



AgEcon SEARCH
RESEARCH IN AGRICULTURAL & APPLIED ECONOMICS

The World's Largest Open Access Agricultural & Applied Economics Digital Library

This document is discoverable and free to researchers across the globe due to the work of AgEcon Search.

Help ensure our sustainability.

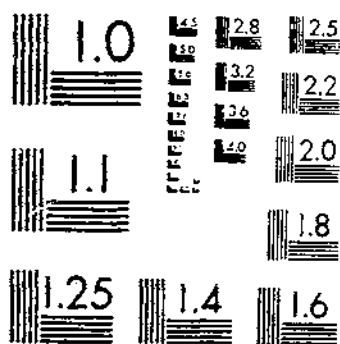
Give to AgEcon Search

AgEcon Search
<http://ageconsearch.umn.edu>
aesearch@umn.edu

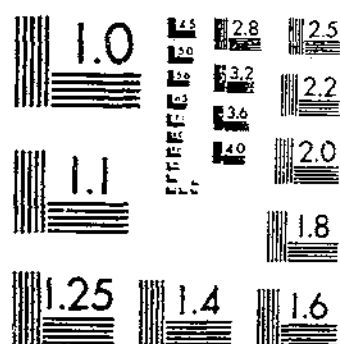
*Papers downloaded from **AgEcon Search** may be used for non-commercial purposes and personal study only. No other use, including posting to another Internet site, is permitted without permission from the copyright owner (not AgEcon Search), or as allowed under the provisions of Fair Use, U.S. Copyright Act, Title 17 U.S.C.*

IB 1476 (1973) USDA TECHNICAL BULLETINS UPDATA
RESPONSES AND RESIDUES IN SUGARBEETS, SOYBEANS, AND CORN IRRIGATED WITH
BRUNS, V. F., CARLILE, B. L., KELLEY, A. D. 1 OF 1

START



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

R

5-

630

USC-1

#1

Responses and Residues in Sugarbeets, Soybeans, and Corn Irrigated With 2,4-D or Silvex-Treated Water

Technical Bulletin No. 1476

DEC 20 1973

DEPT. OF AGRICULTURE

Technical Bulletin No. 1476

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

JAN 21 1974

This publication reports research involving pesticides. It does not contain recommendations for their use, nor does it imply that the uses discussed here have been registered. All uses of pesticides must be registered by appropriate State and/or Federal agencies before they can be recommended.

CAUTION: Pesticides can be injurious to humans, domestic animals, desirable plants, and fish or other wildlife. Use all pesticides selectively, properly, and carefully. Follow recommended practices for the disposal of surplus pesticides and pesticide containers.



Use Pesticides Safely
FOLLOW THE LABEL

U.S. DEPARTMENT OF AGRICULTURE

Responses and Residues in Sugarbeets, Soybeans, and Corn Irrigated With 2,4-D or Silvex-Treated Water

Technical Bulletin No. 1476

1476-1477-1

1476-1477

Agricultural Research Service
UNITED STATES DEPARTMENT OF AGRICULTURE

In Cooperation With
College of Agriculture
Washington State University
and Under Contract With
Pacific Northwest Laboratories
Battelle Memorial Institute

Washington, D.C.

Issued December 1973

For sale by the Superintendent of Documents, U.S. Government Printing Office,
Washington, D.C. 20402 - Price, 35 cents.
Stock Number 0100-02885

JAN 11 1977

PREFACE

The use of pesticides in or near agricultural waters is being scrutinized carefully by a number of State and Federal agencies for possible environmental hazards. The investigations reported in this bulletin provide information on the possible hazards and the margins of safety in irrigating certain farm crops with water that contains 2,4-D or silvex. Although these investigations were conducted in 1967 at the Irrigated Agriculture Research and Extension Center, Prosser, Wash., the results are still pertinent and applicable to many similarly irrigated areas.

CONTENTS

| | Page |
|------------------------------|------|
| Introduction | 1 |
| Investigations | 2 |
| Analytical methods | 2 |
| Laboratory experiments | 5 |
| Field experiments | 10 |
| Summary | 28 |
| Literature cited | 30 |

Trade names are used in this publication solely for the purpose of providing specific information. Mention of a trade name does not constitute a guarantee or warranty of the product by the U.S. Department of Agriculture or an endorsement by the Department over other products not mentioned.

Responses and Residues in Sugarbeets, Soybeans, and Corn Irrigated With 2,4-D or Silvex-Treated Water

By V. F. Bruns, *research agronomist, Irrigated Agriculture Research and Extension Center, Western Region, Agricultural Research Service, Prosser, Wash.*; B. L. Carlile,¹ *formerly senior research scientist, Pacific Northwest Laboratories, Battelle Memorial Institute, Richland, Wash.*; and A. D. Kelley, *agricultural research technician, Irrigated Agriculture Research and Extension Center, Western Region, ARS, Prosser, Wash.*

INTRODUCTION

The control of weeds is a major task in the operation and maintenance of drainage and irrigation systems (23, 25).² Research and development have shown that (2,4-dichlorophenoxy)acetic acid (2,4-D) is generally one of the most effective herbicides for control of broad-leaved weeds that inhabit the banks of such systems (5, 13). Certain formulations of 2,4-D also effectively control several emerged aquatic species such as cattail, waterhyacinth, and waterlily, which may grow at the waterline or directly in water (9, 10, 22, 24). Similarly, 2-(2,4,5-trichlorophenoxy)propionic acid (silvex) effectively controls certain broad-leaved bank weeds, woody plants, and aquatic species, and may be particularly useful on species resistant to 2,4-D and related compounds (8, 9, 27). Silvex and 2,4-D, at normal herbicidal dosages, do not usually injure grasses that are desirable on ditchbanks.

The spraying of weedy plants in or along irrigation and drainage systems, and in or around lakes and reservoirs, without introducing some of the material into the water is extremely difficult, if not impossible. The irrigation of crops with water from conveyance systems or impoundments subjected to such spraying operations poses two major questions. First, what effect will the herbicide in water have on crops? Secondly, will crops, particularly the edible parts, contain unacceptable residues of the herbicide?

¹ Now with the Department of Soil Science, North Carolina State University, Raleigh.

² Italic numbers in parentheses refer to Literature Cited, p. 30.

Several field experiments determined the effects of 2,4-D in irrigation water on certain crops (2, 3, 4, 6). The treatments were applied by furrow irrigation only. In these experiments, the crops tolerated rather high concentrations of 2,4-D. The crops were not analyzed for 2,4-D residues; nor was silvex included in the previous field experiments.

The objectives of these studies were primarily twofold. The first was to gain information on the response of an annual broad-leaved crop, a grass, and a root crop to 2,4-D and silvex in water applied in the field by furrow and sprinkler irrigation. The second was to determine if significant quantities of herbicide residues remained in the crops at normal harvesttime. A considerable amount of preliminary laboratory work was necessary to gain the second objective.

INVESTIGATIONS

The investigations reported herein were conducted jointly with the Pacific Northwest Laboratories, Battelle Memorial Institute, Richland, Wash., under a project entitled, "Degradation and Depletion of Herbicides in Irrigation Waters and Accumulation of Residues in Crops Irrigated with Treated Water." The project was financed by the U.S. Department of Agriculture, Agricultural Research Service contract 12-100-8863(34). The fieldwork was conducted at the Irrigated Agriculture Research and Extension Center, Prosser, Wash., whereas the analytical and other laboratory work was done primarily at the Pacific Northwest Laboratories, Richland, Wash.

Analytical Methods

The basic analytical method used in these investigations involved the conversion of 2,4-D and silvex forms to their respective methyl esters by esterification with boron trifluoride in methanol (12, 17). This derivative can be analyzed with precision and high sensitivity on the gas chromatograph with an electron capture detector.

2,4-D and Silvex in Water

After a water sample was thoroughly mixed, a 500-milliliter (ml) aliquot was taken for analysis. The sample was acidified to pH 2.0 with phosphoric acid and extracted with multiple extractions of chloroform as outlined by Burchfield and Johnson (7). After the chloroform was evaporated, the residue was dissolved immediately in 5 ml of hexane and transferred to a 10-ml volumetric flask with three hexane washings (1 ml each). The hexane was evaporated to near dryness. The residue was then esterified and analyzed by electron capture gas chromatography.

2,4-D and Silvex in Soil

After a soil sample was screened and thoroughly mixed, a 100-g subsample was taken for analysis. The moist soil was transferred to a 1-l Erlenmeyer flask together with enough distilled water to form a slurry. At the same time, a 20-g sample of the soil was oven-dried to determine the moisture content. The slurry was acidified to a pH of 1 to 2 with phosphoric acid, and 100 ml of diethyl ether were added. The mixture was shaken vigorously for 20 min on a mechanical shaker, the liquid phases were decanted into a separatory funnel, and the two layers were allowed to separate. The aqueous layer was re-mixed with the soil slurry, and the solvent phase was collected in a graduated cylinder. Extraction of the soil slurry with diethyl ether (50 ml) was repeated two or more times. All glassware was rinsed three times with diethyl ether (10 ml each), and the rinsings were added to the initial extracts. All extracts were then combined and filtered through a glass filter that contained 25 g of granular, anhydrous sodium sulfate. The solvent was evaporated by a rotary vacuum in a warm water bath (40° C) to the point of dryness. The residue was dissolved immediately in 5 ml of hexane and quantitatively transferred to a 10-ml volumetric flask with three washings of hexane (1 ml each). The hexane was evaporated to dryness under slight vacuum, and the residue was then esterified and analyzed.

2,4-D and Silvex in Plant Material

Basically, the procedure used for isolating 2,4-D and silvex from plant material involved primary extractions with acidified ethanol solution and several additional extractions with diethyl ether as described by Burchfield and Johnson (7). The procedure was modified to include a basic hydrolysis to improve the recovery of 2,4-D and silvex.

Each plant sample was chopped and mixed thoroughly before a 100-g subsample (fresh weight) was taken for analysis. At the same time, a 10-g subsample was oven-dried for moisture determination. The 100-g sample was blended with 300 ml of distilled water, 200 ml of diethyl ether, 40 ml of 10-percent ethanolic sulfuric acid, and 10 g of sodium chloride in a blender at high speed for 3 to 4 min. The homogenate was then transferred quantitatively to large centrifuge bottles and centrifuged at 1,500 revolutions per minute for 5 min. The supernatant was decanted through a glass funnel that contained a glass wool plug into a round-bottom flask. The addition of 50 ml of diethyl ether to the plant residue and the suspending, mixing, centrifuging, and decanting were repeated three times. The

combined extracts were evaporated on a rotary vacuum evaporator to remove the solvent. The aqueous extract was brought to a pH of 10 by the addition of sodium hydroxide and heated over a steam bath for 4 hours. The solution was then acidified with sulfuric acid to pH 1 and placed in a separatory funnel for liquid-liquid extraction. The acidified extract was extracted three times with 100 ml of diethyl ether, the solvent was evaporated to near dryness by rotary vacuum evaporation, and the residue was dissolved in benzene. The residue was then subjected to additional cleanup by column chromatography.

Extract Cleanup

Two procedures of column chromatography were used in the cleanup of extracts from plant material. The initial procedure involved the one-stage separation of methyl esters of 2,4-D and silvex on 200- by 15-ml columns of Florisil. For best results, the Florisil was partly deactivated by adding water (5 percent) and equilibrating before use. The plant extracts were transferred to the top of the column and washed with 100 ml of benzene, and the effluent was discarded. The esters of 2,4-D and silvex were eluted with 20-percent diethyl ether in 100 ml of benzene, and the eluate was carefully evaporated to standard volume for analysis.

A subsequent procedure that utilized a one-step separation of acids of 2,4-D and silvex on 100- by 15-ml columns of basic alumina was adapted to remove a large quantity of interfering plant materials. The concentrated sample extract dissolved in benzene (not esterified) was transferred onto the column. The column was washed with a series of chloroform-ether washes. Acidic phenoxy acids remained on the basic column during this procedure. They were eluted, after the column was dried, by passing 100 ml of a 1-percent solution of sodium bicarbonate through the column. The eluate was acidified to pH 1 with phosphoric acid and extracted three times with 50 ml of diethyl ether. After evaporating the ether to dryness, the herbicide residue was esterified and analyzed by gas chromatography.

Esterification Procedure

Extracts from the water, soil, and plant samples were esterified by the boron trifluoride (BF_3)-methanol procedure, whereby 6 ml of 12.5-percent BF_3 -methanol solution were added to each sample and heated until BF_3 fumes were released (17). The methyl esters of 2,4-D and silvex were then extracted into 2 ml of hexane, and aliquots were taken from the hexane layer for gas chromatographic analysis.

Gas Chromatography Analyses

Samples were analyzed on a Beckman Model GC-4 gas chromatograph equipped with an electron-capture detector, direct on-column injection, and programmed temperature and carrier-gas-differential flow controllers. The chromatograph glass columns were 6 feet long and one quarter of an inch in diameter and packed with 3-percent Beckman Lopol on 100/120 mesh Chromosorb G. Column and detector temperatures were 170° and 220° C, respectively. The carrier gas was helium with a column ionizing flow rate of 20 ml per minute and a column discharge flow rate of 190 ml per minute. The column was purged with carbon dioxide at the rate of 12 ml per minute. A 1- to 5-microliter sample was injected into the chromatograph. Isothermal column temperature was used in the analyses, except for certain plant extracts when temperature programming was utilized to expel extraneous material from the column and reduce time of analysis.

Detector-response curves for the chromatograph were prepared from standard solutions of the pure methyl ester of each acid and compared with the unknowns to determine the amount of 2,4-D or silvex in the samples. The response was recorded by a disk integrater which measured peak areas as a function of the amount injected into the chromatograph.

Laboratory Experiments

Methods and Materials

The stability and recovery of 2,4-D and silvex in and from water, soil, and plant samples were investigated in replicated laboratory experiments before the field studies. Water samples from irrigation canals were collected and thoroughly mixed in a 5-gal carboy. One liter subsamples were spiked with 0, 0.02, 0.1, and 5.0 parts per million (ppm) of the alkanolamine salts of 2,4-D and the propylene glycol butyl ether (PGBE) ester of silvex and stored in the dark at room temperature (23° C) and under refrigeration (5°). After 1 hour, 7 days, and 14 days in storage, duplicate 100-ml aliquots of each subsample were analyzed by procedures described under "Analytical Methods."

Procedures for extracting 2,4-D and silvex from soil were tested on samples of Warden very fine sandy loam that were collected from noncultivated land on the Irrigated Agriculture Research and Extension Center, Prosser, Wash. The samples were spiked with known quantities of the alkanolamine salts of 2,4-D and the PGBE ester of silvex, and recovery percentages were determined after extraction by the procedures described under "Analytical Methods."

The stability of 2,4-D and silvex in soil samples stored at low temperature was measured by treating soil samples with known amounts of the herbicides, storing the samples at -10°C for 6 weeks, and then analyzing for 2,4-D and silvex.

Extraction procedures for plant material were evaluated by collecting samples of foliage and roots of field-grown corn and sugarbeets and spraying them with the alkanolamine salts of 2,4-D and the PGBE ester of silvex at 0.1, 1.0, and 10.0 ppm. Foliage and roots of soybeans grown in nutrient solutions in growth chambers were also sprayed with 2,4-D and silvex at 2 and 20 ppm. The samples were macerated in a blender and analyzed in accordance with the procedures described previously.

In another series of experiments, 4-week-old soybeans grown in nutrient solutions in a growth chamber were treated by adding the 2,4-D or silvex to the nutrient solution of some plants and by placing a drop of herbicide solution at the base of leaves of others. After 2 days, the plants were harvested and analyzed for herbicide residues.

Results

Extraction from water.—The procedure for extraction and analysis was rather efficient. Recoveries 1 hour after spiking the water samples with 2,4-D or silvex ranged from 89 to 95 and from 94 to 100 percent, respectively (table 1).

TABLE 1.—*Recovery of 2,4-D and silvex from canal water in laboratory experiments*

| Herbicide and concentration (ppm) | Recovery— | | | | |
|--|--|----------------------|---------------------|----------------------|---------------------|
| | After 1 hour at 23°C | After 7 days at— | | After 14 days at— | |
| | | 23°C | 5°C | 23°C | 5°C |
| | Percent | Percent | Percent | Percent | Percent |
| 2,4-D: | | | | | |
| 0.02 ----- | 95 | 81 | 97 | 74 | 91 |
| .10 ----- | 93 | 85 | 95 | 72 | 96 |
| 5.00 ----- | 89 | 87 | 88 | 83 | 92 |
| Silvex: | | | | | |
| 0.02 ----- | 100 | 97 | 99 | 97 | 98 |
| .10 ----- | 94 | 95 | 97 | 91 | 94 |
| 5.00 ----- | 96 | 97 | 95 | 96 | 98 |

The 2,4-D levels in the water samples stored at 23°C declined gradually after 1 and 2 weeks in storage (table 1). The percentage

loss tended to decrease with increase in initial concentration. No significant loss was apparent after 14 days of storage at 5°.

Little, if any, silvex was lost from water samples stored for 14 days (table 1). However, the PGBE ester of silvex was hydrolyzed completely to the acid form after 7 days of storage at either 5° or 23° C. Therefore, all samples from later field experiments were handled to insure recovery of both the ester and acid forms of silvex.

Extraction from soil.—The use of the diethyl ether procedure for the extraction of 2,4-D and silvex from soil provided adequate recoveries with minimum interference from extraneous organic material. Recoveries of 2,4-D and silvex averaged 95 ± 4 and 94 ± 3 percent, respectively. Unlike other procedures that were tested, the diethyl ether procedure required no additional cleanup of extracts from the soil samples.

The recovery of 2,4-D and silvex from moist soil stored at -10° C for 6 weeks ranged from 89 to 94 percent. Thus, the losses of chemical from the soil under the conditions of this study were insignificant.

Extraction from plant material.—The average recovery of 2,4-D and silvex added to foliage and roots of corn, sugarbeets, and soybeans ranged from 82 to 97 and from 86 to 96 percent, respectively (table 2). Low recoveries, primarily from green foliage samples, were attributed to interference in the gas chromatograph from extraneous organic material. Recovery percentages were increased by cleaning up the samples on Florisil in chromatography columns.

No 2,4-D or silvex was detected in the foliage of soybeans grown in solutions that contained 0.01 and 0.1 ppm of these compounds; however, measurable quantities (>0.005 ppm) were present in the roots. No symptoms of injury were evident after 2 weeks of growth in the treated solutions.

Soybeans were injured slightly within 24 hours after 20 micrograms of silvex were placed at the base of the leaves. Injury from similar applications of 2,4-D was barely noticeable. Recovery of 2,4-D from foliage and roots 2 days after treatment varied between 70 and 81 and between 8 and 11 percent, respectively (table 3). Similarly, recovery of silvex from foliage and roots varied between 74 and 85 and between 5 and 10 percent, respectively. A small amount of 2,4-D was found in the solution which nourished the plants treated with 20 micrograms of the herbicide. This suggests exudation of 2,4-D from the roots into the solution. No silvex was detected in the nutrient solutions.

Discussion

Inasmuch as the water-soluble amine salt of 2,4-D and the PGBE ester of silvex were used in these studies, the existence of various forms of the herbicides (salts, esters, and ester-hydrolysis products)

TABLE 2.—*Recovery of 2,4-D and silvex added to plant material in the laboratory*

| Plant part | Concentration added | Recovery ¹ | |
|-----------------------|---------------------|-----------------------|---------|
| | | 2,4-D | Silvex |
| | Ppm | Percent | Percent |
| Corn foliage ----- | 0.1 | 86 | 87 |
| Do ----- | 1.0 | 83 | 89 |
| Do ----- | 10.0 | 88 | 91 |
| Corn roots ----- | .1 | 88 | 94 |
| Do ----- | 1.0 | 90 | 94 |
| Do ----- | 10.0 | 94 | 94 |
| Beet foliage ----- | .1 | 85 | 91 |
| Do ----- | 1.0 | 86 | 96 |
| Do ----- | 10.0 | 90 | 80 |
| Beet roots ----- | .1 | 88 | 90 |
| Do ----- | 1.0 | 89 | 90 |
| Do ----- | 10.0 | 97 | 88 |
| Soybean foliage ----- | 2.0 | 82 | 86 |
| Do ----- | 20.0 | 85 | 87 |
| Soybean roots ----- | 2.0 | 87 | 94 |
| Do ----- | 20.0 | 87 | 94 |

¹ Averages of 3 analyses of the treated plant material.

TABLE 3.—*Recovery of 2,4-D and silvex applied in drops to the base of leaves of soybeans grown in nutrient solution*

| | Micrograms of herbicide applied per plant | Material analyzed | Recovery 2 days after treatment ¹ | |
|----------|---|-------------------|--|---------|
| | | | 2,4-D | Silvex |
| | | | Percent | Percent |
| 2 ----- | | Foliage | 72 | 76 |
| Do ----- | | Roots | 10 | 7 |
| Do ----- | | Solution | 0 | 0 |
| 20 ----- | | Foliage | 78 | 82 |
| Do ----- | | Roots | 9 | 7 |
| Do ----- | | Solution | 2 | 0 |

¹ Averages of 3 analyses.

in the collected samples was possible. Over 50 percent of the PGBE ester of silvex was hydrolyzed to the acid form in less than 48 hours in water and 72 hours in moist soil. Because the conversion of the ester form to the acid was rapid, all sample extracts of 2,4-D and silvex were esterified to the methyl ester by BF_3 -methanol before the analyses. When the acid forms of 2,4-D and silvex were present in water and soil samples, good extraction efficiency with organic solvents could be achieved only if the samples were acidified before extraction. Acidification suppressed the formation of the carboxylate ion which cannot be extracted into organic solvents.

The extraction of anionic 2,4-D or silvex from all plant material cannot always be accomplished successfully by acidification. These compounds can form conjugates with natural metabolites in plant material and cannot be extracted with organic solvents unless subjected to some hydrolytic procedure. Recoveries were significantly higher when the raw extract was hydrolyzed in basic solution over a steam bath for several hours. After the hydrolysis, the aqueous solution was acidified again, and the sample subjected to extraction with an organic solvent which extracted the free acids of 2,4-D and silvex.

Generally, the quality of the reagents and solvents used in the procedures was nanograde. Reagent grade solvents were redistilled from a glass still before use. Each solvent was examined by electron-capture gas chromatography to determine its suitability. Glass bottles were used to dispense the solvents, and contact with polyethylene was avoided. All glassware, except volumetric flasks and pipettes, was heat-treated overnight at 300°C to eliminate organic contaminants. Objectionable impurities in the anhydrous sodium sulfate and cleanup adsorbants were removed by heating the solids at 400° for 8 hours.

Gas chromatographic analyses of the methyl esters of silvex and 2,4-D was a convenient and sensitive method if proper attention was given to cleanliness of apparatus and reagents and to handling of sample extracts. The procedures adapted for cleanup of extracts of plant material in these studies did not eliminate all organic contaminants and some column degradation and detector fouling occurred. However, since large numbers of samples were involved, the preparation of new columns and the occasional cleansing of the detector were more expedient than the use of more rigorous cleanup procedures.

The practical lower limits for measurement of 2,4-D and silvex in water, soil, and plants depended primarily on the sensitivity of the instrument, the size of the sample, and the amount of extraneous material that remained in the sample. Because the absolute lower

limit of detection (2:1 signal to noise ratio) is dependent upon the sample and analytical conditions. the practical lower limit of measurement is difficult to define. For most water samples, the detection limits were approximately 0.01 parts per billion (ppb) of silvex and 0.04 ppb of 2,4-D when 500-ml samples were used. For soil samples, the detection limits of the procedure were approximately 0.5 ppb of silvex and 2 ppb of 2,4-D when 100-g soil samples were used.

The analyses of plant material were somewhat more variable because the background peaks for each plant and plant part were different. At the beginning of the study, a detection level of 5 ppb was selected as a goal for minimal measurement of 2,4-D and silvex in plant material, and the extraction and cleanup procedures were carried out accordingly.

Studies showed that significant losses of 2,4-D from treated samples of irrigation water may occur. Studies by previous investigators on the fate of herbicides in water and soil have shown that 2,4-D may be rapidly degraded by biological action when specific micro-organisms are present (1, 11, 18). Because 2,4-D has been used as a herbicide in the Yakima Valley for many years, it is likely that micro-organisms that are adapted to the decomposition of 2,4-D inhabit the water systems of the region.

Field Experiments

Methods and Materials

The experiments were conducted on Warden very fine sandy loam. The soil contained approximately 1.5 percent organic matter and was 3 to 5 feet deep over bedrock.

On February 16, 1967, the experimental site was fertilized, disked, plowed, and packed. Early in April, winter wheat (Gaines) was seeded in the areas which were not occupied by plots or alleyways.

Before and after the chemical treatments, all plots were cultivated or handweeded and irrigated as necessary to maintain optimum weed control and adequate soil moisture for all crops. Injury symptoms after treatments were noted and recorded. Crops were harvested after maturity (dwarf corn was harvested September 14 to 15; soybeans, September 20; sweet corn, September 27 to October 3; and sugarbeets, October 9 to 13) and yields were determined.

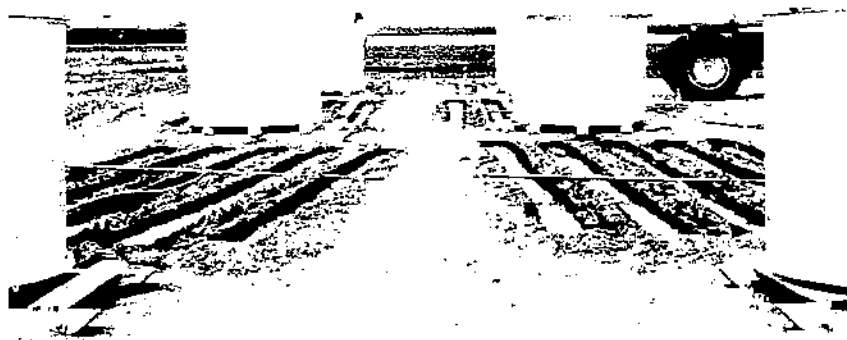
All soil and green plant samples collected for residue analyses were sealed in polyethylene bags and frozen immediately with dry ice in the field. The samples were then stored at -10°C until they were analyzed. Water samples were collected in glass bottles and kept in a refrigerator until they were analyzed.

Furrow irrigation.—Twenty-one plots, each 10 by 12 feet, were laid out on contour with a zero grade within each of three blocks. Each block was divided into three replicates or subblocks. Alleyways between plots and between subblocks were about 2 feet wide (fig. 1).

On April 6, four rows of sugarbeets (U & I Commercial Hybrid Monogerm), 12 feet long and 2 feet apart, were planted in each plot in one block. On May 23, soybeans (Merit) and sweet corn (Ferry Morris Cross) were planted likewise in the other two blocks. After the seedlings were well established, the sugarbeets, soybeans, and sweet corn were thinned to average one plant per 10, 4, and 9 inches of row, respectively.

On August 7 to 9, 2,4-D and silvex were applied to plots at random within each subblock at rates of 0, 0.22, 1.10, or 5.51 parts per million by weight (ppmw) (hereafter referred to as the specified concentrations) in the equivalent of 2 acre-inches of water (0.1, 0.5, or 2.5 lb per acre). The sweet corn was in the early-milk stage, the sugarbeets were 3 to 5 inches in diameter, and the soybeans were 65-percent podded. Six 600-gal tanks on sleds and equipped with valves, hoses, and boom attachments were used to apply the irrigation water and chemicals (fig. 1). The technique is described in previous publications (2, 3, 5). A given tank was used to apply one chemical at one rate only. Each application was made in approximately 1¼ hours.

Measured quantities of 2,4-D or silvex were thoroughly mixed with the appropriate quantity of irrigation water in the 600-gal tanks. The flow of treated water from the tanks was regulated by valves to maintain proper levels of water in the irrigation furrows. The irrigation furrows were dammed at each end of the plots to provide



PN-3374

FIGURE 1.—The arrangement of furrow-irrigated plots and the application of herbicide-treated water by means of tanks, valves, hoses, and boom attachments.

uniform application and wetting and to eliminate effluent during irrigation.

During the furrow-irrigation treatments, the air temperatures ranged from 72° to 92° F. and the wind velocities varied from nearly 0 to 10 miles per hour (mph).

Water samples were collected for analyses from outlets in the boom 15 and 45 minutes after treatments were started. Soil samples were also taken for analyses from a depth of 0 to 6 inches in the crop rows 1 and 7 days after treatment. Samples of roots, foliage, and seeds or seed parts were collected 7 days after treatment and during harvest from each plot, and the replicate samples were composited for residue determinations.

Sprinkler irrigation.—Twenty-one subplots, each 10 by 12 ft. were laid out in semicircular plots within each of three blocks (fig. 2). One subplot of each crop (sugarbeets, corn, and soybeans) was included in each semicircle. Each of the three blocks or replicates contained seven semicircular plots.

On April 5, four rows of sugarbeets were planted at random on one subplot within each semicircle. Similarly, soybeans and dwarf corn (PeeWee B-N.D. 56) were planted on May 23 and June 2, respectively. By June 21, the sugarbeets, soybeans, and dwarf corn



PN-3375

FIGURE 2.—Three rectangular subplots of test crops within a 30-foot semicircular area (main plot) for making sprinkler irrigation treatments.

were thinned to average one plant per 10, 4, and 6 inches of row, respectively.

From August 11 to 17, 2,4-D and silvex were applied randomly at rates of 0.02, 0.22, and 2.21 ppmw (hereafter referred to as the specified concentrations) in the equivalent of 2 acre-inches of water (0.01, 0.1, and 1.0 lb per acre). Each treatment was applied to the three replicated plots simultaneously through three oscillating, half-circle, sprinkler heads at the end of 100-foot, $\frac{3}{4}$ -inch, plastic hoses (fig. 3). The opposite ends of the hoses were connected to a $\frac{3}{4}$ -inch cross at the end of an assembly for mixing and for dispersing the water and 2,4-D or silvex in correct proportions.

The prescribed quantities of 2,4-D or silvex were mixed with 48 gal of water in a 53-gal pressure cylinder (fig. 4). Pressure in the cylinder was maintained at 45 pounds per square inch (psi) with nitrogen gas. The solution in the cylinder was introduced through a flowmeter and into the mixing and dispersing assembly by means of copper tubing. Pressure in the irrigation water supply line and the assembly was maintained at 35 psi. A flowmeter was used to measure the equivalent of 2 acre-inches of irrigation water per treatment.

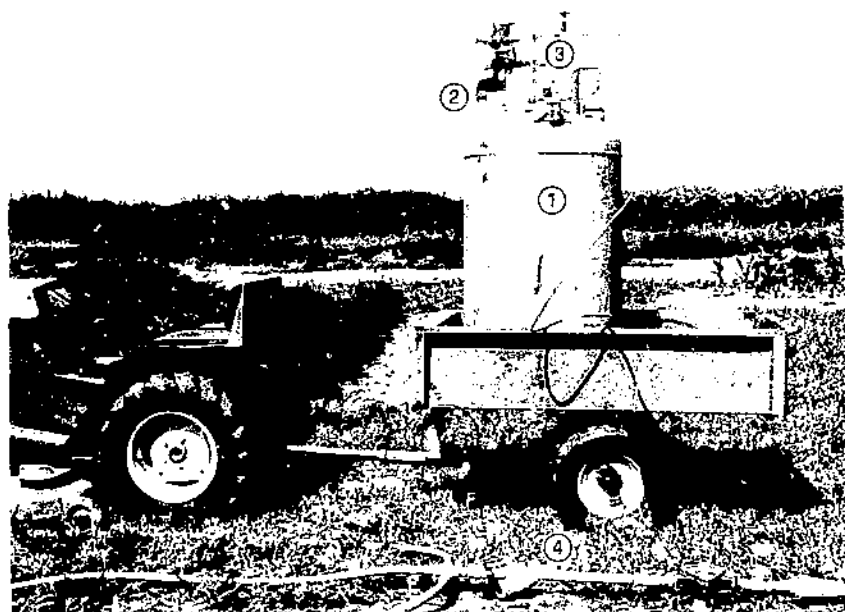
Each treatment was made in 8 hours. The treatments were made between 1:00 a.m. and 9:00 a.m. to avoid interference from strong breezes or winds which frequently occur during midmorning and afternoon in this area. Adjacent subplots were completely covered with pliable sheeting during treatments as an additional safeguard against contamination by drifting particles.

Sugarbeets were 3 to 5 inches in diameter, the short-season dwarf



PN-3376

FIGURE 3.—An oscillating, half-circle sprinkler head attached to the end of a plastic hose and placed at the radial point of the semicircle during a sprinkler irrigation treatment.



PN-3377

FIGURE 4.—Equipment for treating sprinkler-irrigated plots.

1. 53-gallon cylinder. 2. Nitrogen gas cylinder. 3. Meter. 4. Mixing and dispersing assembly; A, Irrigation water supply line; B, flowmeter; C, treated water intake; D, mixer and strainer; E, $\frac{3}{4}$ -inch cross with 3 hoses attached; and F, sampling spout.

corn was in the late-milk stage, and soybeans were 65-percent podded at the time of treatment.

Maximum daytime air temperatures from August 11 to 17 exceeded 100° F. However, air temperatures during the actual treatments ranged from 54° to 71°. Wind velocities varied from approximately 0 to 7 mph.

Water samples for analyses were taken from the mixing and dispersing assembly near the beginning, middle, and end of each treatment. Water samples were also collected from a catch tray or funnel (18 inches in diameter and 12 inches above ground) during treatment to determine losses of the chemicals through volatilization during sprinkler irrigation (fig. 5). Soil samples were taken from a depth of 0 to 6 inches in the crop rows at the end of the treatment and 2 days later to determine herbicidal infiltration. Samples of roots, foliage, and seed or seed parts were collected from each plot 2 days after treatment and during harvest, and the replicate samples were composited for residue analysis.

One-half of each sample of sugarbeet roots collected at harvest-

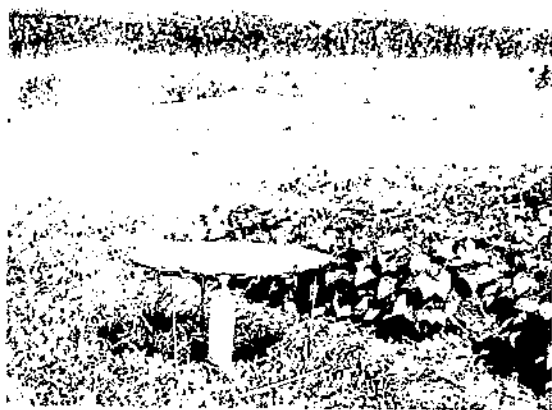
time for residue analysis was used to determine sugar content.³ The analyses for sugar content were made in quintuplet.

Results and Discussion

Analyses of water and soil from furrow-irrigated plots.—In general, the average 2,4-D or silvex concentrations in the water samples as determined by analyses (hereafter called the analytic concentrations) were 94 to 99 percent of the specified concentrations (table 4). The analytic concentrations of 2,4-D in samples from the first applications (sugarbeet plots) at the lowest concentration (0.22 ppmw) were an exception and averaged only 32 percent of the specified concentration. However, such concentrations increased with subsequent treatments until an average of 95 percent of the specified concentration was reached. The 600-gal tanks had been coated with aluminum paint (varnish base) several months before the treatments. The tank and pipe surfaces apparently sorbed appreciable quantities of the chemical, particularly during the early treatments. Various phenoxy compounds reportedly react with or are sorbed by certain paints and metals (15). Such sorption could occur at the high rates and at the low rate of application and be masked by the differences in sorption: concentration ratios. Some sorption of chemicals by sediment in the irrigation water undoubtedly occurred also.

Losses of 2,4-D and silvex from the soil within 7 days after furrow

³ The sugar content of sugarbeet samples was determined by the U-I Sugar Company, Toppenish, Wash.



PN-3378

FIGURE 5.—A plastic catch tray or funnel (18 inches in diameter and 12 inches above ground) used to sample water during sprinkler irrigation treatments.

irrigation with treated water were not significant. Therefore, the data from the analyses of soil samples collected 1 and 7 days after treatment were averaged (table 5).

No 2,4-D was detected in the soil samples from sugarbeet and soybean plots treated at the lowest concentration (0.22 ppmw) and only 0.003 ppmw was found in the samples from the corn plots. On plots treated at 1.10 or 5.51 ppmw, the concentrations of silvex in the soil samples (average 0.17 and 0.97 ppmw) were higher than those of 2,4-D (average 0.11 and 0.48 ppmw). Some of the 2,4-D and silvex undoubtedly was sorbed by organic matter in the furrows and surface soil during treatment.

Analyses of water and soil from sprinkler-irrigated plots.—The analytic concentrations of 2,4-D and silvex in the sprinkler system were 91 to 96 percent of the specified concentrations (table 6). Apparently no 2,4-D (an amine salt form) was lost to the atmosphere during sprinkler irrigation as determined by analyses of water samples from the tray. However, 5 to 10 percent of the silvex (an ester form) was lost to the atmosphere during the sprinkler irrigation treatments.

Losses of 2,4-D and silvex from the soil within 2 days after

TABLE 4.—Concentrations of 2,4-D and silvex in water applied by furrow irrigation

| Crop | Chemical concentration | | | | |
|-----------------|------------------------|-----------------------|----------|--------------------------------|---------|
| | Specified | Analytic ¹ | | Analytic relative to specified | |
| | | 2,4-D | Silvex | 2,4-D | Silvex |
| | | | | | |
| | Ppmw | Ppmw | Ppmw | Percent | Percent |
| Untreated check | 0 | <0.00004 | <0.00001 | -- | -- |
| Sweet corn | .22 | .21 | .21 | 95 | 95 |
| Soybeans | .22 | .17 | .21 | 77 | 95 |
| Sugarbeets | .22 | .07 | .21 | 32 | 95 |
| Sweet corn | 1.10 | 1.07 | 1.03 | 97 | 94 |
| Soybeans | 1.10 | 1.08 | 1.03 | 98 | 94 |
| Sugarbeets | 1.10 | 1.04 | 1.04 | 95 | 95 |
| Sweet corn | 5.51 | 5.24 | 5.44 | 95 | 99 |
| Soybeans | 5.51 | 5.19 | 5.33 | 94 | 97 |
| Sugarbeets | 5.51 | 5.24 | 5.38 | 95 | 98 |

¹ The lowest reliable limits of detection for 2,4-D and silvex were 0.00004 and 0.00001 ppm, respectively. The values were corrected for extraction efficiency and are presented as averages of 2 samples from each of three replicate plots.

sprinkler-irrigation with treated water were not significant. Thus, the data from the analyses of soil samples taken at the end of each treatment and 2 days later were averaged (table 5).

No 2,4-D and only about 0.001 ppmw of silvex were detected in soil samples from plots treated at 0.02 ppmw. The average concentrations of 2,4-D and silvex in the soil samples from plots treated at 0.22 or 2.21 ppmw were approximately 0.02 ppmw for the 0.22 treatments and 0.20 ppmw for the 2.21 treatments. Plant foliage obviously intercepted appreciable quantities of the chemicals during the sprinkler treatments.

CROP RESPONSE TO 2,4-D IN FURROW IRRIGATION WATER

Sugarbeets.—Within 2 weeks after treatment, sugarbeets on plots treated with 2,4-D at 5.51 ppmw (2.5 lb per acre) were wilted and drooped. Some petioles were curved downward abnormally. Injury symptoms were similar but milder on plots treated at 1.10 ppmw (0.5 lb per acre). Growth on plots treated at 0.22 ppmw (0.1 lb per acre) appeared normal.

TABLE 5.—Concentrations of 2,4-D and silvex in soil within 7 days after furrow irrigation and 2 days after sprinkler irrigation with treated water

| Irrigation method and chemical | Concentration ¹ | 2,4-D or silvex concentration ² | | | | |
|-----------------------------------|----------------------------|--|------------------|---------------|---------|-------|
| | | Sugarbeet plots | Soybean plots | Corn plots | Average | |
| Furrow | | | | | | |
| irrigation : | Ppmw | Lbs per acre | Ppmw | Ppmw | Ppmw | Ppmw |
| 2,4-D ----- | 0.22 | 0.1 | <0.002 | <0.002 | 0.003 | 0.001 |
| Do ----- | 1.10 | .5 | .10 | .14 | .09 | .11 |
| Do ----- | 1.10 | .5 | .19 | .19 | .12 | .17 |
| Silvex ----- | .02 | .1 | .027 | .035 | .026 | .029 |
| Do ----- | 5.51 | 2.5 | 1.01 | .98 | .91 | .97 |
| Do ----- | 5.51 | 2.5 | .42 | .62 | .40 | .48 |
| Sprinkler | | | | | | |
| irrigation : | | | | | | |
| 2,4-D ----- | .02 | .01 | <.002 | <.002 | <.002 | <.002 |
| Do ----- | .22 | .1 | .01 | .01 | .03 | .02 |
| Do ----- | 2.21 | 1.0 | .22 | .12 | .28 | .21 |
| Silvex ----- | .02 | .01 | .002 | .001 | .001 | .001 |
| Do ----- | .22 | .1 | .02 | .01 | .03 | .02 |
| Do ----- | 2.21 | 1.0 | .09 | .21 | .30 | .20 |

¹ See tables 4 and 6 for analytical concentrations.

² Dry soil basis. The lowest reliable limits of detection for 2,4-D and silvex were 0.002 and 0.0005 ppm, respectively.

TABLE 6.—Concentrations of 2,4-D and silvex in water applied by sprinkler irrigation

| Chemical | Specified concentration | Concentrations of 2,4-D or silvex | | | |
|------------------|-------------------------|-----------------------------------|----------|--------------------------------|---------|
| | | Analytic ¹ | | Analytic relative to specified | |
| | | Pipe | Tray | Pipe | Tray |
| | | Lb | | | |
| | Ppmw | per acre | Ppmw | Ppmw | Percent |
| Untreated check. | 0 | 0 | <0.00004 | <0.00004 | — |
| 2,4-D | .02 | .01 | .021 | .021 | 95 |
| Do | .22 | .1 | .20 | .20 | 91 |
| Do | 2.21 | 1.0 | 2.12 | 2.15 | 96 |
| Untreated check. | 0 | 0 | <.00001 | <.00001 | — |
| Silvex | .02 | .01 | .020 | .018 | 91 |
| Do | .22 | .1 | .21 | .19 | 95 |
| Do | 2.21 | 1.0 | 2.10 | 2.00 | 95 |

¹ The lowest reliable limits of detection for 2,4-D and silvex were 0.00004 and 0.00001 ppmw, respectively. The values were corrected for extraction efficiency and are presented as averages of 8 samplings during each treatment.

Three weeks after treatment, many of the sugarbeet petioles on plots treated at 5.51 ppmw were twisted and discolored (dark). Many leaves were chlorotic or necrotic and somewhat malformed. Small or younger plants were more severely injured than the large or older plants. Again, injury symptoms were similar but milder on plots treated at 1.10 ppmw. Some symptoms of curly top virus were present and interfered considerably with the evaluations. No definite symptoms of herbicidal injury could be distinguished on plots treated at 0.22 ppmw.

None of the 2,4-D treatments decreased the yields of sugarbeet tops or roots (table 7). Some of the beets on plots treated at 5.51 ppmw possessed abnormal masses of fine roots which were injured or dead at harvesttime.

Soybeans.—Ten days after treatment, the lower leaves on the soybeans were yellowing. Such yellowing was more prevalent on treated than on untreated plots, and it increased in prevalence as the treatment rate increased.

Two weeks after treatment at 5.51 ppmw, the soybean growth was stunted or suppressed. Such stunting or suppression was less obvious on plots treated at 1.10 ppmw. Plants on plots treated at 0.22 ppmw appeared normal.

TABLE 7.—*Yields of sugarbeets, soybeans, and corn after furrow irrigation with 2,4-D or silvex-treated water*

| Chemical | Specified concentration ¹ | Yields per acre ² | | | | | |
|-----------------|--------------------------------------|------------------------------|----------|----------|---------|---------|----------------------|
| | | Sugarbeets | | Soybeans | Corn | | |
| | | Tops | Roots | | Fodder | Shelled | |
| | Ppmw | Lb per acre | Tons | Tons | Bushels | Tons | Bushels ³ |
| Untreated check | 0 | 0 | 19.1 bc | 36.1 a | 49.5 bc | 9.9 a | 203.3 a |
| 2,4-D | .22 | .1 | 20.9 c | 36.7 a | 56.6 c | 10.1 a | 187.1 a |
| Do | 1.10 | .5 | 16.1 abc | 31.9 a | 55.0 c | 10.4 a | 187.8 a |
| Do | 5.51 | 2.5 | 14.6 ab | 31.4 a | 44.7 ab | 8.7 a | 197.5 a |
| Silvex | .22 | .1 | 21.2 c | 36.6 a | 54.5 c | 10.6 a | 190.5 a |
| Do | 1.10 | .5 | 17.0 abc | 34.9 a | 51.9 bc | 10.5 a | 193.4 a |
| Do | 5.51 | 2.5 | 13.5 a | 33.3 a | 37.5 a | 11.1 a | 197.1 a |

¹ See tables 4 and 6 for analytic concentrations.² Any 2 figures in the same column that are not followed by the same letter are significantly different at the 5-percent level of probability, except those under sugarbeet tops, which are significantly different at the 10-percent level, as determined by Duncan's multiple-range test.³ Computed on basis of 15.5-percent moisture.

After 3 weeks, an average of 1, 7, 5, and 21 percent of the soybean leaves were chlorotic or necrotic on plots treated with 2,4-D at 0, 0.22, 1.10, or 5.51 ppmw, respectively. At the same time, much of the terminal leaf growth of soybeans throughout the test area was malformed. Specimens were collected and cultured for pathological tests in the greenhouse.⁴ The tests indicated that the terminal tissues were malformed by a virus known as the tomato big bud strain of aster yellows rather than by the chemical treatment.

The 2,4-D treatments did not decrease the yield of soybean seed (table 7). However, the quality of the seed was somewhat reduced by the high concentration of 5.51 ppmw.

Corn.—Within 1 to 2 weeks after treatment, some of the lower-most leaves of corn were wilted or shrivelled on all plots. However, such wilting or shriveling was more pronounced on plots treated at the highest concentration (5.51 ppmw). As the season advanced, any differences in desiccation were masked by natural maturity. None of the treatments decreased the yield of fodder or shelled corn (table 7).

⁴ P. E. Thomas, plant pathologist, Agricultural Research Service, U.S. Department of Agriculture, conducted the pathological tests.

CROP RESPONSE TO SILVEX IN FURROW IRRIGATION WATER

Sugarbeets.—Two weeks after treatment with silvex at 5.51 ppmw (2.5 lb per acre), sugarbeet petioles were curved downward abnormally and the leaves were wilted. Similar but milder symptoms were noted on plots treated at 1.10 ppmw (0.5 lb per acre). No abnormalities were observed on plots treated at 0.22 ppmw (0.1 lb per acre).

After 3 weeks, many of the petioles were limp, twisted, and bleached on plots treated at 5.51 ppmw. Many leaves, particularly the lower ones, were bleached and somewhat malformed. Again, similar but milder symptoms were observed on plots treated at 1.10 ppmw. Detection of possible chemical injury from treatments at 0.22 ppmw was inhibited by the presence of curly top virus.

None of the treatments decreased the yield of sugarbeet tops or roots significantly at the 5-percent level of probability (table 7). However, the concentration of 5.51 ppmw decreased the yield of tops at the 10-percent level of probability.

A thin layer of tissue immediately beneath the epidermis was broken down in about 25 percent of the larger beet roots harvested from plots treated with silvex at 5.51 ppmw. The thin layer of dark brown, dead tissue was most pronounced in the upper part of the beets. Lesions or splits in the epidermis in the effected areas were common. Such a condition could possibly promote spoilage during the preprocessing, storage period of the sugarbeets. Large, secondary roots developed on a number of the smaller beets. These, in turn, were covered with an abundance of fine roots which were severely injured or dead at harvesttime. Treatments at 1.10 ppmw caused similar responses, but to a lesser degree.

Soybeans.—Two weeks after treatment, growth of soybeans was suppressed by treatments at 5.51 ppmw. Such suppression was less noticeable on plots treated at 1.10 ppmw, and not apparent on plots treated at 0.22 ppmw. Yellowing of the lowermost leaves was more pronounced as the rate of treatment increased.

Three weeks after treatment, 1, 16, 13, and 27 percent of the leaves were chlorotic or necrotic on plots treated with silvex at 0, 0.22, 1.10, or 5.51 ppmw, respectively. Leaf chlorosis was definitely interveinal on plots treated at the highest rate.

Silvex at 0.22 or 1.10 ppmw did not decrease the yield or quality of soybean seed (table 7). However, the concentration of 5.51 ppmw decreased both yield and quality of the seed.

Corn.—Within about 10 days after treatment, the lowermost leaves of corn were somewhat more wilted on plots treated with silvex at 5.51 ppmw than on untreated checks. As the season ad-

vanced, desiccation of the lower leaves was most pronounced on such silvex-treated plots. However, none of the treatments decreased the yield of fodder or shelled corn (table 7).

CROP RESPONSE TO 2,4-D IN SPRINKLER IRRIGATION WATER

Sugarbeets.—Within 4 days, some wilting and drooping of the leaves and some downward curvature of the petioles was noted on plots treated with 2,4-D at 2.21 ppmw (1.0 lb per acre). However, such symptoms of injury disappeared within 10 to 15 days. The foliage of the sugarbeets was not visibly affected by the treatments at 0.02 or 0.22 ppmw (0.01 or 0.1 lb per acre).

The fresh weight yield of sugarbeet tops was from 10 to 15 tons per acre greater on the 2,4-D treated plots than on the untreated plots (table 8). Likewise, the root yields were over 5 tons per acre greater on the 2,4-D-treated plots. The increase in yields without obvious growth differences in the foliage of the plants was remarkable. The laboratory analyses indicated that the sugar content was from 0.7 to 1.7 percent lower in the 2,4-D-treated sugarbeets than in the untreated checks. Nevertheless, the gross sugar production apparently was still higher (200 to 1,600 lb per acre) on the 2,4-D-treated plots. Several investigators have reported increases in growth, yield, protein, nitrate-nitrogen, or potassium nitrate from applications of 2,4-D to plants such as wheat, barley, beans, soybeans, potatoes, or sugarbeets (14, 19, 20, 21, 28). For example, Wort (28) increased root production of sugarbeets 44 percent by applying a composite dust that contained 0.1 percent 2,4-D to the foliage of 1-month-old seedlings. Sugar content was not determined.

Soybeans.—Soybeans were somewhat suppressed 1 week after treatment with 2,4-D at 2.21 ppmw. Two weeks after treatment, the plants were mostly erect, and only about 10 percent of the leaves were chlorotic. By harvesttime, differences between the treated plots and the untreated checks were minor.

Soybeans on plots treated with 2,4-D at 0.02 or 0.22 ppmw appeared normal throughout the season. None of the 2,4-D treatments reduced the yield or quality of the soybean seed (table 8).

Corn.—No visible symptoms of injury were detected in the corn after the treatments with 2,4-D. Moreover, such treatments did not reduce the yield of fodder or shelled corn (table 8).

CROP RESPONSE TO SILVEX IN SPRINKLER IRRIGATION WATER

Sugarbeets.—Within 1 to 2 days after treatment with silvex at 0.22 or 2.21 ppmw, sugarbeets were somewhat wilted and drooped. After 4 days, drooping of leaves and downward curvature of the

TABLE 8.—Yields of sugarbeets, soybeans, and corn after sprinkler irrigation with 2,4-D or silvex-treated water

| Chemical | Specified concentration ¹ | Yields per acre ² | | | | | | | |
|-----------------------|--------------------------------------|------------------------------|---------|----------|-------------|----------|---------|---------|----------------------|
| | | Sugarbeets | | | | Soybeans | Corn | | |
| | | Tops | Roots | Sugar | Gross sugar | | Fodder | Shelled | |
| | Ppmw | Pounds per acre | Tons | Tons | Percent | Tons | Bushels | Tons | Bushels ³ |
| Untreated check ----- | 0 | 0 | 19.5 a | 40.3 a | 16.3 | 6.6 | 52.6 c | 3.3 a | 99.9 a |
| 2,4-D ----- | .02 | .01 | 30.5 bc | 46.2 bed | 14.6 | 6.7 | 49.4 c | 3.2 a | 90.3 a |
| Do ----- | .22 | .1 | 35.2 c | 47.1 cd | 15.6 | 7.4 | 56.0 c | 3.1 a | 87.6 a |
| Do ----- | 2.21 | 1.0 | 29.5 bc | 45.6 bc | 14.7 | 6.7 | 55.3 c | 3.3 a | 87.8 a |
| Silvex ----- | .02 | .01 | 27.0 b | 42.4 ab | 16.0 | 6.8 | 53.8 c | 3.3 a | 87.3 a |
| Do ----- | .22 | .1 | 26.0 b | 50.4 de | 11.5 | 5.8 | 34.7 b | 3.4 a | 100.5 a |
| Do ----- | 2.21 | 1.0 | 26.3 b | 53.1 e | 9.2 | 4.9 | 13.6 a | 3.5 a | 100.3 a |

¹ See tables 4 and 6 for analytic concentrations.

² Any 2 figures in the same column that are not followed by the same letter are significantly different at the 5-percent level of probability, except those under soybeans, which are significantly different at the 1-percent level, as determined by Duncan's multiple-range test.

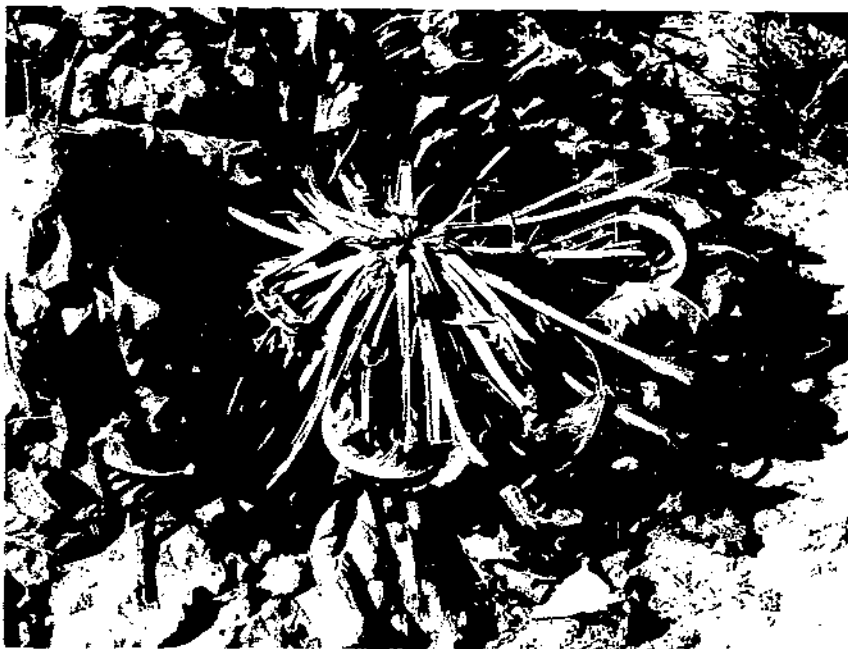
³ Computed on basis of 15.5-percent moisture.

petioles were pronounced (fig. 6). Weeds within the treatment areas, particularly lambsquarters, were injured.

On plots treated at 2.21 ppmw, curvature of the petioles and drooping of the leaves persisted until the sugarbeets were harvested. The petioles were rather brittle and easily broken, particularly near the base. Leaf growth, for the most part, was not killed but was chlorotic and arrested. New growth was sparse and malformed. Treatments at 0.22 ppmw produced similar symptoms, but to a lesser degree. No visible symptoms of injury were observed in sugarbeets treated with silvex at 0.02 ppmw.

Despite the obvious injury to the foliage, the fresh weight yield of sugarbeet tops was about 7 tons per acre greater on the silvex-treated plots than on the untreated checks (table 8). Moreover, root yields were increased about 2, 10, and 13 tons per acre by the silvex treatments at 0.02, 0.22, and 2.21 ppmw, respectively. On the other hand, the treatments at 0.22 or 2.21 ppmw lowered the sugar content of the roots, and the gross sugar yields were 1,600 and 3,400 lb per acre less, respectively, than those from the untreated checks.

Unfortunately the actions of compounds, such as silvex, at sub-



PN-3379

FIGURE 6.—Drooping of sugarbeet leaves and curvature of petioles 4 days after silvex was applied at 2.21 ppmw in 2 acre-inches of water by sprinkler irrigation.

lethal and at lethal dosages within plants are not fully understood. The studies indicated a marked imbalance between the photosynthetic and respiratory processes and an accumulation of water in the foliage and root tissues.

About 30 percent of the sugarbeets harvested from plots treated with silvex at 2.21 ppmw bore an abundance of adventitious, club-like, small roots. Lesions and splits in the epidermis were common, and a breakdown in a thin layer of tissue immediately beneath the epidermis was noted. A few sugarbeets on plots treated at 0.22 ppmw were affected similarly, but to a much lesser degree.

Soybeans.—Within 1 to 2 days after treatment with silvex at 0.22 or 2.21 ppmw, soybeans were wilted and drooped. Within 2 weeks after treatment at 2.21 ppmw, 75 percent of the leaves were chlorotic or necrotic and nearly all plants were decumbent. About 50 percent of the plants were slumped to the ground and about 30 percent of the leaves were chlorotic on plots treated at 0.22 ppmw. The soybeans on plots treated at 0.02 ppmw were erect and growing normally.

The soybean leaves on plots treated with silvex at 0.22 or 2.21 ppmw desiccated prematurely. Yield and quality of seed from such plots were reduced significantly (table 8). Silvex at 0.02 ppmw did not reduce yields, but impaired the quality of the seed slightly.

Corn.—Silvex at 0.02, 0.22, or 2.21 ppmw produced no visible symptoms of injury in the corn. Yields of fodder and shelled corn were not affected significantly (table 8).

2,4-D RESIDUES IN FURROW-IRRIGATED CROPS

Sugarbeets.—No 2,4-D residues were detected in the foliage or roots of sugarbeets 7 days after the furrow irrigation treatments at 0.22 ppmw (0.1 lb per acre) (table 9). At the same time, about 0.1 ppm of 2,4-D was found in the roots on plots treated at 1.10 or 5.51 ppmw (0.5 or 2.5 lb per acre).

At harvesttime, no 2,4-D residues were detected in any of the foliage samples or in roots from plots treated at 0.22 or 1.10 ppmw. Only roots from plots treated at 5.51 ppmw contained any measurable amount of 2,4-D (0.010 ppm).

Soybeans.—No 2,4-D residues were detected in soybean foliage, pod, or root samples collected 7 days after treatment at 0.22 or 1.10 ppmw (table 9). Such samples from plots treated at 5.51 ppmw contained only minute amounts of 2,4-D (<0.1 ppm).

At harvesttime, only soybean roots from plots treated at the high concentration of 5.51 ppmw contained any detectable amount of 2,4-D (0.090 ppm).

Corn.—Only those foliage samples collected 7 days after treatment at 5.51 ppmw contained measurable amounts of 2,4-D (table 9).

No residues were detected in any grain samples. Low concentrations (about 0.1 ppm or less) were found in root samples 7 days after treatment at 1.10 or 5.51 ppmw and at harvesttime.

TABLE 9.—*Residues in plant parts after furrow irrigation with 2,4-D or silvex-treated water*

| Chemical and plant part | Concentration 7 days after treatment at— | | | Concentration at harvest-time after treatment at— | | |
|-------------------------|--|-----------|-----------|---|-----------|-----------|
| | 0.22 ppmw | 1.10 ppmw | 5.51 ppmw | 0.22 ppmw | 1.10 ppmw | 5.51 ppmw |
| | Ppm | Ppm | Ppm | Ppm | Ppm | Ppm |
| 2,4-D: | | | | | | |
| Sugarbeet foliage | <0.005 | <0.005 | 0.08 | <0.005 | <0.005 | <0.005 |
| Sugarbeet roots | <.005 | .084 | .11 | <.005 | <.005 | .01 |
| Soybean foliage | <.005 | <.005 | .05 | <.005 | <.005 | <.005 |
| Soybean pods | <.005 | <.005 | .01 | <.005 | <.005 | <.005 |
| Soybean roots | <.005 | <.005 | .09 | <.005 | <.005 | .09 |
| Corn foliage | <.005 | <.005 | .08 | <.005 | <.005 | <.005 |
| Corn grain | <.005 | <.005 | <.005 | <.005 | <.005 | <.005 |
| Corn roots | <.005 | .072 | .12 | <.005 | .009 | .075 |
| Silvex: | | | | | | |
| Sugarbeet foliage | <.005 | <.005 | .21 | <.005 | <.005 | <.005 |
| Sugarbeet roots | <.005 | .051 | .27 | <.005 | <.005 | -- |
| Soybean foliage | <.005 | .095 | .35 | <.005 | <.005 | <.005 |
| Soybean pods | <.005 | .015 | .02 | <.005 | <.005 | <.005 |
| Soybean roots | .010 | .050 | .15 | <.005 | .050 | .25 |
| Corn foliage | <.005 | <.005 | .28 | <.005 | .009 | .13 |
| Corn grain | <.005 | <.005 | .01 | <.005 | <.005 | .01 |
| Corn roots | <.005 | .074 | .41 | <.005 | .097 | .78 |

SILVEX RESIDUES IN FURROW-IRRIGATED CROPS

Sugarbeets.—No silvex residues were found in sugarbeet foliage, except in samples collected 7 days after treatment at 5.51 ppmw (table 9). Moreover, no silvex was found in root samples, except in those collected 7 days after treatment at 1.10 or 5.51 ppmw. Root samples collected at harvesttime from plots treated at 5.51 ppmw were lost.

Soybeans.—On plots treated at 0.22 ppmw, only the root samples collected 7 days after treatment contained measurable residues of silvex (table 9). Seven days after treatment at 1.10 or 5.51 ppmw, all plant parts contained some residues. However, residues in the foliage and pods apparently dissipated by harvesttime and only the roots retained some silvex.

Corn.—No silvex residues were detected in foliage or grain sam-

ples 7 days after treatment at 0.22 or 1.10 ppmw (table 9). However, residues were found in the roots after such treatments and in all plant parts after treatment at 5.51 ppmw.

Plant parts from plots treated at 0.22 ppmw and grain from plots treated at 1.10 ppmw contained no measurable residues at harvesttime. All other plant parts still contained some silvex (0.01 to 0.78 ppm).

2,4-D RESIDUES IN SPRINKLER-IRRIGATED CROPS

Sugarbeets.—Two days after treatment with 2,4-D at 0.02, 0.22, or 2.21 ppmw (0.01, 0.1, or 1.0 lb per acre) by sprinkler irrigation, all foliage and root samples contained residues (table 10). However, only roots from plots treated at 2.21 ppmw contained a measurable amount of 2,4-D at harvesttime (0.01 ppm).

TABLE 10.—*Residues in plant parts after sprinkler irrigation with 2,4-D or silvex-treated water*

| Chemical and plant part | Concentration 2 days after treatment at— | | | Concentration at harvesttime after treatment at— | | |
|-------------------------|--|-----------|-----------|--|-----------|-----------|
| | 0.02 ppmw | 0.22 ppmw | 2.21 ppmw | 0.02 ppmw | 0.22 ppmw | 2.21 ppmw |
| | Ppm | Ppm | Ppm | Ppm | Ppm | Ppm |
| 2,4-D: | | | | | | |
| Sugarbeet foliage | 0.055 | 0.018 | 0.00 | <0.005 | <0.005 | <0.005 |
| Sugarbeet roots | .073 | .522 | 3.80 | <.005 | <.005 | .01 |
| Soybean foliage | .009 | .061 | .18 | <.005 | <.005 | <.005 |
| Soybean pods | <.005 | .008 | .05 | <.005 | <.005 | <.005 |
| Soybean roots | <.005 | .062 | .52 | <.005 | <.005 | .02 |
| Corn foliage | .008 | .094 | .51 | <.005 | <.005 | <.005 |
| Corn grain | <.005 | .008 | .05 | <.005 | <.005 | <.005 |
| Corn roots | <.005 | .007 | .09 | <.005 | <.005 | .04 |
| Silvex: | | | | | | |
| Sugarbeet foliage | <.005 | .025 | .11 | <.005 | <.005 | <.005 |
| Sugarbeet roots | .105 | .801 | 4.02 | <.005 | <.005 | .08 |
| Soybean foliage | .015 | .104 | .72 | <.005 | <.005 | .03 |
| Soybean pods | <.005 | .017 | .21 | <.005 | <.005 | <.005 |
| Soybean roots | .009 | .321 | .81 | <.005 | .062 | .16 |
| Corn foliage | .010 | .210 | .52 | <.005 | <.005 | .07 |
| Corn grain | <.005 | .044 | .06 | <.005 | <.005 | <.005 |
| Corn roots | .010 | .101 | .45 | <.005 | .008 | .09 |

Soybeans.—All plant parts, except pods and roots from plots treated at 0.02 ppmw, contained some 2,4-D residues 2 days after treatment (table 10). Again, only roots from plots treated at 2.21

ppmw contained measurable amounts of 2,4-D at harvesttime (0.02 ppm).

Corn.—Two days after treatment, 2,4-D residues were detected in all plant parts, except grain and roots from the plots treated at 0.02 ppmw (table 10). Only roots from plots treated at 2.21 ppmw contained detectable amounts of 2,4-D at harvesttime (0.04 ppm).

SILVEX RESIDUES IN SPRINKLER-IRRIGATED CROPS

Sugarbeets.—All foliage and root samples, except foliage samples from plots treated at 0.02 ppmw, contained some silvex residues 2 days after treatment (table 10). However, only roots from plots treated at 2.21 ppmw contained measurable residues at harvesttime (0.08 ppm).

Soybeans.—Silvex residues occurred in all plant parts 2 days after treatment, except in the pods from plots treated at 0.02 ppmw (table 10). No residues were detected in pod samples collected at harvesttime. Moreover, only foliage from plots treated at 2.21 ppmw and roots from plots treated at 0.22 or 2.21 ppmw contained measurable amounts of silvex.

Corn.—All foliage, grain, and root samples contained measurable concentrations of silvex 2 days after treatment, except grain samples from plots treated at 0.22 ppmw (table 10).

No residues were found in the grain samples at harvesttime. At the same time, only foliage from plots treated at 2.21 ppmw and roots from plots treated at 0.22 or 2.21 ppmw contained detectable silvex residues.

Frank, Demint, and Comes (10) found that the maximum concentrations of 2,4-D in the water after field applications of N-oleyl-1,3-propylenediamine salt derivative at 1.9 to 3 lb per acre to control bank weeds along three irrigation laterals were 5.2 to 61.0 ppb. Such concentrations were short in duration because the herbicide dissipated as the water moved downstream. In the most typical treatment, the average level of 2,4-D in the water during the 5 hours required for the treated water to pass a downstream sampling station was 3.6 ppb. The infiltration rate for most soils of this area is one-fourth inch or less per hour. If farmland were irrigated for 8 hours with water that contained an average of 3.6 ppb (total 2 acre-inches), an extremely remote possibility, only 0.0016 pounds of 2,4-D would be applied per acre. In our study, none of the edible plant parts, except sugarbeet roots, contained detectable amounts of 2,4-D residue at harvesttime after sprinkler and furrow irrigation treatments at rates 625 and 1,563 times higher than 0.0016 lb per acre, respectively. Furthermore, the concentrations found in the

sugarbeet roots were only 0.01 ppm and were at least 500 and 2,000 times below the 2,4-D tolerances in effect in 1972 for certain foods and forages for human and livestock consumption, respectively (26).

No detectable residues of silvex occurred in the edible parts of sugarbeets, soybeans, or corn at harvesttime after sprinkler or furrow irrigation treatments at 0.22 ppmw in 2 acre-inches of water (0.1 lb per acre) in mid-August. Silvex is currently registered for use at 5 pounds per acre-foot in ponds and lakes to control submersed aquatic weeds. On the basis of these studies, the irrigation of certain crops with 2 acre-inches of such treated water (1.77 ppm or 0.8 lb per acre) before adequate degradation has occurred should be avoided according to the label because of possible residues and lack of established tolerances.

SUMMARY

Analytical methods for determining 2,4-D and silvex residues in water, soil, and plant material were studied, tested, and modified or developed as necessary in preliminary laboratory experiments. The basic method used in the studies converted the alkanolamine salts of 2,4-D and the P(GBE ester of silvex to the methyl ester by esterification with boron trifluoride in methanol, and the derivatives were measured on a gas chromatograph equipped with an electron capture detector.

By multiple extractions of acidified samples with chloroform, 2,4-D and silvex in water samples could be reliably measured at the 0.00004 and 0.00001 ppm levels, respectively.

With acidification and multiple diethyl ether extractions, quantitative measurements of 2,4-D and silvex in soil at concentrations as low as 0.002 and 0.0005 ppm, respectively, were achieved.

With multiple liquid-liquid extractions and basic hydrolysis, followed by column cleanup procedures, a lower limit of 0.005 ppm in measuring 2,4-D and silvex residues in plant material was achieved.

In field experiments, the alkanolamine salts of 2,4-D and the P(GBE ester of silvex were applied at specified concentrations of 0, 0.22, 1.10, and 5.51 ppmw in 2 acre-inches of water (0, 0.1, 0.5, and 2.5 lb per acre, respectively) by furrow irrigation in mid-August to sugarbeets, soybeans, and sweet corn. The same chemicals were applied to sugarbeets, soybeans, and dwarf corn by sprinkler irrigation at specified concentrations of 0, 0.02, 0.22, and 2.21 ppmw (0, 0.01,

0.1, and 1.0 lb per acre, respectively) in the same amount of water.

On the furrow-irrigated plots, 5.51 ppmw of 2,4-D or silvex injured sugarbeets, soybeans, and sweet corn, but the yields of sugarbeets and corn were not reduced at harvesttime. Both chemicals, at the high rate, reduced the quality of soybean seed, but only silvex decreased the quantitative yields. 2,4-D and silvex at 1.10 ppmw also injured sugarbeets and soybeans somewhat, but not sweet corn. Yields were not affected significantly. At 0.22 ppmw, neither chemical injured the crops visibly or reduced yields.

On the sprinkler-irrigated plots, silvex at 0.22 or 2.21 ppmw injured the foliage of sugarbeets and soybeans markedly and decreased the yield of soybean seed at harvesttime. However, the yields of sugarbeet tops and roots were increased by the treatments. Silvex at 0.02 ppmw reduced the quality of soybean seed, but not the quantitative yields of either soybeans or sugarbeets. The highest concentration of 2,4-D (2.21 ppmw) injured the foliage slightly and temporarily but did not decrease yields of sugarbeets and soybeans. None of the 2,4-D or silvex treatments injured the foliage visibly or reduced the yield of dwarf corn.

With one exception, no edible parts of sugarbeets, soybeans, or corn treated at 0.22 or 1.10 ppmw by furrow irrigation or at 0.02 or 0.22 ppmw by sprinkler irrigation contained detectable amounts of free 2,4-D or silvex residues at harvesttime. The exception was the silvex residue of 0.01 ppm in corn foliage after treatment at 1.10 ppmw by furrow irrigation. At the highest concentrations (5.51 and 2.21 ppmw by furrow and sprinkler irrigation, respectively) 2,4-D residues at harvesttime were detected in the roots of the crops only (edible sugarbeet roots contained 0.01 ppm or less). At the same concentrations, edible parts that contained measurable residues of silvex at harvesttime were corn foliage and grain under furrow irrigation and sugarbeet roots, soybean foliage, and corn foliage under sprinkler irrigation.

In these studies, the 2,4-D was applied at concentrations many times higher than those found during the monitoring of residues in irrigation systems. The concentrations of the residues, if any, in the crops were many times below the tolerances in effect in 1972 for certain foods and forages for human and livestock consumption. Silvex residues in the edible plant parts were also minute, but irrigation of certain crops with silvex-treated water from ponds or lakes before adequate degradation has occurred or adequate tolerances have been established probably should be avoided.

LITERATURE CITED

- (1) ALY, O. M., and FAUST, S. D.
1964. STUDIES ON THE FATE OF 2,4-D AND ESTER DERIVATIVES IN NATURAL SURFACE WATERS. *Jour. Agr. Food Chem.* 12: 541-546.
- (2) BRUNS, V. F.
1954. THE RESPONSE OF CERTAIN CROPS TO 2,4-DICHLOROPHENOXYACETIC ACID IN IRRIGATION WATER. PART I. RED MEXICAN BEANS. *Weeds* 3: 359-376.
- (3) ————
1957. THE RESPONSE OF CERTAIN CROPS TO 2,4-DICHLOROPHENOXYACETIC ACID IN IRRIGATION WATER. PART II. SUGARBEETS. *Weeds* 5: 250-258.
- (4) ———— and CLORE, W. J.
1958. THE RESPONSE OF CERTAIN CROPS TO 2,4-DICHLOROPHENOXYACETIC ACID IN IRRIGATION WATER. PART III. CONCORD GRAPES. *Weeds* 6: 187-193.
- (5) ———— and WOLFE, H. H.
1957. DITCHBANK WEED CONTROL IN WASHINGTON. *Wash. State Col. Ext. Serv. Bul.* 521. 15 pp.
- (6) ———— YEO, R. R., and ABLE, H. F.
1964. TOLERANCE OF CERTAIN CROPS TO SEVERAL AQUATIC HERBICIDES IN IRRIGATION WATER. U.S. Dept. Agr. *Tech. Bul.* 1299. 22 pp.
- (7) BURCHFIELD, H. P., and JOHNSON, D. E.
1965. GUIDE TO THE ANALYSIS OF PESTICIDE RESIDUES. U.S. Dept. Health, Ed., and Welfare, Pub. Health Serv., Off. of Pesticides, Washington, D.C.
- (8) COULTER, L. L.
1954. SILVEX—A NEW SELECTIVE HERBICIDE. *Down to Earth* 9(4): 18-20.
- (9) DAVIDSON, V. E., LAWRENCE, J. M., and COMPTON, L. V.
1962. WATERWEED CONTROL ON FARMS AND RANCHES. U.S. Dept. Agr. *Farmers' Bul.* 2181. 22 pp.
- (10) FRANK, P. A., DEMINT, R. J., and COMES, R. D.
1970. HERBICIDES IN IRRIGATION WATER FOLLOWING CANAL-BANK TREATMENT FOR WEED CONTROL. *Weeds* 18: 687-692.
- (11) GOERLITZ, D. F., and LAMAR, W. L.
1967. DETERMINATION OF PHENOXY ACID HERBICIDES IN WATER BY ELECTRON CAPTURE AND MICROCOLUMETRIC GAS CHROMATOGRAPHY. U.S. Geol. Survey Water-Supply Paper 1817-C, 21 pp.
- (12) GUTENMANN, W. H., and LISK, D. J.
1963. RAPID DETERMINATION OF 4-(2,4-D) AND A METABOLITE, 2,4-D, IN TREATED FORAGE BY ELECTRON AFFINITY SPECTROSCOPY. *Jour. Agr. Food Chem.* 11: 304-306.
- (13) HODGSON, J. M., BRUNS, V. F., TIMMONS, F. L., and others.
1962. CONTROL OF CERTAIN DITCHBANK WEEDS ON IRRIGATION SYSTEMS. U.S. Dept. Agr. *Prod. Res. Rpt.* 60. 64 pp.
- (14) HUFFAKER, R. C., MILLER, M. D., BAGHOTT, K. G., and others.
1967. EFFECTS OF FIELD APPLICATIONS OF 2,4-D AND IRON SUPPLEMENTS ON YIELD AND PROTEIN CONTENT OF WHEAT AND BARLEY AND YIELD OF BEANS. *Crop Sci.* 7: 17-19.
- (15) KELLEY, J. A.
1954. THE EFFECT OF PESTICIDES ON APPLICATION EQUIPMENT. *Down to Earth*, summer 1954. 12-14.

- (16) MARTIN, ALEX C., ERICKSON, RAY C., and STEENIS, JOHN H.
1957. IMPROVING DUCK MARSHES BY WEED CONTROL. U.S. Dept. Int. Cir. 19 [revised], 60 pp.
- (17) METCALF, L. D., and SCHMITZ, A. A.
1961. THE RAPID PREPARATION OF FATTY ACID ESTERS FOR GAS CHROMATOGRAPHIC ANALYSIS. Anal. Chem. 33: 363-364.
- (18) NEWMAN, A. S., and THOMAS, J. R.
1949. DECOMPOSITION OF 2,4-DICHLOROPHENOXYACETIC ACID IN SOIL AND LIQUID MEDIA. Soil Sci. Soc. Amer. Proc. 14: 160-164.
- (19) RIES, S. K.
1971. HERBICIDES AS GROWTH BOOSTERS. Weeds Today 2: 6-8.
- (20) SMITH, R. J., JR.
1965. EFFECTS OF CHLOROPHENOXY HERBICIDES ON SOYBEANS. Weeds 13: 168-169.
- (21) STAHLER, L. M., and WHITEHEAD, E. I.
1950. THE EFFECT OF 2,4-D ON POTASSIUM NITRATE LEVELS IN LEAVES OF SUGAR BEETS. Science. 112: 749-751.
- (22) STEPHENS, J. C., BLACKBURN, R. D., SEAMAN, D. E., and WELDON, L. W.
1963. FLOW RETARDANCE BY CHANNEL WEEDS AND THEIR CONTROL. Amer. Soc. Civ. Engr. Proc. Jour. Irrig. and Drain. Div., 89 (IR2): 31-53.
- (23) TIMMONS, F. L.
1960. WEED CONTROL IN WESTERN IRRIGATION AND DRAINAGE SYSTEMS. U.S. Dept. Agr., Agr. Res. Serv. ARS 34-14, 22 pp. (Joint Rpt. of U.S. Agr. Res. Serv. and U.S. Bur. Reclam.).
- (24) ——— BRUNS, V. F., LEE, W. O., and others.
1963. STUDIES ON THE CONTROL OF COMMON CATTAIL IN DRAINAGE CHANNELS AND DITCHES. U.S. Dept. Agr. Tech. Bul. 1286, 51 pp.
- (25) UNITED STATES BUREAU OF RECLAMATION.
1949. CONTROL OF WEEDS ON IRRIGATION SYSTEMS. 140 pp., illus. Washington, D.C.
- (26) UNITED STATES DEPARTMENT OF AGRICULTURE.
1968. SUMMARY OF REGISTERED AGRICULTURAL PESTICIDE CHEMICAL USES. v. 1. (3), 1-10-7.1-7.7. Washington, D.C.
- (27) WILTSE, MARK G.
1960. AQUATIC VEGETATION CONTROL WITH SILVEX. Weed Soc. Amer. Abs.: 67.
- (28) WORT, D. J.
1966. EFFECTS OF 2,4-D-NUTRIENT DUSTS ON THE GROWTH AND YIELD OF BEANS AND SUGAR BEETS. Agr. Jour. 58: 27-29.

END