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TOXICITY OF 2,4-D IN CALIFORNIA SOILS

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TOXICITY OF AMMONIUM DINITRO-O-SEC-BUTYL PHENOLATE IN CALIFORNIA SOILS

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Toxicity of 2,4-D in California Soils

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Tests on several agriculturally important soils show that under California conditions 2,4-D retained in the soil after spraying may injure subsequent crops unless special measures are taken to supplement natural leaching and decomposition. Once decomposition occurs, crop growth is noticeably stimulated. Spraying gives more satisfactory selective control of weeds than direct application of 2,4-D to the soil. Current studies show the chemical to be practical for brush control and range improvement. Its use as a permanent soil sterilant is not recommended.

Toxicity of Ammonium Dinitro-*o*-sec-Butyl Phenolate in California Soils

(pages 159 to 169)

When used as selective or general contact sprays, dinitro-*o*-sec-butyl phenol compounds decompose too rapidly to create any problem of residual toxicity. Decomposition of dinitro selectives, like many other herbicides, causes considerable stimulation of crop growth. High cost prevents the use of these compounds for soil sterilization. In pre-emergence sprays water-soluble compounds of dinitro-*o*-sec-butyl phenol are not safe for tender crops, but preliminary tests indicate parent substituted phenols may be used.

In order that the information in our publications may be more intelligible it is sometimes necessary to use trade names of products or equipment rather than complicated descriptive or chemical identifications. In so doing it is unavoidable in some cases that similar products which are on the market under other trade names may not be cited. No endorsement of named products is intended nor is criticism implied of similar products which are not mentioned.

**TOXICITY OF AMMONIUM
DINITRO-O-SEC-BUTYL PHENOLATE
IN CALIFORNIA SOILS**

A. S. CRAFTS

TOXICITY OF AMMONIUM DINITRO-O-SEC-BUTYL PHENOLATE IN CALIFORNIA SOILS¹

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The introduction of sodium dinitro-*o*-cresylate (Sinox) as a selective herbicide (Westgate and Raynor, 1940)² provided a great stimulus to chemical weed control. This organic dye was relatively noncorrosive, eliminating the hazards attending the use of sulfuric acid. To control the broad-leaved weeds in one acre of cereal, three pounds of the chemical in the form of one gallon of concentrate sufficed, whereas up to 100 pounds of sulfuric acid had been required. Furthermore, Sinox proved useful in flax, onions, garlic, peas, corn, and other crops not previously sprayed with selective herbicides.

THE PRINCIPLE OF ACTIVATION

Soon after the introduction of Sinox, it was found that the addition of an acid salt such as ammonium sulfate or sodium bisulfate would greatly increase its toxicity to plants. This became known as "activation," and it has become standard practice wherever Sinox solutions are used. In 1945, Crafts and Reiber gave the following chemical explanation for the enhanced toxicity of activated solutions of Sinox.

Sodium dinitro-*o*-cresylate in solution dissociates into the highly polar sodium and dinitro-*o*-cresylate ions. Though readily soluble in the polar solvent water, they are less soluble in the nonpolar waxy cuticle of the plant. Dinitro-*o*-cresol, on the other hand, is an un-ionized compound, soluble in the cuticle and hence able to enter the plant readily.

When an acid salt is added to an aqueous solution of sodium dinitro-*o*-cresylate the reaction $\text{Na}^+ + \text{DNoCr}^- + \text{H}^+ \longrightarrow \text{HDNoCr} + \text{Na}^+$ goes to the right, producing undissociated dinitro-*o*-cresol in the solution. This compound is rapidly absorbed by the plant through the cuticle and as its molecules leave the free solution on the leaves, more are produced by mass action so long as the hydrogen ion concentration is maintained. Many experiments indicate that this reduction in polarity, brought about by the association of the phenolic molecule, is responsible for the increased toxicity resulting from activation. The same chemical mechanism may be used to activate chlorinated phenol compounds.

Since reduction in polarity increases toxicity, another approach to the discovery of more efficient weed killers would be the use of longer side chains on the nitro- or chloro-substituted phenols. Because dinitro-*o*-cresol is more toxic than dinitrophenol, the ethyl-, propyl-, and butyl-substituted compounds should be even more toxic. Testing has proved this to be true (Crafts, 1945).

¹ Received for publication December 2, 1947.

² See "Literature Cited" for complete data on citations referred to in text by name of author and date of publication.

Toxicity increases through the butyl substitution and drops slightly with the amyl substitution, presumably because the dinitro groups become a smaller and hence less effective portion of the total molecule.

Following the discovery of the intense toxicity of dinitro-*o-sec*-butyl and amyl phenols, a number of commercial products based on these compounds appeared on the market, including Dow Contact herbicide, Dow General herbicide, Contax, Chipman General, Stauffer Weed Killer, and Sinox General. Ammonium salts are the active ingredients in Dow Selective, Sprayrite Selective, and Sinox W herbicides. Use of these weed killers, already widespread, will be greatly extended once their manifest advantages are recognized. This is particularly true in countries where hand methods of weed control are still practiced.

PURPOSES OF PRESENT STUDIES

Because the chlorinated and nitrated phenols will find extensive use in agriculture, it is important to know what effects their continued use will have on the soil. We should know:

1. The residual effects of the continued use of these materials as selective herbicides on croplands
2. The effects of accumulation where they are used as general contact herbicides
3. Their toxicity to seedlings when used as fortifying agents in pre-emergence sprays
4. Their possible function as soil sterilants in nontilled areas.

These studies involve nine successive croppings of eight soils treated with varying amounts of the ammonium salt of dinitro-*o-sec*-butyl phenol.

MATERIALS AND METHODS

The soils and methods used in these tests were the same as those described in the preceding paper (Crafts, 1948) except that no percolation and leaching experiments were performed and only Kanota oats were used as indicator plants. The soils used were Aiken clay loam, Egbert loam, Hanford fine sandy loam, Sierra fine sandy loam, Stockton adobe clay, Yolo fine sandy loam, Yolo clay loam, and Yolo adobe clay.

RESULTS

Figures 1-8 illustrate the results of our tests in terms of crop yields 30 days after planting.

Four of the soils used in these tests were employed previously in similar trials with dinitro-*o-cresol*. These were Yolo clay loam, Yolo fine sandy loam, Sierra fine sandy loam, and Stockton adobe clay. When the results (Crafts, 1945) are compared with those of the present study, it is evident that the dinitro-*o-sec*-butyl phenol is considerably more toxic than the dinitro-*o-cresol*. Furthermore, the breakdown in the soil goes on at a considerably slower rate; in three soils, five croppings with the butyl compound gave results comparable to three with dinitro-*o-cresol*. In the Yolo clay loam even nine crops failed to bring down the toxicity to a value comparable with that for the second cropping with dinitro-*o-cresol*.

The graphs indicate that the Sierra and Yolo fine sandy loams may be placed in a high-toxicity group; Yolo adobe clay, Hanford fine sandy loam, and Yolo clay loam in an intermediate-toxicity group; and Stockton adobe clay, Egbert loam, and Aiken clay loam in a low-toxicity group. This is quite similar to the grouping for the soils treated with dinitro-*o*-cresol (Crafts, 1945). It does not follow strictly a grouping based on textural grade nor one based on fertility; evidently the toxicity of the dinitro-substituted phenols is a more complex function than those of arsenic and chlorate.

Although in a few instances the differences in toxicity between runs were not distinct, in most cases toxicity decreased in a regular order with successive cropping. This indicated that decomposition of the dinitro compound was occurring. As with dinitro-*o*-cresol, this decomposition seemed to stimulate production in the soil at concentration levels that had been toxic to previous crops. Crop number seven showed stimulation in all eight soils.

DISCUSSION

Residual Toxicity. It is apparent that, like dinitro-*o*-cresol, dinitro-*o*-sec-butyl phenol compounds could never accumulate in soils in amounts dangerous to crops as a result of normal selective or general contact spraying. For example, to sterilize an acre-foot of soil, weighing roughly 3,600,000 pounds, would require 40 p.p.m. (about 140 pounds of chemical) for the light textures, 100 p.p.m. (about 360 pounds) for the medium group, and 140 p.p.m. (about 500 pounds) for the heavy soils. On the basis of an acre-inch, the corresponding values would be 12.7 pounds, 30.0 pounds, and 41.7 pounds respectively. Since

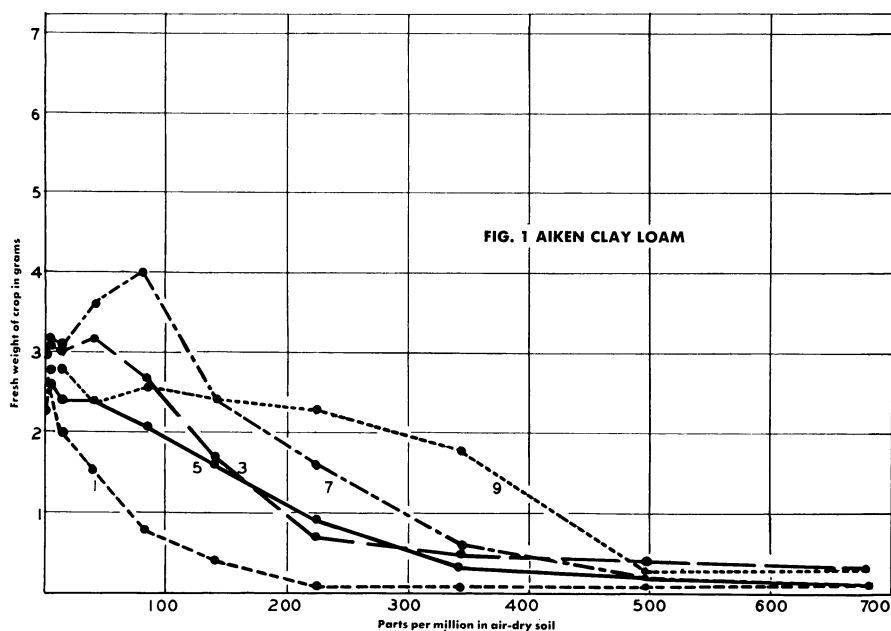


Fig. 1. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

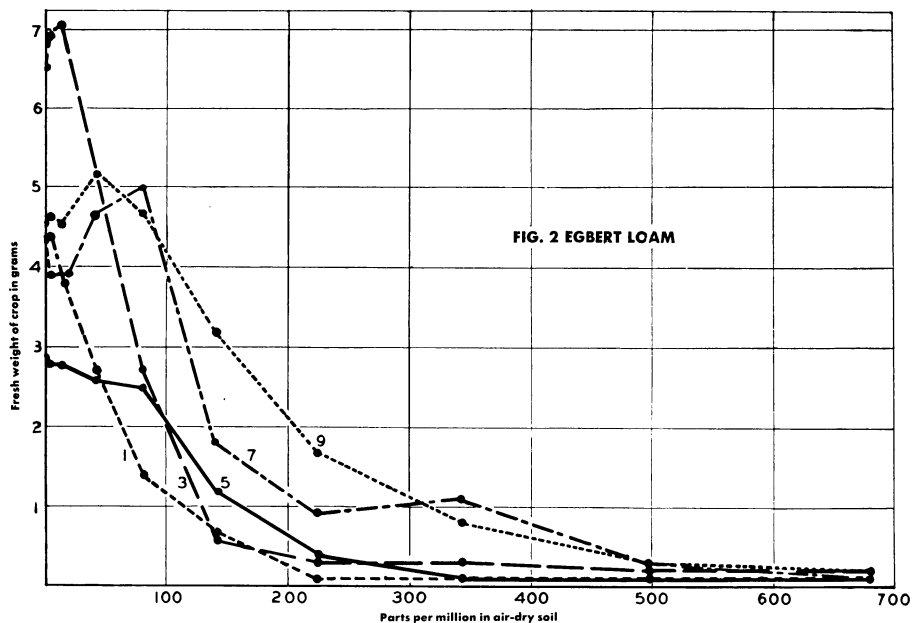


Fig. 2. Toxicity of ammonium dinitro-*o-sec*-butylate in 8 California soils to oats as shown by fresh weight.

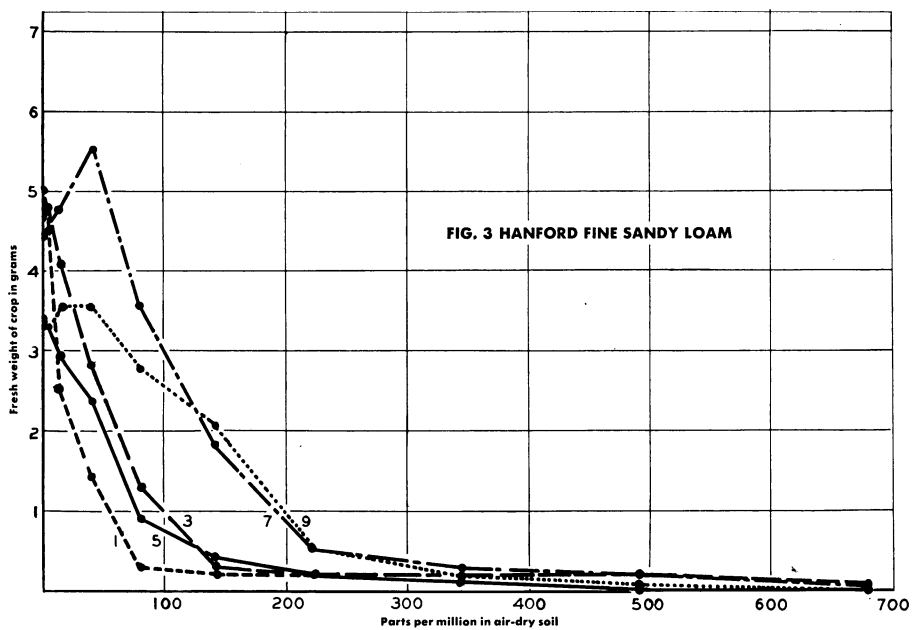


Fig. 3. Toxicity of ammonium dinitro-*o-sec*-butylate in 8 California soils to oats as shown by fresh weight.

selective weed control seldom requires more than one pound of this type of chemical per acre, much of which is absorbed by the weeds, breakdown should normally destroy many times as much as would be needed. On the other hand, to sterilize soils by means of dinitro-*o*-sec-butyl phenol would be out of the question at the present price of this compound.

Tests with Sinox have proved it to be hazardous as a pre-emergence spray. Being readily water-soluble, this chemical may be highly concentrated in a shallow layer of topsoil when light showers follow the spray treatment. Water-soluble compounds of dinitro-*o*-sec-butyl phenol are even more toxic in the topsoil, and they break down at a slower rate. Hence they cannot be used safely in pre-emergence treatments on tender crops.

Recently dinitro herbicides have been used at somewhat higher rates as pre-emergence treatments in cotton, corn, soy beans, and other crops having large vigorous seedlings. Although the crop seedlings are not injured, it seems possible that the herbicide, in the quantities required, might accumulate and eventually give trouble. This might be true in sandy soils underlaid with soil of heavier texture, for once the chemical is leached into the cooler B horizon of the soil, its breakdown would be considerably retarded.

The parent substituted phenols are relatively insoluble in water; their use as fortifying agents in pre-emergence oil spraying should be less hazardous. Preliminary tests in the greenhouse indicate this to be true, but many trials in the field will have to be made before such a procedure can be recommended.

Stimulation. One aspect of the use of dinitro herbicides which is of economic importance is the possible stimulation of crops. Very often cereal crops

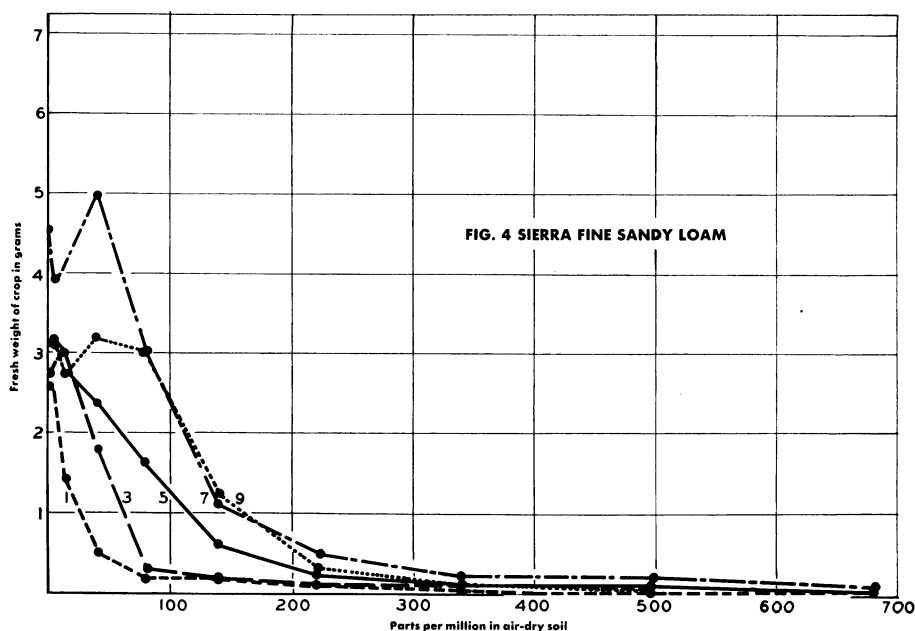


Fig. 4. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

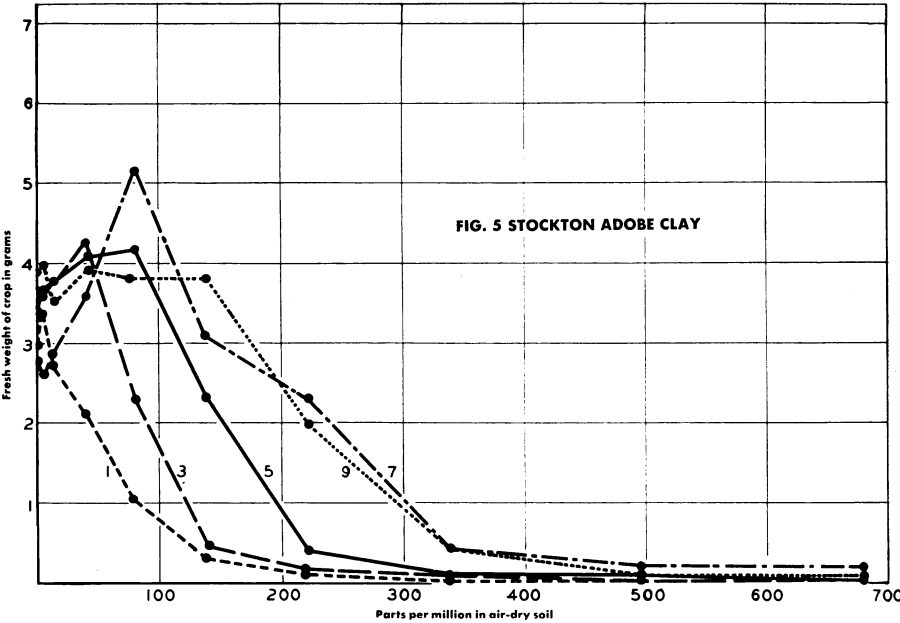


Fig. 5. Toxicity of ammonium dinitro-*o-sec*-butylate in 8 California soils to oats as shown by fresh weight.

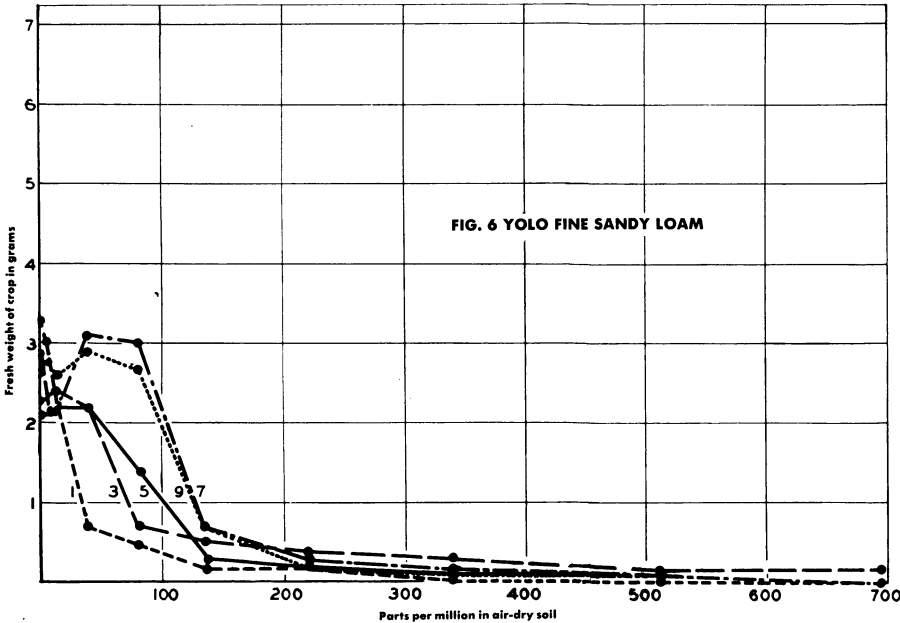


Fig. 6. Toxicity of ammonium dinitro-*o-sec*-butylate in 8 California soils to oats as shown by fresh weight.

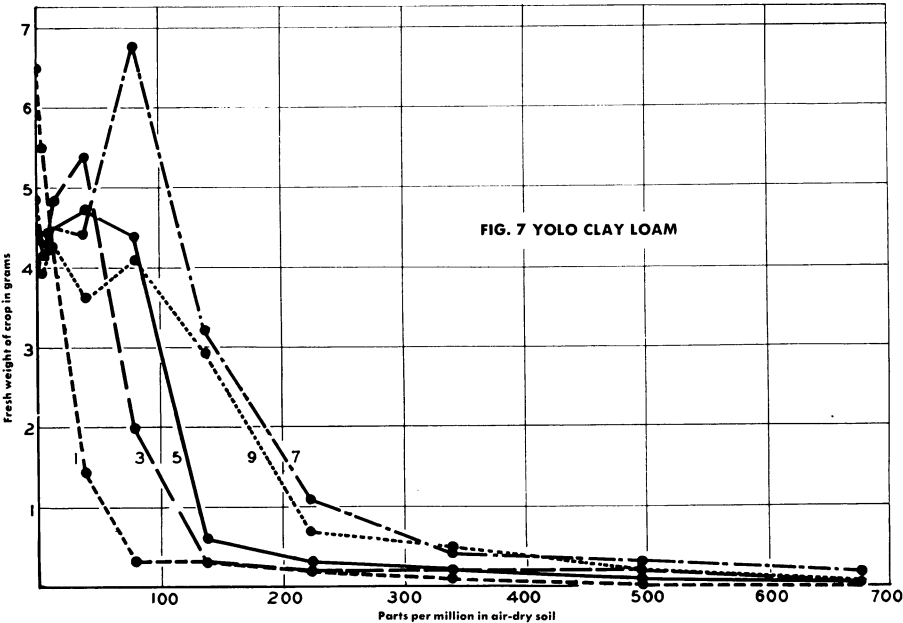


Fig. 7. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

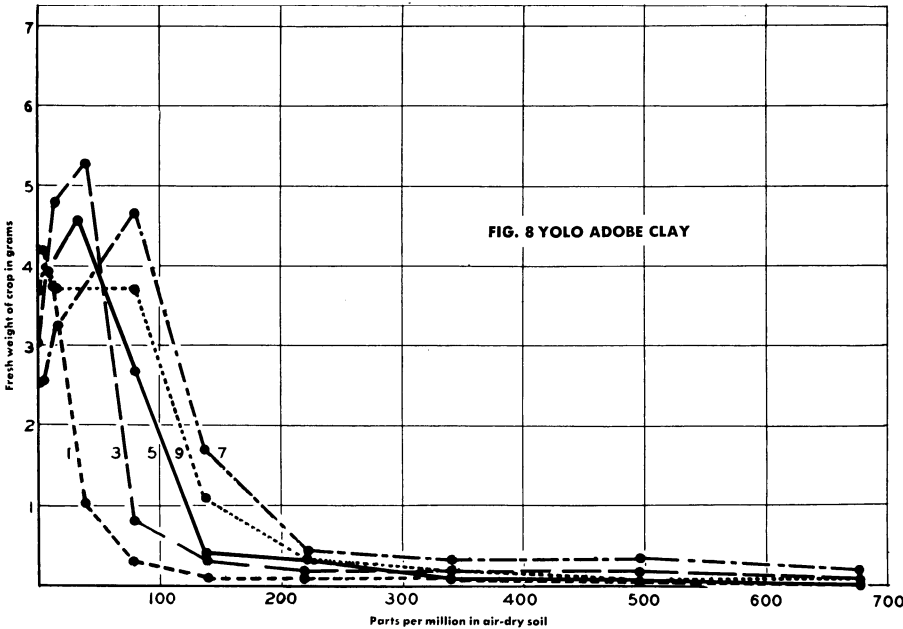


Fig. 8. Toxicity of ammonium dinitro-*o*-sec-butylate in 8 California soils to oats as shown by fresh weight.

sprayed with dinitro selectives are noticeably greener and more vigorous than nearby unsprayed crops. In fact, where plot tests are made by spraying alternate strips through a field, direct comparison shows such stimulation even in areas where, because of a complete lack of weeds in certain parts of the field, weed competition is not a factor.

In the data on toxicity in soils, this stimulating effect is very prominent. Table 1 lists the cases in which crops in treated soils exceeded those in untreated.

Aiken clay loam had cultures exceeding the checks in yield in eight out of nine runs; Egbert loam in seven runs; Hanford fine sandy loam in seven runs; Sierra fine sandy loam in six runs; Stockton adobe clay in eight runs; Yolo fine sandy loam in eight runs; Yolo clay loam in seven runs; and Yolo adobe

TABLE 1
THE NUMBER OF CULTURES OF TREATED SOILS THAT EXCEEDED
IN YIELD THE UNTREATED CONTROL FOR EACH RUN

Run number	Number of soils	Number of cultures
1.....	1	1
2.....	6	14
3.....	8	16
4.....	7	17
5.....	6	14
6.....	7	15
7.....	8	19
8.....	8	20
9.....	8	14

clay in eight runs. Although, in some of these cases, natural variability in yield might explain these high-yielding cultures, it seems highly improbable that they could all be explained on this basis.

These studies on dinitro-*o*-sec-butyl phenol add one more instance to several previously noted (Crafts, 1945, 1948) where the breakdown of toxic chemicals in the soil results in increased yield. In the cases of chlorate and borax, it seems possible that loss of toxicity by decomposition or fixation might be followed by base replacement, making available bases which the crop plants are able to use as nutrients. In the cases where compounds high in nitrogen such as thiocyanate and Ammate are involved, it seems probable that breakdown results in making available nitrogen compounds in sufficient quantities to nourish plants.

Where nitro- or chloro-substituted phenols and 2,4-D compounds are involved, it hardly seems possible that a direct nutrition of plants by the compounds or their decomposition products can be concerned, because they are used in such small quantities. That they are decomposed by soil micro-organisms seems probable, for Zobell (1946) has shown that in the soil there are organisms capable of breaking down many such chemicals. The systematic study of the effects of such breakdown should furnish much valuable information relative not only to the use of herbicides in pest control but possibly also to plant nutrition and crop production.

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