THE FACTORS INFLUENCING THE EFFECTIVENESS OF ARYLOXY ALKANOL ESTERS AND HEMIESTERS AS HERBICIDES

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INTRODUCTION

A great advancement in chemical weed control was the discovery of 2,4-dichlorophenoxyacetic acid by Zimmerman and Hitchcock in 1942 (19 p.409). This chemical was then developed as a herbicide through the investigations of a number of workers. Since that time thousands of tons of 2,4-dichlorophenoxyacetic acid have been used in chemical warfare against weeds. The continued popularity of 2,4-D has been due to its herbicidal effectiveness at low rates of application and the degree of selectivity between different plants.

Generally 2,4-D is used in controlling weeds by applying the chemical to foliage of established plants. It has become evident that the chemical is also effective in checking the germination of seeds in the soil. However, the use of 2,4-dichlorophenoxyacetic acid for controlling germinating seedlings is restricted, because of the likelihood of damage to emerged sensitive crops. A solution to the problem of damage to emergent plants developed when King and Lambrech (18, p.34) discovered the properties of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate. This derivative of 2,4-dichlorophenoxyacetic

acid has no phytotoxic action upon the foliage of plants sensitive to 2,4-D. Once it enters the soil, however, sodium 2-(2,4-dichlorophenoxy)ethyl sulfate displays many of the herbicidal properties of 2,4-D.

Sodium 2-(2,4-dichlorophenoxy)ethyl sulfate has proved to be an effective herbicide for controlling weeds in row crops such as asparagus and strawberries (16, p.131) and (15, p.85).

Two more derivatives of 2,4-D that display properties similar to sodium 2-(2,4-dichlorophenoxy)ethyl sulfate were also discovered. They werebis(2-(2,4-dichlorophenoxy)ethyl) oxalate and 2-(2,4-dichlorophenoxy)ethyl benzoate. Attention was then turned to the possibility of masking the foliar activity of 2,4,5-trichlorophenoxy acetic acid and 2-methyl-4-chlorophenoxyacetic acid. It was found that the corresponding derivatives; sodium2-(2,4,5-trichlorophenoxy)ethyl sulfate and sodium 2-(2-methyl-4-chlorophenoxy)ethyl sulfate also displayed the masking effect of the parent acid.

The objectives of this study were to determine the relative effectiveness of these newly formed herbicides and to determine some of the factors that influence their activity as herbicides.

REVIEW OF LITERATURE

The activity of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate was first reported by King and Lambrech in 1949 (18, p.34). Application of this chemical to foliage gave no epinastic response on tomatoe plants. Slight formative effects did appear but were soon outgrown. Sodium 2-(2,4-dichlorophenoxy)ethyl sulfate was called a germinative toxicant due to its suppression of germinating seedlings when applied to the soil (18, p.34). Nutrient solutions of Sodium 2-(2,4-dichlorophenoxy)ethyl sulfate caused no inhibition of seed germination in petri dishes (20 p.199). Inhibition of seed germination resulted when soil was added to the nutrient media. Studies comparing sterilized and non-sterilized soil showed that sodium 2-(2,4-dichlorophenoxy)ethyl sulfate was not active in inhibiting seed germination when the soil was sterilized (20, p.195). It became evident that sodium 2-(2,4-dichlorophenoxy)ethyl sulfate was changing from an inactive to an active herbicide when it came in contact with non-sterilized soil.

Vlitos (31, p.437) was able to remove the possible physical effects of the soil by showing that water extracts of non-sterile soil would activate sodium 2-(2,4-dichlorophenoxy)ethyl sulfate while sterilized soil

extracts would not. Highly sensitive 2,4-dichlorophenoxyacetic acid plants showed formative effects when the chemical was absorbed from sodium 2-(2,4-dichlorophenoxy)ethyl sulfate treated soil (19, p.307). In an early experiment it was shown that enough sodium 2-(2,4-dichlorophenoxy)ethyl sulfate had been activated within three hours after treatment of soil to inhibit cucumber roots in petri dishes (20, p.195). The concentration of the active form was shown to increase with time.

Concentrated efforts were made to find out the exact nature of the activation phenomenon. Carroll suggested that the activation was due to hydrolysis of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate by bacteria or by acids (9, p.13). In sterilized and non-sterilized nutrient media at different pH levels Carroll was able to show activation of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate when the pH was below four(9, p.13). The compound was also readily converted to its active form in sterile soils of low pH valves (30, p.58). Activation did not occur in sterile soil, if the soil pH was above 5.5. In non-sterile soil the active compound occurred in a pH range of 4.0 to 7.0. On acid hydrolysis sodium 2-(2,4-dichlorophenoxy)ethyl sulfate is converted to 2,4-dichlorophenoxy ethanol and sodium acid sulfate (10, p.411). Carroll emphasized the importance

of purified samples of sodium 2-(2,4-dichlorophenoxy) ethyl sulfate in studying the activation process. Several samples of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate prepared from different procedures indicated that impurities tended to mask the activation (10, p.410). The impurities probably account for the slight formative effects that appear after foliage application of the chemical.

In early studies a microbial factor was considered necessary for the chemical conversion of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate (20, p.206). Carroll was able to show that twenty-six different micro-organisms grown in sterile buffered nutrient solution could activate sodium 2-(2,4-dichlorophenoxy)ethyl sulfate under alkaline conditions. The activation of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate by soil micro-organism was confirmed by Vlitos (31, p.437). He was able to isolate Bacillus cereus var. mycoides and show that it was the organism chiefly responsible for activating Sodium 2-(2,4-dichlorophenoxy)ethyl sulfate. It was also shown that cell-free filtrates of the nutrient broth of Bacillus cereus var. mycoides were capable of activating the sodium 2-(2,4-dichlorophenoxy)ethyl sulfate, to an active form.

Further investigations dealt with the actual identity

of the active compound formed from sodium 2-(2,4-dichlorophenoxy)ethyl sulfate. A quantitative procedure for detecting 2,4-dichlorophenoxy ethanol showed that this compound was rapidly formed in the soil after original treatment of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate (32, p.141). After a longer period of time had elapsed the presence of 2,4-dichlorophenoxyacetic acid could be determined qualatitively (32, p.141). Hence, two active plant growth regulators are formed when sodium 2-(2,4-dichlorophenoxy)ethyl sulfate comes into contact with the soil.

The work by Vlitos compares well with the results obtained by Audus (5, p.887). Soil perfusion studies were made to follow the fate of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate in the soil. By sampling the perfusate periodically and testing it with an appropriate biological assay method the course of activation of sodium 2-(2,4-dichlorophenoxoy)ethyl sulfate could be followed. The first part of the perfusion showed a continual increase in concentration of a herbicidal component up to the sixteenth day. After that time, a rapid fall in toxicity of the perfusate set in. All herbicidal activity was lost within twenty-four hours. The breakdown of 2,4-dichlorophenoxyacetic acid in the soil

perfusion studies agrees well with the pattern set up by sodium 2-(2,4-dichlorophenoxy)ethyl sulfate. This would suggest that the herbicidal form of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate was 2,4-dichlorophenoxyacetic acid (5, p.887). Cross perfusion studies showed that the bacterial flora originally built up in the soil column with sodium 2-(2,4-dichlorophenoxy)ethyl sulfate would decompose subsequent perfusions of either sodium 2-(2,4-dichlorophenoxy)ethyl sulfate or 2,4-dichlorophenoxyacetic acid without a normal fifteen to sixteen day lag period. Further proof as to the indentity of the herbicidal component of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate was established by Audus (5, p.887) with a paper partition chromatogram of the perfusate of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate. The toxic compound that was generated from sodium 2-(2,4-dichlorophenoxy)ethyl sulfate was located in the same position on the chromatogram as when 2,4-dichlorophenoxyacetic acid was chromatographed.

The overall changes of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate appear to be as follows:

sodium 2-(2,4-dichlorophenoxy)ethyl sulfate

step 1
(hydrolysis)

2,4-dichlorophenoxy ethanol Sodium acid sulfate

2,4-dichlorophenoxy ethanol

↓ step 2 (oxidation)

2,4-dichlorophenoxyacetic acid

↓ step 3 (hydrolysis)

2,4-dichlorophenol acetic acid

Step three was postulated by Audus but has not been definately proven (4, p.272). There is considerable evidence, however, in the cross soil perfusion studies conducted by Audus that support this view.

Structurally related compounds 2,4-dichlorophenoxy ethanol, 2,(2,4-dichlorophenoxy)ethyl benzoate and bis(2-(2,4-dichlorophenoxy)ethyl) oxalate were compared with sodium 2-(2,4-dichlorophenoxy)ethyl sulfate (32, p.136-137). It appears that micro-organisms are not a factor in the action of bis(2-(2,4-dichlorophenoxy) ethyl) oxalate, for this chemical, like 2,4-dichlorophenoxy ethanol displayed herbicidal properties in both sterile and non-sterile media. 2-(2,4-dichlorophenoxy) ethyl benzoate also gave root inhibition on sterile media, but it gave greater root suppression on the non-sterile soil media. Of the four chemicals, 2,4-dichlorophenoxy ethanol caused the highest suppression of cucumber roots.

The presence of the growth hormones in the soil

appear to have some effect upon the bacterial flora present. Stevenson and Mitchell (29, p.643) showed that a 0.02% concentration of 2,4-dichlorophenoxyacetic acid in Dextrose agar had a retarding effect on certain groups of bacteria. Lewis and Hamner later showed that concentration of 1000 ppm of 2,4-dichlorophenoxyacetic acid gave no inhibition of bacterial growth (22, p.113). They concluded that under normal rates of application 2,4-dichlorophenoxyacetic acid had no serious effect on soil micro-organisms.

The persistence of sodium 2-(2,4-dichlorophenoxy) ethyl sulfate in the soil is comparable to that of 2,4-dichlorophenoxyacetic acid (20, p.191). This is not too surprising when it is considered that the activated form of sodium 2-(2,4-dichlorophenoxy)ethyl sulfate is 2,4-dichlorophenoxyacetic acid. Many of the factors influencing the activity of 2,4-dichlorophenoxyacetic acid in the soil are likely to pertain to this group of closely related chemicals.

Norman and Newman listed the different ways the activity of 2,4-dichlorophenoxyacetic acid could be lost in the soil (27, p.7). The disappearance of 2,4-dichlorophenoxyacetic acid could occur by leaching, adsorption by soil components, and decomposition of the herbicide by micro-organisms. The amount of 2,4-dichlorophenoxy

acetic acid leached from the soil depends upon the amount of moisture available and the character of the soil. High organic soils greatly inhibit the leachability of the chemical (25, p.150). Normally, inactivated soil adsorption is not a factor (27, p.8).

The major disappearance of 2,4-dichlorophenoxyacetic acid can be accounted to the decomposition by bacteria (13, p.225). Factors that influence the activity of micro-organisms correspondingly influence the persistence of 2,4-dichlorophenoxyacetic acid. In this light, Brown pointed out the persistence of 2,4-dichlorophenoxacetic acid was affected by soil moisture, temperature, addition of manure and auto claving (8- p.315). Mitchell and Marth (24, p.415) demonstrated that 2,4-dichlorophenoxyacetic acid was slowly inactivated when mixed with air-dried soil, and that the emergence of plants from soil, so treated was reduced even after storage for 18 months. They also found that 2,4-dichlorophenoxyacetic acid was readily inactivated when mixed with warm moist soil. Kries (21, p.524) demonstrated that the presence of large amounts of organic matter in soil reduced both apparent activity and persistence of 2,4-dichlorophenoxyacetic acid in unlimed soils and that an application of lime increased its persistence.

The relative residual lengths of 2,4-dichlorophenoxyacetic acid; 2-methyl-4-chlorophenoxyacetic acid; and 2,4,5-trichlorophenoxyacetic acid were studied by DeRose (13, p.222-226). For all the different conditions that were imposed the relative persistence of the three chemicals remained the same. 2,4-dichlorophenoxyacetic acid consistently broke down in the shortest time, while 2-methyl-4-chlorophenoxyacetic acid was intermediate in its breakdown. 2,4,5-trichlorophenoxyacetic acid had the longest residual length.

The relative persistence of 2,4-dichlorophenoxyacetic acid; 2-methyl-4-chlorophenoxyacetic acid and 2,4,5-trichlorophenoxyacetic acid were studied by Audus by using a soil perfusion apparatus (3, p.170). Aerated solutions of the respective chemicals were percolated through soil columns while the concentration of the chemical was followed with a biological assay technique. Three different phases were noted in conducting a perfusion. First there was an immediate drop in the concentration of herbicide in the soil solution. The duration of the lag phase was approximately fourteen days for 2,4-dichlorophenoxyacetic acid and fifty to eighty days for 2-methyl-4-chlorophenoxyacetic acid. The final phase was a rapid disappearance of the herbicide. Subsequent perfusion through a used soil column with the same

herbicide resulted in an immediate breakdown without any lag phase. This was interpreted to mean that a bacterial population had built up that was capable of breaking down that particular herbicide. Comparison of the rates of detoxification of 2,4-dichlorophenoxyacetic acid; 2-methyl-4-chlorophenoxyacetic acid; and 2,4,5-trichlorophenoxyacetic acid in the soil perfusion studies were 100 : 25 : 5, respectively.

Cross perfusion experiments that followed showed that 2,4-dichlorophenoxyacetic acid-enriched soil was capable of breaking down 2-methyl-4-chlorophenoxyacetic acid without a lag period, but not capable of detoxifying a 2,4,5-trichlorophenoxyacetic acid perfusate. In order to breakdown 2,4,5-trichlorophenoxyacetic acid by cross perfusion it was necessary to use 2,4-dichlorophenoxy-acetic acid-enriched soil followed by 2-methyl-4-chloro-phenoxyacetic acid perfusion. The resulting soil column was only capable of breaking down 2,4,5-trichlorophenoxy-acetic acid for a limited time.

Norman and Newman point out that it is not unusual that soil bacteria are capable of breaking down organic herbicides (27, p.7). The soil bacteria are capable of utilizing a great diversity of natural organic compounds. The soil is a great reservour of many different species

that may spring into prominence when the right substrate is present.

METHODS AND MATERIALS

This study was conducted largely in a green house in the summer of 1952. The green house was equipped with florescent lights. Uniform day length was maintained throughout the year by the use of an electric time switch connected to the lights. Adequate temperature was maintained by a hot water heating unit that was thermostatically controlled. During the summer time, when the sun caused excessive heating inside of the greenhouse it was found necessary to white wash the windows to cut down the light intensity. Fans were also used at that time to increase air circulation.

Formulation studies of the different chemicals were done in the Oregon State Agricultural Chemistry Laboratories. The selection of proper solvent and weighing of the chemicals was done in the laboratory, but final emulsions were made in the greenhouse immediately before spraying.

Application of the chemical was done in such a manner as to simulate field application. This was possible through the use of a greenhouse small plot sprayer designed and built at Oregon State College. This machine was simple to operate and dependable for reproducible applications.

The sprayer consists of a small spray tank and nozzle that are connected to an overhead carriage. This carriage is propelled by a constant speed electric motor. Various speeds may be obtained by different diameter driving pulleys. The height of the nozzle above the plot surface is easily adjusted by a set screw located on the carriage. Air pressure is supplied from a small compressor located below the spraying platform. Different spraying pressures were quickly obtained through the use of an adjustable pressure regulator. Spraying vapors are evacuated through an air duct by means of a ventilating fan, located at one end of the spraying unit.

The pots used for the various experiments were waxed paper cartons; 4¼" diameter by 3" deep. Four ¼" holes were punched in the bottom to provide adequate drainage. The only time these particular containers were not used was in Experiment V. Here the limited amounts of the different soil types dictated that smaller containers be used. The soil that was used for the following experiments, when not otherwise indicated, was a Chehalis sandy loam.

The different experiments that were conducted are shown in Table 1.

Only the first three preliminary experiments contained post emergent treatments. All of the treatments

Table 1. Experiments Conducted in the Study of Aryloxy Alkanol Esters

Experiment Number	Title
I.	Plant tolerance to foliar application of four aryloxy alkanol esters at thirty-two pounds per acre.
II.	Activation of sodium 2-(2,4-dichlorophenoxy) ethyl sulfate by homogenate of beet leaves.
III.	Activation of sodium 2-(2 4-dichlorophenoxy) ethyl sulfate by homogenate of beet leaves aided by incubation.
IV.	Comparison of some aryloxy alkanol esters on the germination of three crop plants.
V.	Comparison of residual activity on a sandy soil.
VI.	Effect of soil type upon residual activity.
VII.	Effect of the previous soil treatment upon activity of aryloxy alkanol esters.
VIII.	Effect of the time of spraying upon germinating beans.

of the remaining experiments were pre-emergent. In general the plants were harvested two weeks after they were treated. The harvest data that was recorded was either the plant weight per plot in grams, or germination percentage. During the time an experiment was being conducted observational notes were taken. These notes recorded any unusual differences that would not be shown by harvest data. All treatments in each of the experiments were replicated and randomized.

The list of chemicals used along with their structural formulas are shown in Table 2. Also included in Table 2 is the abbreviated form of the respective chemicals. This abbreviated form will be used throughout the remainder of the thesis. The actual chemicals that were used for the individual experiment are presented in Table 3. Each chemical has been given a number to facilitate the description of the following experiments. For example, 2,4-D was called treatment 1 for the experiments that it was used in. Likewise 2,4-D-S was always called treatment 2. The particular chemicals used in any one experiment are placed in a horizontal row that corresponds with the different experiment numbers.

Experiment I.

Bean, corn and sunflower plants were used as test

Table 2. Structural Formulas of Chemicals Used

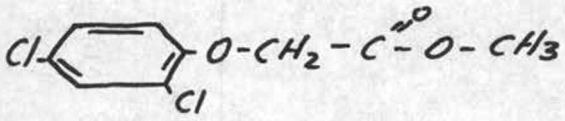
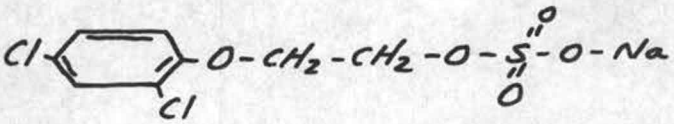
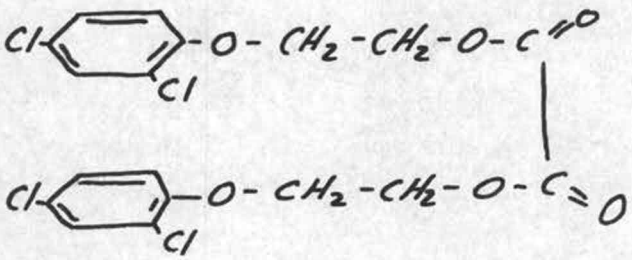
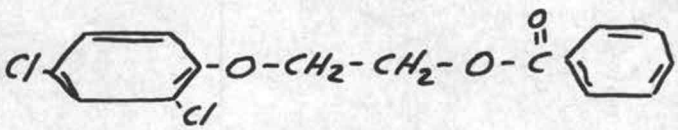
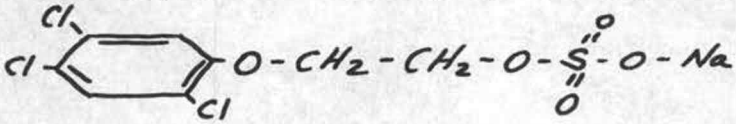
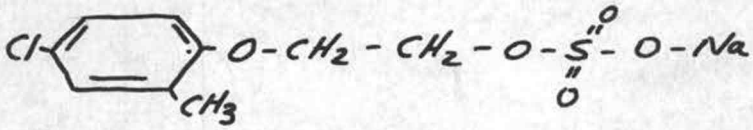
Name and Structure	Abbreviation
Methyl 2-(2,4-dichlorophenoxy)-acetate	2,4-D
	
Sodium 2-(2,4-dichlorophenoxy)ethyl sulfate	2,4-D-S
	
Bis(2-(2,4-dichlorophenoxy)-ethyl) oxalate	2,4-D-O
	
2-(2,4-dichlorophenoxy)ethyl benzoate	2,4-D-B
	
Sodium 2-(2,4,5-trichlorophenoxy)ethyl sulfate	2,4,5-T-S
	
Sodium 2-(2-methyl,4-chlorophenoxy)ethyl sulfate	M.C.P.S.
	

Table 3. Treatments Showing Chemicals and their Rates of Application

Experiments	Treatments					
	1	2	3	4	5	6
I			2,4-D-O 32#/A	2,4-D-B 32#/A	2,4,5-T-S 32#/A	M.C.P.S. 32#/A
II		2,4-D-S 4#/A				
III		2,4-D-S 4#/A				
IV	2,4-D 4#/A	2,4-D-S 4#/A	2,4-D-O 4#/A	2,4-D-B 4#/A	2,4,5-T-S 4#/A	M.C.P.S. 4#/A
V		2,4-D-S 4#/A	4		2,4,5-T-S 4#/A	M.C.P.S. 4#/A
VI		2,4-D-S 4#/A			2,4,5-T-S 4#/A	M.C.P.S. 4#/A
VII	2,4-D 4#/A	2,4-D-S 4#/A			2,4,5-T-S 4#/A	M.C.P.S. 4#/A
VIII					2,4,5-T-S 4#/A	

plants. The number of seeds per crop, per pot planted was five. Post emergent application of treatments 3, 4, 5, and 6 shown in Table 3 were made on two week old plants. The plants were harvested two weeks later.

Experiment II.

Beans were used as an indicator plant to test the activation of 2,4-D-S by a homogenate of beet leaves. This homogenate was prepared by grinding up 100 grams of fresh beet leaves in a Waring blender. A small amount of distilled water was added to facilitate grinding. The slurry was then added to a weighed amount of 2,4-D-S and brought up to volume. One aliquote of this solution was applied immediately to the foliage of bean plants. The remaining portion was incubated in a water bath at 25°C for six hours before applying. The harvest data consisted of visual observations only. 2,4-D-S without any beet homogenate added was applied to serve as a control.

Experiment III.

This experiment differed from Experiment II in that the homogenate was divided into 2 fractions and that different incubation periods were tested. The same homogenizing procedure was used but after grinding was completed the slurry was then filtered. Both the filtrate and precipitate were then placed into two different flasks. A weighed amount of 2,4-D-S was added and this solution was

brought up to volume with distilled water. The concentration of this solution gave a 4#/Acre rate application. Again a 2,4-D-S solution without any beet homogenate was prepared to serve as a control.

All three solutions were then placed in a constant temperature water bath at 25°C and agitated periodically. Aliquots were drawn from each of the solutions after 24 hours, 48 hours and 72 hours had elapsed, and were applied to the foliage of bean plants. Visual observations were taken periodically until a period of two weeks had elapsed after each respective treatment.

Experiment IV.

The three plant species used in this experiment were bean, corn and sunflower. The three crop plants were planted in different pots using five seeds per pot. The two replications of each crop were treated with 1, 2, 3, 4, 5, and 6 listed in Table 3. Treatment number 1 was included as a standard.

It was necessary to formulate 2,4-D-O and 2,4-D-B as emulsive concentrates since they were not water soluble. A combination of xylene and methyl-iosobutyl ketone was used to dissolve these chemicals. An emulsion was then made by adding an emulsifying agent and bringing the solution up to volume with distilled water. At that time it was felt necessary to also treat the

remaining chemicals in the same manner so that all chemicals would be applied under the same conditions.

The plots were harvested twenty-four days after treatment. Germination percentage was used as the criteria for comparing the relative effectiveness of this group of chemicals in suppressing the emergence of the seeds.

Immediately after harvest a seed bed was prepared in each pot. Care was taken not to transfer chemicals from one pot to another by using a common instrument for breaking the crust. This was conveniently done by using the labeling stake of each pot for a stirrer. The same planting schedule was repeated in the soil originally treated to determine if any chemical was still present. The second harvest took place thirty-eight days after treatment of the soil. Again the germination percentage was recorded as the harvest data. The experiment was discontinued after the second harvest.

Experiment V.

A total of sixty pots were filled with soil in this experiment. All sixty of these pots were treated with their respective treatments listed in Table 3 under Experiment V at the same time. Five different plantings were made at two week intervals. Radish seeds were used as the test plant to determine if activity

was present at the different dates. The plant material that was able to grow was harvested two weeks after planting and the total plant weight in grams per pot was recorded. All pots whether planted or not were uniformly watered.

At the end of the eight weeks period it was found necessary to continue planting in order to determine when certain chemicals would break down. A total of seven different plantings were made in this experiment.

Experiment VI.

The sources of twenty-two different soil types used in this experiment are listed in Table 4. The pH and percent organic matter of each soil is included. Percent organic matter was determined by the Walkley and Black's rapid titration method (28, p.223). The pH determinations were made with a Beckman pH instrument.

Six ounce paper cups measuring 3" in diameter by 3½" tall were used in this experiment. These cups were dipped in hot paraffin to increase the length of time they could be used.

Treatments 2, 5, and 6 listed in Table 3 were placed on eighteen of the twenty-two soils. There was not enough soil to place all three treatments on soils numbered 9, 10, 11 and 14 listed in Table 4. Only

Table 4. History and Properties of Soils Used in Experiment V.

No.	Soil Type	Source	pH	Organic Matter (%)
1.	Yahola fine sandy loam	Stillwater, Oklahoma	6.4	0.5
2.	Chehalis Sandy loam	Corvallis, Oregon	5.6	0.4
3.	Chehalis Sandy loam	Monroe, Oregon	5.8	1.3
4.	Chehalis Sandy loam	Corvallis, Oregon	5.3	1.7
5*	Sandy loam	New Brunswich, New Jersey	6.0	1.4
6*	Sandy loam	Santa Clara, Cal.	7.0	0.5
7*	Sandy loam	State College, Mississippi	5.2	0.6
8*	Palouse silt loam	Moscow, Idaho	5.8	1.7
9*	Palouse series (silt loam)	Pullman, Washington	5.8	2.3
10.	Groseclose silt loam	Blaksburg, Virginia	6.9	1.4
11.	Maury silt loam	Lexington, Kentucky	6.0	1.7
12*	Silt loam	State College, Mississippi	5.0	1.2
13.	Mattapex (USDA) silty clay loam	Norfolk, Virginia	6.8	0.7
14.	Terry silty clay loam	Fort Collins, Colorado	7.8	0.8

Table 4. (continued)

No.	Soil Type	Source	pH	Organic Matter (%)
15.	Webster loam	Ames, Iowa	6.4	3.3
16.	Cecil Clay loam	Clemson, South Carolina	5.3	0.5
17.	Decatur clay loam	Auburn, Alabama	5.6	1.8
18*	Clay loam	Columbus, Ohio	5.2	1.4
19.	Wapato clay	Corvallis, Oregon	6.1	3.3
20.	Melbourne clay	Corvallis, Oregon	6.4	1.5
21.	Muck Soil	Madison, Wisconsin	5.8	---
22.	Muck Soil	Layette, Indiana	4.6	---

* Soil type was not given by sender so that soil class was determined from Mechanical Analysis of soil.

treatment number five was placed on these four soils. This made a total of two hundred and forty different pots. Five different plantings were made in the various soils originally treated on October 7, 1952. At each planting date five bean seeds were placed in each pot. The harvest date of each planting was determined when beans in the majority of the control pots had produced the first trifoliate leaf. After each planting the experiment was completely randomized.

Differential watering was accomplished by modification of a wick feeding technique discribed by Elle (14, p.141). A twenty milliliter test tube was fastened to the side of each pot. A 1/8" wick was run from the bottom of each test tube over the side of the cup and down below the soil surface. Overhead watering was used initially to start each planting, but as indidual soils and treatments required more water they were supplemented by placing water in the test tubes. It became necessary to allow a few days to elapse between each harvest and planting date. Planting was initiated then as soon as the soils with certain treatments had dried out sufficiently.

Experiment VII.

Some of the soils previously treated in experiment four were used as the basis of this experiment. The

soils that were chosen after all activity had been lost were the ones where treatments 1, 2, 5 and 6 had been applied to. In addition soil that was steam sterilized at 15 pounds per square inch for four hours was also included. Treatments 1, 2, 5 and 6 listed in table 3 were than applied to each of the different groups of soils. Soil with no previous treatment was also given the same treatments as the other soils. This provided a means of comparing the effect of previous treatment.

Beans were planted in the various groups of soil just prior to treatment. Germination percentage was taken as an index to herbicidal activity. The experiment was concluded at the end of the second harvest.

Experiment VIII.

One hundred and twenty-six pots were planted in experiment eight with five bean seeds per pot. All pots were then watered to saturation to insure even germination. Treatment number five, listed in Table 3, was sprayed on four pots every six hours for five days. Two pots of beans not treated were also examined at each application time in order to note the stage of germination present. Bean seedling samples were washed and placed in formaldehyde for later examination. The experiment was harvested three weeks after planting.

EXPERIMENTAL RESULTS

Experiment I.

The results of applying four aryloxy alkanol esters at thirty-two pounds per acre on beans, corn and sunflower plants are shown in Table 5. M.C.P.S. killed all of the bean and sunflower plant material. Corn plants were not effected by the foliar applications of M.C.P.S. Treatments 2,4-D-O; 2,4-D-B and 2,4,5-T-S did not markedly reduce the plant growth of beans, corn, or sunflower plants when compared with the control.

Table 5. Plant tolerance to foliar application of four aryloxy alkanol esters as measured by average weight per plant

Treatment	Harvest Weight (grams)		
	Bean	Sunflower	Corn
2,4-D-O 32#/Acre	2.5	2.1	0.4
2,4-D-B 32#/Acre	2.7	1.2	0.5
M.C.P.S. 32#/Acre	0	0	0.9
2,4,5-T-S 32#/Acre	1.9	1.1	0.9
Check	2.7	1.4	0.7

Experiment II.

Table 6 contains the observation in connection with attemps to activate 2,4-D-S to its herbicidal form. The results from this experiment were all negative. There was no indication that 2,4-D-S had been activated to a herbicidal form.

Table 6. Activation of sodium 2-(2,4-dichlorophenoxy) ethyl sulfate by homogenate of beet leaves

Treatments	Observations
2,4-D-S	No response
2,4-D-S + Beet Homogenate applied immediately	" "
2,4-D-S + Beet Homogenate incubated six hours	" "
Control	Normal Plants

Experiment III.

The observations for Experiment III are recorded in Table 7. Wherever the incubation period was 72 hours, the growing tips of treated bean plants were retarded in comparison with the growth of the growing tips in the control plants. This observation was made for 2,4-D-S incubated in distilled water as well as for 2,4-D-S incubated with different fractions of beet homogenates.

An increased plant response was observed where 2,4-D-S was incubated for 72 hours with the filtrate of the beet leaf homogenate. Along with the growing tip being retarded, there was a bending of the internodal tissue.

Table 7. Activation of sodium 2-(2,4-dichlorophenoxy) ethyl sulfate by homogenate of beet leaves aided by incubation

Treatments	Observations
2,4-D-S + Beet Homogenate incubated @ 25°C for:	
24 hours	No response
48 hours	" "
72 hours	Growing tip retarded
2,4-D-S + Beet filtrate incubated @ 25°C for:	
24 hours	No response
48 hours	" "
72 hours	Growing tip retarded with slight internodal bending present
2,4-D-S + distilled water incubated @ 25°C for:	
24 hours	No response
48 hours	" "
72 hours	Growing tip retarded
Control	Normal plants

Experiment IV.

The harvest data for this experiment are shown in Table number 8. A major difference in plant tolerance stands out in this experiment. Corn appears to be much more

Table 8. The Effect of Some Aryloxy Alkanol Esters on Germination of Three Crop Plants

Treatments 4#/A	Per-cent Germination for Four Replications					
	Bean		Corn		Sunflower	
	Harvest 1	Harvest 2	Harvest 1	Harvest 2	Harvest 1	Harvest 2
2,4-D	0	40	60	70	0	100
2,4-D-S	10	40	70	95	0	90
2,4,5-T-S	0	0	80	40	0	15
M.C.P.S.	10	25	90	85	0	70
2,4-D-O	100	50	70	65	10	80
2,4-D-B	60	80	80	60	40	95
Check	70	75	90	95	90	100

tolerant to this group of chemicals than either beans or sunflower. This difference holds true for both harvest periods.

In the case of bean germination 2,4-D and 2,4,5-T-S gave complete suppression for the first harvest. At the same time 2,4-D-S and M.C.P.S. only allowed ten percent germination. The 2,4-D-B and 2,4-D-O were not very effective in checking bean germination. For the 2,4-D-B treatment there was sixty percent emergence and 100 percent emergence in the 2,4-D-O treatment.

For the second harvest of beans 2,4,5-T-S did not show any loss of activity. On the other hand 2,4-D; 2,4-D-S; and M.C.P.S. show a marked reduction in effectiveness compared with their relative effectiveness at the first harvest.

Sunflower germination was completely suppressed at the first harvest by 2,4-D; 2,4-D-S; 2,4,5-T-S; and M.C.P.S. The 2,4-D-O and 2,4-D-B chemicals were certainly more effective on sunflower germination at the first harvest than they were on bean germination. Only ten percent germination occurred for the 2,4-D-O treatment and forty percent emergence with the 2,4-D-B.

Another contrast between beans and sunflower is that considerably more germination occurred in the case of sunflower in the second harvest than in the corresponding

planting of beans. The only chemical that retained its herbicidal activity to the second harvest on sunflower was 2,4,5-T-S.

Experiment V.

In Table 9 are shown the results from radish plantings made in the respective treatments at two week intervals after treatment, up to eight weeks. All three chemical treatments were effective in prohibiting radish germination in the pots planted immediately after treatment.

Table 9. The residual activity of three aryloxy alkanol esters as shown by the average harvest weight in grams of radish grown on treated soil at different intervals following treatment

Treatment	Radish plant growth at different intervals				
	0 wks.	2 wks.	4 wks.	6 wks.	8 wks.
2,4-D-S 4#/A	0	3.1	1.7	3.5	3.1
2,4,5-T-S 4#/A	0	0	0	0	0
M.C.P.S. 4#/A	0	0	0.2	1.9	0.3
Control	3.9	2.6	1.5	3.3	3.1

Loss of activity occurred for 2,4-D-S before the second planting was made. M.C.P.S. showed signs of

losing activity at the third planting or after four weeks. Not all of the activity of M.C.P.S. was lost even after the fourth and fifth plantings were made.

In the case of 2,4,5-T-S, the chemical had not shown any loss of activity eight weeks after treatment. The experiment was continued longer than originally planned to determine just when M.C.P.S. and 2,4,5-T-S would break down. The data obtained by continuing this experiment for two more harvest periods is not shown in Table 8. For the planting made 109 days after treatment, M.C.P.S. was completely broken down. At that time 2,4,5-T-S showed a slight loss in activity. The final planting made 146 days after treatment showed that 2,4,5-T-S was completely broken down.

The relative residual length of these three chemicals are summarized in Graph 1.

Experiment VI.

The harvest data for this experimentare presented in Table 10. The plant weight in grams for each harvest date is the average for three replications. A summarization of the residual length of the three chemicals on different soils is found in Graph 2. The length of each bar represents the period of time that bean growth was suppressed by a particular chemical. In determining the residual length, a treatment was not considered

Graph 1. Summarization of the residual activity of three chemicals as shown by the percent growth of radish grown on treated soil at differnt intervals after initial treatment.

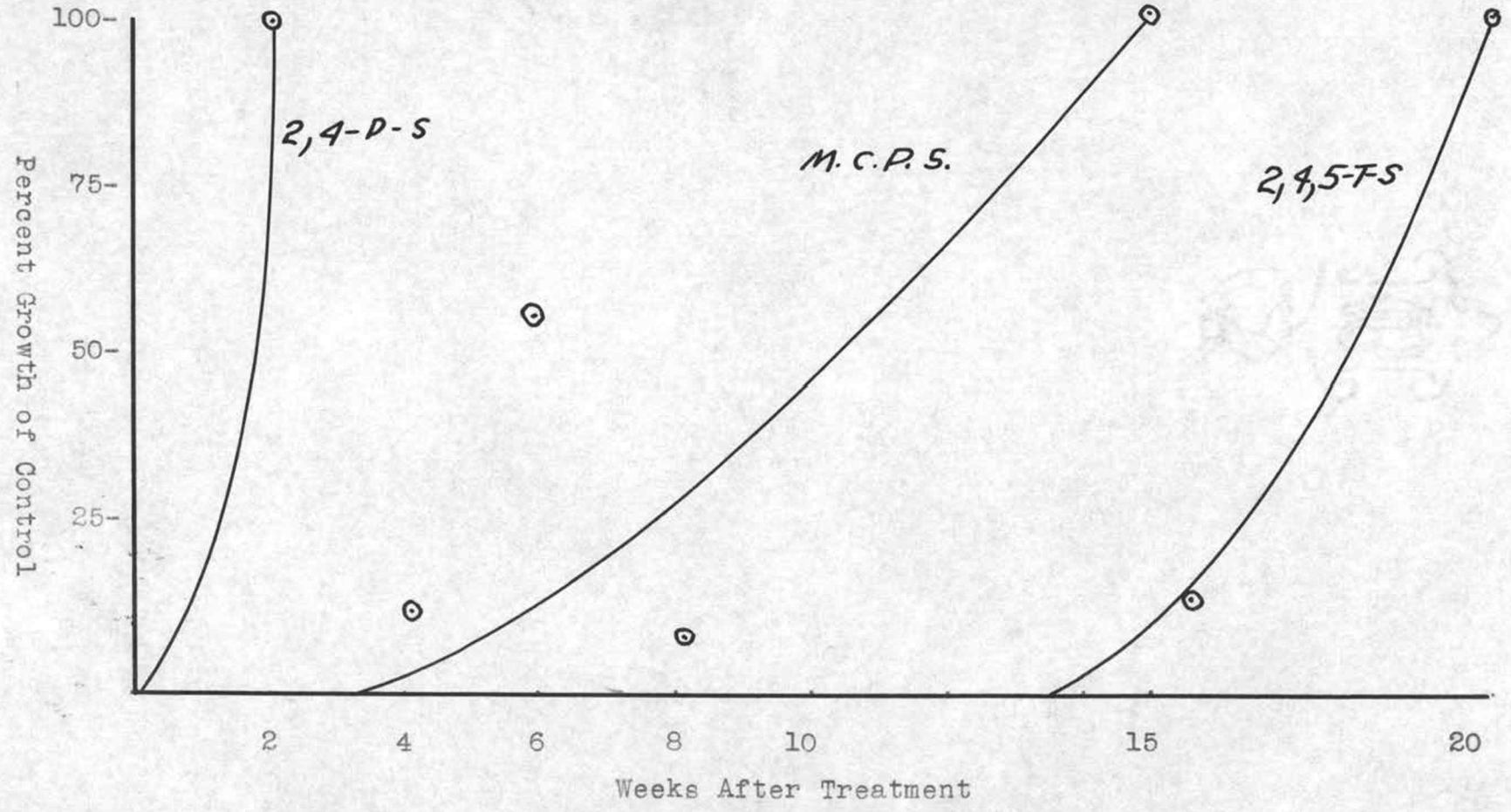


Table 10. The Effect of Soil Type on the Residual Activity of three Chemicals as Measured by the Average Harvest Weight in Grams for Three Replications

Treatments	Harvest Dates 10/28/52	11/18/52	12/12/52	1/9/53	2/25/53
1. Yahola fine sandy loam					
2,4-D-S	0	0.6	6.4	3.8	4.0
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0.6	2.7	4.2
Check	5.1	4.3	2.4	5.3	7.8
2. Chehalis sandy loam					
2,4-D-S	0	1.0	4.0	6.4	10.3
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	4.5	9.0
Check	3.6	5.5	6.8	4.0	10.6
3. Chehalis sandy loam					
2,4-D-S	0	0	4.3	4.7	7.1
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0.4	3.6	7.0
Check	4.3	2.5	1.6	3.1	8.8
4. Chehalis sandy loam					
2,4-D-S	0	2.5	5.2	5.2	10.7
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	1.2	5.3	10.7
Check	6.2	5.7	5.4	5.7	10.7
5. Sandy loam					
2,4-D-S	0	0	6.3	4.3	8.7
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0.1	1.9	6.0
Check	4.7	2.5	5.0	6.4	8.5

Table 10 (continued)

Treatments	Harvest Dates 10/28/52	11/18/52	12/12/52	1/9/53	2/25/53
6. Sandy loam					
2,4-D-S	0	0	0	2.4	7.6
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	1.9	5.4
Check	0.1	0	0.7	0.4	3.7
7. Sandy loam					
2,4-D-S	0	0.8	4.9	6.5	8.1
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	1.5	5.6
Check	6.9	2.2	6.8	6.5	5.1
8. Palouse silt loam					
2,4-D-S	0	0	5.7	7.4	9.4
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	1.9	4.4	7.2
Check	4.2	3.1	6.0	5.2	8.2
9. Palouse series (silt loam)					
2,4,5-T-S	0	0	0	0	0
Check	6.5	3.2	4.3	4.2	10.5
10. Groseclose silt loam					
2,4,5-T-S	0	0	0	0	0
Check	5.5	4.7	5.7	4.5	11.8
11. Maury silt loam					
2,4,5-T-S	0	0	0	0	0
Check	5.4	0.3	2.1	6.3	11.1

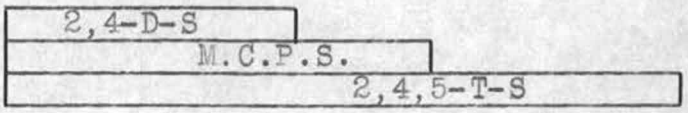
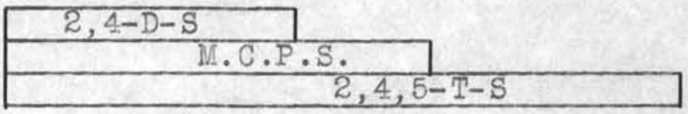
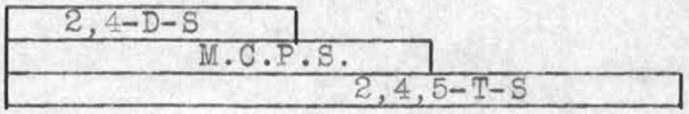
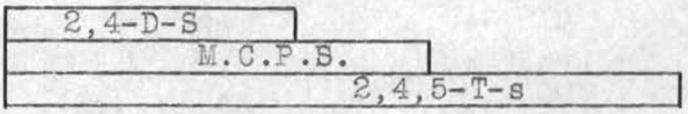
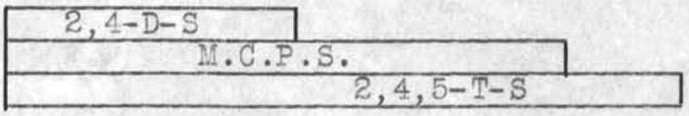
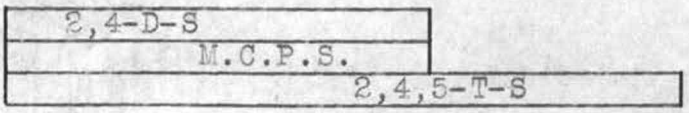
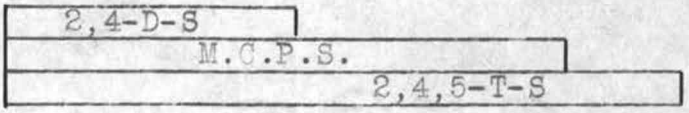
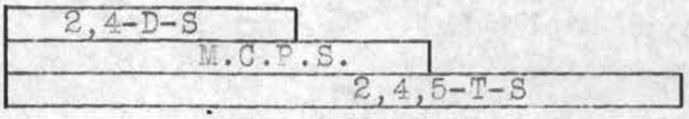
Table 10. (continued)

Treatments	Harvest Dates 10/28/52	11/18/52	12/12/52	1/9/53	2/25/53
12. Silt loam					
2,4-D-S	0	0	5.2	6.6	10.9
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	4.4	6.5
Check	7.3	6.6	5.9	5.2	9.5
13. Mattapex (USDA) silty clay loam					
2,4-D-S	0	1.3	5.5	6.0	8.9
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	2.2	8.7
Check	4.8	3.9	4.6	5.2	9.9
14. Terry silty clay loam					
2,4,5-T-S	0	0	0	0	0
Check	6.6	5.3	5.7	6.1	10.3
15. Webster loam					
2,4-D-S	0	5.5	4.3	5.4	10.3
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	2.1	7.2
Check	6.4	2.7	4.3	6.7	9.1
16. Cecil clay loam					
2,4-D-S	0	0	5.1	6.3	8.1
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	1.4	7.2
Check	3.4	2.4	3.6	5.1	7.8
17. Decatur clay loam					
2,4-D-S	0	0	6.3	5.4	8.0
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	1.5	4.9
Check	2.5	6.7	6.1	6.6	8.6

Table 10.(continued)

Treatments	Harvest Dates 10/28/52	11/18/52	12/12/52	1/9/53	2/2/
18. Clay loam					
2,4-D-S	0	0.5	6.6	6.9	8.5
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	2.1	4.9	8.8
Check	5.8	4.7	5.8	5.7	9.5
19. Wapato clay					
2,4-D-S	0	1.1	6.0	1.7	9.7
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0.1	0	1.0	5.8
Check	5.1	5.9	5.2	6.7	8.9
20. Melbourne clay					
2,4-D-S	0	0	5.4	4.9	8.4
2,4,5-T-S	0	0	0	0	0
M.C.P.S.	0	0	0	0.5	5.4
Check	4.1	7.1	4.8	6.1	10.6
21. Muck soil					
2,4-D-S	0	1.9	6.5	5.4	9.8
2,4,5-T-S	0.1	0	2.2	0.2	0
M.C.P.S.	0	0	0	0.6	3.1
Check	5.8	6.5	5.8	7.0	10.9
22. Muck soil					
2,4-D-S	1.5	0	5.9	6.1	9.9
2,4,5-T-S	3.1	0.3	1.0	0.5	0.2
M.C.P.S.	0.8	1.1	3.7	5.6	13.6
Check	6.2	5.5	6.0	5.0	10.0

Graph 2. Summary Chart of Residual Activity of Tnree Chemicals as shown by the Length of Suppression of Bean Growth

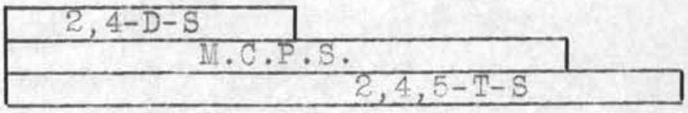
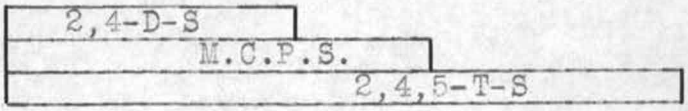
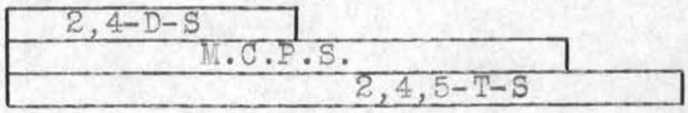
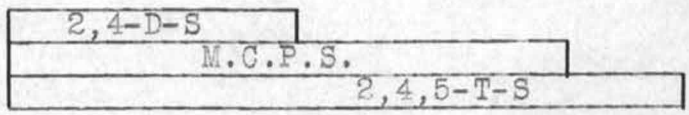
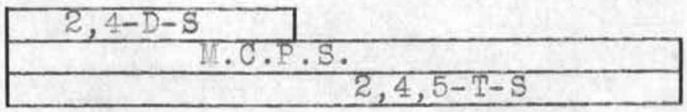
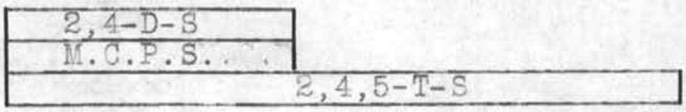
Soil Type	Harvest Periods 1 2 3 4 5
1. Yahola fine sandy loam	
2. Chehalis sandy loam	
3. Chehalis sandy loam	
4. Chehalis sandy loam	
5. Sandy loam	
6. Sandy loam	
7. Sandy loam	
8. Palouse silt loam	

Graph 2.(continued)

Soil Type	Harvest Periods 1	2	3	4	5
9* Palouse series (silt loam)	2,4,5-T-S				
10* Groseclose silt loam	2,4,5-T-S				
11* Maury silt loam	2,4,5-T-S				
12. Silt loam	2,4-D-s	M.C.P.S.	2,4,5-T-S		
13. Mattapex (USDA) silty clay loam	2,4-D-S	M.C.P.S.	2,4,5-T-S		
14* Terry silty clay loam	2,4,5-T-S				
15. Webster loam	2,4,D-S	M.C.P.S.	2,4,5-T-S		
16. Cecil clay loam	2,4-D-S	M.C.P.S.	2,4,5-T-S		

* Only enough soil for one chemical to be tested.

Graph 2. (continued)

Soil Type	Harvest Periods 1 2 2 3 5
17. Decatur clay loam	
18. Clay loam	
19. Wapato clay	
20. Melbourne clay	
21. Muck soil	
22. Muck soil	

active after plant growth was received that equalled fifty percent of the check.

All soils in Experiment VI were capable of activating each of the three chemicals to their respective herbicidal form. The only questionable activation is in the case of the muck soil #22. There did not appear to be a very high degree of chemical activity at the first harvest but each of the three chemicals were still able to reduce plant growth by fifty percent.

The relative order of residual activity of the three chemicals was as follows: 2,4-D-S had the shortest, M.C.P.S. was intermediate, and 2,4,5-T-S had the longest activity.

In practically every soil 2,4-D-S was inactivated by the second harvest date or 42 days after treatment. The only soils that showed any different rate of breakdown of 2,4-D-S was in the case of soil #6, sandy loam and #15, Webster loam. In the case of the Webster loam, soil #15, activity had disappeared at the end of the first harvest, only 21 days after treatment. On the other hand 2,4-D-S activity did not disappear from the sandy loam, soil #6 until the end of the third harvest or 66 days after treatment.

The length of activity for M.C.P.S. was fairly evenly divided between the third and fourth harvest

dates, sixty and ninety-four days after treatment respectively. A considerable difference in activity of M.C.P.S. was obtained with the two muck soils numbers 21 and 22. In the case of Muck soil #22 activity was lost by the end of the second harvest, forty-two days, while effective activity was maintained on muck soil #21 through the fifth harvest, 116 days.

Complete inhibition of growth was received with the treatment of 2,4,5-T-S throughout the five different plantings for the various soil types except in the case of the two muck soils. Even in the case of muck soils #21 and #22 better than fifty percent reduction in plant growth was received. It is to be noted that muck soil #22 was more effective in reducing the activity of 2,4,5-T-S than was muck soil #21.

Experiment VII.

The harvest data of two repeated plantings are shown in Table 11. In the left had column the current soil treatments are listed. The previous soil treatments are listed across the top of the table. For example, the first group shown is where the previous treatment was sterilization of the soil and then treated with 2,4-D; 2,4-D-S; 2,4,5-T-S; M.C.P.S. The results of these treatments are shown under the columns marked Harvest I and Harvest II.

Table 11. The Effect of Previous soil Treatment Upon the Activity of Aryloxy Alkanol Esters as Measured by the Weight of Bean Growth in Grams

Current Soil Treatment	Previous Soil Treatments											
	Sterilized		Non-treated		2,4-D		2,4-D-S		2,4,5-T-S		M.C.P.S.	
	Harvest		Harvest		Harvest		Harvest		Harvest		Harvest	
	1	2	1	2	1	2	1	2	1	2	1	2
2,4-D	0	1.3	0	3.5	0	2.8	0	2.4	0	1.1	0	0.8
2,4-D-S	0	0.5	0	6.1	0.3	1.5	0	6.8	0	0.3	0	3.2
2,4,5-T-S	0	0	0	0	0	0	0	0	0	0	1.1	0
M.C.P.S.	0	0	0	0.7	0	1.1	0	1.9	0	0.1	0	0.8
Check	6.6	4.5	8.5	3.0	7.4	2.4	7.3	3.2	7.7	5.7	7.9	2.7

Previous treatment of the soil did not appear to affect the activity of the four chemicals at the first harvest date. Even sterilized soil, under the conditions present, did not prevent activity of the chemicals. There appeared to be a slight loss in activity in one replication of 2,4-D-S treatment on previously treated 2,4-D soil. Growth was also made in one replication of a 2,4,5-T-S treatment on soil previously treated with M.C.P.S.

The harvest of the second planting in the same treatments show some wide differences. Perhaps the most noticeable result is that none of the previous treatments reduced the activity of 2,4,5-T-S in the second harvest. In all cases 2,4,5-T-S suppressed the growth of planted beans.

Previously sterilized soil apparently reduced the rate of inactivation of the four chemical treatments as shown by comparing the activity of these chemicals on previously non-treated soil. The effect of previously treated 2,4,5-T-S soil is similar to the effect of sterilized soils.

The previously treated 2,4-D soil seemed to reduce the rate of breakdown of 2,4-D-S. On the other hand, previously treated 2,4-D-S soil did not alter the rate of breakdown of the four chemicals at the second harvest

date. Previously treated M.C.P.S. soils apparently reduced the breakdown of the chemical treatments, except in the case of 2,4-D-S. Here the rate of breakdown of 2,4-D-S is comparable to previously non-treated soils.

Experiment VIII.

The final harvest data for Experiment 8 are presented in Table 12. The effectiveness of the chemical is decreasing as the germinating seedling increases in age. In the treatments where spraying occurred within thirty hours after planting, there were no visible signs of germination. For the treatments that occurred thirty-six and forty-two hours after planting, there were a few plants that were able to emerge in each plot but died a few days after emerging.

The treatment made forty-eight hours after planting was the earliest date that any plants were able to emerge and remain alive. Here only one plant was able to grow in replication 4 and attain a weight of 2.0 grams. The amount of plant growth that was obtained from each treatment after forty-eight hours is very eratic.

In each plot, however, there were plants emerging from the soil but, in many cases theydied a few days later. The amount of plant growth that is shown in the varied treatments and replications is the plant material

Table 12. Effect of the Time of Spraying of 2,4,5-T-S Upon Germinating Beans as Measured by Average Plant Weight

Time of spraying after planting (hours)		Harvest Weight (gms.)
0		0
6		0
12		0
18		0
24	(1 day)	0
30		0
36		0
42		0
48	(2 days)	0.5*
54		0.9
60		1.4
66		0
72	(3 days)	2.0
78		1.7
84		3.3
90		1.7
96	(4 days)	2.4
102		1.4
108		4.4
114		1.6
120	(5 days)	2.9
Check		13.8

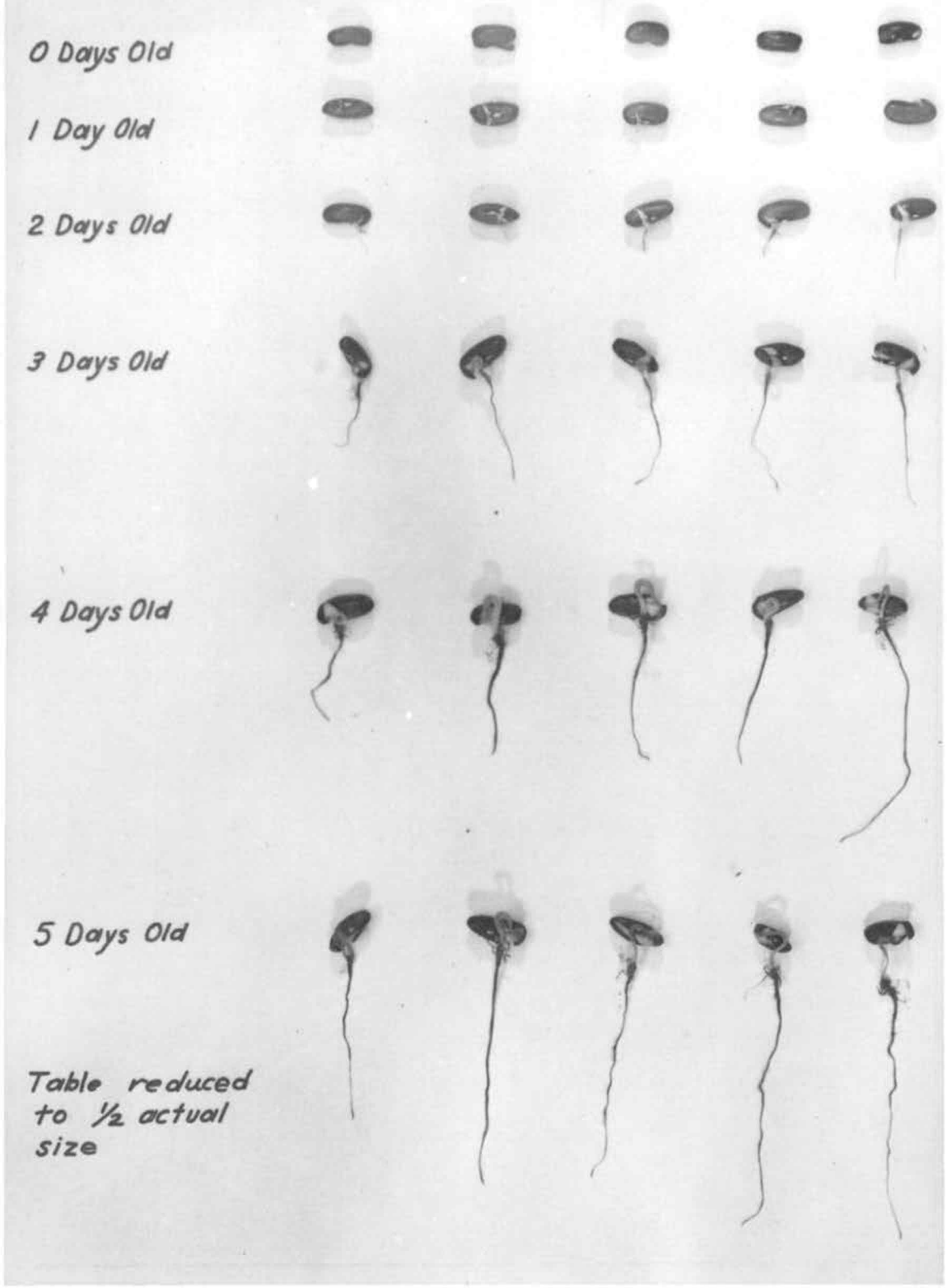
* Average harvest weight for four replications.

that was alive at the time of harvest.

The germinating bean seedlings became more tolerant to 2,4,5-T-S as the interval between planting and spraying was increased. The chemical is still highly effective in reducing plant growth even when applied 120 hours or five days after planting. The growth rate of beans is displayed in Table 13. Germinating bean seeds are shown at one day intervals after planting. It is to be noted that the bean seedlings were the most tolerant when the bean root length was the greatest.

TABLE 13

GROWTH RATE OF BEAN SEEDS



DISCUSSION

It appears that 2,4-D-S does not cause any epinastic response when sprayed upon the foliage of plants, but when it comes into contact with the soil it displays the herbicidal properties of 2,4-D. This phenomenon appears to hold true for the other aryloxy alkanol esters, except for M.C.P.S. When 2,4-D-O; 2,4-D-B; M.C.P.S. and 2,4,5-T-S were applied to the foliage of bean, corn, and sunflower plants, only M.C.P.S. caused a marked reduction in plant growth. In the study where the chemicals were applied to the foliage of plants it is to be emphasized that excessive rates were used. Any inherent toxicity in the chemicals would, consequently, be magnified by the high rate of application. The response caused by M.C.P.S. on plant foliage could have been due to two other factors besides a natural herbicidal property. The sample of M.C.P.S. used was not a purified sample. It could have contained a contaminate, such as 2-methyl-4-chlorophenoxy ethanol that could have killed the bean and sunflower plants. No precautions were taken to prevent the chemicals from entering the soil when the plant foliage was sprayed. Either one or both of these conditions could have taken place and accounted for the toxicity of the treatment. Further investigations utilizing

a purified sample and eliminating any possible contact with the soil would establish if M.C.P.S. per se is active on plant foliage.

The aryloxy alkanol esters were compared in their ability to suppress seed germination of three plant species. There appeared to be wide differences in the ability of the chemicals to suppress germination. The greatest reduction in germination was caused by 2,4,5-T-S and M.C.P.S. On the other hand, 2,4-D-O and 2,4-D-B gave the poorest suppression of germination. The spacial structure of the latter two molecules may be such that they are not attacked easily by micro-organisms. Work conducted by Vlitos (32, p.137) indicated that micro-organisms were not a factor in the activity of 2,4-D-O. At the same time microbial activity did enhance the toxicity of 2,4-D-B.

Corn plants expressed an unusually high tolerance towards all of the chemicals in the germinating stage. Selectivity of the growth regulators between monocots and dicots is largely attributed to differences in plant morphology. In the case of germinating seedlings, however, it appears that this difference would be more likely attributed to an actual difference in plant metabolism.

It is important to note that the three species of plants used are considered large seed crops. King and

Lambrech indicated that the small seeded crops were more susceptible to the aryloxy alkanol esters (20, p.197). This probably stems from the fact that the root systems of the large seeded crops are developed much faster due to the high amount of food reserves present. The growth rate of beans in Table 13 emphasizes just how fast the root system of bean plants can develop. In only five days the bean plants were able to produce a tap root that was four to five inches long.

The importance of the rapid root growth of beans was illustrated when 2,4,5-T-S was applied at different intervals of time after planting. The increasing tolerance of the bean plants to 2,4,5-T-S appeared to be related to the rapidly increasing root system. As the herbicide is concentrated in the top layer of soil, the plant would absorb smaller concentrations of 2,4,5-T-S as the root system grew deeper. The safe use of these chemicals in the field will be influenced by the maturity of the economic crop grown.

There are a few plants that appear to be mildly susceptible to foliar application of 2,4-D-S. For example, beet leaves are severely distorted when sprayed with this chemical. It was felt that the beet leaves contained an enzyme system capable of activating the 2,4-D-S molecule. The results received in this study would certainly not

indicate any activity of this sort. It is possible that the enzyme system was made non-functional when the organization of the cell was disrupted by homogenizing.

Another means of attacking the problem would be to spray growing beet plants and make the homogenate after the herbicidal symptoms develop. The homogenate could then be transferred to a sensitive plant such as beans to test if the active component on the beet leaves was 2,4-D-S per se or an activated form.

The length of time that a herbicide will remain active in the soil is an important factor. There appears to be wide differences in the residual activity of 2,4-D-S, M.C.P.S. and 2,4,5-T-S. It is hard to explain why there should be such wide differences because of the similarity of the three molecules. 2,4,5-T-S differs from 2,4,-D-S in that it only has one more chlorine atom in the five position on the benzene ring. Yet the residual length of 2,4,5-T-S is increased from two weeks to twenty weeks. Soil perfusion studies made by Audus (3, p.177) with the parent acids 2,4-D; M.C.P.A.; and 2,4,5-T showed the same relative order of breakdown as found in this study of the respective derivatives. Audus concluded that the residual activity of the parent acids could be interpreted in terms of the different rates of proliferation or adaption of the relevant bacteria.

It would be expected that different soil types might alter the rate of breakdown of the aryloxy alkanol esters. Actually, though, the different soil types in this study did not appear to effect the relative activities of 2,4-D-S, M.C.P.S. and 2,4,5-T-S. The compound to be consistently broken down first was 2,4-D-S while 2,4,5-T-S was still active when the experiment was concluded after 116 days.

This consistent order of breakdown of the three chemicals on different soil types differs from the residual activity studies made on 2,4-D in the soil. It is possible that the size of the plots were too small in this study to show the differences that may be present. Another improvement in the study of soil effect would be to use an indicator plant that could be planted and harvested more often than bean plants. This would measure the differences between soil types more precisely.

Several different investigators have shown that the rate of breakdown of 2,4-D in the soil could be altered, depending upon the treatment (8, p.321) and (24, p.415). Lime was shown to increase the length of activity, while organic matter or previously treated 2,4-D soil was shown to shorten the length of activity (21, p.524). Previous treatment of the soil also appears to influence the breakdown of some of the aryloxy alkanol esters. One

point that stood out was that none of the treatments were able to shorten the activity of 2,4,5-T-S. On the other hand, 2,4,5-T-S treated soil appeared to increase the residual activity of 2,4-D and 2,4-D-S. Inhibition of growth was certainly not expected on the sterilized soils. Other experiments have shown that sterilization prohibited the activation of these chemicals. Aseptic precautions were not taken so it would have been very easy for the soils to become inoculated with bacteria capable of activating the chemicals.

SUMMARY AND CONCLUSIONS

A series of greenhouse experiments were conducted to determine some of the factors that influence the effectiveness of a class of herbicides designated as aryloxy alkanol esters. Studies were also made of the relative toxicity between different members of this group.

The following factors were found to be present in this greenhouse study:

1. Among the chemicals examined M.C.P.S. was the only aryloxy alkanol ester that showed any herbicidal activity on the foliage of bean and sunflower plants. The remainder of the group did not cause any damage to the foliage of the plants used.

2. All attempts to change 2,4-D-S to an active form by incubation with beet leaf homogenate were unsuccessful.

3. 2,4,5-T-S caused the greatest suppression of beans and sunflower germination out of six different pre-emergent treatments.

4. Corn showed considerable tolerance to the pre-emergent application of the aryloxy alkanol esters.

5. There were large differences in the residual activity of 2,4-D-S, M.C.P.S. and 2,4,5-T-S under greenhouse conditions. 2,4-D-S was broken down within two weeks after application to the soil while M.C.P.S. was active up to fifteen weeks. Radish plants were not able to germinate in 2,4,5-T-S treated soil until twenty-one weeks after treatment.

6. The bacteria responsible for activating 2,4-D-S, M.C.P.S., and 2,4,5-T-S to a toxic compound were present in twenty-two soil types tested.

7. Only minor differences occurred in the rate of breakdown of 2,4-D-S, M.C.P.S. and 2,4,5-T-S on twenty-two different soil types under greenhouse conditions. In all cases 2,4,5-T-S remained active until the experiment was concluded after 116 days.

8. The effect of different soil types will have to be made under field conditions before any conclusions can be made.

9. The activity of the aryloxy alkanol esters in the soil appears to be affected by the treatments that previously occurred in that soil.

10. The time of spraying 2,4,5-T-S in relation to the

germination stage of bean was found to be an important factor in the toxicity of this herbicide. The rapid root growth of beans was postulated to be the reason for the rapid increased tolerance of bean plants to 2,4,5-T-S.

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