Accumulation of Dieldrin and Heptachlor on Corn Leaves in and around a Treated Field

Joseph H. Caro

Corn leaves grown in a field that had been treated with 5.6 kg per hectare of both heptachlor and dieldrin accumulated total insecticide residues to a maximum of over 1.8 ppm. Residue concentrations decreased with height on the plant; leaves 180 cm above ground contained only 20 to 30% as much as those at the 60 cm level. Residues of heptachlor and its conversion product, heptachlor epoxide, were lower than those of dieldrin throughout the growing season, suggesting lesser revolatilization of the latter from leaves. Insecticide residues on plants grown downwind of the treated plot decreased sharply with distance from the treatment. At 30 m away, residues were only 5 to 10% of those within the treated area.

Organochlorine insecticides applied in the field for the control of soil pests contaminate the crops grown in the treated area. The degree of contamination depends primarily upon insecticide, soil, and crop types and the climate during the growing season (Caro, 1969). With crops used for dairy cattle feed, even extremely small accumulations of certain pesticides on the plants will result in measurable residues in the milk. For example, cows feeding for 30 days on alfalfa hay containing less than 0.04 ppm heptachlor residues produced milk containing 0.013 ppm heptachlor epoxide (Waldron *et al.*, 1968). Dieldrin levels in a forage crop as low as 0.02 ppm led to unacceptable contamination of milk (Harris and Sans, 1969). Consequently, it is imperative that crops harvested for forage from areas near sites of pesticide application be free from contaminating residues, yet little information is available as a guide to safe use of these crops. In the study presented here, corn was grown on a field plot that had been treated with heptachlor and dieldrin, and measurements were made of the variation in crop contamination with stage of growth, height above the soil, and distance from the treated area.

EXPERIMENTAL

Treatment. A small watershed at the North Appalachian Experimental Watershed, a USDA research station located at Coshocton, Ohio, was used for the study. The plot (Watershed No. 109) consisted of 0.68 hectare of Muskingum silt loam soil, with an average slope of 12.7%. The normal 4-year crop rotation sequence on the watershed was corn-wheat-meadow-meadow. On April 30, 1969, 5.6 kg per hectare each of dieldrin (active ingredient 1,2,3,4,10,10-hexachloro-6,7-epoxy-1,4,4a,5,6,7,8,8a-octahydro-1,4-*endo*:5,8-*exo*-dimethanonaphthalene) and heptachlor (1,4,5,6,7,8,8-heptachloro-3a,4,7,7a-tetrahydro-4,7-methanoindene) were applied together as an aqueous emulsion, immediately disked into the soil to a depth of 7.5 cm, and corn (*Zea mays*) was planted.

Sample Collection. Corn leaf samples were collected four times during the growing season. A traverse was made on foot, 7.5 m inside the treated plot and parallel to the northeast edge, which was the prevailing leeward side. During the traverse, leaves were stripped by hand from predetermined heights on 10 to 15 equally spaced corn plants, and the leaves collected from each height were composited to form the bulk analytical samples. Bulk samples were wrapped in Teflon sheets, frozen, and transported to the U.S. Soils Laboratory at Beltsville, Md., for analysis. Two other sample collection traverses, parallel to the first but 15 m and 30 m northeast (downwind) of the treated watershed, were made on each of the sampling days.

On June 26, the first sampling day, the young plants were about 85 cm high and had about nine leaves each. The sixth leaf up from the ground, at a height of approximately 60 cm, was sampled. By the second sampling, on July 24, the plants had reached maximum height, 240 cm, but ears had not yet developed. Each plant carried 12 leaves, of which the fourth and tenth from the ground (heights 60 and 180 cm, respectively) were taken. Leaves at the same two heights were also taken on the third sampling day, August 27, at which time ears had developed, but the plants were still green and at maximum height. On the fourth sampling day, October 14, the crop was so withered, brown, and windblown that plant height was only 130 cm. Leaves were hanging vertically on the stalks, so that their heights above the surface could only be estimated. The fourth and tenth leaves from the ground were again sampled.

Pesticide Analysis. The frozen leaves were broken into small pieces in a food chopper and 15- to 30-g samples (3- to 6-g for desiccated leaves) were analyzed in duplicate. Extraction was with 2:1 acetonitrile:water according to Bertuzzi *et al.* (1967). For dieldrin analysis, half the extract was subjected to peroxide cleanup (Glotfelty and Caro, 1970). For heptachlor analysis, the remainder of the extract was cleaned up first on a Florisil column, and then on a column of activated carbon. A third cleanup of this extract, using

U.S. Soils Laboratory, Soil and Water Conservation Research Division, Agricultural Research Service, USDA, Beltsville, Md. 20705

thin-layer chromatography on alumina plates, was required for heptachlor epoxide determinations. Gas chromatography of all clean extracts was conducted using a glass column, 2 mm × 165 cm containing an equal-weight mixture of 10% DC-200 and 15% QF-1 on 100- to 120-mesh Gas Chrom Q. Temperatures of the inlet block, column oven, and ^{63}Ni electron capture detector were 235°, 220°, and 285° C, respectively. Carrier gas (95 to 5 argon:methane) flow rate was 40 ml per min. Typical retention times under these conditions were: heptachlor, 3.0 min; heptachlor epoxide, 4.9 min; and dieldrin, 7.4 min.

RESULTS AND DISCUSSION

Pesticide residues found on the leaves of corn plants grown within the treated area are presented in Table I. The total pesticide concentration reached a maximum of over 1.8 ppm on the lower leaves by the October harvest time, a level that is unacceptable in dairy cattle fodder (Waldron *et al.*, 1968). The increasing pesticide burden was due primarily to steadily increasing dieldrin concentrations. Levels of total heptachlor (heptachlor plus its conversion product, heptachlor epoxide) were much more constant throughout the growing season. At all stages of growth, residue concentrations decreased sharply with height of the leaves of the plants. Concentrations at the 180 cm height were generally 20 to 30% of those at the 60 cm height.

Although some absorption of the pesticides through plant roots may have occurred, the observations are in agreement with deposition from the vapor phase as the primary mechanism of pesticide accumulation by aerial plant parts (Barrows *et al.*, 1969). In a related experiment conducted on the same field during the same season, heptachlor and dieldrin vapor densities were periodically measured in the overlying air. The results, presented in Table II, show that, during growth, the corn plants were continually bathed in pesticide-bearing air. The vapor densities at the upper levels of the crop were always lower than in the air near the ground. Thus, the upper leaves contained less pesticide than the lower leaves (Table I), not only because they were younger and were exposed to the contaminated air for a shorter time, but also because they were exposed to lower concentrations in the air.

Pesticide residues on external plant parts at any given time are the net result of continual adsorption and desorption. Gunther and Blinn (1955) have stated that the major portion of a pesticide adsorbed on the surface of a plant leaf is desorbed by various means before it can be assimilated into cuticular waxes. Of the pesticide that is assimilated, some returns to the surface and some is permanently fixed into subcuticular layers. The magnitudes of the various fractions are not known and little information is available on the rates of deposition or evaporation from the leaves, so that the data cannot be interpreted in detail. However, it may be noted that the amount of residues retained is not large. The total amount of pesticides present in the mature corn leaves was about 4.2 g per hectare. Calculations of the rate of evaporation of the insecticides from the soil, based on the measured concentrations in the air and meteorological data, indicate that this was about equal to the amount of pesticide vapor moving upward through the crop in a single day. Therefore, the corn did not accumulate the pesticides efficiently.

Despite the generally higher concentrations of heptachlor in the air (Table II), less heptachlor than dieldrin was retained on the corn leaves. The relationship held true even when allowance was made for the observed conversion of most of the heptachlor on the leaves to heptachlor epoxide (Table III, last column). Moreover, the heptachlor:dieldrin ratios on the leaves decreased with plant age and were independent of the height of the leaves on the plant. The results suggest that heptachlor, which is more volatile than dieldrin, desorbed from leaf surfaces to a greater extent than dieldrin under the influence of high summer air temperatures.

The epoxidation of heptachlor occurred after deposition on the plant surfaces, since no heptachlor epoxide was found in the air. The conversion evidently was quite rapid, since 72% epoxidation was observed even in the young plants sampled in June and, moreover, little difference was noted in extent of conversion between the older and younger leaves at any stage of growth (Table III). The data also imply that plant pigments, which act as carriers of reactive oxygen, are involved in the epoxidation of heptachlor. The degree of conversion

Table I. Insecticide Contents of Corn Leaves Grown in a Treated Field

Sampling Date, 1969	Corn Height cm	Height Above Ground of Leaves Sampled cm	Insecticide Content, ppm Dry Basis		
			Heptachlor	Heptachlor Epoxide	Dieldrin
June 26	85	60	0.15	0.38	0.56
July 24	240	60	0.05	*a*	0.96
		180	0.01	*a*	0.16
Aug. 27	240	60	0.06	0.51	1.05
		180	0.03	0.14	0.33
Oct. 14	130[b]	<60	0.14	0.37	1.33
		<130	0.03	0.08	0.34

[a] Not determined. [b] Plants desiccated and shriveled.

Table II. Average Heptachlor and Dieldrin Concentrations in the Air Above a Treated Field[a]

Sampling Date, 1969	Height Above Ground, cm	Concentration,[b] ng/m,[3] in Air of		Ratio: Heptachlor to Dieldrin
		Heptachlor	Dieldrin	
May 22	50	74.9	35.6	2.10
	200	17.8	18.7	0.95
July 24	60	166.4	99.7	1.67
	180	80.5	54.0	1.49
Aug. 27	54	76.8	29.5	2.60
	162	29.2	14.6	2.00

[a] Abstracted from unpublished data of A. W. Taylor *et al.*, U.S. Soils Laboratory. [b] Averages of seven to nine 2-hr samplings taken each day.

Table III. Conversion of Heptachlor to Heptachlor Epoxide in Corn Leaves Grown in a Treated Field

Sampling Date, 1969	Height Above Ground of Leaves Sampled cm	% Conversion to Heptachlor Epoxide	Ratio: Heptachlor Plus Heptachlor Epoxide to Dieldrin
June 26	60	72	0.95
Aug. 27	60	90	0.54
	180	83	0.51
Oct. 14	<60	73	0.38
	<130	73	0.32

Table IV. Horizontal Gradient of Insecticide Accumulation by Corn Leaves Sampled on August 27, 1969

Height Above Ground of Leaves Sampled, cm	Location in Field	Insecticide Content, ppm Dry Basis		
		Heptachlor	Heptachlor Epoxide	Dieldrin
60	Within treated area	0.055	0.510	1.05
	15 meters downwind	0.023	0.090	0.23
	30 meters downwind	0.003	0.025	0.07
180	Within treated area	0.029	0.140	0.33
	15 meters downwind	0.006	0.040	0.09
	30 meters downwind	0.001	*a*	0.04

[a] Not determined.

observed on the leaves sampled in October was less than in the August sampling, suggesting that the heptachlor adsorbed during the last stages before harvest when the plants were depigmented underwent little or no epoxidation.

If the corn were to be used for forage, it would probably be harvested near the August 27 sampling day. Although the crop within the treated area was too badly contaminated at that time for use, measurements of residues in the surrounding crop, growing in soil containing less than 0.002 ppm pesticide residues, show (Table IV) that the contamination was confined to areas close to the treatment. The quantities of both heptachlor and dieldrin deposited on plants decreased sharply with distance from the treated area. The pattern was identical for both upper and lower leaves and did not differ appreciably from those obtained on the other sampling days. The data show that, at a distance of 30 m downwind from a treated plot, the corn leaves accumulated 5 to 10% of the residue concentrations found on plants within the treated area. At normal pesticide application rates (0.5 to 2.2 kg per hectare), corn grown at this distance would probably be safe for use as dairy cattle feed.

ACKNOWLEDGMENT

The author thanks the Shell Chemical Co., New York, and the Velsicol Chemical Corp., Chicago, for supplying the insecticides used in the study; W. M. Edwards and A. W. Taylor for assistance in the sample collection; and E. R. Lemon and L. H. Parmele for development of a method for calculation of insecticide evaporation rates from soil.

LITERATURE CITED

Barrows, H. L., Caro, J. H., Armiger, W. H., Edwards, W. M., *Environ. Sci. Technol.* **3,** 261 (1969).
Bertuzzi, P. F., Kamps, L., Miles, C. I., Burke, J. A., *J. Ass. Offic. Agr. Chem.* **50,** 623 (1967).
Caro, J. H., *Phytopathology* **59,** 1191 (1969).
Glotfelty, D. E., Caro, J. H., *Anal. Chem.* **42,** 282 (1970).
Gunther, F. A., Blinn, R. C., "Analysis of Insecticides and Acaricides," pp. 141–147, Interscience, New York, 1955.
Harris, C. R., Sans, W. W., *Pest. Monit. J.* **3,** 182 (1969).
Waldron, A. C., Kaeser, H. E., Goleman, D. L., Staubus, J. R., Niemczyk, H. D., J. AGR. FOOD CHEM. **16,** 627 (1968).

Received for review August 13, 1970. Accepted October 28, 1970.