Photodieldrin Residues in Field Soils

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The organochlorine pesticides fallen from crops or directly applied to control soil inhabitating pests were absorbed or leached into the soil, or co-distilled, volatilized or wind-blown from it, or dissolved into river water. During these processes, it has been suggested that some of these pesticides were attacked by physico-chemical and microbial actions, and became more persistent and toxic products.

The presence of an unknown compound on grass which had been treated with dieldrin and exposed to sun-light was reported by ROBURN (1963). ROBINSON et al. (1966) and ROSEN et al. (1966) obtained this unknown compound by ultraviolet (2537 Å) irradiation of dieldrin, and it was concluded from IR and mass spectra that this compound was photodieldrin (PD), i.e., photochemical isomer of dieldrin. Also, PD was obtained by solid state photolysis (KAWASHIRO et al. 1966, BENSON 1971) and photolysis of dieldrin in solutions (ROSEN and CAREY 1968, HENDERSON and CROSBY 1968). This PD was several times more toxic than the parent compound to house flies and mosquitoes (KHAN et al. 1969), 1.3 to 12.2 times more toxic to fresh water animals (GEORGACAKIS and KHAN 1971), and it biologically concentrated in animals (STANTON et al. 1973). PD was more persistent than the parent compound (IVIE and CASIDA 1970). The presence of PD in soil which had been treated ten years before with aldrin were reported (LICHTENSTEIN et al. 1970), but few reports have been published about PD in the environment.

In the present study, the PD in field soil was identified by electron capture gas-liquid chromatography (GLC-ECD) and a combined gas-liquid chromatography-mass spectrometry system (GC-MS), and those residue levels were determined by GLC-ECD.

METHODS

a) Soil sampling, pretreatment and extraction: About 99 field soil samples of the Kitakyushu area where organochlorine pesticides had been applied 2 to 20 years ago, were taken in quantities of 10 cm in diameter , 15 cm in depth when the vegetables were mature and stored at 0°C until pretreatment. These soils were planted with radishes, cabbages, spinach, carrots, chinese cabbages, cucumbers, turnips, grapes, tomatoes,

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egg plants and lettuce. The soil texture was sand to loam. Pretreatment and extraction procedure of PD and dieldrin from soil samples were the same as in the previous report (SUZUKI et al. 1973).

b) Clean-up of extract: The extracts were cleaned-up by Florisil column chromatography (2x10 cm). The column elution was done successively with a 200 ml portion of 15% (fraction I) and 30% (fraction II) ethyl ether in n-hexane. Dieldrin and PD were eluted in the fraction I and II, respectively, and these fractions were injected into GLC-ECD after adjusting appropriate volume

c) GLC-ECD analysis: The detection and determination of PD and dieldrin were made with a Shimadzu Model GC-5AIEE with a dual electron capture detector and a dual detection system by comparing with authentic samples in different GLC columns. The following columns (3mm in inner diameter and 2m in length, glass) and operational conditions were employed; i) 3% silicone OV-17 on dimethyldichlorosilane-treated Gaschrom Q, 80-100 mesh. The injector, column and detector temperatures were 210°, 190° and 190°C, respectively. The flow rate of high purity nitrogen carrier gas was 100ml/min.. ii) 2% silicone OV-17 and 2% silicone OV-1 on dimethyldichlorosilane-treated Chamelite CS, 80-100 mesh. The injector, column and detector temperatures were 220°, 200° and 200°C, respectively. Flow rate of high purity nitrogen carrier gas was 100ml/min..

d) Preparation of a sample for GC-MS analysis: All of the sample solutions in which the PD were detected were combined, concentrated and cleaned-up again by a Florisil column chromatography. The column (2x10 cm) was eluted with 15% ethyl ether in n-hexane, and the fraction between 250 and 425 ml was taken, and the solvent was evaporated off. The residue was dissolved in 0.3ml toluene and applied to GC-MS analysis. The concentration of PD in this sample solution was about 20 ppm. Ten microliter of this sample solution was injected into GC-MS system.

e) GC-MS analysis: GC-MS measurements were done with a JGC-1100-JMS-01SG-2 (NIPPON DENSHI CO. LTD.) equipped with a total ion monitor detector. The column of GLC (3mm in inner diameter and 2m in length, glass) was packed with 4% silicone OV-17 on a dimethyldichlorosilane-treated Gaschrom Q, 100-120 mesh, and the GLC was programmed from 180°C at 10°C/min.. The injector and mass temperatures were 250°C, and the flow rate of helium carrier gas was 40ml/min..

RESULTS

Dieldrin was detected in 52 soil samples from among 99 in the range of 1.726-0.002 ppm, and in 14 soil samples from among 52, PD was found at the level above 0.001 ppm. Other organochlorine pesticides and their related compounds, α-BHC (7.605-0.002), β-BHC (2.806-0.021), γ-BHC (1.785-0.003), δ-BHC (1.530-0.001), aldrin (1.012-0.002), endrin (0.629-0.016), p,p'-DDE (2.085-0.008), p,p'-TDE (1.554-0.018), p,p'-DDT (9.801-0.015) and o,p'-DDT (1.745-0.007 ppm) were detected, and BHC isomers were especially found in all the soil samples analysed. The residue levels of PD and dieldrin, and the ratio of PD to dieldrin (%) were shown in TABLE I. The typical GLC-ECD chromatogram and GC-MS spectrum of PD were shown in FIG.I and II, respectively.

TABLE I

Dieldrin and Photodieldrin Residues in Field Soils
(ppm on dry matter bases)

Sample Number	Photodieldrin Residues	Dieldrin Residues	PD/D$^{a)}$	Organic Matter Contents
23	0.010	1.291	0.8	6.4
37	0.005	0.555	0.9	2.9
42	0.015	0.426	3.5	6.4
45	0.019	0.721	2.6	8.3
46	0.011	0.694	1.6	8.3
47	0.017	0.687	2.5	8.3
52	0.018	0.702	2.6	7.7
59	0.035	1.024	3.4	6.9
64	0.010	0.484	2.1	10.2
65	0.016	0.506	3.1	10.0
66	0.018	0.692	2.6	9.2
85	0.024	0.348	6.9	8.8
90	0.004	0.628	0.6	8.0
99	0.013	0.554	2.3	2.1

a)Photodieldrin/Dieldrin x 100(%).

In these GC-MS analyses, PD lost a chlorine atom $[M-Cl]^+$. This was due to the thermal instabilities of PD (PD was eluted from the column at 310°C). But comparing with an authentic spectrum, they were identical. The PD was detected in soil samples at a concentration between 0.035 and 0.004 ppm.

DISCUSSION

In the Kitakyushu area, aldrin had been mainly applied as dust to control vegetable pests, and application of it was done directly to the soil surface and incorporated into the soil.

The greater amounts of aldrin in the soil was readily converted to dieldrin by physico-chemical and microbial actions (LICHTENSTEIN and SCHULZ 1965). From these dieldrin formed in solid state on the soil surface and incorporated with soil particles, PD was formed photochemically and microbially.

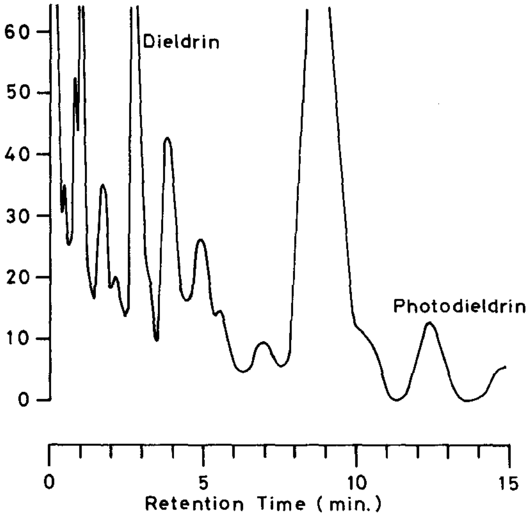

Fig. 1. Typical Gas Chromatogram of Photodieldrin in Soil Sample (3% silicone OV-17 column)

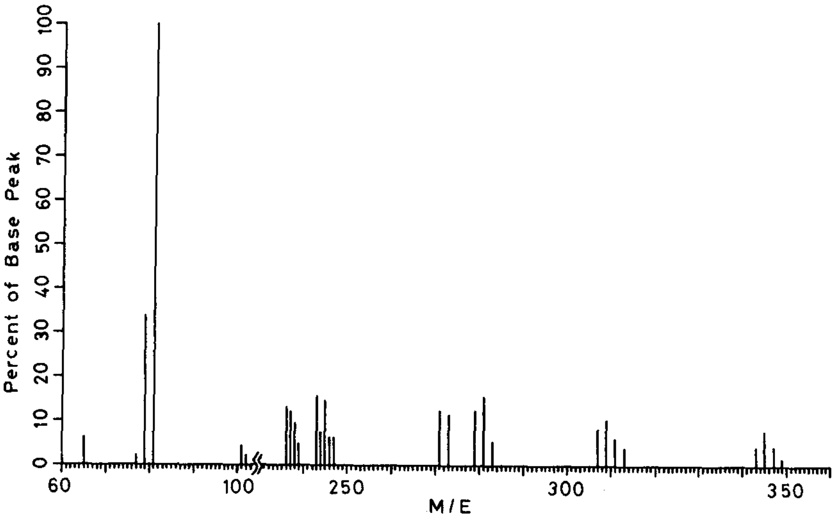

Fig. 2. GC-MS Spectrum of Photodieldrin in Soil

In laboratory experiments using ultraviolet (2537 Å) light, the PD formation rate with or without benzophenone as a photosensitizer was 77% or less than 1% for 21 hr irradiation (ROSEN and CAREY 1968), and in a field experiment, PD was formed on the leaf of an apple tree which had been treated with dieldrin (HARRISON et al. 1967). Also IVIE and CASIDA (1970, 1971a and 1971b) reported that rotenone was the most active on conversion of dieldrin to PD in experiments of sun-light irradiation of pesticides among various photosensitizers.

Aldrin incorporated into soil was absorbed at first by the surface of soil organic matter and remained for a long time (EDWARDS 1966). Conversion of dieldrin to PD by microorganisms was reported by employing those isolated from a rat intestine, rumen stomach contents of a cow, water, soil, bottom sediments of the Lake Michigan (MATSUMURA et al. 1970) and algae of the Hawaiian coast (PATIL et al. 1972).

But in this study, all of the agricultural fields in which PD residues were detected had been planted with cucumbers. This is assumed to be due to the following reasons: The cucumber grows in the most humid and hot season of the year when many pests appear, so, much pesticides were applied to the soil surface or incorporated into soil. At the same time, the strong UV light of summer irradiated the dieldrin on the soil surface which had been applied with aldrin or dieldrin, and photoisomer formed on them.

LICHTENSTEIN et al. (1970) reported that the soil which had been treated with aldrin at five yearly dosages of 5 pounds per acre from 1958 to 1962, contained 0.015 ppm of PD (1.6% of dieldrin) and other more polar metabolites which could not identified. In this study, PD/dieldrin ratio was 6.9 to 0.6%. Judging from these results, the PD residues in Japanese agricultural fields were formed from dieldrin by a photochemical and microbial action.

Organic matter in soil which surface was substrated for retention of organic chemicals were not correlative to PD levels in the soils (TABLE I).

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