

Use of Carbon to Reduce the Uptake of Insecticidal

Soil Residues by Crop Plants

Effects of Carbon on Insecticide Adsorption and Toxicity in Soils

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Laboratory and field tests determined the effect of activated carbon (Norit) on the adsorbance of insecticidal residues to soils, the toxicity of insecticides in soils, and the penetration of these residues into the roots of crop plants. Peas were grown in the laboratory in aldrin, dieldrin, heptachlor, or heptachlor epoxide treated loam soil or quartz sand. Carbon added to soils at 1000 (800 pounds per acre, 3 inches deep), 2000, or 4000 p.p.m. considerably reduced the penetration of the insecticides into the roots and greens of the pea plants. A 96% reduction of the penetration of aldrin into pea roots was achieved with carbon at 1000 p.p.m. in a quartz sand and at 4000 p.p.m. in a loam soil. A 96%

reduction of dieldrin or heptachlor and heptachlor epoxide into pea roots was achieved with carbon at 2000 p.p.m. in a loam soil. Carbon in soil prevented the total extraction of the insecticides and reduced the toxicity of the insecticide residues to *Drosophila melanogaster* Meigen. This binding of the residues to the carbon-soil complex increased with time. Field test results, although similar, were not so striking as in the laboratory. Treatment of the soil with carbon could reduce insecticidal residues in crops to such an extent that a farmer could use a soil of abnormally high insecticidal content.

Measurable amounts of insecticidal residues in our food present a variety of problems. If a chemical is nontoxic to humans and causes no harm to living cells, residual amounts in food could be tolerated. However, the lack of detailed knowledge concerning the potential effects of agricultural chemicals on humans and animals has necessitated the establishment of legal limits.

Recently, more sensitive analytical methods were used, and formerly nonmeasurable amounts of residues of agricultural chemicals were detected in raw agricultural products. Since many tolerance levels were set on the basis of the sensitivity of a specific analytical method, the detection of residues by new methods had an effect on the whole concept of tolerance levels.

One major problem concerning the food supply emerged when several crops grown in insecticide treated soil were found to contain within their edible parts measurable amounts of some insecticides. These residues were usually chlorinated hydrocarbons. The amounts that penetrated into the plant parts were dependent on the nature of the chemical, the soil type, and the particular crop (Lichtenstein, 1959, 1960). The availability of these chemicals for penetration into the plant root systems is also dependent on these factors. Chlorinated hydrocarbons disappear faster from soils of low organic matter content and persist longest in muck soils of high organic matter content (Lichtenstein and Schulz, 1959b; Lichtenstein *et al.*, 1960; Harris and Lichtenstein, 1961). The insecticides are apparently bound to organic matter in the soil, making them less available to the biological, physical, and chemical action of environmental factors, which are responsible for the disappearance of a chemical through

breakdown into nontoxic products, or through volatilization from the soil. When insecticides are bound to the organic materials, their toxicity to insects is reduced (Edwards *et al.*, 1957). LD_{50} values for *Drosophila melanogaster* (Meigen) increased with an increase in organic matter in the soil. Harris and Lichtenstein (1961) showed that the amounts of aldrin volatilized from soils decreased with increasing amounts of organic matter. The amount of insecticidal soil residues that penetrated into various crops decreased when the plants were grown in soils of higher organic matter content (Lichtenstein, 1959). In one of these studies, carrots were grown in a sandy loam (organic matter = 2.6%), silt loam (organic matter = 3.6%), and in a muck soil (organic matter = 45%). These soils contained lindane residues at concentrations of 0.96, 0.90, and 6.66 p.p.m., respectively. Carrots from these soils contained lindane residues of 5.99, 2.41, and 0.40 p.p.m., respectively. This same trend was observed with other crops grown in these soils. Lichtenstein *et al.* (1967) showed that in pea plants, grown in diazinon, parathion, aldrin, or lindane treated quartz sand, all the insecticides except diazinon accumulated within the roots. Apparently, all the insecticides were translocated into the greens, yet the organophosphorus compounds were metabolized and detoxified. Lindane residues in green plant parts were the highest among the insecticides tested. Part of the aldrin, after its penetration into the pea roots, was epoxidized into the more water soluble dieldrin which then was translocated to a small extent into the aerial parts of the pea plants.

Root crops, whose edible parts grow in soils treated with insecticides, are directly exposed to an insecticidal environment. Therefore, relatively high amounts of insecticidal residues are being found in carrots, potatoes, radishes, etc. However, large differences exist in the ability of plants to pick up or to prevent the penetration of

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insecticides into their systems. Some soils contained sufficient insecticidal residues to make it questionable whether or not crops could be grown in these soils without exceeding the legal tolerance levels. Therefore, the addition of an adsorbent to a soil has been tested to prevent undesirable side effects of pesticidal chemicals (Ahrens, 1964). Buchholtz (1967) was able to protect crop plants grown in herbicide contaminated soils by adding carbon to these soils. Rodriguez *et al.* (1960) demonstrated that activated carbon alleviated the phytotoxic effects of DDT on beans, and Thurston (1953) reported similar effects with carbon in DDT contaminated soils.

The effects of activated carbon on the penetration of aldrin, dieldrin, heptachlor, and heptachlor epoxide from soils into crop plants, were studied in laboratory and field experiments under controlled conditions during 1967 at the University of Wisconsin. Four series of experiments were performed: (1) the effect of carbon in soil on toxicity and extraction recoveries of insecticides from soils (laboratory experiment); (2) the effect of carbon and soil type on the uptake of aldrin by pea plants (laboratory experiment); (3) the effect of carbon on the uptake of insecticidal residues from aldrin or heptachlor treated field plots by radishes, peas, carrots, and potatoes; and (4) the effect of carbon in a loam soil on the uptake of dieldrin, heptachlor, and heptachlor epoxide by pea plants (laboratory experiment).

PROCEDURE

Application of Insecticides and Carbon. The soil used was a Carrington silt loam, free of any insecticidal residues. A quartz sand of minimum sorptive qualities and minimal microorganism activities was also used for comparison purposes in experiment 2. Insecticides used in laboratory experiments were analytical grade aldrin, dieldrin, heptachlor, or heptachlor epoxide. They were applied to the soil in an acetone solution, followed by mixing of the soil (Lichtenstein and Schulz, 1959a). In field experiments, soils had been previously treated with commercial formulations of aldrin or heptachlor (Lichtenstein and Schulz, 1965).

The carbon used in this study was Norit H. G. 7732, activated carbon, Grade A (American Norit Co., Jacksonville, Fla.). This material was applied under laboratory conditions as a powder, followed by thorough mixing and moistening of the soil. Under field conditions, however, the carbon was first mixed with water and then applied to the soil. After these soil treatments, plants were grown in these soils.

Plant Growing and Harvest Procedure. In laboratory experiments, pea plants (Alaska Wilt Resistant) were grown in quartz sand or a loam soil within nonglazed clay pots (opening = 15-cm. diameter) as described by Lichtenstein *et al.* (1967). The plants grew for 19 days (experiment 2) or 26 days (experiment 4). The pots containing quartz sand were watered during the growing period with nutrient solution added to the saucers as necessary, while only water was added to the loam soils.

At harvest time, the greens from each pot were cut 1.0 to 1.5 cm. above the soil surface. The soil and the roots in each pot were separated by pouring the top layer of soil carefully into a plastic bag. The roots were then

gently pulled out. The remainder of the soil was added to the bag and frozen for future extraction and analyses.

The roots were placed on a 10-mesh sieve and washed with tap water to remove soil particles. They were then dried with blotting paper, placed into individual plastic bags, and frozen for future analyses. This procedure did not differentiate between residues within the root system and those adhering to the outside of the root epidermis. Analytical data referring to residues "within" the root are to be understood and interpreted in that way.

Under field conditions, radishes (Early Scarlet Globe), peas (Alaska Wilt Resistant), carrots (Red Cored Chantenay), and potatoes (Russet Sebago) were grown in two 30-foot (9.15-meter) rows each on 30 × 24-foot (9.15 × 7.32-meter) sized experimental plots. For comparison with the laboratory experiments, every other pea plant was harvested 26 days after seeding by clipping the greens 1 to 1¼ inches (2.5 to 3.0 cm.) above the ground. The remainder of the pea plants, however, grew for a total of 2 months when the pea seeds were harvested. To reduce the sampling errors, the edible parts of all the carrots, potatoes, and radishes were harvested and brought into the laboratory for processing. Each edible part was brushed with warm water to remove adhering soil particles, then rinsed with acetone from a wash bottle, and immediately rinsed again with warm water. All crop parts were then macerated with a food grinder (Hobart, Model-215 food cutter). The ground material was mixed, and aliquots were placed into plastic bags within 1-quart cartons, frozen, and held until extraction.

Extraction Procedures. Soil samples were processed as described by Lichtenstein and Schulz (1959a, b). If the soils were dry or unusually wet, they were either moistened or air dried until soil conditions close to field moisture levels were obtained. This course was necessary to obtain as complete a recovery of the insecticides as possible. Quartz sand, however, was not dried prior to extraction because it was found that insecticidal residues were lost from quartz sand while the water was evaporated. The sand and loam were passed through an 8-mesh screen both for mixing purposes and for removal of root particles.

Roots and greens of peas were cut with scissors into 0.5 to 1 cm. pieces and placed into an extraction jar. To facilitate grinding of this plant material, some hexane-washed quartz sand (half the weight of plant material) was added. Soils and crops were extracted as described by Lichtenstein *et al.* (1967). Pea seeds were extracted with redistilled acetonitrile, followed by partitioning the insecticidal residues into redistilled hexane.

Cleanup Procedures. Extracts containing the equivalent of 5 to 10 grams of plant material were passed through a 10-gram Florisil P.R. (60- to 80-mesh, pesticide residue grade, Floridin Co.) column (20-mm. diameter) and eluted with 150 ml. of 15% ether in redistilled hexane.

After an analysis of extracts from pea plants by gas-liquid chromatography, the following additional cleanup of the extracts was performed prior to thin-layer chromatography. The extracts were concentrated in a flash evaporator to 2 or 3 ml. This concentrate was then subjected to the "Sweep cleanup" procedure (Storherr and Watts, 1965) with the Kontes Sweep co-distillation apparatus. Insecticidal residues were passed through boro-

silicate glass wool packed sweep columns and eluted with redistilled acetone at 245° C.

Analytical Procedures. The extracts were all analyzed by gas-liquid chromatography (Lichtenstein *et al.*, 1967). Thin-layer chromatography was used for further identification of insecticidal residues in extracts of pea roots or pea greens from experiment 2. Aliquots of these extracts were spotted on aluminum oxide G containing calcium sulfate as a binder (Merck, Darmstadt, Germany). The chromatograms were developed with 5% acetone in hexane, followed by spraying with reagents as described by Mitchell (1957) and subsequent exposure to ultraviolet light for 30 minutes to make spots visible.

RESULTS AND DISCUSSION

Experiment 1. The effect of carbon in soil on toxicity and extraction recoveries of insecticides from soil is discussed. The amount of insecticidal residues penetrating from soils into plant tissues is to some extent dependent on the insecticidal concentration in the soil (Lichtenstein, 1959). To evaluate possible differences in insecticidal penetration into plant tissues due to carbon treatments of soil, the amount of insecticidal residues in soil and carbon-treated soil has to be known. For this purpose, experiments were conducted to test the persistence or recovery of aldrin, dieldrin, heptachlor, or heptachlor epoxide in and from soil not treated with carbon in comparison to those that had been treated with carbon.

Dieldrin was applied to loam soils at either 5 or 20 p.p.m. Afterwards, one half of these soils was also treated with carbon at 2000 p.p.m. An identical experiment was conducted, except that a mixture of heptachlor and heptachlor epoxide was applied, each at either 2.5 or 10 p.p.m. Soils that had been treated at 5 p.p.m. were held at room temperature in aluminum foil covered clay pots for 30 days, and those that were treated at 20 p.p.m. were held for 15 days only.

Samples of the soils that were taken initially after the insecticidal and carbon applications were extracted by stirring in a homogenizer for 15 to 20 minutes with 200 ml. of a 1 to 1 mixture of redistilled hexane and redistilled acetone. From soil samples obtained at the end of the incubation period, however, three 100-gram portions were used for extractions. One part was extracted like the initial soil samples. The second 100-gram portion of soil was extracted four times in a homogenizer, each time with a 1 to 1 mixture of hexane and acetone. The four solvent fractions obtained were finally combined. The solvent remaining in the soil was filtered off by suction with a Buchner funnel and added to the previously pooled solvents. The third 100-gram soil portion was extracted in a Soxhlet extractor with redistilled acetonitrile for a period of 20 hours. The insecticidal residues were then partitioned into hexane, followed by concentration of the extract to volume and analysis.

In addition, bioassays were performed with these soils by exposing vinegar flies (*Drosophila melanogaster* Meigen) directly to duplicated 5-gram soil samples as described by Edwards *et al.* (1957). Mortality counts were made at intervals over a 24-hour exposure period. These tests

were conducted immediately after the application of dieldrin or aldrin at 20 p.p.m., or heptachlor and heptachlor epoxide at 10 p.p.m. each. After 15 days of soil incubation at room temperature, the soils were again tested by this bioassay procedure.

Initially, there were no differences in insecticidal recoveries from carbon-free soils and carbon-treated soils (Table I). However, after the soils stood for 15 days, lower insecticidal recoveries were obtained from those soils that also contained carbon. These insecticides probably could not dissipate faster in carbon-treated soils. Under standard cleanup procedures with Florisil, carbon is not used with aldrin and dieldrin residues. This is due to the strong retention of these insecticides by activated carbon. For this reason, the soils were extracted by different methods. With carbon-free soils, no appreciable increase in insecticidal recoveries was noticed with these extraction procedures. However, with carbon-treated soil, more residues were recovered from the soil following four extractions with hexane-acetone (1 to 1) or by a continuous Soxhlet extraction for 20 hours. But even with these additional extraction procedures, only 83 to 88% of the residues recovered from carbon-free soil could be extracted from the carbon-treated soil after 15 days of soil incubation. Apparently insecticidal residues in soils are increasingly bound to the soil-carbon complex as time progresses, making it impossible to fully recover these residues by standard extraction methods.

Results obtained after 30 days of soil incubation were similar, except that only 57 to 78% of the residues recovered from the carbon-free soil could be extracted from the carbon-treated soil. A similar experiment was conducted with aldrin, applied to the soil at 20 p.p.m. Residues recovered initially were very much alike. However, after 15 days of soil incubation the amounts of aldrin plus dieldrin residues recovered by a 200-ml. hexane-acetone extraction from the carbon treated soil (10.95 p.p.m.) were only 65% of that recovered from the carbon-free soil (16.78 p.p.m.). Four extractions of the carbon-treated soil with 200-ml. portions of hexane and acetone (1 to 1) increased this figure to 81% (13.55 p.p.m.).

Bioassay tests gave additional information relative to the binding of insecticides in the soil. Although the concentration of the insecticidal residues in the carbon-free and carbon-treated soils were identical immediately following the insecticidal applications, insect mortalities observed in a given time were considerably higher with carbon-free soils than with carbon-treated soils (Table I). With aldrin, 97% of the flies had died after a 3-hour exposure period to carbon-free soil and only 16% after an equal exposure to carbon-treated soil. These figures were 4% or no mortality for dieldrin and 98 or 6% for heptachlor- and heptachlor epoxide-treated soils. Results obtained 15 days after the insecticidal applications were similar (Table I). The insecticides were bound to the soil-carbon complex to such an extent that they were not as available for toxic action to the insects nor for extraction by organic solvents. This phenomenon increased with the aging of the insecticidal soil residues.

Experiment 2. The effect of carbon and soil type on the uptake of aldrin by pea plants was studied. A loam soil and quartz sand were treated with aldrin at 20 p.p.m.

Table I. Effect of Different Extraction Methods on Recoveries of Insecticidal Residues from a Loam Soil, Experiment 1—Laboratory

		Applied to Loam Soil, P.P.M.							
		Dieldrin 20				Heptachlor, 10 and H. Epoxide, 10			
		None		Carbon, 2000		None		Carbon, 2000	
Extraction Method ^a	Day	Recovered from Soil							
		Dieldrin				Heptachlor and H. Epoxide			
		P.p.m.	%I ^b	P.p.m.	%I	P.p.m.	%I	P.p.m.	%I
I 200	0	18.31		17.82		20.90		21.48	
% Mort/4 hr. ^c	0	26		4		100		70	
I 200	15	17.61 = 100		12.53 = 71		16.54 = 100		13.74 = 83	
II 4 × 200	15	18.22 = 103		15.32 = 87		17.13 = 104		14.19 = 86	
III Soxhlet	15	16.45 = 93		14.49 = 83		15.97 = 96		14.51 = 88	
% Mort/4 hr.	15	55		0		100		0	
% Mort/8 hr.	15	100		0				43	
Mort/24 hr.	15			20				100	

^a I 200: Extracted in homogenizer with 200 ml. of hexane-acetone (1 to 1); II 4 × 200: Extracted in homogenizer four times with 200 ml. of hexane-acetone (1 to 1) each; III Soxhlet: Extracted in Soxhlet apparatus with acetonitrile.

^b Residues recovered in % of those that were extracted from carbon free soils with extraction method I (200 ml. of hexane-acetone, 1 to 1), 15 days after the insecticidal applications.

^c % mortality observed after exposure of *Drosophila melanogaster* for 4 to 24 hours directly to soils immediately or 15 days after the insecticidal and carbon applications.

Four clay pots each (controls) were then filled with either aldrin treated loam or aldrin treated sand. After that, the remaining aldrin treated loam or quartz sand was treated in addition with carbon at either 1000, 2000, or 4000 p.p.m. (800, 1600, or 3200 pounds per acre, 3 inches deep). Four clay pots each were then filled with aldrin-treated loam or sand that contained carbon at one of the three concentrations. This then resulted in 16 clay pots for each soil type of which four contained only aldrin-treated soil and the remainder contained aldrin plus carbon at three different concentrations. Following the insecticide and carbon applications, aliquots of these soils were removed for initial analyses.

Pea plants were grown, as described, for a period of 19 days. No growth differences could be observed between plants from carbon-free soils and those that grew in carbon-treated soils. After harvesting of the plants, analyses were performed on the soils, the roots, and the pea greens (Table II).

Analyses of the quartz sand and the loam soil immediately following treatment indicated aldrin concentrations of 19 ± 0.3 p.p.m. in the sand and 18 ± 0.5 p.p.m. in the loam samples. After the harvest of the pea plants 19 days later, sand samples still contained aldrin residues from 17.9 to 18.9 p.p.m. No effect of carbon on the recovery of insecticidal residues from the sand could be observed. However, extracts of carbon-treated loam soils contained 30 to 37% less aldrin and dieldrin residues than the extracts from carbon-free loam soils. Based on previous results, the authors assumed that the residues were not extracted as efficiently 19 days after the carbon had been applied to the loam soil. Though different concentrations of carbon had been used, the amounts of aldrin residues recovered from the carbon treated soils were similar. Since the reduction in the extraction efficiency due to carbon did not occur with quartz sand, this retention of insecticidal residues must be related to the joint action of loam soil and carbon particles. During the 19-day incubation period, insecticides became bound to the loam-

carbon mixture to such an extent that they could no longer be fully extracted.

Plant material, however, was extracted in the absence of carbon, thus assuring a more reliable picture of the actual insecticidal concentrations in the plant tissues. Results obtained with gas-liquid chromatography were also confirmed by thin-layer chromatography. Only aldrin and dieldrin were detected by this latter method.

Pea roots, grown in aldrin-treated quartz sand, picked up relatively large amounts of insecticidal residues, the concentrations being 3.1 times larger in the roots than in the sand itself. However, roots grown in sand containing also carbon at concentrations of 1000 or 4000 p.p.m. contained insecticidal residues that amounted to only 13 and 7% of the aldrin and dieldrin residues in the respective sand-carbon mixtures. The addition of carbon to the sand resulted in a 96 to 98% reduction of aldrin and dieldrin residue within the pea roots (Figure 1). With loam soils a similar trend was noticeable but not so striking. Roots from loam that had been treated only with aldrin contained insecticidal residues at concentrations similar to those in the soil (92% of the soil residue). However, the addition of carbon at 1000, 2000, and 4000 p.p.m. to the soil resulted in insecticidal residues within the roots that amounted to 36, 30, or 6% of the determined soil residues. A 96% reduction in insecticidal penetration from the loam soil into the roots was achieved only when carbon was added at a concentration of 4000 p.p.m. (Figure 1).

Pea greens, after having grown in aldrin-treated quartz sand, contained insecticidal residues at a concentration of 2.21 p.p.m., of which 78% were in the form of dieldrin. Residues in pea greens from loam soil were all in the form of dieldrin. Though the carbon-free sand and loam contained similar amounts of insecticides, the amount of residues that had penetrated into roots from the loam soil were only 2% of the amounts that were in pea greens from quartz sand. The effects of the soil type in retaining insecticidal residues and preventing their penetration into the plant system is obvious. A 99 and 60% reduction in

Table II. Effects of Carbon in Quartz Sand and Loam Soil on the Uptake of Aldrin from Soils into Pea Plants, Experiment 2—Laboratory

		Aldrin Applied at 20 P.P.M. Plus						
		Carbon, P.P.M.						
		1000		2000		4000		
		Recovered after 19 Days, at Harvest ^a						
		P.p.m.	P.p.m.	%R ^b	P.p.m.	%R	P.p.m.	%R
Peas grown in quartz sand								
Sand	A ^c	18.88 ± 0.56	18.75 ± 0.26		^d		17.93 ± 0.4	
	D ^c	0.02 ± 0	Trace				Trace	
	T ^c	18.90 ± 0.56	18.75 ± 0.26				17.93 ± 0.4	
Roots	A	49.98 ± 3.0	2.23 ± 0.21	96	^d		1.15 ± 0.34	98
	D	7.92 ± 0.08	0.19 ± 0.02	98			0.03 ± 0.01	99
	T	57.90 ± 3.1	2.42 ± 0.23	96			1.18 ± 0.35	98
Greens	A	0.48 ± 0.35	^e		^a		0.01 ± 0	98
	D	1.73 ± 0.80	0.02 ± 0.02	99			0.02 ± 0	99
	T	2.21 ± 1.1	0.02 ± 0.02	99			0.03 ± 0	99
Peas grown in a loam soil								
Loam	A	16.46 ± 0.07	12.13 ± 0.19	26	10.72	35	10.88 ± 0.51	33
	D	0.69 ± 0.09	0.22 ± 0.05	68	0.11	84	0.11 ± 0.01	84
	T	17.15 ± 0.02	12.35 ± 0.15	30	10.83	37	10.99 ± 0.52	36
Roots	A	13.51 ± 2.91	3.22 ± 0.02	76	2.36	83	0.46 ± 0.02	97
	D	2.50 ± 0.10	1.21 ± 0.03	52	0.94	62	0.24 ± 0.01	90
	T	16.01 ± 3.0	4.43 ± 0.05	72	3.30	80	0.70 ± 0.02	96
Greens	A	^e	^e		^e		^e	
	D	0.05 ± 0.01	0.02 ± 0.01	60	0.02	60	^e	
	T	0.05 ± 0.01	0.02 ± 0.01	60	0.02	60	^e	

^a Results are the average of duplicated experiments.
^b %R = per cent reduction of insecticidal residues due to carbon treatment of soil as compared with residue levels obtained in the absence of carbon treatment.
^c A = aldrin; D = dieldrin; T = total of aldrin plus dieldrin.
^d No data available.
^e No measurable amounts of residues were detected.

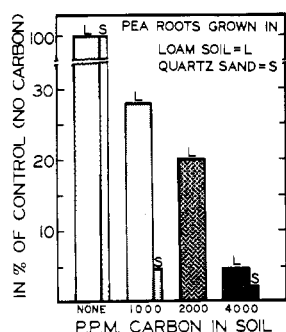


Figure 1. Aldrin and dieldrin residues in pea roots after growing in aldrin treated loam or sand that contained various concentrations of carbon

insecticidal residues in pea greens was achieved with carbon at 1000 p.p.m. in sand and loam, respectively. No measurable amounts of residues could be detected in pea greens that had grown in loam soil containing carbon at 4000 p.p.m.

Carbon prevented to a large extent the penetration of insecticidal residues into pea roots and also reduced proportionately the translocation of residues into the pea greens.

Experiment 3. The effect of carbon on the uptake of insecticidal residues by radishes, peas, carrots, and potatoes from aldrin or heptachlor treated field plots was studied. In these experiments, field plots were used that had been treated with either aldrin or heptachlor at a rate of 5 pounds per acre each year over the 5-year period of 1958–1962 (Lichtenstein and Schulz, 1965). These soils contained, after five additional years in May of 1967, residues that were totally in the form of dieldrin or mixed residues of heptachlor and heptachlor epoxide (Table III). Portions of these field plots were treated with carbon in May of 1967 to test under field conditions the effect of carbon as previously described. For that purpose, 30 × 24-foot (9.15 × 7.32-meter) plots, originally treated with aldrin or heptachlor, were divided into two 15 × 24-foot (4.58 × 7.32-meter) parts. Soil samples consisting of 24 cores (1 by 6 inches or 2.54 × 15.24 cm. deep) each were collected from each half and analyzed. After that, carbon was applied to the eastern half of each plot at a rate of 2000 p.p.m. For soil treatment purposes, each 15 × 24-foot plot was subdivided into 13 15-foot × 22-inch strips in the east-west direction and also into 13 24-foot × 14-inch strips in the south-north direction. Measured amounts of carbon were then thoroughly mixed with 2-gallon quantities of water and spread as uniformly as possible with a sprinkling can over each of the 26 strips. This crosswise treatment was used to attain a more uni-

Table III. Effects of Carbon in Soil on the Uptake of Aldrin (A), Dieldrin (D), Heptachlor (H), and Heptachlor Epoxide (HO) Residues from Soils into Various Crops, Experiment 3—Field Plots

	Applied to Loam Soil, 1958-1962									
	Aldrin ^a					Heptachlor ^a				
	Recovered in p.p.m. before carbon application, 1967									
	I ^b		II ^c		III ^b		IV ^c			
Soil	A + D	%D ^d	A + D	%D	H + HO	%HO ^d	H + HO	%HO		
	1.18	99	1.21	99	0.78	78	0.87	78		
	Carbon Applied to Soil, P.P.M.									
	None		2000 ^e			None		2000 ^e		
	Recovered at harvest, p.p.m.									
	A + D	%D	A + D	%D	%R ^e	H + HO	%HO	H + HO	%HO	%R
Soil	0.94	98	0.85	98	10	0.49	82	0.58	81	
Radish I ^f	0.06	99	0.02	100	67	0.08	99	0.03	100	62
Radish II ^g	0.05	100	0.01	99	80	0.10	100	0.03	100	70
Pea greens	0.07	100	0.05	100	30	0.05	100	0.03	100	45
Pea seeds	Trace	100	^h			^h		^h		
Carrots	0.32	100	0.15	100	53	0.36	84	0.30	87	16
Potatoes	0.07	100	0.02	100	71	0.05	92	0.02	100	60

^a Aldrin or heptachlor applied to 24 × 30-foot plots at five yearly dosages of 5 pounds per 5-inch acre.

^b Half (24 × 15 feet) of aldrin or heptachlor contaminated plots to which no carbon was added.

^c Half (24 × 15 feet) of aldrin or heptachlor contaminated plots to which carbon was added to an approximate depth of 5 inches at a rate of 2000 p.p.m.

^d %D, %HO = Dieldrin (D) or heptachlor epoxide (HO) in per cent of total residues (aldrin + dieldrin, or heptachlor plus heptachlor epoxide) recovered.

^e %R = per cent reduction of insecticidal residues due to carbon treatment of soil as compared with residue levels obtained in the absence of carbon.

^f Radishes grown from May 25 to June 26, 1967.

^g Radishes grown from July 13 to August 14, 1967, after an additional application of carbon at 2000 p.p.m. had been made to a soil strip 15 feet long and 0.5 foot wide.

^h No measurable amounts detected.

form application. Immediately after treatment, the plots were rototilled to a depth of approximately 5 inches.

Two 30-foot rows of radishes, peas, carrots, or potatoes were then grown in the east-west direction, thus covering both the carbon treated portion and the carbon-free portion of the 30 × 24-foot plot. Radishes were harvested late in June of 1967. To test the effect of a higher concentration of carbon in the soil on insecticidal penetration into radishes, an additional amount of carbon was applied at 2000 p.p.m. to the same two strips (15 × 0.5-foot) where radishes had grown previously. A second crop of radishes was then grown during July and August 1967 in the carbon-free soil and in soil strips that had been treated twice with carbon, each time at 2000 p.p.m. Harvesting, processing, and analyses of all crops were performed as described.

The amounts of insecticidal residues recovered at harvest time from both the carbon-free soil and carbon-treated soil were very similar (Table III). Radishes grown in carbon-treated soil contained only 20 to 38% of the insecticidal residues found in those grown in carbon-free soil. This represents a reduction of 80 to 62% in insecticidal uptake. The increased amount of carbon in soil attained through a second soil-strip treatment in July did not result in a further reduction in insecticidal uptake by radishes.

Insecticidal residues in unpeeled potatoes from carbon-treated soil were only 30 to 40% of those that had grown in carbon-free soil, representing a 70 to 60% reduction in insecticidal content. The actual concentration of in-

secticides in unpeeled potatoes from carbon treated soil amounted to 0.02 p.p.m. Considering that approximately 75% of these residues are located within the potato peels (Lichtenstein, 1960), insecticidal concentrations in those parts of the potato that are mostly consumed by humans would then amount to only 0.005 p.p.m.

Carrots, which usually pick up more insecticidal residues from soils than any other crop (Lichtenstein, 1959, 1960; Lichtenstein *et al.*, 1965), were less affected by the soil carbon treatment than were radishes or potatoes. Yet carrots from carbon-treated soils contained dieldrin residues that amounted to 47% of those that were grown in soils containing dieldrin but no carbon. Least affected by carbon were carrots in heptachlor-treated soil, where only a 16% reduction occurred.

Insecticidal residues recovered from pea greens were similar (0.03 to 0.07 p.p.m.) to those that were found under laboratory conditions in pea greens from plants that had grown in loam soil treated with aldrin at 20 p.p.m. (Table II). No insecticides could be detected in the seeds.

Heptachlor treated soils and plants grown therein contained in addition to heptachlor and heptachlor epoxide, γ -chlordane, a component of commercial heptachlor formulations. These results were confirmed by thin-layer chromatography. The concentration of γ -chlordane in carbon-free and carbon-treated soils amounted to 0.68 and 0.83 p.p.m., respectively, in radishes 0.03 and 0.01 p.p.m., in all carrots 0.16 p.p.m., and in potatoes 0.03 and 0.01 p.p.m. Pea greens did not contain measurable amounts of this compound.

Commercial formulations of heptachlor contain in addition to 1 pound of actual heptachlor 0.25 to 0.3 pound of γ -chlordane (Velsicol Chemical Corp., 1967). During the 5-year soil treatment, a total of 25 pounds of actual heptachlor had been applied which also resulted in an application of 6.25 to 7.5 pounds of γ -chlordane. Since chlordane is more persistent than heptachlor (Lichtenstein and Polivka, 1959), 5 years after the last insecticidal application more γ -chlordane than heptachlor and heptachlor epoxide were present in the soil.

To test the different toxicities of heptachlor and γ -chlordane to vinegar flies, these insects were exposed to dry residues of heptachlor or γ -chlordane. After a 3-hour exposure period, 50% mortalities were registered with 1.5 μ g. of heptachlor and 7.5 μ g. of γ -chlordane, indicating that the latter compound is 5-times less toxic to *Drosophila melanogaster* Meigen than is heptachlor.

Experiment 4. The effect of carbon in a loam soil on the uptake of dieldrin, heptachlor, and heptachlor epoxide by pea plants is discussed. Loam soils treated under field conditions in Wisconsin at relatively high dosages of aldrin or heptachlor for several years until 1962 contained, in spring of 1967, only dieldrin or heptachlor and heptachlor epoxide (Table III). Since under field conditions these are the primary residues after aldrin or heptachlor soil treatments, experiments were also conducted in the laboratory with these insecticides.

Dieldrin was applied to loam soil at 5 p.p.m. After thorough mixing, one portion of this treated soil was used to fill four clay pots, while the remainder was also treated with carbon at 2000 p.p.m. This carbon treated soil was then placed into four additional clay pots. The same procedure was repeated with a mixture of heptachlor and heptachlor epoxide, each at a concentration of 2.5 p.p.m. Finally, 16 clay pots were obtained, of which eight contained dieldrin-treated soil and eight contained heptachlor-

and heptachlor epoxide-treated soil. One half (four pots) of each insecticide treated soil also contained carbon. Samples were removed from these soils for initial analyses. Pea plants were then grown in these soils for 26 days. At that time plants or soils from two pots of the same treatment were pooled, resulting in duplicated samples of soils and pea plants for extraction and analysis.

Residues recovered from soils immediately following the insecticidal application were very similar (Table IV). No retention effect of carbon was noticed at that time. However, after a 26-day holding period the amount of dieldrin recovered from carbon-treated soil was only 45% of the amount that could be extracted from the carbon-free soil. Similar results were obtained with heptachlor- and heptachlor epoxide-treated soils. The authors assume, however, that all soils contained similar amounts of insecticidal residues and that the "reduction" of the insecticide content in the carbon-treated-soil was only an apparent one due to extraction inefficiencies.

The reduction in the penetration of insecticidal residues from soils into roots—due to the presence of carbon in soil—was very pronounced. The amounts of dieldrin or heptachlor and heptachlor epoxide that had penetrated from treated soils into pea roots were only 4 or 3% of the amounts that penetrated pea roots in the absence of carbon. This then represents a reduction of 96 or 97% in insecticidal penetration into the roots. Although roots from carbon-free soil contained dieldrin at a concentration of 6.6 p.p.m. and heptachlor and heptachlor epoxide at a combined concentration of 10.2 p.p.m., no measurable amounts of these insecticides could be detected in the pea greens.

The effects of carbon in preventing the penetration of insecticidal residues from soils into plant tissues were more striking in these laboratory experiments than in those conducted under actual field conditions (Table III).

Table IV. Effects of Carbon in Soil on the Uptake of Insecticidal Residues from Soils into Pea Plants, Experiment 4—Laboratory

	Applied to Loam Soil, P.P.M.						
	Dieldrin, 5			Heptachlor, 2.5, H. Epoxide, 2.5			
	None	Carbon, 2000		None		Carbon, 2000	
Recovered initially after soil treatment ^a							
	Dieldrin (D)			Heptachlor (H) and H. Epoxide (HO)			
	P.p.m.	P.p.m.	%R ^b		P.p.m.	P.p.m.	%R
Soil D	4.46	4.21	5	H	2.37	2.22	7
				HO	2.40	2.20	8
				H + HO	4.77	4.42	7
Recovered after 26 days at harvest ^a							
Soil D	4.61 ± 0.05	2.05 ± 0.14	55	H	2.15 ± 0.08	1.23 ± 0.05	43
				HO	2.42 ± 0.06	1.03 ± 0.03	57
				H + HO	4.57 ± 0.14	2.26 ± 0.08	51
Pea roots D	6.65 ± 0.64	0.27 ± 0.07	96	H	3.86 ± 0.33	0.11 ± 0.02	97
				HO	6.37 ± 0.26	0.17 ± 0.03	98
				H + HO	10.23 ± 0.59	0.28 ± 0.05	97
Pea greens D	Trace	c		H	c	c	
				HO	c	c	

^a Results are the average of duplicated experiments.

^b %R = per cent reduction of insecticidal residues due to carbon-soil treatment as compared with residue levels obtained in the absence of carbon treatment.

^c No measurable amounts detected.

It should be borne in mind, however, that under field conditions the mixing of carbon with the soil was not so thorough as in the laboratory. In addition, the carbon-treated field soil was in contact with untreated soils and plant roots could have penetrated into the carbon-free soil layers. Under field conditions the effects of weathering, such as rain and temperature changes, and of necessary soil cultivating during the growing season undoubtedly had also some influence on the effectiveness of carbon in the soil.

Apparently, treatment of the soil with carbon could in some cases reduce the amount of insecticidal residues in crops to such an extent that a farmer could use a soil of abnormally high insecticidal content. Further experiments would be necessary, however, to determine the condition under which plants would have to be grown so that no measurable residues within the plant parts would be found. Another important question pertains to the effect of carbon on the soil. Though no effects on plant growth could be detected in any of our experiments, the effects, if any, of carbon on nutrient uptake should also be studied. A soil of higher sorptive capacity due to the addition of carbon might be desirable from the point of view of reduced insecticidal translocation but might also present problems in terms of insect or weed control.

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