 0.3 0.2	6.0 6.7 6.0 5.9 5.9 5.8 5.2 2.8 0.4 0.2	3.8 4.0 4.0 3.9 4.4 4.5 6.2 0.5 0.3 0.3

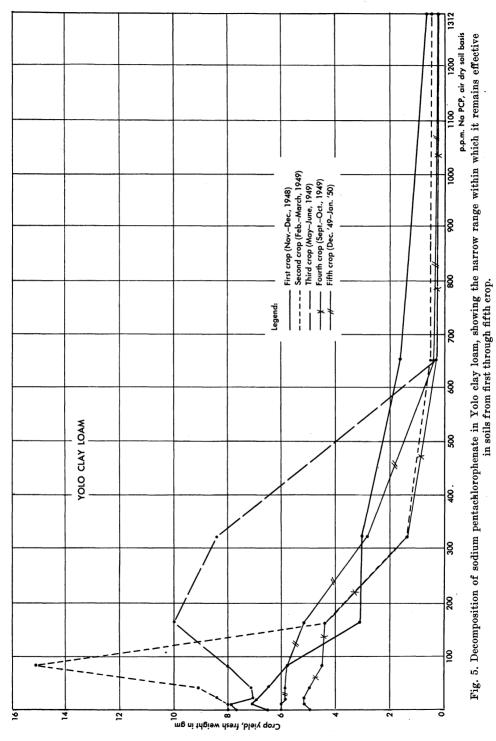


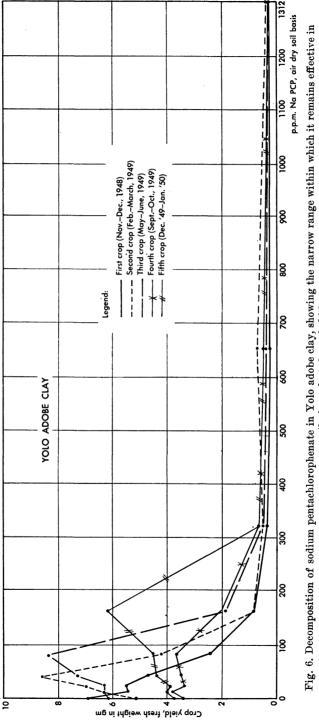












soils from first through fifth crop.

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