Organochlorine Insecticide Residues in Agricultural Soil and Legume Crops in Northeastern Saskatchewan

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Soil samples from 20 fields in northeastern Saskatchewan were analyzed by electron capture gas chromatography for residues of organochlorine insecticides. More than 0.01 p.p.m. of dieldrin was present in soil from 16 fields, while four had no detectable residue. Heptachlor, heptachlor epoxide, endrin, and aldrin were present in soil from ten fields. Sweet clover and alfalfa collected from the same fields contained more than 0.01 p.p.m. of dieldrin in 16 samples. The highest level of dieldrin in soil was 0.3 p.p.m. and in plants was 0.1 p.p.m. DDT or its degradation products could not be detected in any plant or soil sample.

Organochlorine insecticides have been used in large quantities to control agricultural insect pests for about 20 years. Considerable information is now available on the persistence and degradation of these insecticides under controlled laboratory and field conditions. The extent to which residues of these materials occur in agricultural soil as a result of widespread application is known for only two areas in Canada (Duffy and Wong, 1967; Harris *et al.*, 1966). However, neither study presents data on residues in the crops grown in those soils. Studies of this type are important to determine the extent of contamination of soils and crops and to monitor residues in them effectively.

The purpose of this study was to determine the levels of organochlorine insecticide residues in soil and legume crops in the northeastern agricultural area of Saskatchewan.

MATERIALS AND METHODS

The northeastern agricultural area of Saskatchewan is a mixed farming area of approximately 1,250,000 cultivated acres. The soils of the area are fine- to medium-textured clay and sandy loams. The principal crops are cereal grains grown in a rotation that might include summer fallow, rapeseed, and a legume crop, either sweet clover or alfalfa. Sweet clover, a biennial, is sown with the cereal crop and in the following year may be plowed down for soil improvement, cut for silage, or harvested for seed. Alfalfa, a perennial, also sown with a companion cereal grain is cut for hay or harvested for seed for three or four years before being plowed down.

Soil and Crop Sampling. In September 1966, soil and foliage samples were collected from 16 sweet clover and four alfalfa fields throughout the area. All sweet clover was first-year crop; one alfalfa was first-year crop, and the remainder were at least two years old. No attempt was made to determine the history of insecticide application to these fields. A soil sample consisted of 20 cores, each core 2 inches in diameter and 6 inches long, taken at random throughout a field. A foliage sample consisted of 20 one-square-foot areas of the growing crop cut off at the soil surface, taken at random throughout a field. Samples were stored in plastic bags at −18° C. until analyzed two to three months later.

Organic Matter in Soil. The dry combustion method was used to determine organic carbon. The soil sample is heated in a furnace at 925° ± 25° C., the evolved CO_2 is absorbed in a known amount of standard NaOH, the CO_2 is precipitated as $BaCO_3$, and the excess NaOH is back-titrated with standard HCl. The amount of carbon present in the original sample is calculated from this back-titration.

The amount of organic matter in the soil can be calculated approximately by the equation: organic carbon × 1.724 = organic matter.

If inorganic carbonates are present in the sample, inorganic carbon must be determined on a separate sample. The inorganic carbon then is subtracted from the total carbon, as determined above, to obtain organic carbon.

Reagents. Reagent grade hexane, benzene, and petroleum ether (30° to 60° C.) were refluxed with dry Na and distilled through a Vigreux column. Reagent grade isopropyl alcohol and diethyl ether were purified by distillation. Nanograde acetonitrile (Mallinckrodt Chemical Co.) was used without further purification.

Florisil commercially activated at 1200° F. was reheated at 130° C. for 3 hours and deactivated with 0.7% water prior to use (Wood, 1966).

Gas Chromatography. Aerograph Hi-Fy Model 600-D gas chromatograph with electron capture detector was used as the analytical instrument. Two columns were used: a 5-foot × 1/8-inch i.d. aluminum column packed with 4% SE30 on 80- to 100-mesh Chromosorb W, and a 5-foot × 1/8-inch i.d. aluminum column packed with 2% QF-1 on 80- to 100-mesh Chromosorb W. The operating conditions for the SE30 column were: carrier gas, oxygen-free nitrogen; flow rate, 130 ml. per minute; temperatures, injector 180°, column 175°, and detector 175° C.; electrometer range and sensitivity, 1 and 4, respectively. The QF-1 column was maintained at 160° C. with a carrier gas flow rate of 60 ml. per minute and the other parameters the same as the SE30 column. This column was used to separate dieldrin and DDE because they had the same re-

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tention time in the SE30 column. Samples in which dieldrin was detected by the SE30 column were re-examined by the QF-1 column for the presence of DDE. The columns were conditioned for 3 days by injecting standard solutions of various insecticides until peak areas were linearly related to the quantities of compounds, indicating no breakdown in the column.

Extraction and Cleanup. The soil samples were dried at room temperature and screened through a 20-mesh sieve. The large clay lumps were pulverized in a hammer mill and screened, and the whole sample was mixed thoroughly. One hundred grams of the soil (average moisture content 2 to 4%) was shaken with 200 ml. of a 1 to 1 hexane–isopropyl alcohol mixture for 1 hour and filtered. The residue was re-extracted twice with 50-ml. portions of the same solvent mixture and filtered. The combined filtrate was partitioned into petroleum ether after dilution with 500 ml. of a 2% solution of sodium chloride. The petroleum ether layer was dried with sodium sulfate and concentrated to about 10 ml. The concentrated solution was then chromatographed on a 3-inch Florisil column and eluted with 200 ml. of 6% diethyl ether in hexane (eluate I) followed by 200 ml. of 15% diethyl ether in hexane (eluate II). The two fractions were concentrated to 50 to 70 ml., transferred to a 100-ml. volumetric flask, made up to the mark with hexane, and examined by gas-liquid chromatography.

Sweet clover and alfalfa plant samples were chopped into small pieces and mixed thoroughly, and 20-gram portions were used for analysis. The methods of extraction and cleanup were the same as described by Saha and McDonald (1967b) for wheat plants.

Recoveries of lindane, heptachlor, aldrin, heptachlor epoxide, gamma-chlordan, dieldrin, endrin, DDT, DDE, and DDD at 0.1 and 0.01 p.p.m. added to air-dry soil were 90 to 100%. After this work was completed, studies on the recovery of aged dieldrin-C^{14} residue from soil indicated that 1 to 1 hexane–isopropyl alcohol mixture extracted 62% of the residue from a silt loam soil (Saha, 1968b) and 50 to 60% from loamy sand, sandy loam, clay loam, and heavy clay soil (Saha, 1968a). Recoveries of the same pesticides added to sweet clover and alfalfa were 90 to 105%. The minimum amount of these insecticides detectable in plants and soil, except DDT and its metabolites, was 2 p.p.b.; 10 p.p.b. of DDT and its metabolites could be detected. Although residues could be detected in concentrations as low as 2 p.p.b., quantitative determinations were made only for residues present in concentrations of 0.01 p.p.m. or more. The amount of a given insecticide present in a particular sample was determined by the standard curve method of Gutenmann and Lisk (1963).

Thin-Layer Chromatography. All soil and plant samples indicating more than 0.02 p.p.m. of any residue were analyzed by thin-layer chromatography according to Kovacs (1963). The identity of a suspected insecticide in plant or soil extract (after cleanup) was proved by comparing its R_f value with that of the authentic sample.

Chemical Confirmation. The presence of dieldrin in a particular sample was further confirmed by treatment with HBr and acetic anhydride reagent when the gas-chromatogram peak due to dieldrin disappeared (O'Donnell *et al.*, 1955). The sensitivity of this method was 0.01 p.p.m. of dieldrin. Aldrin, heptachlor, and γ-chlordan were not confirmed by any chemical conversion procedure. Since no DDT or its metabolite was detected by gas chromatography in any of the samples, the question of their confirmation did not arise.

RESULTS AND DISCUSSION

Residues in Soil. Eighty per cent of the soil samples contained aldrin and/or dieldrin residues of 0.01 p.p.m. or more (Table I). Of these, 44% contained 0.01 to 0.04 p.p.m., 31% contained 0.05 to 0.09 p.p.m., and 25% contained 0.10 to 0.30 p.p.m. Twenty-five per cent of the samples contained residues of heptachlor, heptachlor epoxide, or γ-chlordan in concentrations of 0.01 to 0.04 p.p.m.; 15% contained endrin residue of 0.01 to 0.02 p.p.m.; 15% contained no detectable residue; 35% contained residue of only one insecticide; and 50% contained residues of two or more insecticides.

The level of dieldrin residue in these soil samples is much lower than in samples of soil from the Maritime Provinces of Canada, where concentrations of 0.75 to 4.0 p.p.m. were found (Duffy and Wong, 1967). In 16 of 32 soil samples from southwestern Ontario concentrations of dieldrin ranged from 0.10 to 1.60 p.p.m. (Harris *et al.*, 1966). The purposes for which the insecticides were applied and the mode and rate of application of the insecticides in eastern and western Canada may partially explain the differences in residue levels found. In eastern Canada, for control of insects of root crops, the insecticides were usually incorporated into the soil at substantial dosages. In northeastern Saskatchewan, for control of cutworms, rapeseed insect pests, and sweet clover weevil, the insecticides were applied as foliar sprays to the growing crop or as granules with the seed at not more than 8 ounces of toxicant per acre per treatment.

Virtually no residues of DDT or its metabolites were found in these samples, in sharp contrast to the high levels of DDT recorded for eastern Canadian soils (Duffy and Wong, 1967; Harris *et al.*, 1966). Actually, for the last 10 to 12 years DDT has had only very limited use in northeastern Saskatchewan.

Residues in Sweet Clover and Alfalfa. Eighty per cent of the legume crop samples from the 20 fields contained 0.01 p.p.m. or more of dieldrin (Table I). The highest concentration of dieldrin was 0.10 p.p.m. in one sweet clover and one alfalfa sample. Residues of other insecticides were either undetectable or present in only trace amounts.

In every instance where dieldrin occurred in the soil the legume crop also contained dieldrin residue. The ratio of concentration of dieldrin in soil to dieldrin in sweet clover or alfalfa was 1 to 1 to 6 to 1. This is as high as the uptake by carrots from contaminated soil (Lichtenstein, *et al.*, 1964), and much higher than by wheat plants (Saha and McDonald, 1967b). In an earlier experiment (Saha and McDonald, 1967a), sweet clover grown in soil treated the previous year with 8 pounds of endrin or aldrin per acre contained 0.14 and 0.09 p.p.m. of endrin and dieldrin, respectively. Wheat, oats, and barley plants grown at the same time in plots in the same field had 0.03 to 0.05 p.p.m. of endrin and 0.03 to 0.04 p.p.m. of dieldrin. The soil

Table I. Organochlorine Insecticide Residues in Agricultural Soil and Legume Crops in Northeastern Saskatchewan in 1966[a]

Sample	Organic Matter in Soil, %	Residues in Soil, P.P.M.[b]						Dieldrin Residue in Crop, P.P.M.[c]
		Heptachlor	Heptachlor epoxide	γ-Chlordan	Aldrin	Dieldrin	Endrin	
				Sweet Clover				
1	1.9	[d]	0.01	[d]	[d]	0.06	[d]	0.03
2	2.4	[d]	[d]	[d]	[d]	0.02	0.01	0.01
3	2.4	[d]	[d]	[d]	0.02	0.06	[d]	0.03
4	2.5	[d]	[d]	[d]	[d]	0.01	0.02	0.01
5	2.7	[d]	[d]	[d]	[d]	0.02	0.01	0.01
6	2.9	[d]	[d]	[d]	[d]	[d]	[d]	[d]
7	3.0	0.04	0.01	0.02	[d]	0.10	[d]	0.06
8	3.1	[d]	[d]	[d]	[d]	0.01	[d]	0.01
9	3.2	[d]	0.02	[d]	[d]	0.02	[d]	0.01
10	3.4	[d]	[d]	[d]	[d]	[d]	[d]	[d]
11	3.5	[d]	[d]	[d]	[d]	[d]	[d]	[d]
12	3.8	[d]	[d]	[d]	0.05	0.03	[d]	0.03
13	5.0	0.01	[d]	[d]	[d]	[d]	[d]	[d]
14	5.5	[d]	[d]	[d]	[d]	0.03	[d]	0.02
15	6.0	[d]	[d]	[d]	[d]	0.11	[d]	0.03
16	6.8	[d]	[d]	[d]	[d]	0.04	[d]	0.01
				Alfalfa				
17	1.6	[d]	[d]	[d]	[d]	0.13	[d]	0.10
18	3.2	0.01	0.01	[d]	0.01	0.08	[d]	0.04
19	3.7	[d]	[d]	[d]	0.02	0.06	[d]	0.01
20	4.1	[d]	[d]	[d]	[d]	0.30	[d]	0.10

[a] No DDT or metabolites detected in any soil or crop sample.
[b] Average of duplicate analyses, oven-dry basis. True recovery of dieldrin by this method as shown by studies on extraction of dieldrin-C^{14} from soil is 50 to 60% (Saha, 1968a,b).
[c] Average of duplicate analyses, fresh weight basis. Moisture content of plant material 75 to 80%. No other insecticide detected or concentration less than 10 p.p.b.
[d] Not detectable or concentration less than 10 p.p.b.

residues were 1.20 p.p.m. of endrin and 0.90 p.p.m. of combined aldrin and dieldrin. Alfalfa grown in soil treated with 1.0 pound of heptachlor per acre (soil residue of 0.7 p.p.m. of heptachlor and epoxide) had 0.20 to 0.30 p.p.m. of heptachlor epoxide (King *et al.*, 1966). Alfalfa and sweet clover apparently absorb more residue from soil than do cereal crops. Bailey and White (1964) stated that the bioactivity of an insecticide is lowest in soils that are high in organic matter, and vice versa. The organic matter content of the soils under investigation here is generally low (Table I). Eighty per cent of the soils had 2 to 5% organic matter, and the highest organic matter content was 6.8%. Uptake of residues by plants growing in such soils would be expected to be high, as was observed.

Since sweet clover and alfalfa are used as cattle feed, the presence of dieldrin in them can lead to residues in milk and meat. Gannon *et al.* (1959a) found 0.014 and 0.076 p.p.m. of residue in milk of cows fed 0.1 and 0.25 p.p.m. of dieldrin, respectively, in their daily ration. Steers fed at the same levels stored 0.3 and 0.8 p.p.m. of dieldrin in their body fat, respectively (Gannon *et al.*, 1959b). Williams *et al.* (1964) found 0.02, 0.06, and 0.11 p.p.m. of residue in the milk of cows fed 0.05, 0.15, and 0.30 p.p.m. of dieldrin in their daily ration. Dieldrin levels in the feed in those two studies are close to the observed dieldrin level in sweet clover and alfalfa (0.01 to 0.1 p.p.m.) in the present survey. Thus small amounts of dieldrin might be present in the milk and meat of cows consuming these contaminated forage crops alone as their total diet.

ACKNOWLEDGMENT

The authors thank L. A. Gadallah and R. B. Woodford for technical assistance.

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Received for review February 25, 1968. Accepted April 22, 1968. Contribution No. 301, Canada Agriculture Research Station, Saskatoon, Canada.