Residues of Dieldrin, Lindane, DDT, and Parathion in a Light Sandy Soil after Repeated Application throughout a Period of 15 Years

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From 1953 on, dieldrin, lindane, DDT, and parathion, in two concentrations, were sprayed on crops several times a year. In addition, soil treatment with these insecticides took place once a year. Soil and crop samples were taken regularly throughout the whole period. The results of residue analyses of soil samples taken after 15 yr in layers of 10 cm (3.9 in.) to a depth of 60 cm are reported here. In this light sandy soil, DDT and dieldrin were much more persistent than lindane. Parathion disappeared rather soon. Below 20 cm, traces of only dieldrin and DDT were found.

Literature on insecticides in soils has been excellently reviewed (Edwards, 1966). The present paper concerns an experiment started in 1953 at Wageningen and continued almost without interruption for 15 yr, up to 1968. The aim, originally, was to determine the influence of pesticides on the yield and quality of crops. It was soon obvious, however, that the experimental plots were too small to provide reliable results on crop yields. From then on, the persistence of the insecticides in the cultivated soil and their uptake by crops were investigated. Changes in the soil fauna caused by the application of lindane, DDT, and parathion were also studied (Van de Bund, 1965). Soil samples to a depth of 15 cm were regularly taken and analyzed. Finally soil samples were taken to a depth of 60 cm, subdivided into six layers of 10 cm each. The results of the analyses of these samples are the subject of this paper.

METHODS AND MATERIALS

The experimental field at Wageningen (Climatic Data, Table I) was divided into plots of 12 m^2 each. These plots were separated by sunken concrete slabs up to about 1 m below soil level. The ground water level is always below that level. The plots were subdivided into six parts. These six parts were planted with different field crops: potatoes, beets, turnips, carrots, chicory, lettuce, and leek. Crop rotation was applied each year; each plant species was planted in the next part of the plot in a clockwise direction. The soil was light sandy and contained about 3% organic matter. Organic manure was applied every other year (Van de Bund, 1965).

Before the start of the experiment, no insecticide was used on the plots. During the experiment only the insecticides mentioned in Table II were applied. The field was protected against spray drift or run-off from neighboring fields through a nontreated zone.

Each insecticide (of technical quality) was applied on three plots. On the plots B and C, a water emulsion (1.2 l/12 m^2) of the insecticide was sprayed on the crops. Both were treated three to five times a year. The pesticide residues in the soil of these plots result only from run-off of the spray during the application, and the washing-down by rain afterwards. Plot D was given a soil treatment once a year, early in the season before sowing or planting; a water emulsion (50 l/12 m^2) of the insecticide was poured directly onto the soil. The insecticide was left on the soil surface after its application. Two soil treatments took place in 1961. At harvest time the crops, mainly root crops, were removed, with the residues remaining on or in these plants.

Table II gives the total quantity of active material applied per plot of 12 m^2 per yr. The 1955 soil application was given during the winter 1955/1956 (in Table II mentioned under 1956 together with the application in spring 1956). Plot D of dieldrin was treated with a 2% powder in 1953 and 1954. The technical DDT contained about 25% *o,p'*-DDT.

The soil samples for this investigation were taken on 1/21/-1969 with a special soil borer. This consists of a stainless steel tube about 75 cm long, which inside contained a tube with a capacity of 100 ml (diameter 3.6 cm, inner length 10 cm). The small tube had a loose bottom that could be fastened by a simple turning of a rod with which it and the outer tube were driven into the soil. In each plot six drilling operations were performed to a depth of 60 cm. The samples of each layer of 10 cm (0.9 ± 0.1 kg) taken from the same plot were collected in plastic bags and stored at ice-box temperature until they were analyzed.

After thorough mixing by hand, 30.0 g of soil were taken out of each bag, placed in a 100 ml flask, and shaken with a mixture of 30 ml of benzene and 15 ml of 2-propanol for 18 hr on a shaking-machine. After standing overnight, 3.0 ml of supernatant was thoroughly mixed with 7 ml of a 3% solution of sodium sulfate in water in an 11-ml test tube with glass stopper on a Vortex mixer. The layers were separated by centrifuging and the upper layer was analyzed by glc with an electron capture detector after appropriate dilution if necessary. In the case of parathion, 20 ml of extract was washed with 75 ml of a 3% sodium sulfate solution in a separation

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Table I. Some Climatological Data of Wageningen[a]

Season	Mean Daily Max. Temp. in °C	Mean Daily Min. Temp. in °C	Mean Precipitation in mm
Winter Dec.–Feb.	5.2	0.2	196
Spring March–May	13.7	4.6	140
Summer June–Aug.	21.5	12.3	260
Autumn Sept.–Nov.	14.2	7.1	190

[a] Climatological Data of Netherlands Stations.

funnel, and the benzene layer dried with sodium sulfate. Of the dried extract, 10 ml was evaporated till nearly dry, taken up in 1.0 ml of hexane, and analyzed by glc using a phosphorus detector.

The benzene had been purified by treatment with concentrated sulfuric acid and fractionation. The 3% sodium sulfate solution in water was extracted with pure benzene prior to use. All glasswork had been rinsed with a little pure benzene.

The analyses were performed on a Varian Gas Chromatograph, Model 204-1B using colums of borosilicate glass packed with 5% Dow 11 on Chromosorb-W 70/80 ($^1/_8$″ × 129 cm, for dieldrin and lindane), 10% FS 1265 on Gaschrom Z 80/100 mixed with a same quantity support coated with 10% Dow 200 (12,500 cS) ($^1/_8$″ × 120 cm for DDT), or 5% Apiezon L on Aeropak 30 70/80 ($^1/_8$″ × 132 cm for parathion). The last mentioned specially conditioned with Silyl-8 (Pierce Chemical Co.).

The calculations were based on the over-dry weight of the soil (105° C until constant weight was attained).

Precoated tlc plates Silica Gel F 254 (E. Merck AG, Darmstadt), layer thickness 0.25 mm, were used for the separation of *p,p'*-DDE, *o,p'*-DDT, *p,p'*-DDT, and *p,p'*-DDD. They were developed with hexane in a closed tank saturated with vapor of hexane and diethyl ether. The spots showed up under UV light. Extracts representing about 2 g of soil were spotted on the plate after a cleanup with Nuchar Attaclay and a subsequent concentration to 0.2 ml.

RESULTS AND DISCUSSION

The results of the analyses are recorded in Table III. Most figures are the mean of the results of two independent determinations. The total amount of insecticide per plot of 12 m² can be calculated from the figures given in Table III. (The specific gravity of the oven-dry soil is set at 1.3, one layer is 1560 kg.) Table IV gives the results of these calculations. In plot D of lindane very small amounts of a compound with the same retention distance as γ-PCCH (γ-pentachlorocyclohexene) were found: 0.01 ppm at 0 to 10 and 10 to 20 cm (Yule *et al.*, 1967). No paraoxon was found in the parathion plots.

Table III. Quantities of Dieldrin, Lindane, DDT, DDE, and Parathion (in ppm) after Regular Application for 15 Years of the Insecticides

Compound	Plot	Soil Layer in Cm 0–10	10–20	20–30	30–40	40–50	50–60
Dieldrin	B	1.25	0.23	0.02	0.01	...	...
	C	2.29	0.86	0.02	0.01	...	...
	D	7.33	2.50	0.05	0.03	0.02	0.01
Lindane	B	0.09	0.01	...	...	...	...
	C	0.34	0.07	...	...	...	...
	D	1.30	0.23	...	...	...	...
p,p'-DDT	B	3.53	0.56	0.01	0.01	...	...
	C	8.94	1.05	0.02	0.01	0.01	...
	D	59.6	9.22	0.15	0.10	0.11	0.13
o,p'-DDT	B	0.78	0.07	...	...	...	...
	C	1.77	0.22	...	...	...	...
	D	12.9	2.02	0.04	0.02	0.02	0.02
p,p'-DDE	B	0.39	0.07	...	...	...	...
	C	0.77	0.11	0.01	0.01	...	...
	D	3.33	0.51	0.02	0.02	0.02	0.02
Parathion	B	0.01	...	...	...	...	...
	C	0.02	...	...	...	...	...
	D	0.06	0.02	...	...	...	...

The presence of *p,p'*-DDE in the DDT plots could be confirmed by tlc. The quantities are recorded in Tables III and IV. No *o,p'*-DDE was found. The column used for the estimation of DDT did not separate *p,p'*-DDD from *p,p'*-DDT completely. So it was necessary to perform this separation by tlc at first. The DDD spots (invisible under UV) were extracted with benzene and the extracts subjected to glc. The upper layers only were investigated in this way. In the plots B and C, 0 to 10 cm, was found 0.1 and 0.2 ppm, respectively, in plot D 0 to 10 cm, 1.2 ppm, and D 10 to 20 0.1 ppm. The DDT used in these experiments was of technical quality like all the other insecticides and a sample of it contained some DDD and traces of DDE. Therefore these results are not conclusive about the metabolism of DDT in the soil.

About half a year after the last application practically all the

Table II. Total Quantity Active Material Applied per 12 m² per Year in Grams

(1 g/12 m² = 0.74 lb/acre = 0.83 kg/ha)

Insecticide	Plot	Year 1953	'54	'56	'57, '58, '59	'60	'61	'62, '63, '64, '65	'66	'67, '68	Total
Dieldrin	B	0.4	...	0.7	0.7	1.0	1.0	1.4	2.1	1.7	16
	C	0.7	...	1.4	1.4	2.1	2.1	2.8	4.2	3.5	33
	D	3.4	6.8	9.8	4.9	4.9	9.8	4.9	4.9	4.9	83
Lindane	B	0.3	...	0.3	0.3	0.5	0.5	0.7	1.0	0.8	8
	C	0.6	...	0.7	0.7	1.0	1.0	1.3	2.0	1.7	16
	D	2.4	2.4	3.4	1.7	1.7	3.4	1.7	1.7	1.7	30
DDT (incl. 25% *o,p'*-DDT)	B	1.8	...	1.8	1.8	2.7	2.7	3.6	5.4	4.5	43
	C	3.6	...	3.6	3.6	5.4	5.4	7.2	10.8	9.0	86
	D	23.5	23.5	48.0	24.0	24.0	48.0	24.0	24.0	24.0	407
Parathion	B	0.5	...	0.6	0.6	0.9	0.9	1.2	1.8	1.5	14
	C	1.0	...	1.2	1.2	1.8	1.8	2.4	3.6	3.0	29
	D	3.4	3.4	19.2	9.6	9.6	19.2	9.6	9.6	9.6	151

Table IV. Total Amount Residue in Grams per Plot of 12 m^2 after 15 Years of Repeated Application

Compound	Plot	Applied	Recovered	% Recovered
Dieldrin	B	16	2.4	15
	C	33	5.0	15
	D	83	15.5	19
Lindane	B	8	0.2	3
	C	16	0.6	4
	D	30	2.3	8
p,p'-DDT	B	32	6.4	20
	C	64	15.6	24
	D	305	108	35
o,p'-DDT	B	11	1.3	12
	C	22	3.1	14
	D	102	23	23
p,p'-DDE	B	...	0.71	...
	C	...	1.4	...
	D	...	6.1	...
Parathion	B	14	0.02	0.1
	C	29	0.03	0.1
	D	151	0.13	0.1

parathion disappears. By comparing the figures of Table IV with reports of earlier analyses (Pesticides Reports, 1963, 1965) it can be assumed that a stationary state has been reached. In the last years there has not been a significant increase in the residue level.

In plots B and C, a quantity of insecticide probably did not reach the soil because it was applied by spraying. This can also be concluded from the figures in Table IV. Only the more persistent insecticides are found in the deeper layers, although it is a negligible percentage.

For the chlorinated hydrocarbons, the yearly dose is smaller than the quantity still present in the soil after a stationary state has been reached, especially for dieldrin and DDT (Tables II and IV).

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