

## Dieldrin and Chlordane Residue in Agriculture Fields

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Long-lived organochlorine insecticides were prohibited from agricultural use in early 1970's in the advanced nations. But these pesticides are detected even now in field soils (Martijn et al. 1993) and foodstuffs (Yoshida et al. 1992; McDougall et al. 1995). The breakdowns of organochlorine insecticides in soil were often explained by four components model (Edwards 1966), and the fourth half-lives are important to long-term persistences. Long-term residue survey was not reported on organochlorine insecticides in Japan except for Nakamura (1990).

In this study the organochlorine insecticides were surveyed in three fields in Nara, Japan, and the residue of dieldrin (1,2,3,4,10,10-hexachloro-1*R*,4*S*,4*aS*,5*R*,6*R*,7*S*,8*S*,8*aR*-octahydro-6,7-epoxy - 1, 4 : 5, 8 - dimethanonaphthalene,  $C_{12}H_8Cl_6O$ ) was found in a field, and the residues of chlordanes (1, 2, 4, 5, 6, 7, 8, 8-octachloro-2, 3, 3*a*, 4, 7, 7*a*-hexahydro-4, 7-methano-1*H*-indene,  $C_{10}H_6Cl_8$ ) and nonachlor (1, 2, 3, 4, 5, 6, 7, 8, 8-nonachloro-2, 3, 3*a*, 4, 7, 7*a*-hexahydro-4,7-methanoindene,  $C_{10}H_5Cl_9$ ) were found in two fields. The persistences of these residues were followed for the estimations of the fourth half-lives.

### MATERIALS AND METHODS

All the analytical standards were supplied by Wako Pure Chemicals Inc. (Chuou, Ohsaka, Japan) and dissolved in toluene and diluted with toluene for use as working standards. Florisil<sup>®</sup> was also supplied by Wako Pure Chemicals Inc., and added 10v/w% of H<sub>2</sub>O and shaken vigorously for 3 min, and left a few hours. Organic solvents and anhydrous Na<sub>2</sub>SO<sub>4</sub> were the pesticide grades.

Three fields (A, B, C) selected for this study are at the north east area of Nara Basin in Japan at lat. 34°38'N and long. 135°50'E. The normal temperature is 14°C and the normal amount of rainfall 1600 mm/year in this region (National Astronomical Observatory 1996). Field A is square with sides 20 m, and the soil character was silt. Fields B and C are both rectangle with sides 20 m and 50 m, and the soil characters were sandy silt and silt respectively.

Soil samplings were begun from Oct. 1991 in field A, from Oct. 1989 in field B, and from Apr. 1991 in field C, and continued twice per year as a rule. The soil was collected in 0-10 cm depth with core sampler, and removed gravel and plant pieces over 2 mm. The moisture contents of the soil samples were measured as the weight loss rates by drying at 110°C. The results in three fields were 30-60% when rice paddy, 10-30% when the other crops were planted.

The soil sample was weighed to be 10 g as dry weight, and added 50 mL of acetone, and shaken for 30 min. The suspension was filtered with Toyo 5A filter paper; the residue was washed with 5 ml of acetone 3 times. The filtrate and washings were joined and added 50 ml of n-hexane and 100 mL of 10% NaCl aq, and shaken for 5 min. The lower layer was removed and the upper layer was washed with 50 ml of 10% NaCl aq 3 times. The washed solution was dehydrated by 20 g of anhydrous  $\text{Na}_2\text{SO}_4$  and evaporated. The residue was dissolved by 2 mL of n-hexane, and the solution was loaded into florisil column (10 v/w% hydrated, 3 g, 12 mm $\phi$ ). The column was eluted by 30 mL of diethylether/n-hexane (5+95), and the eluate was evaporated. The residue was dissolved by n-hexane, and analysed by gas chromatography with electron capture detector (GC-ECD) and GC mass spectrometry (GC-MS). The recovery rates and detection limits of four chemicals were 85-95% and 0.001  $\mu\text{g/g-dry}$ .

GC analyses were carried out by following instruments and conditions. GC-ECD: Instrument; HP 5890, Column; J&W DB-17 and DB-1 0.25  $\mu\text{m}$  x 0.25 mm $\phi$  x 30 m, Injector; He, 150 kPa, 230°C; Injection; split (50:1), 3  $\mu\text{L}$ , Oven temp.; 140°C(1 min)  $\rightarrow$  (10°C/min)  $\rightarrow$  300°C (5 min), Detector;  $\text{N}_2$ , 80 ml/min, 300°C. GC-MS: Instrument; HP 5890, 5971, Column; HP Ultra-2 0.11  $\mu\text{m}$  x 0.20 mm $\phi$  x 25 m, Oven temp.; 110°C(1 min)  $\rightarrow$  (10°C/min)  $\rightarrow$  300°C, Injector; He, 50 kPa, 200°C, Injection; splitless, 1  $\mu\text{L}$ , Ionization; EI.

## RESULTS AND DISCUSSION

Organochlorine insecticide dieldrin (DLD) residue was detected to the amount of about 0.05  $\mu\text{g/g-dry}$  from soils of field A. The mass-chromatogram of the soil sample detected the residue of DLD is presented in Figure 1. Total ion chromatogram gave an isolated peak at the retention time of DLD as the upper figure, the mass-spectrum of which agreed well with DLD standard as the lower figure. This residue is guessed the result of the agricultural use of aldrin or DLD products before 1975. The following determinations for ca. 5 years are shown in figure 2. The regression analyses on two points of field A resulted that the fourth half-lives ( $T_{1/2}$ ) of DLD were 26, 24 years in these soils, and their 95% confidence intervals ranged 12 years to infinity, 11 years to infinity respectively.

In 1960-70's the estimated  $T_{1/2}$  of DLD varied widely in Japan and USA as follows. Nishimoto et al. (1971) investigated in Kohchi, Japan for 3 years, and reported that  $T_{1/2}$  of DLD in field soil was

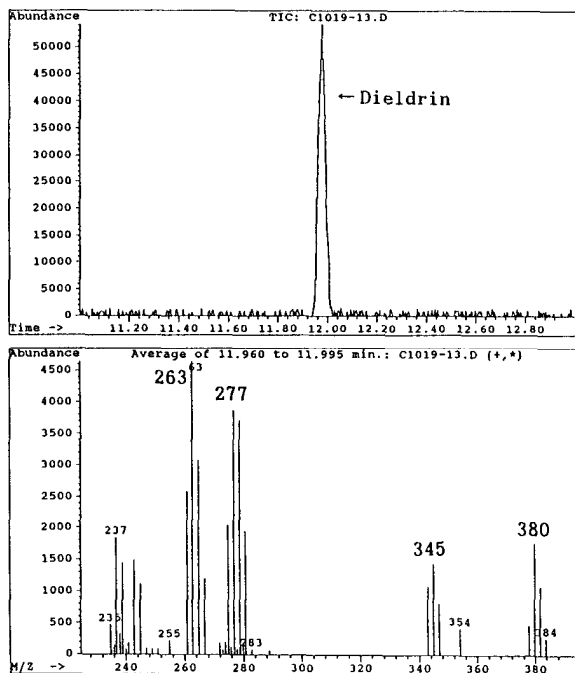


Figure 1. Masschromatogram of the soil sample that detected the residue of dieldrin

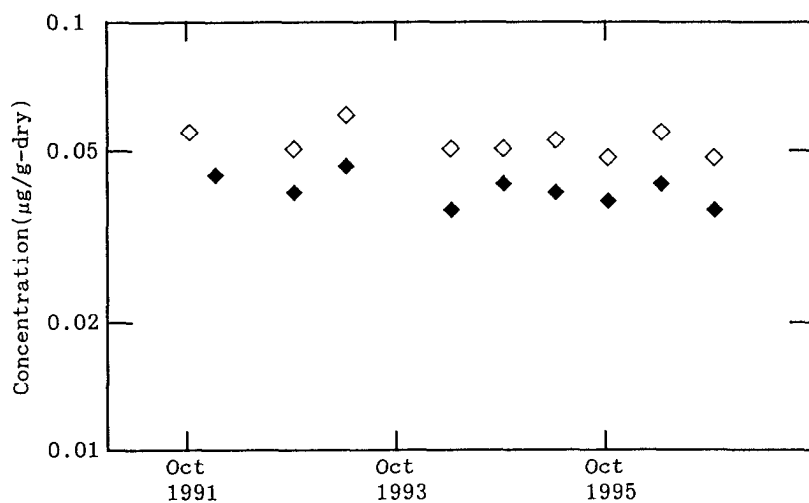


Figure 2. Persistence of dieldrin in an agriculture field  
 ◇, ◆ Field A north, south

1 year. Hankawa (1974) examined in Hiroshima, Japan for 1.5 years, and estimated that T1/2 of DLD in two field soils were 1.0, 1.7 years respectively. Edwards (1966) reviewed 13 reports and generalized that T1/2 of DLD in soil was about 2 years. Lichtenstein et al. (1970) examined in Wisconsin, USA for 11 years, and T1/2 of DLD in field soil can be read about 3 years from their figure. Freeman et al. (1975) investigated in Ohio, USA for 7 years, and summarized that 95% disappearance time of DLD in field soil was 13 years. These reports can be concluded that T1/2 of DLD in field soil is some years. On the other hand, Suzuki et al. (1975) examined in Kitakyushu, Japan for 2 years, and reported "A little or no decrease of DLD residues in the field soils was observed in the experimental term." Hermason et al. (1971) investigated in California, USA for 9 years, and estimated that T1/2 of DLD in field soil was 13 years.

Nakamura (1990) investigated in Saitama, Japan during 1971-86, and described "the average of DLD residue amounts in 50 field soils was 0.288 ppm in 1971 and decreased to 0.088 ppm in 1972, but did not decrease in following 15 years at the level of 0.1 ppm". Martijn et al. (1993) examined in Wageningen, Netherlands, and reported that T1/2 of DDTs in soil was estimated to be about 15-20 years, and DLD seemed to be more persistent. These reports in 1990's and this study suggest that DLD residue in soil is seriously persistent in the temperate region and colder.

Organochlorine insecticides trans-chlordane (tr-CD), cis-chlordane (cis-CD) and trans-nonachlor (tr-NC) were detected in fields B and C. Heptachlor, heptachlor-epoxide and oxy-chlordane were not found. The mass-chromatogram of the soil sample detected the residue of CDs is presented in Figure 3. Total ion chromatogram gave the isolated peaks at the retention times of tr-CD, cis-CD and tr-NC as the upper figure, the mass-spectra of which agreed with the standards as the lower figure. These residues are guessed the result of the agricultural use of heptachlor or chlordane products before 1975. As the ratio of three chemicals were in the range of tr-CD: cis-CD: tr-NC= 10:4-5:4-7 through the measurements, the sum of tr-CD, cis-CD and tr-NC is named chlordanes (CDs) in this study. The residue amounts of CDs in field soil B, C were about 0.015, 0.020 µg/g-dry at the beginning of this study. The following determinations for ca. 5 years are shown in figure 4. The regression analyses on fields B and C resulted that T1/2 of CDs were 7, 6 years in these soils, and their 95% confidence intervals ranged 5-11, 5-9 years respectively.

There has been no report on T1/2 of CDs in field soil in Japan. Edwards (1966) reviewed 8 reports and generalized that T1/2 of CDs in soil was about 1 year. Hermason et al. (1971) investigated in California, USA for 9 years, and estimated that the T1/2 of CDs in field soil was 5 years. T1/2 of CDs estimated in this study seems to be far from that of Edwards', near to Hermason's, similar to T1/2 of DLD.

In conclusion, the fourth half-lives of dieldrin and chlordanes in

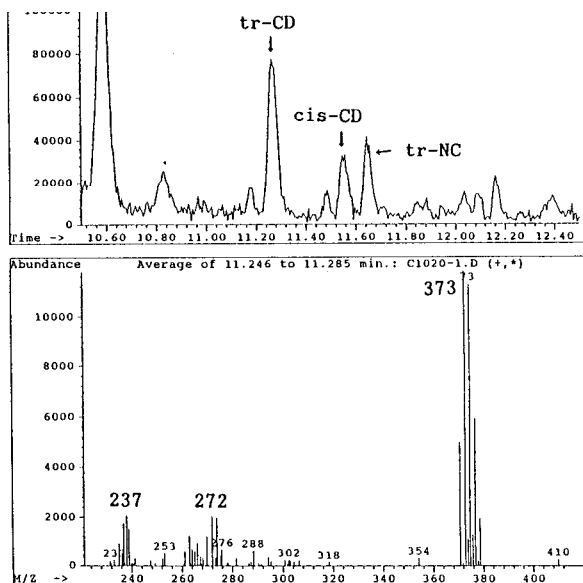


Figure 3. Masschromatogram of the soil sample that detected the residues of chlordanes

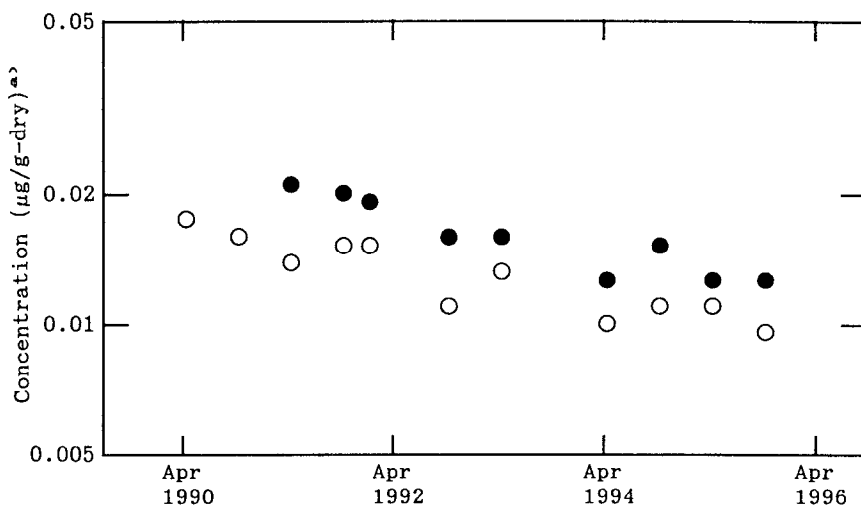


Figure 4. Persistences of chlordanes in two agriculture fields  
 ○ ; Field B ● ; Field C  
 a) Figure represents the sum of trans-chlordane, cis-chlordane and trans-nonachlor

some agricultural fields in Nara, Japan were estimated about 25 years, 7 years with 95% confidence intervals 11 years to infinity, 5-11 years respectively. The serious persistence of dieldrin in field soil is likely to cause the contamination of foodstuffs for several decades in Japan.

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