CHLORINATED HYDROCARBONS DEPOSITED IN BIOLOGICAL MATERIAL [1,2]

I. PLANTS AND PLANT PRODUCTS

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Editorial Note: Chlorinated hydrocarbon insecticides have been used to control pests on many plants of economic importance, on livestock and in soil. These uses have led to deposition of this group of insecticides in a host of biological material ranging from tobacco to eggs. This is the first of three review papers which will provide background information on different materials which have become contaminated and the levels of insecticide residues present. The first paper will discuss contamination of plants and their products; the second, animals and their products; and the third, soil and bodies of water.

Plants or their products may become contaminated with chlorinated hydrocarbons either through direct application of the insecticide to the plant in an attempt to control pests or through growth in soil which contains residues from previous years.

Vegetables

Guyer *et al.* *(36)* treated spinach with 0.25 lb lindane or one lb DDT per acre in attempts to control maggots. Fresh spinach harvested one day later contained 5.4 ppm lindane or 71 ppm DDT while the same spinach after canning had only 0.3 ppm lindane or 18 ppm DDT. After one week, levels were reduced to less than 0.05 ppm lindane or 3.8 and 1.4 ppm DDT in fresh and canned spinach respectively.

Snap beans, tomatoes and collards were treated with insecticides which contained 5% DDT, 10% methoxychlor, 20% toxaphene, 2% endrin or 1% lindane in studies by Brett and Bowery *(10)*. After treatment, endrin disappeared from tomatoes in one day, from snap beans in 3 days and from collards in 4 days. The highest initial level was found in collards (17.3 ppm) and lowest in tomatoes (0.31 ppm). Lindane disappeared from tomatoes after one, snap beans after 4 and collards after 12 days. The highest initial level again was found in collards (7.77 ppm) while the lowest was in tomatoes (0.28 ppm). The highest initial toxaphene level also appeared in collards (168 ppm) and the lowest in tomatoes (four ppm). At the end of the study (12 and 13 days after treatment), collards had the highest toxaphene residue (4.9 ppm) while tomatoes had the lowest (0.15 ppm). Results obtained with DDT or methoxychlor were similar except methoxychlor disappeared from tomatoes 7 days after treatment. Data from this study clearly indicated that highest residues of chlorinated hydrocarbons were present initially and persisted for longer periods in leafy vegetables than in those which produced a fruiting body. Other studies by Waites and Van Middlene *(91)* on DDT residues in snap beans, collards and leaf lettuce gave similar results.

Wallis and Carter *(92)* tested a variety of vegetables for methoxychlor residues after the crop had been sprayed with 1.75 or 3.0-3.5 lb per acre of insecticide. Green onions contained 13.8 to 23.0 ppm methoxychlor immediately after spraying and, after 8 days, contained 1.1 to 1.5 ppm. Initially, green beans had residues of 20.9 to 50.4 ppm and after 10 days, 1.0 to 10.8 ppm remained. Summer squash had initial residues of 2.9 to 8.4 ppm which were reduced to zero after 7 days. Immediately after treatment, okra contained up to 3 ppm which was completely eliminated 14 days later. Egg plant, initially, had residues of 1.7 to 8.2 ppm. This was completely eliminated one day later. Residues of 0.4 to 2.4 ppm were found in pumpkins immediately after treatment. Three days later 0.9 to 2.3 ppm were noted. Methoxychlor was completely eliminated from bell peppers 7 days after treatment, although initially residues of 0.9 to 5.4 ppm were present. Tomatoes contained 0.5 to 2.3 ppm initially and up to 0.6 ppm 7 days later. Initial residues of 1.1 to 1.7 ppm were detected in cucumbers and 3 days later 0.8 to 1.1 ppm remained. Immediately after application to kohlrabies, residues of 0.2 to 3.7 ppm were found. The contamination level after 7 days was 2.5 to 5.1 ppm. Turnip roots, initially, contained up to 1.0 ppm methoxychlor and after 7 days, up to 0.6 ppm.

Peppers were sprayed with different formulations of DDT at rates of one and 2 lb per acre in tests reported by Menzer, *et al.* *(69)*. Average residues detected immediately after spraying ranged from 6.7 to 10.5 ppm. During the ensuing 24 hr, 0.55 in of rain fell and peppers were again examined. Average residues were not appreciably different from

[1]Portions of this paper were presented at the Residues in Foods Conference conducted by the Food Science Department, Michigan State University, East Lansing on March 27-28, 1961.

[2]First in a series of three review papers on this subject which will appear in this Journal.

those noted initially. Seven days later 1.2 to 8.1 ppm of insecticide were noted as average values. Highest residue levels were noted when treatment consisted of 2 lb of insecticide plus 4 oz of a sticker-spreader per acre.

Menzer, *et al.* *(69)* extended these studies by determination of DDT residues in peppers at different stages during commercial processing. Residues in unwashed peppers ranged from 2.8 to 8.4 ppm. After the first wash, 2.1 to 5.3 ppm remained and after the second wash, 0.8 to 3.7 ppm were observed. Canned peppers contained from 0.5 to 4.4 ppm DDT.

Vegetables may become contaminated with insecticides through growth in treated soils. San Antonio *(79)* tested different crops grown in lindane treated soils for residues of the insecticide. He reported levels up to 25 ppm in carrots, sweet potatoes and in plants of snap bean, tomato, wheat, and potato which had grown on soils with either 5 or 10 ppm lindane present initially.

Soils were treated with aldrin, chlordane, DDT, dieldrin and toxaphene *(73)*. Various vegetables were then planted and, after harvesting, were analyzed for insecticide residues. When aldrin was added at the rate of 4 lb per acre, no residue was detected in shelled lima beans. Sweet potatoes contained 0.03 ppm each of aldrin and dieldrin while radishes were free from aldrin but had 0.24 ppm dieldrin. Chlordane was added to soil at the rate of 10 lb per acre. No residue was detected in broccoli, eggplant, bell pepper, cauliflower, cabbage, or collard. Residues of 0.01 ppm were found in tomatoes, 0.04 ppm in sugar beet roots and lettuce, 0.08 ppm in cantaloupes and cucumbers, 0.16 ppm in turnip roots and tops, 0.43 ppm in sweet potatoes, 0.50 ppm in rutabagas, and 1.51 ppm in carrots. No DDT was observed in sweet potatoes and 0.2 ppm was noted in shelled lima beans when 10 lb insecticide was added to the acre. Residues of DDT were not observed in any of the following crops when they were grown in soil previously treated with 20 lb insecticide per acre: cauliflowers, collards, broccoli, turnips, eggplants, kale or brussel sprouts. Potatoes and red beets contained 0.5 ppm each and bell peppers had 0.2 ppm insecticide. Dieldrin was added to soil at the rate of 4 lb per acre. No residue was found in radishes but sugar beet roots contained 0.11 ppm. Three pounds of toxophene were added per acre. No residues were found in sugar beet or red beet roots. Potatoes contained 0.3 ppm and radishes 0.4 ppm.

Heptachlor was applied at the rate of 0.5–2 lb per acre to the seed furrow together with ammonium phosphate in attempts to control the sugar-beet root maggot *(2)*. Sugar beets contained 0.01 ppm heptachlor and 0.02 ppm heptachlor epoxide at all rates of insecticide application.

Roberts, *et al.* *(78)* added insecticides to soil in the drill with fertilizer. Heptachlor, aldrin, dieldrin, toxaphene and DDT were added at the rates of 2, 2, 2, 10, and 5 lb per acre, respectively. Sweet potatoes grown in soils receiving the different treatments contained 0.11 ppm heptachlor, 0.06 ppm aldrin, 0.06 ppm dieldrin, 0.11 ppm toxaphene or 0.01 ppm DDT.

Several investigators have reported that flavors of vegetables may be affected by insecticides. Hening, *et al.* *(41)* noted an off-flavor in pureed squash prepared from squash grown in aldrin-treated soil. When soil was treated with chlordane, no off-flavors were noted in squash, carrots, peas, beans, spinach, red beets or tomatoes. Carrots and squash grown on soils treated with chlordane, aldrin or dieldrin appeared deeper in color than those from untreated soils. This effect was not observed when soil was treated with DDT.

Gyrisco, *et al.* *(39)* studied the effect of lindane-treated soil on flavor of potatoes and red kidney beans. The soil was treated for 2 consecutive years prior to growth of these crops. An application of one lb insecticide per acre was used. Potatoes grown on treated soil and tested for flavor were judged "probably-off" to "strongly-off". No flavor differences were detected in red kidney beans.

No adverse effect was noted on the flavor of turnips, parsnips or carrots when these crops were grown in soils treated with 3 or 6 lb per acre of heptachlor or 5 or 10 pounds per acre of chlordane *(51)*. During one growth season an additional 20 lb per acre of chlordane were applied to soil in which carrots were grown. Flavor was not affected by this treatment.

Murphy, *et al.* *(74)* evaluated a variety of vegetables for off-flavors caused by growth in soils previously treated with insecticides. Benzene hexachloride, lindane or toxaphene treatments resulted in off-flavors in about 50% of vegetable samples. When mixtures of insecticides were used, those containing toxaphene produced off-flavors in 14% of the samples. Off-flavors from toxaphene were most pronounced in potatoes. The same crop also suffered in flavor when grown on endrin-treated soil. Chlordane, DDT and heptachlor, when used individually, generally did not induce off-flavors. Ten to 13% of samples from soils treated with chlordane, heptachlor, lindane or endrin showed improvements over controls in flavor quality.

Lindane was used to control mushroom flies in studies reported by Weigel and Gilpin *(94)*. When 0.5 lb insecticide per acre was applied to mushroom beds, yield was not affected. An application of one lb or more per acre depressed yields. No appreciable residues were detected in mushrooms harvested 5 days after application. Slight occasional off-flavors were found in canned mushroom pieces and cream of mushroom soups made from mushrooms grown in beds treated with 0.25, 0.5 or 1.0 lb of lindane per acre at least 7 days before harvest. Mushrooms harvested 3 days after treatment had musty off-flavors which made both pieces and soup inferior in flavor quality.

FRUIT

Hoskins *(42)*, as early as 1949, was concerned with residues of DDT, DDE or methoxychlor on different sprayed fruits. He reported DDT was present in the range up to 30.5 ppm on apples, apricots, grapes, peaches, pears, prunes, and raisins.. A higher level (20.5 to 35.6 ppm) was found in olives. The DDE content in apples, apricots and prunes varied from 0.14 to 38.5 ppm with the higher level present in apricots. Methoxychlor residues ranged from 0.18 to 32.4 ppm in apples and apricots. Again, the highest level appeared in apricots.

The deposition on peaches of five different chlorinated hydrocarbons applied 40, 30, 20 or 10 days before harvesting fruit was studied by Fahey, *et al.* *(20)*. When DDT was applied 10 days before harvesting, peaches contained 24.6 ppm of insecticide. The level dropped to 5.3 ppm when the insecticide was applied 40 days before harvesting. Results with chlordane, heptachlor, dieldrin and endrin were similar although quantities of residues were different. Peach trees were sprayed with a solution of 2 lb of 50% wettable DDT powder per 100 gal on May 27, June 5, June 17, July 4 and July 15, 1957. On August 22 a solution containing one-half the above-mentioned concentration of insecticide was used. At harvest time, on September 16, peaches from trees which received all 6 sprays contained an average of 9.7 ppm DDT. Peaches from trees which received the first 5 sprays contained an average of 5.3 ppm while those from trees which received the last 3 sprays only contained 5.0 ppm. A residue of 1.6 ppm DDT was detected in peaches from trees which received the last spray only.

Lemons and oranges were treated with neotran (bis (p-chlorophenoxy) methane) to control the red mite of citrus fruits *(47)*. The pulps of both citrus fruits were virtually free of the insecticide while peels contained 11.4 to 15.2 ppm one day after treatment and 6.8 to 9.5 ppm 32 to 36 days later.

Blinn, *et al.* *(6)* studied the deposition of various insecticides on lemons and oranges. Chlordane (4 lb of 50% powder per 100 gallons of water) was used for a full coverage spray. Seven days later residues in and on the peel averaged 15.0 ppm. After 21 days this was reduced to 9.0 ppm and after 34 days, 5.6 ppm remained. Similar tests were conducted with dieldrin (2 lb of 50% powder per 100 gal of water). Seven days after spraying, an average of 31.4 ppm dieldrin appeared in and on the peel. This was reduced to 7.3 ppm after 21 days and further reduced to 6.2 ppm after 34 days. Heptachlor residues were studied after trees were sprayed with a solution of 4 lb of 25-% insecticide per 100 gal of water. After 7 days the average residue detected was 8.4 ppm. This dropped to 3.6 ppm after 21 days and to 1.7 ppm after 34 days. Lower heptachlor residues were noted when either 2 lb of heptachlor powder or one qt. of emulsifiable heptachlor concentrate was mixed with 100 gal of water instead of 4 lb of powder. Blinn, *et al.* *(6)*, reasoned that initial dissipation of the chemical occurred while it remained primarily on the surface of fruit and was subjected to physical and chemical action of weathering. Later, less rapid decreases occured after the chemical had penetrated into waxes and oils of the fruit where it undergoes change.

DDT and TDE were used in sprays at the rate of 2.5, 5.0 or 10.0 lb per acre in attempts to control a variety of orangeworms *(4)*. Residues of DDT in mature oranges, when 2.5 lb of insecticide per acre were used, ranged from 1.0 ppm 7 days after treatment to 0.3 ppm after 42 days. When 5 lbs of insecticide per acre were used, residues of 2.0 ppm after 7 days and 0.9 ppm after 42 days were noted. A treatment with 10 lb of DDT resulted in a residue of 3.1 ppm 7 days later and 2.4 ppm after 42 days. Residues of TDE followed the pattern noted with DDT.

Wolfe, *et al.* *(95)* investigated DDT residues on apples grown in central Washington after trees were sprayed with the insecticide during the growing season. Residues ranged from 0.3 to 12.4 ppm with an average of 3.0 ppm for all samples, both washed and unwashed apples. In general, higher DDT residues were found in unwashed apples and in those from trees which had received a greater number of cover sprays.

The use of DDT with a sticker-spreader to control the grape berry moth resulted in deposits of 17 to 23 ppm insecticide on grapes immediately after the final application *(85)*. At harvest time the residue was generally in excess of 7 ppm. Most of this deposit was contributed by the final spray applied for control of the second brood of grape berry moths. When only the original applications were used, 2.5 to 4.0 ppm insecticide were found in grapes. Elimination of the sticker-spreader reduced the residue to below 7 ppm at harvest. Combined effects of weathering and growth caused a reduction of DDT deposits at harvest which ranged from 37 to 64% and averaged 51%.

The flavor of some fruits has been affected by the presence of insecticides in soil *(37, 38, 52)*. Gyrisco and Burrage *(37)* found "obvious off-flavors" in strawberries grown on dieldrin-treated soil. Off-flavors were noted in jams produced from berries grown on soils treated with aldrin, benzene hexachloride or dieldrin. These unsatisfactory flavors were also observed in canned berries and fresh-frozen fruit. Benzene hexachloride also imparted an off-odor to strawberries while chlordane did not affect their odor or flavor. Other experiments by Gyrisco, *et al.*, *(38)* showed that flavor and odor of strawberries were unaffected when plants which produced the berries 12 to 24 months later were planted in soils treated with one, 2 or 4 lb per acre of aldrin, lindane, dieldrin or heptachlor.

Lindane, when applied to vines or melons produced musty flavors in a large portion of cantaloupes *(52)*. The frequency with which musty flavors appeared was related to the insecticide formulation used. Fifty-eight per cent of samples had the off-flavor when an emulsion concentrate was used. This was reduced to 44% with a wettable powder and further reduced to 10% with dust.

NUTS

Reynolds, *et al.* *(76)* determined levels of benzene hexachloride in peanut butter made from peanuts grown on land a year following cotton which had been sprayed with the insecticide. Peanut butter contained from 0.20 to 0.50 ppm BHC when cotton was treated with 3.8 lb of the gamma isomer per acre. When the rate was increased to 5.14 lb per acre, peanut butter contained 0.45 to 0.90 ppm benzene hexachloride.

WHEAT

Lindane and methoxychlor have been suggested for use on stored wheat *(35, 80)*. There was very little loss in lindane activity during 15 months of storage when wheat was treated with 4, 8 or 12 ppm of insecticide. Initial levels were 2.8, 5.1 and 7.7 ppm respectively and after 15 months they were 2.3, 4.0 and 7.4 ppm respectively.

Samples of wheat were treated with either methoxychlor or lindane in studies by Schesser, *et al.* *(80)*. The wheats were milled 9 to 10 days after treatment or after 18-24 months of ageing. Ageing by itself failed to eliminate these insecticides from grain. Cleaning of grain before milling somewhat reduced methoxychlor levels but had little effect on lindane. Highest levels of insecticide were found in the bran portion of milled wheat, followed in order by shorts, germ and flour. The flour portion contained from 0.3 to 1.8 ppm methoxychlor when the initial treatments ranged from 5 to 50 ppm. Lindane was present in flour at the rate of 1.3 to 2.6 ppm when the initial treatments were 2.5 to 7.5 ppm. Since the greatest portion of insecticide was present in shorts and bran, it appeared to be retained by the pericarp.

Laboratory studies were conducted by Strong, *et al.* *(84)* in which methoxychlor was added to wheat (15 ppm) to control the rice weevil and confused flour beetle. An emulsion, wettable powder and tetrachlorethylene solution of the insecticide were used. Samples of treated wheat having 10 or 13% moisture were held at 60° or 90°F. Whole grain, before cleaning, contained 4.2 to 12.1 ppm insecticide. Samples of wheat with different moisture levels held at 60°F were similar in residue content. Higher residue levels were noted in high moisture wheat when held at 90°F. Ranges of methoxychlor content found in different fractions of milled wheat were: *(a)* clean-out (prior to milling) - 19.76 to 101.6 ppm; *(b)* flour - 1.65 to 6.6 ppm; *(c)* bran - 13.18 to 28.4 ppm; *(d)* shorts - less than 2.0 to 13.38 ppm and *(e)* middlings - less than 2.0 to 5.65 ppm. These data verify those previously discussed *(80)* in regard to location of insecticide residues on kernels of wheat.

Highest levels of insecticide in flour and bran were noted when wheat was treated with the emulsion or wettable powder. Shorts and middlings from wheat treated with the tetrachlorethylene solution were higher in residue level than those from the other treated grain.

TOBACCO

TDE and endrin are the major chlorinated hydrocarbons used on flue-cured tobacco for control of the tobacco hornworm. Both are usually applied more frequently and closer, in time, to harvesting or priming than other compounds. Bowery, *et al.* *(8)* conducted extensive studies on TDE and endrin residues in green and processed tobacco and in cigarettes. Tobacco was sprayed with one lb TDE per acre before the second, fourth and sixth priming. Levels of TDE in green tobaccos one day after treatment were 460, 196 and 68 ppm respectively. After 5 to 7 days they had decreased to 69, 89 and 52 ppm. Use of 3 lb TDE per acre, applied as a dust, resulted in residues of 2,667, 167 and 582 ppm one day after treatment and 86, 82 and 149 ppm respectively 5 to 7 days after dusting. Dusting tobacco with endrin (0.4 lb per acre) before the second, fourth and sixth priming resulted in the presence of 316, 31 and 114 ppm respectively after one day and 33, 10 and 6 ppm respectively after 5 to 7 days. Flue curing of tobacco reduced the TDE content by 41% and endrin content by 42%. Stemming, shredding, redrying, ageing for 2 years and cigarette manufacturing failed to appreciably reduce further the contents of either insecticide in tobacco.

Tests on tobacco samples from commercial auction markets showed an average of 39.0 ppm TDE present in 1956, 28.6 ppm in 1957 and 43.7 ppm in 1958. Analyses for endrin indicated an average of 1.5 ppm present in 1957 and 2.2 ppm in 1958. TDE residues in different American cigarettes averaged 11.7 to 13.4 ppm. The average for endrin was 0.16 ppm. Smoke from cigarettes with an average of 10.3 to 14.7 ppm of TDE contained an average of 1.6 to 1.7 ppm TDE and 0.6 to 1.4 ppm dehydrochlorinated TDE.

PASTURES AND HAY

Pasture and hay crops have been treated with a variety of chlorinated hydrocarbons to control insects. Residues on these crops are of concern since after ingestion by cattle, they may appear in meat or milk. Alfalfa was treated with heptachlor in two different studies *(16, 57)*. In one, an application of about 0.25 lb per acre resulted in an initial contamination of 13.3 ppm. The insecticide had disappeared completely 14 days later. The use of about one-eighth lb gave similar results although the initial level was only 3.76 ppm. In the other study the highest initial level, 4.81 ppm, was encountered when 5 lb of heptachlor granules were applied per acre. Heptachlor persisted for more than 30 days regardless of application used (spray 0.25 lb per acre; dust 0.42 lb per acre; granules 3 and 5 lbs per acre). Aldrin was applied to alfalfa at a rate of 5 oz per acre. Initially 6.02 ppm were found in forage but none remained 14 days after treatment. An application of 0.25 lb dieldrin per acre resulted in an initial contamination of 3.65 ppm. Insecticide residues persisted on plants for over 30 days.

Fahey, *et al. (21)* noted that appreciable (in excess of 0.5 ppm, residues of lindane remained on alfalfa for 24 to 31 days if it was 15 inches or more in height at the time of spraying. No measureable residues were found at harvest time (20 days after treatment) if alfalfa was not over 12 in in height when it was sprayed.

Aldrin was applied to Ladino clover as a dust or in granulated attapolgite or vermiculite formulations *(15)*. Higher residues were encountered when dust was used. Residues had decreased to less than 0.1 ppm 14 days after 1.0 lb per acre was applied regardless of formulation used. Dosages of 2.1 to 2.4 lb per acre required more than 14 days to reduce levels below 0.1 ppm.

Peanut hay was treated with 28.5 to 36.0 lb per acre of a 2% DDT dust from 9 to 35 days before harvesting *(90)*. At 9 days a residue of 8.0 ppm was noted and after 35 days this had dropped to 0.8 ppm.

Corn was treated on July 11, 1957 with 20 lb per acre of a granulated formulation containing 5% heptachlor in an attempt to control the European corn borer *(49)*. Residues of heptachlor on corn ranged from 1.44 ppm one day after treatment to 0.55 ppm after 4 days. Less than 0.01 ppm was found after 8, 18, 32 and 102 days. Heptachlor epoxide present after one day was 0.04 ppm; after 4 days, 0.15 ppm; after 8 days, 0.07 ppm; after 18 days, 0.06 ppm; and after 32 days, 0.03 ppm. No heptachlor was found in corn stover samples collected 120 days after insecticide application. Experiments were conducted on residues of toxaphene in pangolagrass *(89)*. This grass, widely used in Florida for pasture purposes, is frequently treated with toxaphene to control caterpillars. Initial residues of 102 ppm were observed when 2 lbs of a 10% dust was applied per acre. Residues after 14 days ranged from 2.1 to 6.0 ppm for all treatments (one or 2 lb per acre of 10% dust; one or 2 pounds per acre of 40% wettable powder; one or 2 pounds per acre of a 60% emulsifiable concentrate).

Huddleston, *et al (43)* sprayed parts of five townships in an area near Norwich, N. Y. (Chenango Valley) with DDT in an attempt to control the gypsy moth. One lb of insecticide in one gal of mixed oil solvents was applied per acre by means of an airplane flown at a height of 20 feet. Pastures and hay from the sprayed area were tested periodically for DDT residues. Insecticide residues on pastures from five farms ranged from 21.6 to 348 ppm initially, 12.6 to 100.8 ppm after 7 days, 4.1 to 60 ppm after 30 days and 2.2 to 17.6 ppm after 60 days. Hay, harvested 120 days after treatment contained from 1.8 to 43.2 ppm insecticide.

Recent studies *(26,34)* have shown that aldrin is converted to the more residual and equally toxic dieldrin in alfalfa, soybeans, corn and carrots. This reaction may also occur in other plants. Other work *(27)* has shown that heptachlor is converted to its epoxide by alfalfa, soybeans and corn. These reactions also occurred when insecticides were absorbed by plants from contaminated soils *(62)*. This change is of importance since the new compounds are more persistant in plant tissue and also more toxic to insects and mammals.

REFERENCES

The complete list of references cited will be included with the third paper of this series.