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Fate of [^{14}C]Aldrin in Crop Rotation under Outdoor Conditions

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[^{14}C]Aldrin was applied to soils (about 3 kg/ha) in outdoor boxes at various locations (Germany, England, and United States), and crops were cultivated (maize, wheat, sugar beets, and potatoes). In the following year, crop rotation experiments were carried out in the same soils without retreatment; in addition, wheat was grown in soils retreated with [^{14}C]aldrin (3.5 kg/ha). After the harvest of both years, the distribution of aldrin and major metabolites (dieldrin; photodieldrin; hydrophilic metabolites including dihydrochlordene dicarboxylic acid; an unidentified nonpolar compound X; and unextractable metabolites) was determined in plants, soils, and leaching water. Two further conversion products, photoaldrin and aldrin-*trans*-diol, occurred in trace amounts only in a few samples. Metabolic pathways for aldrin under outdoor conditions are presented. The distribution of radioactive residues in soils and plants as well as their quantitative chemical composition are discussed, and comparisons are made between the different experimental sites, the crops, the first and second year, and retreated and nonretreated samples. The quantitative results are compared to those of field trials.

One rational of the experiments discussed in this paper was to yield a model which combines the advantages of small-scale laboratory experiments, i.e., the possibility of using ^{14}C-labeled compounds and, consequently, detecting and determining all metabolites including highly hydrophilic or unextractable ones, with the advantages of field experiments, i.e., normal agricultural conditions.

In previous papers, we reported outdoor studies with [^{14}C]aldrin in potatoes (Klein *et al.*, 1973), sugar beets (Kohli *et al.*, 1973b), wheat, and maize (Weisgerber *et al.*, 1974b), following soil application at various locations (Birlinghoven/Germany; Sittingbourne/UK; Modesto/Calif.) at the rate of about 3 kg/ha (dose recommended for agricultural practice). During the year after these soil treatments, crop rotation experiments were carried out with wheat, potatoes, sugar beets, and maize. In Experiments 1–7 (Table 1), crops were cultivated in the same soils without further treatment; in Experiments 8 and 9 (Table 1), wheat was grown in soils retreated with [^{14}C]aldrin (3.5 kg/ha). This paper gives a summary and evaluation of the results of both years.

EXPERIMENTAL

The plants were grown in boxes 60 × 60 × 60 cm, constructed from water-resistant plywood. The base of the box contained holes to permit the drainage of excess water

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TABLE 1

SURVEY OF CROP ROTATION EXPERIMENTS

Experiment	Location	[^{14}C]Aldrin soil treatment, first year	Crop, first year	Results for first year summarized in	[^{14}C] Aldrin soil treatment, second year	Crop, second year	Results for second year summarized in
1	Birlinghoven/Ger.	2.9 kg/ha	Sugar beets	Table 2	Nil	Wheat	Table 7
2	Sittingbourne/U.K.	3.2 kg/ha	Sugar beets	Table 2	Nil	Wheat	Table 7
3	Birlinghoven/Ger.	2.9 kg/ha	Wheat	Table 3	Nil	Potatoes	Table 8
4	Sittingbourne/U.K.	3.2 kg/ha	Wheat	Table 3	Nil	Potatoes	Table 8
5	Birlinghoven/Ger.	2.9 kg/ha	Potatoes	Table 4	Nil	Sugar beets	Table 9
6	Sittingbourne/U.K.	3.2 kg/ha	Potatoes	Table 4	Nil	Sugar beets	Table 9
7	Modesto/Calif.	3.0 kg/ha	Maize	Table 5	Nil	Maize	Table 10
8	Birlinghoven/Ger.	2.9 kg/ha	Maize	Table 6	3.5 kg/ha	Wheat	Table 11
9	Sittingbourne/U.K.	3.2 kg/ha	Maize	Table 6	3.5 kg/ha	Wheat	Table 11

which was collected in a metal splash tray. The box was wrapped in aluminium foil on the outside to prevent temperature increases due to sunlight. The bottom 25 mm of the box was packed with stone chips about 25 mm in diameter, and the stones were covered with a 25-mm layer of well-rotted turf. The box was filled with soil to 1 cm from the top. The soil was allowed to settle for 1 month before planting. The box was sunk into a

FIG. 1. Survey on the outdoor experiments with [^{14}C]aldrin.

large pit so that the upper surface of the soil was level with the surrounding ground. The soils were typical for crop growing in the three locations. Fertilizers were applied as in agricultural practice. The [^{14}C]aldrin was applied as a diluted 30% emulsifiable concentrate using commercial surfactants. Application rates of [^{14}C]aldrin are included in Table 1. The concentrate was diluted 100 times with water before application. The insecticide was incorporated in the soil to a 10-cm depth, and crops were sown in each

box. Air temperature, humidity, and pressure, as well as rainfall, were recorded during the vegetation period.

Figure 1 is a photograph of the experimental boxes along with a plan of the base and a side view of the boxes.

The leaching water drained from the boxes at a depth of >60 cm was collected and analyzed.

Detailed information on working up procedures and on analytical methods are given in the previous papers (Klein *et al.*, 1973; Kohli *et al.*, 1973b; Weisgerber *et al.*, 1974b). The identification of conversion products was carried out by comparison with chromatographic data and mass spectra of authentic reference compounds; in the case of hydrophilic metabolites, methylation was included in the isolation procedure.

RESULTS AND DISCUSSION

Table 1 gives a survey on the crop rotations in the experiments.

IDENTIFICATION OF CONVERSION PRODUCTS

Already after the first vegetation period, several conversion products were observed in all samples in varying concentrations. The quantitative data for the major metabolites or metabolite groups in the first year are listed in Tables 2–6, those of the second year in Tables 7–11. The following description of metabolite identification relates to both years.

One main product in plants and soil was identical to dieldrin (Fig. 2) which has been known to be an aldrin metabolite in various organisms and soil for many years (summary: Korte *et al.*, 1962; FAO/WHO, 1968).

A considerable portion of the radioactivity present in plants and soil was a mixture of very hydrophilic substances, the main compound of which was found to be *dihydrochlordene dicarboxylic acid.* This substance, a product resulting from oxidative ring cleavage of aldrin (Fig. 2), has also been observed in rabbits treated with the major dieldrin metabolite in animals, aldrin-*trans*-diol (Korte, 1972; Oda and Müller, 1972) (Fig. 2); later on, dihydrochlordene dicarboxylic acid was also detected directly after dieldrin application to animals (Baldwin *et al.*, 1972). In the leaching water of these outdoor experiments, which was drained from the experimental boxes at a depth of about 60 cm, dihydrochlordene dicarboxylic acid constituted more than 90% of the radioactivity present (Moza *et al.*, 1972).

The other substances from the hydrophilic group could not be identified in soils and plants. In the leaching water, however, a hydrophilic byproduct was identified as *aldrin-trans-diol* (Fig. 2), the major animal metabolite of aldrin (Korte and Kochen, 1966) and dieldrin (Korte and Arent, 1965) mentioned above. It cannot be excluded that this substance is also a byproduct in the hydrophilic metabolite group of plants and soils; the attempts to detect it in these extracts, however, failed due to high amounts of biological byproducts which occurred much less in water extracts (i.e., detection limit in water is better than in soils or plants).

Preferably in the upper soil layers, a conversion product was detected, the polarity of which was between that of aldrin and dieldrin upon tlc (thin-layer chromatography). Since this substance (*metabolite X* in Tables 2–11) was decomposed upon purification, it could not be identified. It is noteworthy that the compound occurred in traces in many

TABLE 2

RESIDUES OF [14C]ALDRIN AND ITS CONVERSION PRODUCTS IN SUGAR BEETS AND SOIL, FOLLOWING SOIL APPLICATION[a]

Sample	GERMANY						UNITED KINGDOM					
	Aldrin	Metabolite X	Dieldrin	Hydrophilic metabolites (extracted) + photodieldrin	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Hydrophilic metabolites (extracted) + photodieldrin	Unextracted residue	Total residue
Soil												
0–10 cm from surface	0.87	0.02	0.68	0.10	0.21	1.88	1.28	0.07	0.69	0.18	0.28	2.50
10–20 cm from surface	0.38	0.01	0.28	0.05	0.06	0.78	0.01	<0.01	0.01	0.01	0.10	0.13
20–40 cm from surface	0.08	<0.01	0.07	0.02	0.03	0.21	<0.01	<0.01	<0.01	<0.01	0.03	0.04
40–60 cm from surface	0.01	<0.01	0.01	0.02	0.01	0.05	<0.01	<0.01	<0.01	<0.01	0.02	0.03
Peel	0.03	<0.01	0.51	0.15	<0.01	0.70	0.01	0.03	0.26	0.16	<0.01	0.46
Peeled beets	<0.01	<0.01	<0.01	0.05	<0.01	0.06	<0.01	<0.01	<0.01	0.04	<0.01	0.05
Leaves	<0.01	<0.01	0.01	0.03	<0.01	0.04	<0.01	<0.01	<0.01	0.05	<0.01	0.05

[a] Values are expressed as equivalent parts per million of aldrin.

TABLE 3

RESIDUES OF [^{14}C]ALDRIN AND ITS CONVERSION PRODUCTS IN WHEAT AND SOIL FOLLOWING SOIL APPLICATION[a]

	GERMANY							UNITED KINGDOM						
Sample	Aldrin	Metabolite X	Dieldrin	Photo-dieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Photodieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue
Soil														
0–10 cm from surface	1.09	nd[b]	0.52	nd	0.09	0.17	1.87	2.00	0.11	0.42[c]	0.05	0.14	0.15	2.87
10–20 cm from surface	0.45	nd	0.21	nd	0.05	0.07	0.78	<0.01	<0.01	<0.01	nd	<0.01	0.05	0.05
20–40 cm from surface	0.09	nd	0.05	nd	0.02	0.02	0.18	<0.01	<0.01	<0.01	<0.01	<0.01	0.05	0.05
40–60 cm from surface	<0.01	nd	<0.01	nd	<0.01	0.01	0.01	<0.01	nd	<0.01	<0.01	<0.01	0.02	0.03
Roots	0.07	nd	0.79	0.02	0.18	0.05	1.11	0.57	nd	2.92	0.02	0.82	0.31	4.64
Low stems, 8 cm	—	—	—	—	—	—	—	0.10	nd	0.69	0.02	0.11	<0.01	0.92
Straw	<0.01	nd	0.07	<0.01	0.04	<0.01	0.12	0.02	nd	0.11	<0.01	0.05	<0.01	0.18
Husks	<0.01	nd	0.01	<0.01	0.01	<0.01	0.03	0.01	nd	0.01	<0.01	0.02	<0.01	0.04
Grain	<0.01	nd	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	nd	<0.01	<0.01	<0.01	<0.01	0.01

[a] Values expressed as equivalent parts per million of aldrin.
[b] nd = none detected.
[c] Including 5% of radioactivity as photoaldrin.

samples, but higher amounts (>2%) were found only in the upper soil layers from England. For plants, larger amounts were observed in sugar beets than in other crops. The reason for this fact can be given only when the compound is identified.

The known photoisomerization product of dieldrin, *photodieldrin* (Fig. 2), was found preferably in leaves or straw (5–10% of the total residues); smaller amounts were detected in soils, especially in soil with wheat or maize. The dependence of photodieldrin formation in soil upon the plants may be explained by the different capabilities of the plants to shade the soil or by metabolic reactions; the question cannot be decided

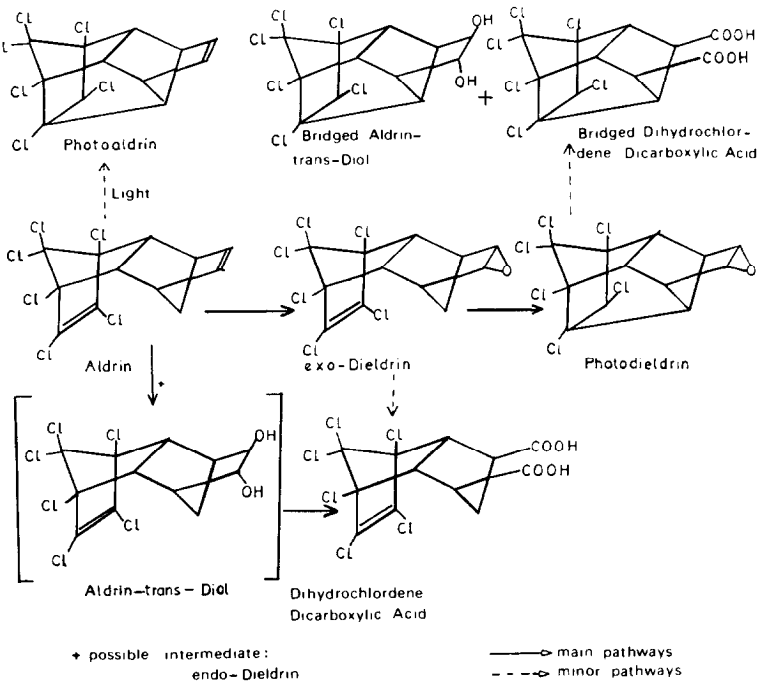

FIG. 2. Conversion pathways of aldrin in plants and soil under outdoor conditions.

in experiments under normal outdoor conditions. The theory of metabolic photodieldrin-formation is supported by the following observation: Since photodieldrin is not a photoproduct of aldrin but of its conversion product dieldrin, the photoproduct of aldrin itself, photoaldrin (Fig. 2), should be found in higher concentrations than photodieldrin when aldrin is applied to soil; but this did not occur. Photoaldrin was not at all detected in plants. In soils, it was observed only in traces (<0.5% of the total residues); higher concentrations (up to 5%) were found only in the wheat soils from England. It should also be mentioned that metabolic formation of photodieldrin has been reported for microorganisms (Matsumura, 1972).

Besides these metabolites, plant and soil extracts contained, in varying concentrations, radioactive products which were *not extractable with organic solvents*. Their percentage of total radioactivity was highest in the deeper soil layers from England and was low in most of the plant samples. From a combined soil sample, 55% of these residues could be solubilized with dilute ammonia or sodium hydroxide, and this solubilized portion was identified as dihydrochlordene dicarboxylic acid. It may be

TABLE 4

RESIDUES OF [^{14}]ALDRIN AND ITS CONVERSION PRODUCTS IN POTATOES AND SOIL FOLLOWING SOIL APPLICATION[a]

Sample	GERMANY						UNITED KINGDOM					
	Aldrin	Metabolite X	Dieldrin	Hydrophilic metabolites (extracted) + photodieldrin	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Hydrophilic metabolites (extracted) + photodieldrin	Unextracted residue	Total residue
Soil												
0–10 cm from surface	0.58	0.01	0.62	0.11	0.11	1.43	0.59	0.01	0.40	0.74	0.27	2.01
10–20 cm from surface	0.23	nd[b]	0.26	0.05	0.08	0.62	<0.01	<0.01	<0.01	0.01	0.06	0.07
20–40 cm from surface	0.02	<0.01	0.02	0.02	0.03	0.09	<0.01	nd	<0.01	0.01	0.03	0.04
40–60 cm from surface	<0.01	<0.01	<0.01	0.02	0.03	0.05	<0.01	nd	<0.01	0.01	0.01	0.02
Roots	0.20	nd	1.68	0.38	0.08	2.34	0.58	nd	2.26	0.76	0.33	3.93
Peel	0.10	nd	0.39	0.12	0.01	0.62	0.36	nd	1.16	0.14	0.02	1.68
Peeled tubers	<0.01	nd	0.04	0.02	<0.01	0.06	<0.01	nd	0.08	0.02	<0.01	0.10
Leaves	<0.01	nd	0.06	0.04	0.01	0.11	0.03	nd	0.53	0.85	0.43	1.84

[a] Values expressed as equivalent parts per million of aldrin.
[b] nd = none detected.

TABLE 5

RESIDUES OF [14C]ALDRIN AND ITS CONVERSION PRODUCTS IN MAIZE AND SOIL FOLLOWING SOIL APPLICATION IN MODESTO, CALIFORNIA[a]

Sample	Aldrin	Metabolite X	Dieldrin	Photodieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue
Soil							
0–10 cm from surface	0.50	nd[b]	1.17	nd	0.25	0.30	2.22
10–20 cm from surface	0.01	nd	0.01	nd	0.02	0.08	0.12
20–40 cm from surface	<0.01	nd	<0.01	nd	0.02	0.02	0.04
40–60 cm from surface	<0.01	nd	<0.01	nd	<0.01	0.03	0.04
Roots	—	—	—	—	—	—	—
Leaves	0.03	nd	0.06	0.05	0.23	0.03	0.40
Stem	<0.01	nd	0.05	nd	0.02	<0.01	0.08
Husks	<0.01	nd	<0.01	<0.01	0.02	<0.01	0.03
Grain	<0.01	nd	<0.01	nd	<0.01	<0.01	<0.01
Core	<0.01	nd	<0.01	nd	<0.01	<0.01	<0.01

[a] Values expressed as equivalent parts per million of aldrin.
[b] nd = none detected.

TABLE 6

RESIDUES OF [^{14}C]ALDRIN AND ITS CONVERSION PRODUCTS IN MAIZE AND SOIL FOLLOWING SOIL APPLICATION[a]

	GERMANY							UNITED KINGDOM						
Sample	Aldrin	Metabolite X	Dieldrin	Photo-dieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Photodieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue
Soil														
0–10 cm from surface	0.78	nd[b]	0.55	0.02	0.07	0.16	1.58	1.30	0.11	0.72	nd	0.19	0.30	2.62
10–20 cm from surface	0.18	<0.01	0.16	nd	0.04	0.06	0.45	<0.01	nd	<0.01	<0.01	0.01	0.05	0.06
20–40 cm from surface	0.03	nd	0.04	nd	0.02	0.03	0.12	<0.01	<0.01	<0.01	nd	<0.01	0.03	0.04
40–60 cm from surface	<0.01	nd	0.01	nd	0.01	0.03	0.05	<0.01	nd	<0.01	nd	<0.01	0.02	0.02
Roots	0.30	nd	3.64	nd	2.42	0.84	7.20	0.19	nd	1.49	0.06	0.69	0.03	2.46
Leaves	0.01	<0.01	0.03	0.02	0.08	<0.01	0.15	<0.01	nd	0.01	nd	0.06	0.03	0.10
Stem	<0.01	nd	0.03	<0.01	0.01	<0.01	0.04	<0.01	nd	0.02	nd	0.01	<0.01	0.03
Husks	<0.01	nd	<0.01	<0.01	0.01	0.02	0.04	<0.01	nd	<0.01	nd	<0.01	<0.01	<0.01
Grain	<0.01	nd	<0.01	nd	<0.01	<0.01	0.01	<0.01	nd	<0.01	nd	<0.01	<0.01	<0.01
Core	<0.01	nd	<0.01	nd	0.01	<0.01	0.01	<0.01	nd	<0.01	nd	<0.01	<0.01	<0.01

[a] Values expressed as equivalent parts per million of aldrin.
[b] nd = none detected.

TABLE 7

RESIDUES OF [14C]ALDRIN AND ITS CONVERSION PRODUCTS IN WHEAT AND SOIL FOR THE SECOND YEAR[a]

	GERMANY							UNITED KINGDOM						
Sample	Aldrin	Metabolite X	Dieldrin	Photo-dieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Photodieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue
Initial concentration[b]	0.87	0.02	0.68	nd[c]	0.10	0.21	1.88	1.28	0.07	0.69	nd	0.18	0.28	2.50
Soil														
0–10 cm from surface	0.18	nd	0.44	0.01	0.11	0.14	0.88	0.40	0.06	0.50	0.06	0.20	0.27	1.49
10–20 cm from surface	0.02	<0.01	0.19	0.01	0.05	0.07	0.34	0.01	<0.01	0.02	<0.01	0.02	0.05	0.10
20–40 cm from surface	0.01	nd	0.01	nd	0.02	0.04	0.08	<0.01	<0.01	0.01	<0.01	0.01	<0.01	0.03
40–60 cm from surface	<0.01	nd	<0.01	nd	0.03	0.03	0.07	<0.01	<0.01	0.01	<0.01	0.01	<0.01	0.02
Roots	0.29	0.06	2.83	0.06	0.33	0.41	3.98	0.52	nd	2.14	0.11	0.50	0.49	3.76
Low stems, 8 cm	0.03	nd	0.90	0.04	0.14	0.06	1.17	0.07	nd	0.64	0.04	0.18	0.08	1.01
Straw	<0.01	nd	0.06	0.01	0.04	0.01	0.12	0.01	nd	0.06	0.01	0.09	0.01	0.18
Husks	<0.01	nd	<0.01	<0.01	0.01	0.01	0.02	<0.01	nd	<0.01	<0.01	<0.01	0.01	0.02
Grain	<0.01	nd	<0.01	<0.01	<0.01	0.01	0.01	<0.01	nd	<0.01	<0.01	0.01	<0.01	0.01

[a] Soil treatment 1 year prior to planting. Values are expressed as equivalent parts per million of aldrin.
[b] Soil 0–10 cm from surface, at harvest of sugar beet in the first year.
[c] nd = none detected.

TABLE 8

RESIDUES OF [^{14}C]ALDRIN AND ITS CONVERSION PRODUCTS IN POTATOES AND SOIL, SECOND YEAR[a]

	GERMANY							UNITED KINGDOM						
Sample	Aldrin	Metabolite X	Dieldrin	Photo-dieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Photodieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue
Initial concentration[b]	1.09	nd[c]	0.52	nd	0.09	0.17	1.87	2.00	0.11	0.42	0.05	0.14	0.15	2.87
Soil														
0–10 cm from surface	0.44	nd	0.54	0.01	0.08	0.11	1.18	0.36	0.01	0.45	0.01	0.13	0.22	1.18
10–20 cm from surface	0.08	<0.01	0.13	<0.01	0.02	0.03	0.27	<0.01	<0.01	<0.01	nd	0.02	0.06	0.09
20–40 cm from surface	0.02	nd	0.04	<0.01	0.01	0.02	0.09	<0.01	<0.01	<0.01	<0.01	0.01	0.04	0.05
40–60 cm from surface	0.01	nd	0.01	nd	0.01	0.02	0.05	<0.01	<0.01	<0.01	<0.01	0.02	0.03	0.05
Roots	0.08	nd	2.71	0.09	0.40	0.08	3.36	0.06	nd	0.74	0.02	0.14	0.11	1.07
Peel	0.06	nd	0.52	nd	0.03	0.01	0.62	0.07	<0.01	0.36	0.01	0.02	0.02	0.48
Peeled tubers	<0.01	<0.01	0.03	<0.01	<0.01	<0.01	0.04	<0.01	nd	0.04	<0.01	<0.01	<0.01	0.05
Leaves	0.01	nd	0.08	0.02	0.03	0.02	0.16	0.03	nd	0.10	0.03	0.11	0.10	0.37

[a] Soil treatment 1 year prior to planting. Values are expressed as equivalent parts per million of aldrin.
[b] Soil 0–10 cm from surface, at harvest of wheat crop in the first year.
[c] nd = none detected.

TABLE 9

RESIDUES OF [14C]ALDRIN AND ITS CONVERSION PRODUCTS IN SUGAR BEETS AND SOIL, SECOND YEAR[a]

Sample	GERMANY							UNITED KINGDOM						
	Aldrin	Metabolite X	Dieldrin	Photo-dieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Photodieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue
Initial concentration[b]	0.58	0.01	0.62	nd[c]	0.11	0.11	1.43	0.59	0.01	0.40	nd	0.74	0.27	2.01
Soil														
0–10 cm from surface	0.09	<0.01	0.52	0.01	0.11	0.12	0.85	0.26	0.01	0.48	<0.01	0.16	0.23	1.14
10–20 cm from surface	0.02	<0.01	0.14	nd	0.04	0.05	0.25	<0.01	<0.01	<0.01	nd	0.01	0.04	0.05
20–40 cm from surface	<0.01	<0.01	0.02	nd	0.01	0.03	0.07	<0.01	<0.01	<0.01	nd	0.01	0.03	0.04
40–60 cm from surface	<0.01	<0.01	0.02	nd	0.01	0.02	0.06	<0.01	<0.01	<0.01	nd	0.01	<0.01	0.01
Peel	<0.01	<0.01	0.13	<0.01	0.04	0.01	0.18	0.01	<0.01	0.05	nd	0.01	<0.01	0.07
Peeled beets	<0.01	nd	<0.01	<0.01	<0.01	<0.01	0.01	<0.01	<0.01	0.01	nd	0.02	<0.01	0.03
Leaves	<0.01	nd	<0.01	<0.01	0.02	<0.01	0.03	<0.01	<0.01	0.01	nd	0.03	<0.01	0.05

[a] Soil treatment 1 year prior to planting. Values are expressed as equivalent parts per million of aldrin.
[b] Soil 0–10 cm from surface, at harvest of potato crop in the first year.
[c] nd = none detected.

TABLE 10

RESIDUES OF [^{14}C]ALDRIN AND ITS CONVERSION PRODUCTS IN MAIZE AND SOIL IN MODESTO, CALIFORNIA, SECOND YEAR[a]

Sample	Aldrin	Metabolite X	Dieldrin	Photodieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue
Initial concentration[b]	0.50	nd[c]	1.17	nd	0.25	0.30	2.22
Soil							
0–10 cm from surface	0.01	<0.01	0.15	0.01	0.02	0.09	0.28
10–20 cm from surface	<0.01	<0.01	0.01	<0.01	0.01	0.07	0.09
20–30 cm from surface	<0.01	<0.01	<0.01	<0.01	0.02	0.03	0.05
30–40 cm from surface	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.03
40–60 cm from surface	<0.01	<0.01	<0.01	<0.01	<0.01	0.03	0.03
Leaves	<0.01	nd	0.08	0.02	0.18	0.10	0.38
Stem	<0.01	nd	0.04	<0.01	0.04	0.01	0.09
Husks	0.01	nd	0.06	0.01	0.06	0.02	0.16
Grain	<0.01	nd	<0.01	<0.01	<0.01	0.01	0.01
Core	<0.01	nd	<0.01	<0.01	<0.01	<0.01	<0.01

[a] Soil treatment 1 year prior to planting. Values are expressed as equivalent parts per million of aldrin.
[b] Soil 0–10 cm from surface, at harvest of maize crop in the first year.
[c] nd = none detected.

TABLE 11

RESIDUES OF [14C]ALDRIN AND ITS CONVERSION PRODUCTS IN WHEAT AND SOIL, SECOND YEAR: SOIL TREATMENT 1 YEAR PRIOR TO PLANTING AND RETREATMENT IMMEDIATELY BEFORE PLANTING[a]

	GERMANY							UNITED KINGDOM						
Sample	Aldrin	Metabolite X	Dieldrin	Photo-dieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue	Aldrin	Metabolite X	Dieldrin	Photodieldrin	Hydrophilic metabolites (extracted)	Unextracted residue	Total residue
Initial concentration[b]	0.78	nd[c]	0.55	0.02	0.07	0.16	1.58	1.30	0.11	0.72	nd	0.19	0.30	2.62
Soil														
0–10 cm from surface	0.41	0.04	0.67	0.03	0.15	0.25	1.55	1.43	0.08	0.65	0.02	0.18	0.38	2.74
10–20 cm from surface	0.05	<0.01	0.21	<0.01	0.08	0.15	0.49	0.01	<0.01	0.01	<0.01	0.02	0.09	0.13
20–40 cm from surface	<0.01	<0.01	0.02	<0.01	0.03	0.07	0.12	0.01	<0.01	0.01	<0.01	0.01	0.05	0.08
40–60 cm from surface	<0.01	<0.01	0.02	<0.01	0.01	0.06	0.09	<0.01	<0.01	<0.01	<0.01	0.01	0.05	0.07
Roots	1.79	nd	7.71	0.30	1.19	1.54	12.53	3.43	nd	6.73	0.43	2.17	2.03	14.79
Low stems	0.28	0.02	3.28	0.23	1.10	0.24	5.15	0.31	nd	2.66	0.20	0.74	0.21	4.12
Straw	<0.01	nd	0.16	0.04	0.22	0.07	0.49	0.01	nd	0.11	0.01	0.38	0.07	0.58
Husks	<0.01	nd	<0.01	<0.01	0.04	0.02	0.06	<0.01	nd	<0.01	<0.01	<0.01	<0.01	0.02
Grain	<0.01	nd	<0.01	<0.01	<0.01	0.02	0.03	<0.01	nd	<0.01	<0.01	<0.01	0.01	0.03

[a] Values are expressed as equivalent parts per million of aldrin.
[b] Soil 0–10 cm from surface, at harvest of maize in the first year.
[c] nd = none detected.

TABLE 12

COMPARISON OF ALDRIN/DIELDRIN RESIDUES AFTER ALDRIN SOIL APPLICATION IN FIELD TRIALS AND ^{14}C EXPERIMENTS

Crop	Field Trials (ppm)				^{14}C Experiments[a] (mean ppm)
	Application rate (kg/ha)	References	Mean value or range	Highest value	
Potatoes, whole	2–4	Shell, private communication, 1968	0.04–0.06	0.10	0.17
	2–4	Shell, private communication, 1974	0.08	0.24–0.27	
Potatoes, peeled	2–4	Shell, private communication, 1968	0.01–0.03	0.03	0.06
	3–4	Lee, 1968/U.K. Ministry of Agriculture	0.01	0.14	
Potatoes, whole (treated 1 year prior to planting)	2.5	Shell, private communication, 1974	0.04	0.11	0.10
Sugar beets, whole	2–4	Shell, private communication, 1974	<0.01–0.05	0.05	0.04
	2–3	Onsager *et al.*, 1970	0.06	0.06	
Sugar beets, whole (treated 1 year prior to planting)	2–4	Shell, private communication, 1974	<0.01	0.02–0.03	0.02
	2–3	Onsager *et al.*, 1970	0.01	0.01	
Sugar beet leaves	1–6	Shell, private communication, 1974	≦0.01	0.01	≦0.01
Maize kernels	1–6	Shell, private communication, 1974	<0.01–0.02	0.02	<0.01
Maize leaves, dry	1–6	Shell, private communication, 1974	0.01–0.07	0.07	0.04
Wheat grains	1–6	Shell, private communication, 1974	<0.01–0.01	0.01	<0.01
Wheat straw	2–4	Shell, private communication, 1974	<0.01–0.16	0.16	0.10

[a] Application rate for ^{14}C experiments was 3 kg/ha.

concluded that the unextractable radioactivity is neither aldrin nor dieldrin, but hydrophilic metabolites which are firmly bound to soil complexes (e.g., humic acids), cell wall constituents (e.g. lignin), or other macromolecules and are liberated only when the complexes are destroyed, e.g., with alkali. Similar soil- or plant-bound residues were found in higher amounts for N-containing pesticides and were partly elucidated (Chin *et al.*, 1973; Yih *et al.*, 1968; Golab and Amundson, 1975; Hsu and Bartha, 1976). Furthermore, it cannot be excluded that part of the unextractable radioactivity is normal biological plant constituents resulting from assimilation from $^{14}CO_2$ or other low molecular weight degradation products.

The metabolites identified thus far from outdoor experiments indicate at least two independent major metabolism pathways (besides the abiotic minor pathway to photoaldrin); these are shown in Fig. 2. Both pathways are started by an attack on the most reactive molecule site, i.e., the nonchlorinated double bond. The first metabolism pathway is the epoxidation by mixed-function oxidases resulting in dieldrin which may be rearranged by light and/or metabolism to form photodieldrin. Both epoxy groups, those of dieldrin and of photodieldrin, are chemically stable and react only very slowly. The hydrolysis of dieldrin to form aldrin-*trans*-diol, a normal metabolic pathway for animals (Korte and Arent, 1965; Feil *et al.*, 1970; Baldwin *et al.*, 1972), has not been demonstrated in plants or normal soils thus far; the hydrolysis of photodieldrin to form the corresponding bridged diol in soil is only 1% within 1 year (Weisgerber *et al.*, 1975a). Similarly, the dihydrochlordene dicarboxylic acid is formed from dieldrin very slowly (Kohli *et al.*, 1973a), as is the formation of the corresponding bridged acid from photodieldrin (Weisgerber *et al.*, 1975a). These data suggest that the first metabolism pathway of aldrin in soil and plants, the epoxidation, has a "dead end" in respect to skeleton degradation.

In contrast to dieldrin, aldrin is decomposed to dihydrochlordene dicarboxylic acid in relatively high rates by the second metabolism pathway, without the intermediacy of dieldrin. The intermediacy of aldrin-*trans*-diol in this pathway was confirmed experimentally: After application of the ^{14}C-labeled diol to plants, 8% of the recovered radioactivity has been converted to dihydrochlordene dicarboxylic acid within 4 weeks, and after application to soil, more than 80% (Kilzer *et al.*, 1974). The high conversion rate of the *trans*-diol could be the explanation for the fact that it is not found in soils or plants. Thus, the second major metabolism pathway of aldrin implies the oxidation of the double bond to form the diol, followed by oxidative ring cleavage to form dihydrochlordene dicarboxylic acid. Of course, there could exist additional possibilities for the formation of the acid.

The oxidative ring cleavage was also observed for other cyclodiene insecticides, e.g., for isodrin (Weisgerber *et al.*, 1975b) or heptachlor (Weisgerber *et al.*, 1974a). In these cases, however, the resulting dicarboxylic acids were unstable and were degraded further by losses of carbon atoms. A stable final product for both insecticides was, among others, Prill's acid.

QUANTITATIVE RESIDUE MEASUREMENTS

Distribution Pattern of Total Residues in both years

Whereas the results for the first year after soil treatment (1969) are summarized in Tables 2–6, Tables 7–10 show the residues of aldrin and conversion products in soils

and rotation crops cultivated in the second year after aldrin application, without further application (Experiments 1–7). Table 11 shows the residues in soil and rotation crops after reapplication in the second year. In the first lines of Tables 7–11, the concentration of radioactive substances in the upper soil layers at the end of the first year, resulting from application and metabolism during the first growing season, is recorded.

As a summary of the data in the tables, it may be established that the residues of radioactive substances are highest in the upper soil layer (0–10 cm from the surface). They decrease in the soil with depth, and in the individual parts of plants, with distance from the soil surface; the ratio of the hydrophilic metabolites to the total residue increases in the same direction. The experiments in England showed mostly higher residues in the plants, a slower leaching of radioactivity in the soil, and higher rates of conversion to hydrophilic substances than did the experiments in Germany. Slower leaching of radioactivity in soil in England than in Germany may be attributable to differing rainfall regimes and could account for the higher percentage of hydrophilic components observed in plants in the experiments in England.

Total residues in crop are lower for sugar beet than for potatoes and wheat, both in absolute terms and as a percentage of the total residue in the soil in which they were grown. On the contrary, the ratio of hydrophilics to total residue is highest in sugar beet. Thus, it may be concluded that, although uptake of total residues from soil into sugar beet occurs less readily than with wheat or potatoes, the reverse is true for the uptake of hydrophilic compounds.

Unintended Residues (Second Year without Retreatment)

The upper soil layers (0–10 cm in depth) show, after the harvest of the second year, in comparison to those taken after the harvest of the first year, much lower residues (average: about one-half, when comparing the total residues, as shown in the last columns of Tables 7–10), containing a lower percentage of aldrin and a higher percentage of conversion products than in the first year. The residues in the lower soil layers, as well as in the plants, however, have decreased only slightly in comparison to the first year; in several samples, they are the same or somewhat higher.

However, comparisons between wheat, potato, and sugar beet samples are not significant since they have been grown each year in different soils each containing a differing initial distribution of aldrin and metabolites. Thus, final residues in crops must result from a combination of original soil residue, uptake capability, and metabolism capability for each type of residue of the separate plant type. Direct comparisons between the first and second year are possible for maize from the United States, since this plant was grown twice in the same soil. The residues of the maize kernels were at the detection limit in both years; the residues in leaves decreased in the second year from 0.40 to 0.38 ppm. A slight increase of residues may be due to lower crop weights, for example, for maize stems, caused by different water content on the day of sampling.

Residues following Retreatment

Table 11 shows the radioactive residues in wheat and soil from Experiments 8 and 9 with soils treated with aldrin in the first and second years. The first line shows the concentration in soil after the harvest of the first year.

The residues after retreatment are, as expected, higher than those in the wheat grown in soils which had not been retreated (Experiments 1 and 2). Compared to the first year,

the residues in the soils were either increased only slightly or not at all. In the plants, some samples, especially roots and lower stems, showed high residues which exceeded those in the surrounding soil. In the grain, total residues of 0.03 ppm were observed at both locations, but in each case the residues of aldrin and dieldrin were below the limit of determination.

Unchanged aldrin did not exceed detection limits in deeper soil layers and in the edible parts of crops, even after a second application.

COMPARISON TO FIELD DATA

For a critical evaluation of this outdoor ^{14}C experimental model, the data must be compared to those obtained from real agricultural field conditions. Since analytical methods for unlabeled residues are available only for aldrin and dieldrin, not for hydrophilic or unextractable residues, comparisons can be undertaken only for these two substances. Nevertheless, these are sufficient for a rough estimate of the usefulness of these model experiments to predict agricultural conditions. Direct comparison of soil residue data on a parts per million basis after equal dosage are not significant since in agriculture the dose is applied by spraying, and a considerable portion drifts off before reaching the soil surface. An identical application method is not possible for radiolabeled substances. However, when the residues in the samples under consideration are expressed as percentage of the initial residue in the soil immediately after the application, data are obtained which are relatively independent of the dose, but do depend on soil texture and climate. These data are comparable to those obtained from our ^{14}C model experiments.

A series of field studies on soil residues was conducted recently by Elgar (1975). The mean value obtained from these studies was lower than that from our ^{14}C experiments, but, since deviations between individual field data were high, the ^{14}C experiments are not outside the range of values. The slightly raised residues in the ^{14}C experiments may be due to the application method: Since field application is carried out by spraying, the insecticide may evaporate faster from the small droplets than from the normal drops in the ^{14}C experiment.

In the same study (Elgar, 1975), the mean percentage of dieldrin (based on the sum of aldrin and dieldrin) was found to be between 20 and 66% after 1 year, depending on the soil type. The corresponding mean value of our ^{14}C experiments was 41% dieldrin.

Comparisons of crop residues between ^{14}C experiments and field experiments are shown in Table 12. The table shows, for the ^{14}C experiments, slightly higher data due to the higher soil residues discussed above, but they are within the range of field data.

CONCLUSION

As compared to field data for aldrin and its metabolite dieldrin, the data from these ^{14}C experiments are higher than the mean values of various field data, but they are within the range of field value variations. This small deviation of the results of the ^{14}C model experiments from agricultural practice may be neglected in comparison to the great advantages of the model in the identification and assessment of conversion products for which analytical detection methods are not available.

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