July 18, 1967

To the Graduate Council:

I am submitting herewith a thesis written by James T. Barron entitled "The Effect of Preparation and Thermal Processing on Residues of DDT, Heptachlor, and Their Metabolites in Turnip Greens and Roots (Brassica rapa)." I recommend that it be accepted for nine quarter hours of credit in partial fulfillment of the requirements for the degree of Master of Science, with a major in Food Technology.

Major Professor

We have read this thesis and recommend its acceptance:

H. McCarty

Leo J. Hardin

E. A. Kinsella

Accepted for the Council:

Vice President for
Graduate Studies and Research

THE EFFECT OF PREPARATION AND THERMAL PROCESSING ON RESIDUES OF DDT, HEPTACHLOR, AND THEIR METABOLITES IN TURNIP GREENS AND ROOTS (*BRASSICA RAPA*)

A Thesis

Presented to

the Graduate Council of

The University of Tennessee

In Partial Fulfillment

of the Requirements for the Degree

Master of Science

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by

James T. Barron

August 1967

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CHAPTER I

INTRODUCTION

Most data available on pesticide residues are based on samples of food obtained from the grower or from the market in a fresh state. Until recently, very little attention has been given to the effects of commercial processing on pesticide residues in food.

Williams (108) indicated that the most common chlorinated hydrocarbon insecticides that were found in a representative "market basket" by the Food and Drug Administration were DDT, TDE, and DDE. Heptachlor and heptachlor epoxide also were found frequently.

The Food and Drug Administration (3) has established tolerances of 7.0 p.p.m. for DDT and TDE, and a zero tolerance for heptachlor and heptachlor epoxide. No tolerance was set for DDE. At present, the determination of residues is made on the raw agricultural commodities rather than the finished processed product.

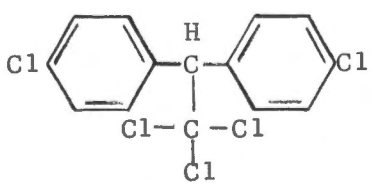
This study was made to determine the effects of normal preparation and thermal processing on residues of DDT, heptachlor, and their metabolites in turnips and turnip greens.

CHAPTER II

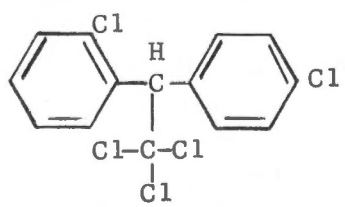
REVIEW OF LITERATURE

I. PHYSICAL AND CHEMICAL PROPERTIES OF DDT AND HEPTACHLOR

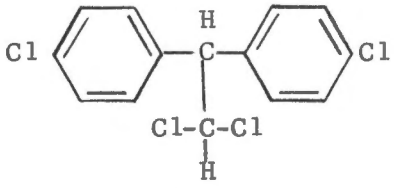
DDT, whose name was derived from the name dichloro-diphenyl-trichloroethane, was first synthesized and described by Zeidler (110) as a new chemical. The properties would be of interest to future generations of organic chemists. The original Baeyer reaction, between chloral and chlorobenzene in the presence of concentrated sulfuric acid, is still the most widely used method of preparation, commercial or otherwise (39). In the production of DDT, 66-77 per cent of the product is p,p'-DDT; 8-21 per cent o,p'-TDE; and 0.3-4.0 per cent p,p'-TDE (50). Other products include o,p'-TDE, p,p'-DDE, and o,p'-DDE in insignificant amounts.



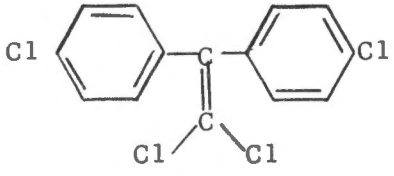
p,p'-DDT
1,1,1-trichloro-2,2-bis
(p-chlorophenyl)ethane



p,p'-DDT
1,1,1-trichloro-2-
(o-chlorophenyl)-2-
(p-chlorophenyl)ethane



p,p'-TDE
1,1-dichloro-2,2-bis
(p-chlorophenyl)ethane



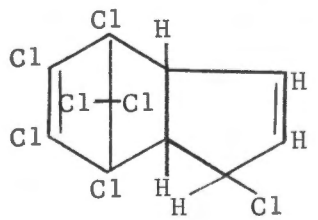
p,p'-DDE
1,1-dichloro-2-bis
(p-chlorophenyl)ethylene

Pure p,p'-DDT is a white crystalline compound occurring in long tabular biaxial needles (23), with a melting point between 108.5° and 109°C. (39). Gunther (46) reported that solutions of pure, p,p'-DDT in 95 per cent ethanol, exhibit a maximum absorption at 236 mμ, with two other peaks at 221 mμ and 265 mμ. DDT is readily soluble in fat soluble solvents, but is practically insoluble in water, dilute acids, and alkalies (39).

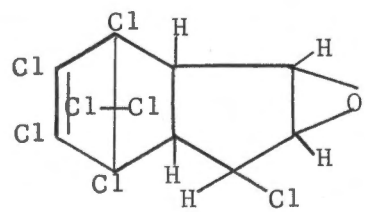
DDT is relatively stable and will decompose only when heated to temperatures above 195°C. (6). Impure samples containing iron or aluminum salts will be catalytically decomposed at lower temperatures by dehydrochlorination, forming DDE. However, no catalytic decomposition by ferric salts will occur in dioxane, motor oil, soy bean oil, and methylated naphthalene (36).

DDT is decomposed readily in solvents containing chloro- or nitro- groups, such as dichlorobenzene, ethylene chloride, and nitrobenzene, and by basic organic compounds such as methylamine or dimethylamine (69). Ultraviolet light (35) and sunlight (22, 68) also were shown to decompose DDT.

Heptachlor, the generic name of 1,4,5,6,7,8,8-heptachlor-3a,4,7,7a-tetrahydro-4,7-endomethanoindene, was first described as a specific insecticide by March (74). Although first found as an isomer of technical chlordane, it later was found that heptachlor could be synthesized by the action of sulfuryl chloride on the condensation product of cyclopentadiene and hexachloropentadiene in carbon tetrachloride in the presence of benzoyl peroxide (39).



Heptachlor
1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-endomethanoidene



Heptachlor Epoxide
1,4,5,6,7,8,8-heptachloro-2,3-epoxy-3a,4,7,7a-tetrahydro-4,7-methanoidene

Heptachlor, in the pure crystalline state, is a white solid with a melting point of 95°-96°C. (39). Unlike chlordane, a closely related compound, it is not dehydrohalogenated readily by alkali (95).

Nakatsugwa, Ishida, and Dahm (85), and Wong and Terriere (109) found that liver microsomes contain an enzyme which will convert heptachlor to heptachlor epoxide. The enzyme was found to require reduced nicotinamide-adenine dinucleotide phosphate (NADPH) and oxygen. Earlier, Ghazal et al. (42) found that the addition of DDT to isolated liver microsomes greatly increased their activity. Gilleth, Chan, and Terriere (43) found that DDT will induce the synthesis of microsomal epoxidase, causing an extremely rapid conversion of heptachlor to the more toxic heptachlor epoxide.

II. PHYSICAL AND CHEMICAL ASPECTS OF CHLORINATED HYDROCARBON INSECTICIDES ON PLANTS

Gunther and Blinn (48) defined the portion of an insecticide spray or dust which reaches the surface of the plant as "deposit," and the portion that remains after run-off, evaporation, or sloughing as the "residue." Further, the external residue is that portion of the residue which remains outside the cuticle, and the internal residue, as that portion which penetrates the cuticle.

Crafts and Foy (26) reported that most foliar applied substances enter the leaf tissue by diffusion as a vapor through the stomata, mass movement as a liquid through the stomata, and diffusion through the cuticle and epidermal walls. Oils and insecticides of a lipophilic nature, including DDT and heptachlor, will penetrate the cuticle more readily than compounds of a more polar nature. Stomata also are penetrated by oils or lipophilic insecticides (91).

Orgell (89) proposed cuticular penetration of insecticides as a three step process--absorption of the penetrant at the cuticle-spray interface, absorption of the penetrant into the cuticle by absorption on internal surfaces or by solution within the cuticle, and desorption into the plasma membrane of the cell. Franke (38) reported the uptake, as well as excretion, of various lipophilic pesticides by the ectodesmata, which are structures on outer surfaces of epidermal cells resembling plasmodesmata. Another mode of entry was thought to be through cracks in the cuticle (91).

Roots do not absorb lipophilic insecticides as rapidly as hydrophilic ones (81). However, toxic amounts of lipophiles have appeared in plants. Ishii and Hirano (56), and Tsukano and Suzuki (103), reported the absorption of lindane (gamma isomer of hexachlorocyclohexane) by rice seedlings in a sand culture. Both groups of workers reported that the aerial concentration of lindane was about one-third as great as the concentration in the roots.

The accumulation of DDT in horse bean was reported by Bogdarina and Odumanova-Dunaeva (11). They noted that the penetration of the insecticide was specific for different plant organs and dependent upon the concentration of insecticide and the addition of minerals (selenium or sulfur). Ordas, Smith, and Meyer (88) reported that potatoes grown in soil fortified with heptachlor had a high residue on the peel, but only a trace in the pulp, indicating that transmigration did not occur. Work by Lichtenstein, Myrdal, and Schulz (64) indicate that although heptachlor was readily absorbed by the epidermal layer of carrot, there was no major transmigration within the root. Spencer (99), and Gannon and Decker (40) noted of the chlorinated hydrocarbon insecticides, only two have significant metabolic products in plants. These were heptachlor epoxide from heptachlor, and dieldrin from aldrin.

Marth (75) in his review of pesticide residues in biological material pointed out that, in all instances, pesticide residues on plants have decreased with time. He also points out that chlorinated hydrocarbons on plants will be dissipated according to several factors.

III. PERSISTENCE AND BEHAVIOR OF CHLORINATED HYDROCARBON INSECTICIDES IN THE SOIL

Lichtenstein (62) lists eight factors which effect the breakdown or persistence of insecticides in the soil. The factors include the insecticide itself, the soil type, moisture, microorganisms, soil temperature, crop, cultivation of the soil, and the mode of insecticidal application and formulation.

The characteristics of the insecticide itself was important in residue considerations. Heptachlor was extremely stable and its metabolite, heptachlor epoxide, was more stable and toxic than heptachlor itself (66). Wilkenson, Finlayson, and Morley (107) reported that a single application of heptachlor gave toxic residues (mainly heptachlor epoxide) after nine years, even though the land was under continuous cultivation. DDT is relatively stable in soil, and will not be degraded unless common soil microorganisms are present (13).

Chlorinated hydrocarbon insecticides will persist in soils of high organic matter longer than in those of low organic matter (13, 66). In muck soil, where organic matter constitutes about 50 per cent of the dry weight, insecticides were bound to the soil particles such as to render the same amount of pesticide less effective as compared to a sandy soil (65). Moisture, although more important in the breakdown of phosphate and carbamate insecticides, was an important factor in the persistence of chlorinated hydrocarbons. High moisture caused the release the pesticides from soil particles and provided a

favorable medium for microorganisms which act upon insecticides (67). Recently, Mendel et al. (78) showed that Aerobacter aerogenes, a common soil microorganism, possesses a specific metabolic pathway for the reductive dechlorination of DDT to TDE. Perthane (1,1-dichloro-2,2-bis(p-ethylphenyl)ethane) showed no reduction, while methoxychlor was reduced only slightly.

Soil temperature influenced the rate of volatilization of insecticides as well as breakdown by chemical and biological factors (65, 66). Cover crops such as alfalfa will tend to decrease the volatilization of insecticides; hence, will cause a greater persistence of the insecticide (60). Lichtenstein et al. (63) reported that amounts of heptachlor and aldrin translocated into carrots significantly reduced the amount of insecticide in the soil.

The last two factors effecting the persistence of residues in the soil are cultivation of the soil and mode of application and formulation of the insecticide. Cultivation increases the disappearance or residues from the soil (67). In the application of aldrin, the greatest losses were noted when it was applied as an emulsion and left on the surface, probably through volatilization. The greatest persistence was noted when aldrin was applied in a granular form and incorporated into the soil (63).

IV. CHLORINATED HYDROCARBON INSECTICIDE RESIDUES IN AND REMOVAL FROM FOOD

In total diet samples collected over a 2 year period, the Food and Drug Administration (108) found that residues of DDT, TDE, and DDE were widely distributed and were present in concentrations ranging from 0.3 to 0.001 p.p.m. Residues of heptachlor and heptachlor epoxide were found also.

In collards dusted with DDT, at the rate of 3 lb./acre, residues of 63.0 and 0.6 p.p.m. were found after the final application and 13 days later, respectively (14). Waites and van Middelem (104) recovered 34.5, 18.6, and 6.7 p.p.m. DDT from collards treated 3, 7, and 14 days earlier.

Guyer, Reath, and Haisley (49) reported that fresh spinach contained 71 p.p.m. DDT one day after spraying, and 6.7 p.p.m. 13 days after spraying, while the canned product contained 18 and 1.4 p.p.m., respectively. Dawsey, Woodham, and Lofgren (29) were unable to detect heptachlor or heptachlor epoxide in turnip greens grown in soil previously treated with heptachlor. However, they did find 0.2 p.p.m. heptachlor in the roots. Muns, Stone, and Foley (84) reported that no residue was recovered from turnips grown in soil fortified with DDT. Lichtenstein et al. (63) recovered 4.3 p.p.m. DDT from radishes grown in fortified soils, while Dawsey, Woodham, and Lofgren (29) reported the recovery of 0.05 p.p.m. heptachlor and 0.15 p.p.m. heptachlor epoxide. When heptachlor was applied to sugar beets at the rate

of 1.5 lb./acre, a residue of 0.01 p.p.m. heptachlor and 0.02 p.p.m. heptachlor epoxide was recovered (2).

In a study of insecticides in 5 carrot varieties, Lichtenstein, Myrdal, and Schulz (64) concluded that there was no significant difference in absorption of heptachlor among the 5 varieties. Four of the varieties contained 70 to 86 per cent of the residues in the peel, which would be removed during normal processing, while the other variety contained only 50 per cent in the peel, the remainder being in the pulp. The vertical distribution of the residue within the root itself corresponded closely to the vertical distribution of the insecticide in the soil, indicating very little, if any, translocation of the insecticide within the plant.

In a review, Maloney (73) noted that only a small number of insecticides, when applied to the soil or to the growing crop, caused definite off-flavors, particularly in vegetables processed by heat. Gilpin, Parks, and Reynolds (44) conducted palatability studies on turnips, carrots, and other vegetables grown on soils fortified with BHC (hexachlorocyclohexane), DDT, TDE, and heptachlor. Of all the insecticides, only BHC caused a significant flavor change. Birdsall, Weckel, and Chapman (10) reported that turnip greens were relatively free from flavor changes caused by heptachlor. Johnston (59) reported that lindane applied to cucumbers caused no off-flavors to the resulting pickles after fermentation when lindane was applied at normal rate. However, when it was applied at an excessive rate, the pickles were found inferior in flavor to pickles from untreated cucumbers.

Of special interest to the food canning industries are processes which reduce insecticide residues to a level below the tolerances set by the Food and Drug Administration.

Although residues have been reported in sugar beets (2), Johnson (57) noted that no insecticide residues have been recovered from refined beet sugar. He suggested two reasons for this--primary juice purification with lime would remove residues with the carbonate cake, and crystallization of the sugar from the liquor, an excellent purification process in itself, would eliminate any residues getting past primary purification.

Cook (25) showed that when insecticides were applied at equal rate to different crops, the initial residue after application varied directly with the surface area per unit weight of the product. Crops such as turnip green or alfalfa, therefore, would have a much higher residue than a crop such as tomatoes when equal amounts of insecticides were applied.

Marth (75) pointed out that residues will be dissipated prior to processing according to the crop, the type of insecticide, the time between final application and harvest, and environmental conditions such as rainfall, temperature, and wind velocity.

Tressler (102) reported the destruction of 20 to 27 per cent of the DDT residues during the processing of tomato juice for 25 min. at 212°F. Dormal et al. (30) found that blanching reduced DDT residues in spinach by 20 to 40 per cent. Carlin, Hibbs, and Dahm (21), in a study on insecticide residues in canned and frozen green beans,

noted a reduction in DDT from 3.62 p.p.m. in the initial field sample to 0.0 p.p.m. in canned samples stored 12 months.

In another study of DDT residues in green beans, Hemphill et al. (53) found that washing and trimming reduced residues slightly, while various cooking methods reduced residues even more. Boiling caused a reduction of 53 per cent; pressure cooking, 63 per cent; and microwave heating, 54 per cent.

Farrow, Elkins, and Cook (34) investigated the conversion of DDT to TDE during the thermal processing of spinach. They found that after the normal thermal processing time, 52 per cent of the DDT was converted to TDE, DDE, or breakdown products which did not register on electron-capture detectors. At four times the normal thermal process, 78 per cent of the DDT was decomposed.

Johnston (59) found that lindane residues did not adversely effect the fermentation of cucumbers. In exaggerated amounts, however, lindane altered the microflora of the cucumber brine. The principal alteration was the inhibition of growth in several species of yeast. Slade (98) suggested that the ability of lindane to block the physiological activity of an organism was due to the similarity of its molecular spatial configuration to that of i-inositol.

Other effects which may serve to break down DDT during processing are the ability of bases to decompose DDT to TDE or DDE (46, 69), and the ability of iron and aluminum salts to dehydrochlorinate DDT to form its ethylene analog DDE (36, 37).

The physical removal of residues from food products during normal processing has not been extensively investigated. Washing was shown to significantly reduce levels of toxaphene and DDT in tomatoes (27). Lichtenstein, Myrdal, and Schulz (64) showed that the majority of heptachlor and heptachlor epoxide residues were in the epidermal layers of carrot. They concluded that peeling would have removed a major portion of these residues.

Crosby (27) estimated that roughly half the residues in canned fruits and vegetables may be removed by preparative practices such as washing, trimming, and peeling, while the remainder may be removed by thermal processing.

V. PESTICIDE RESIDUE CLEANUP METHODS

In most cleanup methods, there are two separate steps--gross extraction and cleanup, or, separation of the pesticide from any interfering material. The extraction and cleanup procedure depends upon the type of material from which the pesticide was to be extracted and the type of pesticide which was to be extracted (33).

The cleanup methods for chlorinated hydrocarbon insecticide residues have been reviewed by several authors (9, 33, 76). However, the official methods as recognized by the Food and Drug Administration are described, in detail, in the Pesticide Analytical Manual (7).

Various procedures have been worked out for the extraction of chlorinated hydrocarbons. One of the most widely used is extraction

with acetonitrile. The Mills-Onley-Gaither method (80) was the first method which utilized acetonitrile as an extraction solvent. The use of acetonitrile eliminated several time consuming and cumbersome steps of earlier methods. Mills, Onley, and Gaither (80) macerated the tissue in a blender, using acetonitrile as the extraction solvent. Saha (96) modified this slightly for low moisture samples, such as cereal grains, using a Soxhlet extraction with acetonitrile as the solvent. In a recent collaborative study of extraction methods for leafy green vegetables, Burke and Porter (20) concluded that the acetonitrile extraction of Mills, Onley, and Gaither (80) had the highest extraction efficiency of the several methods studied.

Other extraction systems which have been used are isopropyl alcohol (IPA)-hexane mixtures (51, 61, 79), IPA-benzene mixtures (51), ethyl acetate (105), and methylene chloride (8).

Hardin and Sarten (51) concluded that IPA-hexane and IPA-benzene gave suitable recoveries (83-95 per cent) of DDT from collards. The principal difficulty, however, was the ease with which emulsions were formed and their difficulty of removal. This problem was partially remedied by the addition of sodium sulfate. The principal advantage of this solvent system was its ability to remove plant waxes and some other types of fatty material. Using the IPA-hexane method for extraction, Burke and Porter (20) found the average recovery to be about 92 per cent.

The Watts-Storherr method (105) of extraction using ethyl acetate was found to be generally unacceptable for the recovery of

chlorinated hydrocarbon insecticides, but acceptable for organophosphate insecticides. The recovery of TDE from kale by this method averaged 74 per cent (20). Of all the extraction methods investigated by Burke and Porter (20), the methylene chloride extraction of Benson and Finocchiaro (8), which was used originally for carbamate insecticides, was the poorest, giving only 65 per cent recovery.

The cleanup of the extract is usually affected by the use of some type of column chromatography; however, other methods have been found to be suitable.

Florisil, a synthetic magnesium trisilicate, first was used for pesticide residue determination by Mills (79) and is probably the most widely used absorbent because of its reasonable reproducible properties (9). Florisil is standardized by calcination at 1250°F. for 3 hr. and holding at 135°C. until just prior to use (19). Other workers, however, standardized its activity by calcination, then added a known amount of water to partially inactivate the Florisil (83).

The cleanup used in the Mills-Onley-Gaither (80) method utilizes activated Florisil eluted with 6 and 15 per cent ethyl ether in petroleum ether, and is generally accepted as being the most suitable method for a wide range of pesticides in low fat materials. Onley (87) modified the Mills-Onley-Gaither (80) method to be used for residues in fluid whole milk by the addition of dioxane to the second elution. Moats and Kotula (83) devised a Florisil column using a large

volume of eluent and high elution rate to shorten the time required for cleanup to about one-half that of the Mills-Onley-Gaither method.

Moats (82) developed a column of some merit using a charcoal-celite mixture as an absorbent with 20 per cent ethyl ether in acetone as an eluent. It is suitable for cleanup of most chlorinated hydrocarbon insecticides, especially those in solution with plant pigments and waxes. This method is, however, very time consuming.

Other column absorbents which have found limited use in the cleanup of pesticide residues are magnesium oxide-celite mixtures (80), activated charcoal (5), attapulgite clay (86), cellulose (106), and polyethylene coated alumina (55).

Many times, when the concentration of fatty and waxy material in a sample was great, methods other than column chromatography were used. One of the principal methods used in cases such as these was saponification (76). The disadvantages of this procedure was the instability of several chlorinated hydrocarbon insecticides such as DDT and its analogs to the strong alkali used for saponification. However, it was useful for removal of fats from samples containing the cyclodiene insecticides such as heptachlor, aldrin, dieldrin and chlordane.

Davidow (28) used a hexane slurry of 30 gm. celite, 9 ml. concentrated sulfuric acid, and 9 ml. fuming sulfuric acid to render up to 5 gm. of fat. However, this method, too, was limited to just a few insecticides.

McKinley and Savary (77) used an acetone precipitation of fat to remove a major portion of interfering material from pesticide residues in various animal fats. This was followed by further cleanup on a Florisil column. Good recoveries were obtained with most chlorinated hydrocarbon insecticides.

At very low pressures, most of the commonly used insecticides are sufficiently volatile to sublime or distill at moderate temperatures, and if the accompanying plant extractives have appreciably higher vapor pressures, effective separations can be obtained. Farrow and Elkins (33) adapted vacuum sublimination as a direct cleanup procedure for low fat materials and a secondary cleanup for fatty materials. The general procedure was to evaporate all solvent then apply a vacuum, reducing the pressure to about 2.5 u Hg, for 15 to 30 min. Over the temperature range of 30° to 60°C., recoveries of several insecticides have ranged from 90 to 100 per cent.

Other procedures which have found limited use as cleanup procedures include paper chromatography (52), and thin layer chromatography (1).

VI. GAS-LIQUID CHROMATOGRAPHY OF CHLORINATED HYDROCARBON INSECTICIDE RESIDUES

Gas-liquid chromatography or, as it was more commonly known, gas chromatography, was that chromatographic method by which components of a gaseous mixture are separated by elution through a column consisting of a stationary non-volatile liquid phase on an inert support and a mobile vapor phase (97).

A simple theory of gas chromatography has been presented by Phillips (93) who states that the rate of elution of a gas through the column will be dependent upon the gas's distribution coefficient--that is, the ratio of the number of molecules of the gas in the liquid phase to the number of molecules in the vapor phase at equilibrium. A mixture of gases, therefore, was eluted in the inverse order of their distribution coefficients.

The optimum column size for gas chromatography of chlorinated hydrocarbon insecticides appears to be from 3 to 6 ft. in length and 3 to 4 mm. i.d. Diatomaceous earth in various grades was the most widely used solid support material and had the advantages of being relatively inert, having a high ratio of surface area to volume, and having reasonable mechanical strength (9). Glass micro-beads were investigated as a possible support; however, they were found to offer no advantage over diatomaceous earth (45).

From chromatography of chlorinated hydrocarbon insecticides, an important property of a support material was the absence of any tendency to decompose the insecticide. Goodwin, Goulden, and Reynolds (45) found the main source of decomposition in diatomaceous earth columns to be active sites which could be eliminated by the mixing of small amounts of polar stationary phase with the non-polar stationary phase. Adsorption of the sample by the support material, another problem encountered with diatomaceous earth columns, has been eliminated by acid and alkali washing; and active hydroxyl groups, by conversion to their trimethylsilyl derivatives with hexamethyldisilizane (17).

Selection of a stationary phase for a gas chromatographic column was based on the separation which it offered the material being analyzed. For separations of chlorinated hydrocarbon insecticides, Beynon and Elgar (9) recommended dimethyl silicone base greases. These greases, however, will not separate p,p'-TDE from o,p'-DDT. Recently, Burke and Holswade (18) and Henley, Kruppa, and Supina (54) developed a mixed-phase silicone packing which will accomplish this separation.

The electron capture detector, which is the most sensitive detector available for the determination of pesticide residues, was developed by Lovelock and Lipsky (72). In an ionized gas, the negative charge carriers may be either free electrons or negative molecular ions. The process leading to the formation of gaseous negative ions is the reversible reaction in which neutral molecules (M°) capture free electrons (e^-):

$$M^\circ + e^- \rightleftharpoons M^- + \text{energy} .$$

A beta radiation source, such as tritium foil, is used as a source of free electrons. The carrier gas, such as nitrogen or argon, must be relatively inert and possess a very low electron capturing ability. A potential is applied, and a standing current is set up across the cell. When molecules with electron capturing abilities enter the detector, electrons are absorbed and the standing current drops. It is this current drop which is measured (24).

Lovelock (70, 71) found that compounds such as organic halogens, highly unsaturated hydrocarbons, polynuclear aromatics, nitro-compounds,

and olefinic esters possess very high electron affinities. The measurement of the electron affinities of many compounds has revealed an interesting correlation with the biological activity of a compound.

Goodwin, Goulden, and Reynolds (45) were the first to recognize the potential of the electron capture detector for chlorinated hydrocarbon insecticides and described a procedure for analysis of residues to a concentration of 0.1 p.p.m. The detector since has been used widely for analysis of residues in crops, soils, animal tissues, and food products. Optimum conditions for operation has been reviewed by Burke and Guiffrida (16). These workers recommend a 6 ft. x 4 mm. glass column packed with 10 per cent DC200 dimethyl silicone oil on 80 to 90 mesh, acid- and base-washed, and silanized diatomaceous earth. The column and detector were maintained at 200°C. and 120 ml./min. of nitrogen is passed through the column.

Some chlorinated hydrocarbon insecticides, notably DDT and endrin, are decomposed during gas chromatography (94). Burke and Guiffrida (16) reported that DDT will break down to form compounds with the same retention time as TDE and DDE. This reaction may be a reductive dechlorination or hydrogenolysis of DDT as a result of contact with Fe^{+2} associated with the stainless steel parts of many gas chromatographs or of elevated column temperatures (90). Farrow (32) recommended the injection of pure p,p'-DDT standards as a method of checking for such decomposition.

Lovelock (71) showed that the response of the electron capture detector may be quantitized. Over about 40 per cent of the current

range of the detector response at optimum activity, the peak height of the response may be related to the sample weight as follows:

$$I = I_o e^{-kc} ,$$

where

I = current flowing in detector at sample peak maximum,

I_o = detector standing current,

c = sample weight, and

k = a constant.

Lovelock (71) pointed out that the relationship has a formal analogy to Beer's Law. Gaul (41) compared five methods of quantitative calculation of gas chromatographic peaks in pesticide residue analysis--peak height, product of peak height and width of the peak at half height, "area" as a product of retention time and peak height, electrical disk integrator attached to the recorder, and triangulation. No significant difference was found among the results of the five methods. The only method for which the calculated quantities were usually higher than the injected quantities was the disk integrator method.

CHAPTER III

MATERIALS AND METHODS

I. EXPERIMENTAL DESIGN

On March 12, 1966, four plots, 60 ft. by 12 ft., were prepared for planting at Mound Range No. 5, U. T. Knoxville Farms. All plots were disked to a depth of 5 in. and heptachlor applied to plots No. 2 and No. 4 at the rate of 10 lb./acre. The plots were then disked again to insure an even distribution of heptachlor.

On April 1, 6-12-12 fertilizer was applied to all plots at the rate of 500 lb./acre. The plots then were culti-packed. Purple Top globe turnip (Brassica rapa) seed, which had been obtained from a local seed company, were broadcast over the plots at the rate of 3 lb./acre.

On April 28, May 4, and May 18, an emulsion of technical DDT (78 per cent p,p'-isomer) was applied to plots No. 3 and No. 4 at the rate of 1.5 lb./acre. A cart mounted sprayer with nozzles mounted 1.5 ft. apart on a 6 ft. boom was used to apply the DDT.

The plots were partially harvested on May 21. Prior to sampling, the weight of the leaves from each plot was adjusted to 16 lb. Each 16 lb. lot was divided into 8 lb. sub-lots to facilitate handling during the washing process. Each sub-lot was washed by submersion and agitation for 2.5 min. in 18.5 gal. warm (95°F.) water, followed by a similar wash for 2.5 min. in cold water. The sinks were

thoroughly cleaned between washings. The two sub-lots from each lot were recombined and thoroughly mixed.

The leaves were spread on blanching trays, and blanched for 3 min. in an atmospheric steam blancher. Blanched leaves were packed into eight No. 2½ cans and filled to within .25 in. from the top of the can with 1.5 per cent NaCl brine. The cans were sealed and placed into the retort immediately.

The cans were sterilized in a retort for 75 min. at 252°F. (15 lb. steam), then air cooled. The cans from plot No. 3 were sterilized at reduced steam pressure (10-13 lb.). The cans from plot No. 4 were placed into a -20°F. air blast freezer for 2 days, were allowed to thaw, and then were sterilized as the other samples. All cans were stored at room temperature. The sterilization time exceeded the time recommended by the National Canners Association (4) by 10 min.

Thirty-five gm. random samples were taken in three replications as follows: after the final DDT application; at harvest, after adjustment of lot weight; after washing and recombining the sub-lots; after blanching; after sterilization; and after 6 months storage. The leaves were sampled by randomly selecting about 100 gm. of leaves, chopping them with a knife, mixing, and selecting a 35 gm. sample. The contents of the cans were sampled by mixing the contents of three cans which had been drained on a No. 8 size sieve, chopping, mixing and finally randomly selecting three 35 gm. samples. Three 50 ml. samples of fill liquor were taken, extracted into acetonitrile, and stored in a 0°F. still air freezer. The drained weights of the canned

samples were not recorded. The leaf samples were placed in 12 oz. screw cap jars and placed in a -20°F. air blast freezer. They later were moved to a 0°F. still air freezer and held there until analyzed.

The statistical design of the leaf experiment was six process levels and four treatment levels with three replications.

The turnip roots were allowed to mature until July 12, when they were harvested by hand. Lots from each plot were adjusted to 30 lb. prior to sampling. Each lot was washed statically with cold water for one min., then for 3 min. in a rotary pea washer (Food Machinery Corp.).

The washed turnips were peeled in a hot (180°F.) 10 per cent lye bath for 7 min., then were washed statically with cold water to remove any remaining lye. The turnips were cut traversely once, then were quartered longitudinally. Eight No. 2½ cans were packed to within .5 in. of the top. The cans were filled to within .25 in. of the top with 2.5 per cent NaCl brine, sealed, and placed into the retort immediately. The cups were sterilized for 35 min. at 240°F. (11 lb. steam). This process, also, exceeded the recommended process time (4) by 5 min. The cans were air cooled, and stored at room temperature.

Thirty-five gm. random samples in three replications were taken as follows: at harvest, after adjustment of lot weight; after washing; after peeling and second washing; after sterilization; and after 6 months storage. The canned turnips and fill liquor were sampled similarly to the canned green samples.

The statistical design of the root experiment was five levels of processes and four levels of treatment with three replications.

II. SAMPLE PREPARATION FOR GAS CHROMATOGRAPHY

The Mills-Onley-Gaither (80) cleanup method for pesticide residues in non-fatty foods was used to prepare all samples for gas chromatography.

Reagents

Acetonitrile--AR grade. Distill 1 gal. with 30 gms. phosphorus pentoxide, and 1 ml. 85 per cent phosphoric acid. Discard the first 50 ml. and last 100 ml. fraction.

Petroleum ether--30°-60°C. boiling, AR grade. Redistill, discarding first 50 ml. and last 100 ml. from each distillation. Check the purity by means of gas chromatography.

n-Hexane--AR grade. Redistill, discarding first 50 ml. and last 100 ml. fraction of each distillation. Check the purity by means of gas chromatography.

Ethyl ether--anhydrous, AR grade. Place in separatory funnel and wash twice with portions of distilled water equal to about half the volume of the ether. Wash once more with 50-100 ml. saturated NaCl solution. Drain the washed ether into a glass stoppered Erlenmeyer flask with a large excess of anhydrous sodium sulfate. Place the Erlenmeyer flask on a Burrell wrist-action shaker for 20-30 min.

Elution solvent--6 per cent ethyl ether in redistilled petroleum ether.

Florisil--80-100 mesh, pesticide grade. Activate by storing at 150°C. at least 48 hr. Store at 150°C. until ready to use.

Celite 545--(Johns-Manville Company).

Sodium sulfate--anhydrous AR grade.

Apparatus

Chromatographic columns (Konte's Glass Company, Vineland, New Jersey)--300 mm. x 23 mm. i.d. with teflon stopcock.

Separatory funnels--500 ml. and 1000 ml. with teflon stopcock.

Graduated cylinders--100 ml. and 250 ml. with 24/40 ℧ glass stoppers.

Kudera-Danish concentration apparatus (Konte's Glass Company)--500 ml. size fitted with 3-ball Snyder column.

Suction filtration apparatus--11 cm. Buchner funnel fitted with a No. 8 rubber stopper; 35/42--24/40 ℧ reducing adapter; and 24/40 ℧ vacuum take-off adapter (Konte's Glass Company).

Flint glass bottles (Sargent)--15 ml. with screw cap containing conical polyethylene liner.

The sample was removed from its storage jar and placed in a pint Mason jar. The sample jar then was flushed out, into the Mason jar, with 150 ml. acetonitrile. Ten gm. of Celite 545 was added to the sample, an Oster blending head affixed to the jar and the sample macerated--90 sec. for leaf samples and 120 sec. for root samples.

A vacuum filtration apparatus was placed on a 250 ml. graduated cylinder and the macerated sample filtered with vacuum. An additional 50 ml. portion of acetonitrile was used to rinse the jar. The volume of the filtrate was noted and recorded.

The acetonitrile extract then was placed into a 1000 ml. separatory funnel. One hundred ml. of petroleum ether was measured into the 250 ml. graduate used for the acetonitrile extract; the volume was noted and recorded. The petroleum ether then was added to the acetonitrile extract, and shaken for 1-2 min. to insure thorough mixing, thereby forcing the pesticide residues into the petroleum ether phase. Ten to twenty ml. saturated NaCl solution was added to break any emulsion which may have formed.

Five to six hundred ml. distilled water was added and thoroughly mixed, forcing any residues remaining in the acetonitrile phase into the petroleum ether phase. After allowing the phases to separate, the aqueous phase was discarded. The petroleum ether extract was washed twice more with 100 ml. portions of distilled water to remove any acetonitrile remaining. The petroleum ether extract then was drained into a 100 ml. glass stoppered graduated cylinder, and the volume noted.

The sample weight remaining after extraction was determined by the following formula:

$$S_r = S_o \times \frac{F}{T} \times \frac{E}{P} \quad ,$$

where

S_r = remaining sample weight,

S_o = original sample weight,

T = total volume (ml. acetontrile added + ml. acetonitrile rinse + ml. H_2O in sample - 5 ml. shrinkage),

F = ml. acetonitrile filtrate,

E = ml. petroleum ether extract, and

P = ml. petroleum ether added.

About 15 gm. anhydrous sodium sulfate was added to the graduate containing the petroleum ether extract. The cylinder was then stoppered and inverted several times to remove any moisture present. The extract was transferred to a Kuderna-Danish concentration flask and the graduate rinsed twice with 15 ml. portions of petroleum ether. Two glass beads were added to the concentration flask, a 3-ball Snyder column attached, and the extract concentrated to a volume of about 5 ml. on the steam bath.

The concentrated extract was transferred from the receiver tube to a 10 ml. volumetric flask. Two 1 ml. portions of petroleum ether were used to rinse the receiver tube. The solution was not brought to volume.

A chromatographic column was prepared by placing 40 gm. Florisil in a column and topping this with a 0.5 in. layer of anhydrous sodium sulfate. The column was packed by either tapping with a rubber mallet or by vibrating with a "Vibrogun" mechanical vibrator.

The extracts were brought to volume with petroleum ether and inverted several times to mix. The column was pre-wetted with 60 ml. petroleum ether, the pre-wet discarded, and a Kuderna-Danish concentration flask placed as a receiver.

A suitable aliquot of the extract--2 ml. for the leaf samples and 4 ml. for the root samples--was added, and small portions of the elution solvent used to force the extract on to the Florisil. The column was eluted with 200 ml. solvent, regulating the elution rate to about 5 ml./min.

A 3-ball Snyder column was affixed to the concentration flask. This was placed on a steam bath and the eluent concentrated to about 5 ml. The receiver tubes were removed from the concentration flask, and the solvent allowed to evaporate to dryness at room temperature. The residue was taken up in n-hexane and its volume adjusted to 10 ml. This was transferred to a 15 ml. flint glass bottle and stored at 4°C. until analyzed.

III. GAS CHROMATOGRAPHY OF SAMPLES

A Micro Tek Model DSS162 gas chromatograph equipped with a 150 μc. tritium foil electron capture detector, was operated with an inlet temperature of 190°C., a column temperature of 175°C., and a detector temperature of 195°C. Purified nitrogen was used as the carrier gas with a flow rate of 70 ml./min. and an inlet pressure of 40 p.s.i. The column was a 60 x 1/8 in. i.d. spiral aluminum tube packed with 60-80 mesh, acid washed, silanized, Chromosorb W coated with 5 per

cent Dow DC-11 silicone grease (w/w). The detector attinuation was 10^2 x 128 or 10^2 x 32, depending upon the range of residue concentrations in the sample.

Prepared standard solutions of 100 p.p.m. (w/v), p,p'-DDT, p,p'-TDE, and DDE in n-hexane, obtained from Analabs, Incorporated (Hamden, Conn.), were combined and diluted to a suitable working range of 0.005 p.p.m. to 1.0 p.p.m. Crystalline standards of heptachlor and heptachlor epoxide were provided by the Velsicol Chemical Corporation (Chicago, Illinois). From these, working standard solutions, ranging from 0.005 p.p.m. to 1.0 p.p.m., were prepared.

All samples were analyzed for DDT, TDE, DDE, heptachlor, and heptachlor epoxide. With the particular column used, o,p'-DDT and p,p'-TDE were eluted off the column at the same time, showing on the recorder graph as a single peak. Following the recommendation of Burke (15), the peak was treated as TDE, and reported as such. The p,p'-DDT peak was treated as DDT. The relative recorder response and retention times of the five standards are shown in Figure 1.

Four µl. injections were used for all samples. Samples representing leaves from the DDT and DDT + heptachlor treated plots were chromatographed at a detector attenuation of 10^2 x 128 because of the relatively high concentrations of DDT, TDE, and DDE. All leaf samples from these treatments required further dilutions, from 0.5 to 0.01, with n-hexane to bring the residue concentration to within a readable range. In most cases it was necessary to dilute and chromatograph the same sample several times to determine the residues of each insecticide.

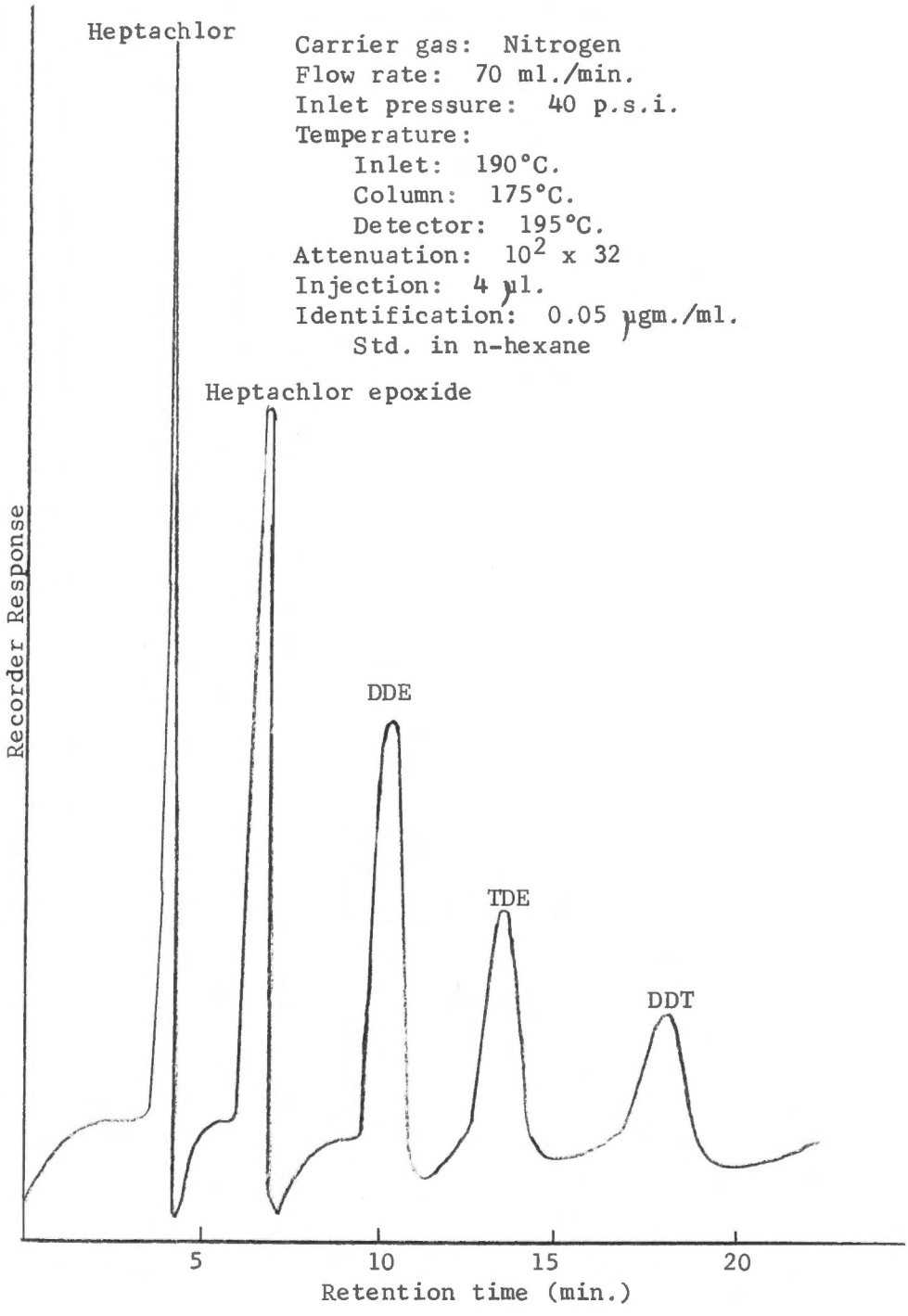


Figure 1. Chromatogram of five chlorinated hydrocarbon insecticides.

The leaf samples from the control and heptachlor treated plots taken after the final spray application and after harvest were also chromatographed at a detector attenuation of 10^2 x 128; however, no dilution was required.

All other samples, both leaf and root, were chromatographed at a detector attenuation of 10^2 x 32 which is about four times as sensitive as the attenuation of 10^2 x 128. No further dilutions were required for the DDT residues in the root samples except for samples from the DDT + heptachlor plot taken after the final spraying.

The chromatographic peaks were quantitated by determining the peak area through triangulation procedures (15), and the apparent concentration determined, in µgm./ml. standard/4 µl. injection, from a standard curve prepared by determining the peak areas of standards which were linearly plotted. The actual residue concentration was found by the following formula:

$$R = \frac{C}{S \times D} ,$$

where

R = residue concentration (p.p.m.),

C = apparent residue concentration (µgm./ml. hexane/4 µl.),

S = sample concentration (gm./ml. hexane/4 µl.), and

D = dilution factor.

Two check procedures were used to eliminate possible sources of error. A study was made to determine the percentage of pesticides recoverable from the cleanup procedure. For this study, turnip greens

and roots were purchased locally and divided into three 10 gm. lots each. To each lot, prior to blending with acetonitrile, each of the insecticides studied was added to give residues of 50 p.p.m., 0.05 p.p.m., and 0.0 p.p.m. They were then cleaned up by the procedure previously described. The percentage recoveries of the various insecticides may be found in Table I.

The other check procedure, recommended by Farrow (32), was the determination of DDT decomposition during gas chromatography. A suitably large injection of p,p'-DDT was injected daily to determine this. Throughout the gas chromatography of the samples, no column decomposition of DDT was noted.

IV. EVALUATION OF DATA

The data were adjusted to give a composite DDT residue and a composite heptachlor residue. The composite DDT residue was determined by the following formula:

$$\text{Composite DDT} = \text{DDT} + 1.079\ \text{TDE} + 1.111\ \text{DDE},$$

where 1.079 and 1.111 are the ratios of the molecular weight of DDT to the molecular weights of TDE and DDE respectively. The composite heptachlor residues were determined by the following formula:

$$\text{Composite heptachlor} = \text{heptachlor} + .975\ \text{heptachlor epoxide},$$

where .975 is the ratio of the molecular weight of heptachlor to the molecular weight of heptachlor epoxide. The preceding adjustments were carried out by the Data Transgenerator subroutine, TRAN, on the IBM Model 7040 digital computer (92).

TABLE I

CLEANUP RECOVERY PERCENTAGES OF SEVERAL INSECTICIDE RESIDUES IN TURNIP GREENS AND ROOTS

Sample Type[1]	Initial Concentration (p.p.m.)	Insecticide Recovery (Percentage of Original Concentration)				
		DDT	TDE	DDE	Heptachlor	Heptachlor Epoxide
G	50	97.5	95.2	96.1	99.0	98.2
R	50	93.6	94.6	86.0	93.5	94.3
G	0.5	90.6	90.0	88.2	92.2	89.5
R	0.5	83.6	85.5	82.6	80.8	87.3
G	0	--	--	--	--	--
R	0	--	--	--	--	--

[1] G indicates a leaf sample; R, a root sample.

The analysis of variance of the original and adjusted data was calculated by the ANOVAR subroutine (12) on the IBM Model 7040 digital computer. The effects of treatment and processing were determined by Duncan's new multiple range test (31); and effects of treatment times process interactions, by least significant differences (100). Correlation between residue concentrations and composite residue concentrations were determined by the BMD02D subroutine on the IBM Model 7040 digital computer.

CHAPTER IV

RESULTS AND DISCUSSION

A. DDT AND DDT METABOLITE RESIDUES IN TURNIP GREENS

Results of the analyses for DDT and DDT metabolites are shown in Tables II through IX. Large differences were found between the samples taken from the plots sprayed with DDT and the samples taken from the plots which had not been sprayed. As processing proceeded, DDT and DDT metabolite residues decreased.

Analyses of variance of the data, shown in Table II, indicate that treatment was significant at the .01 probability (p) level. Process and treatment x process interaction were significant at the .01 p level with composite DDT residues, DDT residues, and TDE residues; and, at the .05 p level with DDE.

The mean residues of DDT and DDT metabolites from each treatment are shown in Table III. In all cases there was no significant difference between the control and the heptachlor treated plots. The DDT and DDT metabolite residues from the DDT + heptachlor treated plots were found to be significantly less than the residues from the DDT treated plot, although they received the same DDT application. The difference may be attributed to the low residues found in the samples from the DDT + heptachlor treated plot taken after the final spray.

TABLE II

ANALYSIS OF VARIANCE OF DDT AND DDT METABOLITE RESIDUES IN TURNIP GREENS

		Mean Squares			
Source	D. F.	Composite DDT	DDT	TDE	DDE
Treatment	3	14618.60**	6974.63**	758.53**	50.08**
Process	5	4250.38**	3708.94**	42.55**	3.66*
T x P	15	2270.20**	1838.25**	27.29**	3.27*
Error	48	19.19	9.49	1.72	1.18

TABLE III

EFFECT OF INSECTICIDE TREATMENT ON DDT AND DDT METABOLITE RESIDUES IN TURNIP GREENS

Treatment	Means[1]			
	Composite DDT[2]	DDT	TDE	DDE
Control	0.270 a	0.232 a	0.029 a	0.006 a
Heptachlor	0.218 a	0.142 a	0.049 a	0.020 a
DDT	56.771 b	40.283 b	11.555 b	3.316 b
DDT + Heptachlor	39.295 c	24.547 c	10.996 b	2.308 c

[1] All means are expressed as p.p.m., and are the mean of eighteen observations.

[2] Means not followed by the same letter are significantly different at .01 p level.

TABLE IV

EFFECT OF PREPARATION AND THERMAL PROCESSING ON THE DDT AND DDT METABOLITE RESIDUES IN TURNIP GREENS

	Means[1]			
Process	Composite DDT[2]	DDT[2]	TDE[2]	DDE[3]
Final Spray	36.046 a	30.124 a	3.949 a	1.393 a
Harvest	56.630 b	44.405 b	8.707 b	2.320 a
Wash	16.708 c	10.735 c	3.879 a	1.508 ab
Blanch	18.189 c	12.044 c	4.914 ac	0.063 b
Thermal Process	7.696 d	0.317 d	5.506 c	1.141 ab
Storage	9.572 d	0.180 d	6.989 c	1.484 ab

[1] All means are expressed as p.p.m., and are the average of eighteen observations.

[2] Means not followed by the same letter are significantly different at the .01 p level.

[3] Means not followed by the same letter are significantly different at the .05 p level.

TABLE V

EFFECT OF TREATMENT x PROCESS INTERACTION ON COMPOSITE DDT RESIDUE IN TURNIP GREENS[1/]

	Treatment			
Process	Control	Heptachlor	DDT	DDT + Heptachlor
Final Spray	1.396	.809	122.298	19.679
Harvest	.073	.126	115.978	110.345
Wash	.062	.145	31.501	35.124
Blanch	.049	.132	37.048	35.491
Thermal Process	.015	.050	15.668	15.010
Storage	.025	.048	18.094	20.118

L. S. D.[2/] = 9.585

[1/] All values are expressed as p.p.m., and are the mean of three observations.

[2/] L. S. D. value for treatment x process interaction at .01 level of significance.

TABLE VI

EFFECT OF TREATMENT x PROCESS INTERACTION ON DDT RESIDUES IN TURNIP GREENS[1/]

Process	Treatment			
	Control	Heptachlor	DDT	DDT + Heptachlor
Final Spray	1.287	.628	103.033	15.547
Harvest	.037	.074	92.797	84.713
Wash	.037	.074	20.233	22.593
Blanch	.028	.077	24.703	23.370
Thermal Process	.000	.000	.787	0.481
Storage	.000	.000	.143	0.575

L. S. D.[2/] = 6.741

[1/] All values are expressed in terms of p.p.m., and are the mean of three observations.

[2/] L. S. D. value for treatment x process interaction at .01 level of significance.

TABLE VII

EFFECT OF PROCESS x TREATMENT INTERACTION ON TDE RESIDUES IN TURNIP GREENS[1/]

	Treatment			
Process	Control	Heptachlor	DDT	DDT + Heptachlor
Final Spray	.095	.114	12.863	2.720
Harvest	.023	.036	16.427	18.343
Wash	.017	.046	5.319	10.136
Blanch	.015	.041	9.758	9.844
Thermal Process	.006	.030	11.330	10.657
Storage	.016	.027	13.635	14.277

L. S. D.[2/] = 2.871

[1/] All values are expressed as p.p.m., and are the mean of three observations.

[2/] L. S'. D. value of treatment x process interaction at .01 level of significance.

TABLE VIII

EFFECT OF TREATMENT x PROCESS INTERACTION ON DDE RESIDUES IN TURNIP GREENS[1]

Process	Treatment			
	Control	Heptachlor	DDT	DDT + Heptachlor
Final Spray	.004	.049	4.512	1.007
Harvest	.008	.012	4.483	4.777
Wash	.005	.018	4.837	1.171
Blanch	.004	.009	1.412	1.093
Thermal Process	.005	.015	2.095	2.449
Storage	.006	.016	2.560	3.353

L. S. D.[2] = 1.802

[1] All values are expressed as p.p.m., and are the mean of three observations.

[2] L. S. D. value for treatment x process interaction at .05 level of significance.

TABLE IX

CORRELATION MATRIX OF DDT AND DDT METABOLITES IN TURNIP GREENS

	DDT	TDE	DDE
Composite DDT	0.9870	0.7643	0.6989
DDE	0.6178	0.7098	
TDE	0.6548		

The mean residues of DDT and DDT metabolites at each process level are shown in Table IV, page 39. In all cases, the residues found in samples taken after the final spray were significantly (.01 p level) than those found in the samples taken at harvest. This is attributed to low residues in samples taken from the DDT + heptachlor treated plots after the final spray. Washing significantly reduced (.01 p level) all residues except the DDE residues. There was no significant difference between the residues found after washing and those found after blanching; however, the residues after blanching were generally numerically higher than after washing. Although a detailed study was not made to explain the higher residues, in a simple study of weights of a given quantity of leaves it was noted that there was about a 30 per cent increase over fresh weight after washing and about a 5 per cent increase over fresh weight after blanching. Therefore, the lower residues encountered after washing are probably due to dilution as well as actual removal.

Thermal processing significantly reduced (.01 p level) the composite DDT and DDT residues, while TDE and DDE were not significantly different. This observation is consistent with the findings of Farrow, Elkins, and Cook (33). In all cases, there was no significant difference between the residues in samples taken after thermal processing and those taken after 6 months storage.

The means of the treatment x process interaction are found in Tables V through VIII, pages 40-43. In all cases, there were no significant differences between the residues in samples from the control

and heptachlor treated plots. Although no DDT was applied to either the control or heptachlor treated plots, small residues of DDT and DDT metabolites were present; these findings may be attributed to drift of the DDT spray or to DDT contamination from prior applications. The trends in residues caused by processing seem similar, though insignificant, to the decreases found in samples from the two plots where DDT had been intentionally applied.

Although the same amount of DDT was applied to both plots, the residues taken in samples from the DDT + heptachlor treated plot taken after the final spray were significantly less than similar samples from the DDT treated plot. The low residues in question may have been caused by poor sampling or by an error in dilution either during gas chromatography or during the cleanup procedure.

Other than the difference between the samples from the DDT and DDT + heptachlor treated plots taken after final spray, there was no significant difference between composite DDT residues (Table V, page 40) in samples from two plots at similar process levels. Washing significantly reduced (.01 p level) the composite DDT residues, as did thermal processing. There was no significant difference between the composite DDT residues in samples from the DDT treated plot taken after final spray and at harvest. In samples from both plots, there was no significant reduction caused by blanching or by 6 months storage.

Other than the differences previously noted, there was no significant difference in DDT residues (Table VI, page 41) found in samples from the DDT and DDT + heptachlor treated plots at similar

levels of processing. Washing significantly reduced (78 and 71 per cent) the DDT residues, as did thermal processing (97 and 98 per cent). No significant reduction of DDT was affected by blanching or by 6 months storage.

There are no significant differences between TDE residues (Table VII, page 42) in samples from DDT and DDT + heptachlor treated plots at similar levels of processing, except for those residues in samples taken after the final spray and after washing. The low residue in the samples from the DDT treated plot taken after washing was probably due to an error in analysis; had this been a case of poor sampling, the difference would have been reflected in DDT and DDE residues.

In samples from both plots, washing significantly reduced TDE residues. In samples from the DDT + heptachlor treated plot, there was no significant difference after blanching. Thermal processing caused an insignificant increase in TDE residues in samples from both plots. In samples from the DDT + heptachlor treated plot, the TDE residue was significantly increased after 6 months storage.

With exceptions similar to those noted with TDE residues, there are no significant differences between DDE residues (Table VIII, page 43) in samples from the DDT and DDT + heptachlor treated plots at similar levels of processing. Because of the irregularity of data, no conclusions could be made about the effects of washing and blanching. A small but insignificant increase in DDE was noted after thermal processing and after 6 months storage.

Examination of the fill liquor showed the residue concentration to be essentially zero. Scattered traces of DDE and TDE were found, which could be expected on the basis of relative solubilities of the insecticides in water.

The correlation matrix of DDT and DDT metabolites is found in Table IX, page 44. There was a very high correlation between DDT and composite DDT residues which would be expected on the basis of DDT being the major component of the composite DDT residue. Other correlations were not as high as the DDT-composite DDT correlation, indicating that processing had different effects on each residue.

Overall, washing is an effective means of reducing DDT, TDE, and probably DDE. Thermal processing caused a drastic reduction in DDT, and small insignificant increases in TDE and DDE. This observation is consistent with the findings of Farrow, Elkins, and Cook (34) who showed that during thermal processing of spinach DDT was converted to TDE, DDE, and other compounds which are not detected by the method used. During storage, the decomposition of DDT seemed to continue as indicated by the decrease in DDT and increases in TDE and DDE. Blanching does not significantly reduce the residues. This is contrary to the findings of Dormal et al. (30) who noted that blanching reduced DDT residues. However, it was indicated that they used a hot water blanch rather than a steam blanch.

II. HEPTACHLOR AND HEPTACHLOR EPOXIDE RESIDUES IN TURNIP GREENS

The results of the experiments on heptachlor and heptachlor epoxide are found in Tables X through XVI. In the experimental design the data from the DDT treated plot were excluded. Except for scattered traces of heptachlor, the heptachlor and heptachlor epoxide residue concentration was zero.

From the analyses of variance (Table X), treatment was significant at the .01 p level for the composite heptachlor, heptachlor, and heptachlor epoxide residues. Process was significant at the .01 p level for the composite heptachlor and heptachlor residues, but was not significant for heptachlor epoxide residues. The treatment x process interaction was significant at the .01 p level for the composite heptachlor and heptachlor residues; and, at the .05 p level for heptachlor epoxide residues.

The effect of insecticide treatments are found in Table XI. The composite heptachlor and heptachlor residues in samples from the control plot were significantly different (.01 p level) from residues in samples from the heptachlor and DDT + heptachlor treated plots. The heptachlor epoxide residues in samples from the control plot were not significantly different from those found in samples from the heptachlor treated plot, but were significantly different from those in samples from the DDT + heptachlor plot.

The effect of process on residues of composite heptachlor, heptachlor, and heptachlor epoxide are found in Table XII, page 52.

TABLE X

ANALYSIS OF VARIANCE OF HEPTACHLOR AND HEPTACHLOR EPOXIDE RESIDUES IN TURNIP GREENS

Source	D. F.	Mean Squares		
		Composite Heptachlor	Heptachlor	Heptachlor Epoxide
Treatment	2	.0060**	.0032**	.0010**
Process	5	.0011**	.0012**	.0002 n.s.
T x P	10	.0011**	.0006**	.0003*
Error	36	.0003	.0001	.0001

TABLE XI

EFFECT OF INSECTICIDE TREATMENT ON HEPTACHLOR AND HEPTACHLOR EPOXIDE RESIDUES IN TURNIP GREENS

Treatment	Means[1]		
	Composite Heptachlor[2]	Heptachlor	Heptachlor Epoxide
Control	.000 a	.000 a	.000 a
Heptachlor	.036 b	.027 b	.010 ab
DDT + Heptachlor	.024 b	.010 c	.015 b

[1] All values are expressed as p.p.m., and are the mean of eighteen observations.

[2] Means not followed by the same letter are significantly different at the .01 p level.

TABLE XII

EFFECT OF PREPARATION AND THERMAL PROCESSING ON HEPTACLOR AND HEPTACHLOR EPOXIDE RESIDUES IN TURNIP GREENS

Process	Means[1]		
	Composite Heptachlor[2]	Heptachlor	Heptachlor Epoxide
Final Spray	.033 a	.029 a	.004 a
Harvest	.032 a	.023 ab	.009 a
Wash	.026 ab	.014 bc	.012 a
Blanch	.009 c	.007 cd	.002 a
Thermal Process	.010 bc	.001 d	.010 a
Storage	.011 bc	.001 d	.011a

[1] All values are expressed as p.p.m., and are the mean of nine observations.

[2] Means not followed by the same letter are significantly different at the .01 p level.

TABLE XIII

EFFECT OF TREATMENT x PROCESS INTERACTION ON COMPOSITE HEPTACHLOR EPOXIDE RESIDUES IN TURNIP GREENS[1/]

	Treatment		
Process	Control	Heptachlor	DDT + Heptachlor
Final Spray	.000	.076	.024
Harvest	.000	.061	.033
Wash	.000	.060	.018
Blanch	.000	.009	.017
Thermal Process	.000	.005	.025
Storage	.000	.005	.029

L. S. D.[2/] = .039

[1/] All values are expressed as p.p.m., and are the mean of three observations.

[2/] L. S. D. value of treatment x process interaction at the .01 level of significance.

TABLE XIV

EFFECT OF TREATMENT x PROCESS INTERACTION ON HEPTACHLOR RESIDUES IN TURNIP GREENS[1/]

	Treatment		
Process	Control	Heptachlor	DDT + Heptachlor
Final Spray	.000	.065	.022
Harvest	.000	.052	.015
Wash	.000	.031	.012
Blanch	.000	.009	.012
Thermal Process	.000	.001	.000
Storage	.000	.001	.000

L. S. D.[2/] = .017

[1/] All values are expressed as p.p.m., and are the mean of three observations.

[2/] L. S. D. value for treatment x process interaction at .01 level of significance.

TABLE XV

EFFECT OF TREATMENT x PROCESS INTERACTION ON HEPTACHLOR EPOXIDE RESIDUES IN TURNIP GREENS[1/]

	Treatment		
Process	Control	Heptachlor	DDT + Heptachlor
Final Spray	.000	.011	.002
Harvest	.000	.009	.019
Wash	.000	.030	.006
Blanch	.000	.000	.005
Thermal Process	.000	.004	.026
Storage	.000	.004	.030

L. S. D.[2/] = .027

[1/] All values are expressed as p.p.m., and are the mean of three observations.

[2/] L. S. D. value for treatment x process interaction at .01 level of significance.

TABLE XVI

CORRELATION MATRIX OF HEPTACHLOR AND HEPTACHLOR EPOXIDE IN TURNIP GREENS

	Heptachlor	Heptachlor Epoxide
Composite Heptachlor	0.8891	0.7618
Heptachlor Epoxide	0.3809	

There was no significant difference among composite heptachlor residues in samples taken after the final spray, at harvest, and after washing; however, the residues in samples taken after final spray and at harvest were significantly different at the .01 p level from the residues in samples taken after blanching, after thermal processing, and after 6 months storage.

No single process had any effect on the heptachlor residues; however, the heptachlor residues in samples taken after washing were significantly less than those found in samples taken after the final spray, but not significantly different from those found in samples at harvest. The residues in samples taken after blanching were significantly less than those in samples taken at harvest, but not those in samples taken after washing. There was a small, but insignificant, decrease of heptachlor residues taken after thermal processing. No process had a significant effect on heptachlor epoxide residues.

The effect of treatment x process interaction on composite heptachlor, heptachlor, and heptachlor epoxide residues are found in Tables XIII through XV, pages 53-55. The residue concentration of all control samples was zero; processing, therefore, had no measurable effect.

Among the composite heptachlor residues (Table XIII, page 53) in samples taken from the heptachlor treated plots after the final spray, at harvest, and after washing, there were no significant differences. Blanching, however, significantly reduced the composite heptachlor residue. There was no significant effect by processing

on composite heptachlor residues in samples from the DDT + heptachlor treated plot.

There was a significant difference between the heptachlor residues (Table XIV, page 54) in samples from the heptachlor and DDT + heptachlor treated plots at the first three levels of processing. In the last three levels of processing, however, no difference was found among residues in samples taken from the two plots. In samples from the heptachlor treated plot, washing significantly reduced the heptachlor residue, as did blanching. Thermal processing reduced the heptachlor residues further; however, the reduction was not significant. No significant reduction was noted between successive processing steps in samples from the DDT + heptachlor treated plot; however, the residue reduction followed the same general trend as in the samples from the heptachlor treated plot.

No significant differences among heptachlor epoxide residues (Table XV, page 55) were noted between successive processing steps from either the heptachlor or DDT + heptachlor treated plots. Although the data were irregular, it was noted that heptachlor epoxide residues were comparatively greater than heptachlor residues after thermal processing and 6 months storage.

No residues of either heptachlor or heptachlor epoxide were found in the fill liquor of the canned samples.

The correlation matrix of heptachlor and heptachlor epoxide are found in Table XVI, page 56. There was a high correlation between heptachlor and composite heptachlor residues. The correlation between

heptachlor and heptachlor epoxide residues were very low (+.3809) indicating that processing had different effects on each one. A conversion of heptachlor to heptachlor epoxide would be one possible explanation for such a low correlation.

Overall, heptachlor residues were reduced with successive processing steps; the largest reductions were caused by washing and blanching. Thermal processing, though insignificantly, further reduced heptachlor residues.

Heptachlor epoxide residues occurred irregularly among the samples and no conclusions could be made. However, the ratio of heptachlor epoxide to heptachlor was greater after thermal processing, suggesting that some conversion of heptachlor to its epoxide was affected.

Street et al. (101) showed that the presence of DDT will decrease the amount of heptachlor and heptachlor epoxide retained in animal tissue. A comparison of the heptachlor and heptachlor epoxide residues (Tables XIV and XV, pages 54-55) in samples from the heptachlor and DDT + heptachlor treated plots after the final DDT application and at harvest suggests that an analogous situation may exist in plants.

III. DDT AND DDT METABOLITES IN TURNIP ROOTS

Results of the analyses for DDT and DDT metabolite residues are found in Tables XVII through XXIV. Large differences were found in DDT and DDT metabolite residues between samples from those plots

TABLE XVII

ANALYSIS OF VARIANCE OF DDT AND DDT METABOLITE RESIDUES IN TURNIP ROOTS

		Mean Squares			
Source	D. F.	Composite DDT	DDT	TDE	DDE
Treatment	2	.0390**	.0164**	.0017**	.0005**
Process	4	.0387**	.0171**	.0015**	.0005**
T x P	8	.0143**	.0062**	.0006**	.0002**
Error	30	.0006	.0003	.000025	.000005

TABLE XVIII

EFFECT OF INSECTICIDE TREATMENT ON DDT AND DDT METABOLITE RESIDUES IN TURNIP ROOTS

Treatment	Means[1]			
	Composite DDT[2]	DDT	TDE	DDE
Control	.002 a	.000 a	.001 a	.001 a
DDT	.048 b	.031 b	.009 b	.006 b
DDT + Heptachlor	.104 c	.067 c	.022 c	.012 c

[1] All values are expressed as p.p.m., and are the mean of fifteen replications.

[2] Means not followed by the same letter are significantly different at the .01 p level.

TABLE XIX

EFFECT OF PREPARATION AND THERMAL PROCESSING ON DDT AND DDT METABOLITE RESIDUES IN TURNIP ROOTS

Process	Means[1]			
	Composite DDT[2]	DDT	TDE	DDE
Harvest	.127 a	.084 a	.025 a	.014 a
Wash	.129 a	.076 a	.024 a	.014 a
Peel	.006 b	.002 b	.003 b	.001 b
Thermal Process	.003 b	.000 b	.001 b	.001 b
Storage	.002 b	.000 b	.001 b	.001 b

[1] All values are expressed as p.p.m., and are the mean of nine observations.

[2] Means not followed by the same letter are significantly different at the .01 p level.

TABLE XX

EFFECT OF TREATMENT x PROCESS INTERACTION ON COMPOSITE DDT RESIDUES IN TURNIP ROOTS[1]

	Treatment		
Process	Control	DDT	DDT + Heptachlor
Harvest	.003	.107	.272
Wash	.003	.116	.237
Peel	.003	.008	.007
Thermal Process	.002	.003	.003
Storage	.001	.003	.002

L. S. D.[2] = .054

[1] All values are expressed as p.p.m., and are means of three observations.

[2] L. S. D. value of treatment x process interaction at .01 level of significance.

TABLE XXI

EFFECT OF TREATMENT x PROCESS INTERACTION ON DDT RESIDUES IN TURNIP ROOTS[1/]

	Treatment		
Process	Control	DDT	DDT + Heptachlor
Harvest	.001	.073	.179
Wash	.001	.076	.152
Peel	.000	.004	.001
Thermal Process	.000	.001	.000
Storage	.000	.001	.000

L. S. D.[2/] = .039

[1/] All values are expressed as p.p.m., and are the mean of three observations.

[2/] L. S. D. value of treatment x process interactions at .01 level of significance.

TABLE XXII

EFFECT OF TREATMENT x PROCESS INTERACTION ON TDE RESIDUES IN TURNIP ROOTS[1/]

	Treatment		
Process	Control	DDT	DDT + Heptachlor
Harvest	.001	.019	.055
Wash	.001	.023	.049
Peel	.001	.003	.004
Thermal Process	.001	.001	.001
Storage	.000	.001	.001

L. S. D.[2/] = .012

[1/] All values are expressed as p.p.m., and are the mean of three observations.

[2/] L. S. D. value of treatment x process interactions at .01 level of significance.

TABLE XXIII

EFFECT OF TREATMENT x PROCESS INTERACTION ON DDE RESIDUES IN TURNIP ROOTS[1/]

Process	Treatment		
	Control	DDT	DDT + Heptachlor
Harvest	.001	.011	.029
Wash	.001	.014	.027
Peel	.001	.001	.001
Thermal Process	.001	.001	.001
Storage	.001	.001	.001

L. S. D.[2/] = .002

[1/] All values expressed in terms of p.p.m., and are means of three observations.

[2/] L. S. D. value of treatment x process interaction at .01 level of significance.

TABLE XXIV

CORRELATION MATRIX OF DDT AND DDT METABOLITES IN TURNIP ROOTS

	DDT	TDE	DDE
Composite DDT	0.9994	0.9950	0.9848
DDE	0.9839	0.9802	
TDE	0.9911		

sprayed with DDT and plots not sprayed. The residue concentration in samples from the heptachlor treated plot were essentially zero, except for scattered traces of DDT, TDE, and DDE. In the statistical design of this portion of the experiment, therefore, the data from the heptachlor treated plot were omitted. With all residues, as processing of the roots proceeded the residues decreased.

Analyses of variance of the data, found in Table XVII, page 60, indicate that treatment, process, and treatment x process interaction were all significant at the .01 p level for residues of DDT and DDT metabolites, as well as the composite DDT residue. The average residues of DDT and DDT metabolites in samples from each treatment plot are shown in Table XVIII, page 61. The average residues of DDT and DDT metabolites in samples from each plot were significantly different from each other at the .01 p level. In all cases, the samples from the control plot had the minimum residue; and the DDT + heptachlor treated plot, the greatest residue.

The average residues of the composite DDT, DDT and DDT metabolite residues from each processing level are found in Table XIX, page 62. In all cases, there was no significant difference among the residues in samples taken at harvest and after washing. Lye peeling, which removed the epidermis and cortex, significantly reduced DDT, TDE, and DDE residues. There was no significant difference among the residues in samples taken after lye peeling, after thermal processing, or after 6 months storage.

The effects of treatment x process interaction on DDT and DDT metabolite residues are found in Tables XX through XXIII, pages 63-66. In all cases, there was no significant difference among the residues in samples from the control plot. The composite DDT residues (Table XX, page 63) from the DDT treated plots were significantly less at the first two levels of processing than the residues in samples from the DDT + heptachlor treated plots. Lye peeling signifantly reduced the composite DDT residues in samples from both the DDT and DDT + heptachlor treated plots. DDT and DDT metabolite residues (Tables XXI, XXII, and XXIII, pages 64-66) followed the same trend as the composite DDT residues.

No residues of DDT or DDT metabolites were found in the fill liquor of the canned samples.

The correlation matrix of DDT and DDT metabolites in turnip roots is found in Table XXIV, page 67. All combinations of the residues possess a very high correlation which indicates that processing influences the residues similarly, as opposed to the wide range of correlations of DDT and DDT metabolite residues in turnip greens.

Lye peeling, in all cases, caused a significant reduction in all residues. This observation indicates that the majority of DDT, TDE, and DDE residues are contained in the epidermis or cortex, which is removed by peeling, and very little of the residue is translocated into the pith. Lichtenstein, Myrdal, and Schulz (64) reported similar findings in carrots.

IV. HEPTACHLOR AND HEPTACHLOR EPOXIDE RESIDUES IN TURNIP ROOTS

The results of the experiments on heptachlor and heptachlor epoxide residues in turnip roots are found in Tables XXV through XXXI. In the statistical design of this part of the experiment, the data from the DDT treated plot were omitted. There were no heptachlor or heptachlor epoxide residues recovered from samples in this plot; the inclusion of such data would have led to false significance.

Analyses of variance of the data shown in Table XXV indicate that all effects--treatment, process, and treatment x process interaction--were significant at the .01 p level. The effects of insecticide treatment may be found in Table XXVI. In all cases--the composite heptachlor, heptachlor, and heptachlor epoxide residues--there was no significant difference between residues in samples from the control and DDT + heptachlor treated plots. The residues in samples from the heptachlor treated plot were significantly different at the .01 p level from residues in samples from the other plots.

The processing effects are found in Table XXVII. There was no significant difference in composite heptachlor residues in sample taken at harvest and after washing. Lye peeling significantly reduced the composite heptachlor residue. Thermal processing and storage, though insignificantly, reduced the residues.

Washing significantly reduced the heptachlor residues (Table XVII). This was the only occasion in which washing significantly

TABLE XXV

ANALYSIS OF VARIANCE OF HEPTACHLOR AND HEPTACHLOR EPOXIDE RESIDUES IN TURNIP ROOTS

		Mean Squares		
Source	D. F.	Composite Heptachlor	Heptachlor	Heptachlor Epoxide
Treatment	2	.0020**	.0003**	.0008**
Process	4	.0012**	.0003**	.0003**
T x P	8	.0007**	.0001**	.0003**
Error	30	.00003	.000008	.000028

TABLE XXVI

EFFECT OF INSECTICIDE TREATMENT ON HEPTACHLOR AND HEPTACHLOR EPOXIDE RESIDUES IN TURNIP ROOTS

Treatment	Means[1]		
	Composite Heptachlor[2]	Heptachlor	Heptachlor Epoxide
Control	.003 a	.002 a	.001 a
Heptachlor	.025 b	.010 b	.015 b
DDT + Heptachlor	.008 a	.003 a	.005 a

[1] All values are expressed as p.p.m., and are the mean of fifteen observations.

[2] Means not followed by the same letter are significant different at .01 *p* level.

TABLE XXVII

EFFECT OF PREPARATION AND THERMAL PROCESSING ON HEPTACHLOR AND HEPTACHLOR EPOXIDE RESIDUES IN TURNIP ROOTS

	Means[1]		
Process	Composite Heptachlor[2]	Heptachlor	Heptachlor Epoxide
Harvest	.027 a	.014 a	.014 a
Wash	.021 a	.009 a	.012 a
Peel	.006 b	.001 c	.006 b
Thermal Process	.004 b	.000 c	.004 b
Storage	.001 b	.000 c	.000 b

[1] All values are expressed as p.p.m., and are the mean of nine observations.

[2] Means not followed by the same letter significantly different at the .01 p level.

TABLE XXVIII

EFFECT OF TREATMENT x PROCESS INTERACTION ON COMPOSITE HEPTACHLOR RESIDUES IN TURNIP ROOTS[1/]

	Treatment		
Process	Control	Heptachlor	DDT + Heptachlor
Harvest	.007	.065	.010
Wash	.001	.043	.017
Peel	.002	.007	.010
Thermal Process	.001	.007	.004
Storage	.001	.001	.001

L. S. D.[2/] = .016

[1/] All means are expressed in terms of p.p.m., and are the mean of three observations.

[2/] L. S. D. value of treatment x process interaction at .01 level of significance.

TABLE XXIX

EFFECT OF TREATMENT x PROCESS INTERACTION ON HEPTACHLOR RESIDUES IN TURNIP ROOTS[1/]

Process	Treatment		
	Control	Heptachlor	DDT + Heptachlor
Harvest	.006	.029	.007
Wash	.000	.019	.008
Peel	.002	.001	.000
Thermal Process	.000	.000	.000
Storage	.000	.000	.000

L. S. D.[2/] = .006

[1/] All values are expressed in terms of p.p.m., and are the mean of three observations.

[2/] L. S. D. value for treatment x process interaction at .01 level of significance.

TABLE XXX

EFFECT OF TREATMENT x PROCESS INTERACTION ON HEPTACHLOR EPOXIDE RESIDUES IN TURNIP ROOTS[1/]

	Treatment		
Process	Control	Heptachlor	DDT + Heptachlor
Harvest	.002	.038	.003
Wash	.000	.026	.010
Peel	.001	.006	.010
Thermal Process	.000	.007	.004
Storage	.000	.000	.000

L. S. D.[2/] = .014

[1/] All values are expressed as p.p.m., and are the mean of three observations.

[2/] L. S. D. value for treatment x process interaction at .01 level of significance.

TABLE XXXI

CORRELATION MATRIX OF HEPTACHLOR AND HEPTACHLOR EPOXIDE IN TURNIP ROOTS

	Heptachlor	Heptachlor Epoxide
Composite Heptachlor	0.9418	0.9661
Heptachlor Epoxide	0.8230	

reduced a residue in the root samples. Lye peeling also caused significant reduction of the heptachlor residues. There was no significant difference among heptachlor residues in samples taken after lye peeling, after thermal processing, and after 6 months storage. There was no significant difference between heptachlor epoxide residues found in samples taken at harvest and those taken after washing. Lye peeling, as was the case with all other residues, significantly reduced the heptachlor epoxide residues.

Effects of the treatment x process interaction are found in Tables XXVIII through XXX (pages 74, 75, and 76). The composite heptachlor residue (Table XXVII, page 73) in samples at the first two levels of processing from the heptachlor and DDT + heptachlor treated plots were significantly different; however, in the last three levels of processing, there was no statistical difference among composite heptachlor residues in samples taken from either plot. In samples taken from the heptachlor treated plot, washing significantly decreased the composite heptachlor residue, as did lye peeling. Thermal processing and storage had no significant effect. No significant successive processing effects were noted in the control and DDT + heptachlor treated plots.

Washing significantly reduced the heptachlor residues (Table XXIX, page 75) in samples taken from the heptachlor treated plot, but not in samples from the DDT + heptachlor treated plot. Lye peeling, as observed with other insecticides, significantly reduced heptachlor

residues in samples from both heptachlor and DDT + heptachlor treated plots. Thermal processing and 6 months storage had no significant effect.

There were no significant differences among heptachlor epoxide residues (Table XXX, page 76) in root samples from the control and DDT + heptachlor treated plots. Washing had no significant effect on heptachlor epoxide residue in samples from the heptachlor treated plot; however, lye peeling significantly reduced the heptachlor epoxide residues. Thermal processing and 6 months storage had no significant effect on the residues.

No heptachlor or heptachlor epoxide residues were found in the fill liquor of the canned samples.

The correlation matrix for heptachlor and heptachlor epoxide residues in turnip roots is found in Table XXXI, page 77. All three combinations showed very high correlation, indicating that processing had similar effects on both heptachlor and heptachlor epoxide.

Lye peeling, as previously noted in samples containing DDT and DDT metabolite residues, was an effective means of removing both heptachlor and heptachlor epoxide residues. This lends support to the observations of Lichtenstein, Myrdal, and Schulz (64), and Ordas, Smith, and Meyer (88) that chlorinated hydrocarbon insecticides are found almost exclusively in the epidermal cells of roots and tubers, and that there is very little transmigration of residues into the pith.

Again noted, as in the turnip green samples, the retention of heptachlor and heptachlor epoxide was significantly less in samples

from the DDT + heptachlor treated plots. These observations further suggest that an interaction between DDT and heptachlor, analogous to that observed by Street et al. (101) in animal tissue, may also occur in plant tissue.

Because of the low concentration of the residues, it was not possible to show that thermal processing has a significant effect on heptachlor and heptachlor epoxide residues in roots.

CHAPTER V

SUMMARY

A study was made to determine the effect of preparation and thermal processing on residues of DDT, heptachlor and their metabolites in turnip greens and roots.

Under the conditions of the experiment reported in this paper, it was found that:

1. The washing of turnip greens reduced residues of DDT, TDE, and heptachlor, but had no significant effect on DDE or heptachlor epoxide.

2. Blanching reduced the level of heptachlor in turnip greens, but had no effect on DDT and DDT metabolites, or on heptachlor epoxide.

3. Thermal processing effectively reduced the concentration of DDT probably by conversion to TDE and DDE which were slightly, but insignificantly, increased. Thermal processing had no effect on heptachlor or heptachlor epoxide.

4. Storage of the canned greens at room temperature had a significant effect on TDE only, which was increased.

5. In the washing process of turnip roots, only residues of heptachlor were significantly reduced.

6. Peeling of turnip roots in a lye bath effectively removed residues of all the insecticides studied.

7. Results of the data suggest that a DDT-heptachlor interaction, previously observed only in animal tissue, also may be present in plant tissues.

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APPENDIX

TABLE XXXII

RESIDUES OF DDT, DDT METABOLITES, HEPTACHLOR, AND HEPTACHLOR EPOXIDE IN TURNIP GREENS

Source[1]	Rep.	Insecticide[2]				
		Heptachlor	Heptachlor Epoxide	DDE	TDE	DDT
C-1	1	.000	.000	.005	.108	1.334
C-1	2	.000	.000	.005	.088	1.348
C-1	3	.000	.000	.002	.088	1.179
C-2	1	.000	.000	.009	.018	.029
C-2	2	.000	.000	.010	.019	.033
C-2	3	.000	.000	.005	.034	.050
C-3	1	.000	.000	.004	.017	.037
C-3	2	.000	.000	.006	.014	.036
C-3	3	.000	.000	.006	.019	.040
C-4	1	.000	.000	.004	.015	.028
C-4	2	.000	.000	.004	.015	.031
C-4	3	.000	.000	.005	.015	.028
C-5	1	.000	.000	.003	.005	.001
C-5	2	.000	.000	.006	.009	.001
C-5	3	.000	.000	.006	.010	.001
C-6	1	.000	.000	.008	.024	.001
C-6	2	.000	.000	.002	.003	.001
C-6	3	.000	.000	.010	.022	.001
C-7	1	.000	.000	.000	.000	.000
C-7	2	.000	.000	.000	.000	.000
C-7	3	.000	.000	.000	.000	.000
C-8	1	.000	.000	.000	.000	.000
C-8	2	.000	.000	.000	.000	.000
C-8	3	.000	.000	.000	.000	.000
H-1	1	.069	.013	.061	.146	1.019
H-1	2	.042	.010	.017	.043	.336
H-1	3	.085	.053	.068	.153	.529
H-2	1	.042	.003	.019	.033	.075
H-2	2	.058	.007	.009	.032	.070
H-2	3	.060	.001	.009	.041	.075

TABLE XXXII (continued)

Source[1]	Rep.	Insecticide[2] Heptachlor	Heptachlor Epoxide	DDE	TDE	DDT
H-3	1	.063	.077	.016	.052	.075
H-3	2	.015	.007	.022	.041	.076
H-3	3	.016	.005	.018	.044	.073
H-4	1	.002	.000	.018	.035	.078
H-4	2	.000	.000	.010	.044	.077
H-4	3	.004	.000	.010	.044	.075
H-5	1	.000	.005	.018	.036	.000
H-5	2	.000	.002	.012	.023	.001
H-5	3	.002	.007	.013	.031	.001
H-6	1	.000	.003	.017	.028	.001
H-6	2	.000	.004	.017	.026	.001
H-6	3	.000	.001	.015	.027	.001
H-7	1	.001	.002	.000	.000	.000
H-7	2	.000	.000	.000	.000	.000
H-7	3	.000	.000	.000	.000	.000
H-8	1	.000	.000	.000	.000	.000
H-8	2	.000	.000	.000	.000	.000
H-8	3	.000	.000	.000	.000	.000
D-1	1	.000	.000	5.232	11.15	94.86
D-1	2	.003	.000	3.583	13.37	101.12
D-1	3	.000	.001	4.720	14.07	113.21
D-2	1	.000	.000	3.482	17.34	100.40
D-2	2	.000	.000	4.142	16.80	89.92
D-2	3	.000	.000	5.467	15.14	88.07
D-3	1	.000	.000	.171	4.35	21.01
D-3	2	.000	.000	4.779	4.82	18.26
D-3	3	.000	.000	9.562	6.77	21.43
D-4	1	.000	.000	.017	7.14	18.09
D-4	2	.000	.000	2.024	10.18	28.05
D-4	3	.000	.000	2.177	11.95	27.97
D-5	1	.000	.000	1.915	10.63	.866
D-5	2	.000	.000	3.326	11.82	.833
D-5	3	.000	.000	2.043	11.54	.662
D-6	1	.000	.000	2.108	9.695	.163
D-6	2	.000	.000	3.387	16.56	.000
D-6	3	.000	.000	2.185	14.65	.265

TABLE XXXII (continued)

Source[1]	Rep.	Insecticide[2]				
		Heptachlor	Heptachlor Epoxide	DDE	TDE	DDT
D-7	1	.000	.000	.000	.000	.000
D-7	2	.000	.000	.002	.000	.000
D-7	3	.000	.000	.001	.001	.000
D-8	1	.000	.000	.001	.000	.000
D-8	2	.000	.000	.000	.000	.000
D-8	3	.000	.000	.000	.000	.000
DH-1	1	.022	.002	1.079	2.540	14.34
DH-1	2	.022	.002	.918	2.536	15.47
DH-1	3	.023	.002	1.207	3.084	16.83
DH-2	1	.018	.036	5.252	20.17	91.07
DH-2	2	.009	.017	4.150	17.39	82.50
DH-2	3	.019	.003	4.928	17.47	80.57
DH-3	1	.017	.010	1.153	10.53	25.64
DH-3	2	.010	.005	.947	8.977	23.64
DH-3	3	.008	.003	1.412	10.90	18.50
DH-4	1	.008	.005	.836	9.800	22.71
DH-4	2	.012	.007	1.527	11.45	27.36
DH-4	3	.015	.004	.916	8.282	20.04
DH-5	1	.001	.021	2.808	10.42	.629
DH-5	2	.001	.023	2.756	11.77	.362
DH-5	3	.000	.034	1.963	9.781	.442
DH-6	1	.000	.022	3.182	11.01	.356
DH-6	2	.000	.034	1.982	14.50	.435
DH-6	3	.000	.012	4.894	17.32	.934
DH-7	1	.000	.001	.002	.001	.000
DH-7	2	.000	.000	.000	.000	.000
DH-7	3	.000	.000	.000	.000	.000
DH-8	1	.000	.000	.000	.000	.000
DH-8	2	.000	.000	.000	.000	.000
DH-8	3	.000	.000	.000	.000	.000

[1] Letter indicates test plot from which samples was taken: C, control; H, heptachlor; D, DDT; DH, DDT + heptachlor. Number indicates process level from which samples was taken: 1, final spray; 2, harvest; 3, wash; 4, blanch; 5, thermal process; 6, storage; 7, fill liquor from samples taken after thermal process; 8, fill liquor from samples taken after storage.

[2] All values are expressed as p.p.m.

TABLE XXXIII

RESIDUES OF DDT, DDT METABOLITES, HEPTACHLOR, AND HEPTACHLOR EPOXIDE IN TURNIP ROOTS

Source[1/]	Rep.	Insecticide[2/]				
		Heptachlor	Heptachlor Epoxide	DDE	TDE	DDT
C-1	1	.003	.000	.001	.001	.001
C-1	2	.011	.005	.001	.001	.001
C-1	3	.004	.000	.001	.001	.001
C-2	1	.000	.000	.001	.001	.001
C-2	2	.000	.000	.000	.000	.000
C-2	3	.000	.000	.001	.001	.001
C-3	1	.001	.000	.001	.001	.000
C-3	2	.003	.001	.001	.001	.000
C-3	3	.001	.000	.001	.001	.001
C-4	1	.000	.000	.001	.001	.000
C-4	2	.000	.000	.000	.000	.000
C-4	3	.000	.000	.001	.000	.000
C-5	1	.000	.000	.001	.001	.000
C-5	2	.000	.000	.001	.000	.000
C-5	3	.000	.000	.000	.000	.000
C-6	1	.000	.000	.000	.000	.000
C-6	2	.000	.000	.000	.000	.000
C-6	3	.000	.000	.000	.000	.000
C-7	1	.000	.000	.000	.000	.000
C-7	2	.000	.000	.000	.000	.000
C-7	3	.000	.000	.000	.000	.000
H-1	1	.034	.027	.001	.001	.001
H-1	2	.031	.048	.001	.001	.001
H-1	3	.022	.041	.001	.001	.001
H-2	1	.023	.019	.001	.001	.001
H-2	2	.016	.035	.001	.001	.001
H-2	3	.018	.023	.001	.001	.001
H-3	1	.002	.006	.001	.001	.001
H-3	2	.000	.008	.001	.001	.000
H-3	3	.001	.004	.001	.000	.000
H-4	1	.000	.002	.001	.000	.000
H-4	2	.000	.011	.001	.001	.001
H-4	3	.000	.008	.001	.001	.000

TABLE XXXIII (continued)

Source[1]	Rep.	Insecticide[2]				
		Heptachlor	Heptachlor Epoxide	DDE	TDE	DDT
H-5	1	.000	.000	.001	.000	.000
H-5	2	.000	.000	.000	.000	.000
H-5	3	.000	.000	.000	.000	.000
H-6	1	.000	.001	.000	.000	.000
H-6	2	.000	.000	.000	.000	.000
H-6	3	.000	.000	.000	.000	.000
H-7	1	.000	.000	.000	.000	.000
H-7	2	.000	.000	.000	.000	.000
H-7	3	.000	.000	.000	.000	.000
D-1	1	.000	.001	.006	.010	.040
D-1	2	.000	.000	.012	.021	.068
D-1	3	.001	.001	.016	.026	.113
D-2	1	.000	.000	.015	.035	.110
D-2	2	.000	.000	.016	.018	.063
D-2	3	.001	.000	.010	.016	.055
D-3	1	.000	.000	.002	.006	.008
D-3	2	.000	.000	.001	.001	.001
D-3	3	.000	.000	.001	.001	.001
D-4	1	.000	.000	.001	.001	.001
D-4	2	.000	.000	.001	.001	.001
D-4	3	.000	.000	.000	.001	.001
D-5	1	.000	.000	.001	.001	.001
D-5	2	.000	.000	.001	.001	.001
D-5	3	.000	.000	.001	.001	.001
D-6	1	.000	.000	.000	.000	.000
D-6	2	.000	.000	.001	.001	.000
D-6	3	.000	.000	.000	.000	.000
D-7	1	.000	.000	.000	.001	.000
D-7	2	.000	.000	.002	.000	.000
D-7	3	.000	.000	.000	.000	.000
DH-1	1	.001	.001	.024	.057	.163
DH-1	2	.014	.007	.032	.060	.218
DH-1	3	.007	.001	.032	.047	.156
DH-2	1	.008	.003	.031	.060	.193
DH-2	2	.004	.015	.028	.048	.129
DH-2	3	.012	.017	.026	.039	.135

TABLE XXXIII (continued)

Source[1]	Rep.	Insecticide[2]				
		Heptachlor	Heptachlor Epoxide	DDE	TDE	DDT
DH-3	1	.000	.006	.001	.001	.001
DH-3	2	.000	.022	.001	.001	.001
DH-3	3	.000	.002	.001	.001	.001
DH-4	1	.000	.000	.001	.001	.000
DH-4	2	.000	.009	.001	.001	.000
DH-4	3	.000	.002	.001	.001	.000
DH-5	1	.000	.009	.001	.001	.000
DH-5	2	.000	.000	.001	.001	.000
DH-5	3	.001	.000	.001	.001	.000
DH-6	1	.000	.000	.000	.000	.000
DH-6	2	.000	.001	.001	.001	.000
DH-6	3	.000	.000	.000	.000	.000
DH-7	1	.000	.000	.000	.000	.000
DH-7	2	.000	.000	.000	.000	.000
DH-7	3	.000	.000	.000	.000	.000

[1] Letter indicates test plot from which sample was taken: C, control; H, heptachlor; D, DDT; DH, DDT heptachlor. Number indicates process level from which sample was taken: 1, harvest; 2, wash; 3, peel; 4, thermal process; 5, storage; 6, fill liquor from samples taken after thermal process; 7, fill liquor from samples taken after storage.

[2] All values expressed as p.p.m.

VITA

The author was born November 25, 1943, in Medford, Oregon. He was graduated from Lakenheath American High School, R. A. F. Lakenheath, Suffolk, United Kingdom. He attended Texas A and M University, College Station, from 1961 to 1965 and received a B. S. degree in Food Technology. In September 1965, he was appointed Assistant in Food Technology at The University of Tennessee, Knoxville. Since that time he has been working to complete the requirements for the degree, Master of Science.