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Fungicide Procymidone Residue in Agriculture Land

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Long-lived organochlorine insecticides were prohibited 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). The breakdown of organochlorine insecticides in soil were often explained by four components model (Edwards 1966), and the fourth half-lives are important to long term persistence. But these of the pesticides except for organochlorine insecticides are rarely discussed.

In this study, two fields were investigated the persistence of organochlorine fungicide procymidone (Sumilex™, 3-(3,5-Dichlorophenyl)-1,5-dimethyl-3-azabicyclo[3,1,0]hexane-2,4-dione, $C_{13}H_{11}Cl_2NO_2$) in soils, and the translocation to the plants from soils.

MATERIALS AND METHODS

Solvents and anhydrous Na_2SO_4 used in this study were the grade for pesticide residue analysis. Florisil PR™ was supplied by Wako Pure Chemicals Inc. (Ohsaka, Japan), and added 10v/w% water and then shaken vigorously for 5 min, and leaved for a few hours. Analytical standard of procymidone was also supplied by Wako Pure Chemicals Inc. and dissolved in toluene and diluted adequately.

Two fields (A,B) selected for this study are both at the north east area of Nara Basin in Japan at lat.34°38'N and long.135°50'E. In this region, the normal temperature is 14°C and the normal amount of rainfall 1600 mm/year (National Astronomical Obsevatory 1994). Fields A and B are both rectangle with sides 20m and 50m, and the soil characters were sandy silt and silt respectively.

Two greenhouses were constructed in each field for strawberry production, which were fumed with fungicide procymidone once a year (field A 1984-88, field B 1985-89) in late November or early December for gray mold control. The amounts of fumed procymidone were 0.3 g/year/m^2 x 5 years = 1.5 g/m^2.

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The soil samplings were began from Oct 1989 in field A and from Apr 1991 in field B, and continued four times per year to Jan 1992 and reduced the sampling rate to twice per year as a rule. The sampling points A1,B1 were chosen the center of the greenhouses, and A2 between two greenhouses. The soil were collected in 0-10cm depth with core sampler, and removed gravel and plant pieces over 2mm.

The moisture contents of the soil samples were measured as the weight loss rates by drying at 110°C. The results in both fields were 30-60% when rice paddy, 10-30% when the other crops planted.

The soil sample was weighed to be 10g as dry weight, and added 50ml of acetone, and shaken for 30min. The suspention was filtered with Toyo 5A filter paper, the residue was washed with 5ml of acetone three times. The filrate and washing were joined and added 50ml of n-hexane and 100ml of 10%NaClaq, and shaken for 5 min and settled. The lower layer was removed and the upper layer was washed with 50ml of 10%NaClaq three times. The washed solution was dehydorated by 20g of anhydrous Na_2SO_4 and evaporated. The residue was dissolved by 2ml of n-hexane, and the solution was loaded into florisil column (10v/w%hydrated, 3g, 12mmϕ). The column was eluted by 30ml of diethylether/n-hexane (1+9) and the eluate was evaporated. The residue was dissolved with n-hexane, and quantified by Gasschromatography-Electron Captuer Detector(GC-ECD) and qualified by GC-Massspectormetry(GC-MS). The recovery rate and detection limit of procymidone were 90±7% and 0.005µg/g-dry.

The crop sampling were carried out on spring 1990 and spring 1991. The sampled vegetables were washed out soils with water, and shaken off the water. The crop sample was weighed log-raw and added 50ml of acetone and homogenized for 2 min. The following procedure was same as soil sample.

The GC analyses were carried out by following instruments and conditions. GC-ECD: Instrument; HP-5890, Column; J&W DB-17 and DB-1 0.25µmx0.25mmϕx30m, Injector; He, 150kPa, 230°C, Injection; splite(50:1), 3µl, Oven temp.; 140°C(1min) → (10°C/min)~300°C(5min), Detector; N_2 80ml/min, 300°C. GC-MS : Instrument; HP-5890, 5971, Column; HP Ultra-2 0.11µmx0.20mmϕx25m, Injector; He, 50kPa ,200°C, Injection; spliteless, 1µl, Oven temp.; 110°C(1min) → (10°C/min) → 300°C, MS; EI 70eV, 180°C.

RESULTS AND DISCUSSION

Organochlorine fungicide procymidone residues were detected 0.11, 0.06 µg/g-dry from soils of the centers of greenhouses(points A1, B1), where had been stopped fuming with procymidone about a year before. The procymidone residue between greenhouses (point A2) was 0.025 µg/g-dry.

Figure 1 represents the mass-chromatogram of the soil sample detected the residue of procymidone. In the upper figure, total ion chromatogram gave an isorated peak at the retention time of procymidone, the mass-spectrum of which agreed well with procymidone standard as the lower figure.

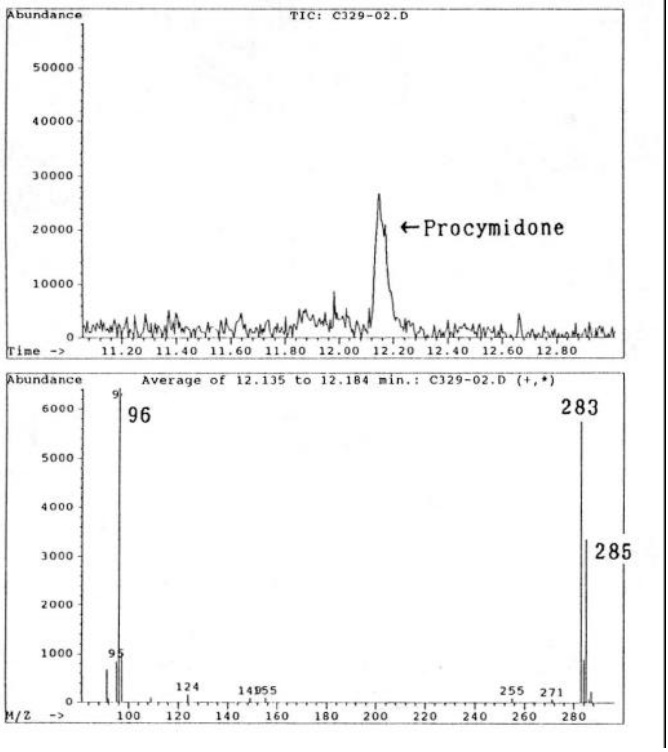

Figure 1. Masschromatogram of the soil sample detected the residue of procymidone

Figure 2 represents the result of following measurements for several years. The concentrations of point A2 in sampling period significantly lower than Al, and both Al and A2 seem to decrease in same rates. These data suggested the strong absorption of procymidone to soil. The regression analysis on points A1,B1 resulted that the fourth half-lives of procymidone in these soils were 2.1, 2.4 years, and their 95% confidence interval ranged 1.7-2.7, 1.8-3.7 years respectively.

Walker and Sarah (1990) applied procymidone sandy clay loam field in Warwick UK, and reported that the following measurement of procymidone residue for 60 days resulted that the half-life of procymidone was 60 days. Fujinami et al. (1981) investigated the half-lives of procymidone in field soils in Japan, and reported 3-4 month when rice paddy, 4-7 month when the other crops planted. But these values were estimated by the data within a year from loading procymidone, and are considerably shorter than fourth harf-life.

Table 1 represents uptakes of procymidone to crops from soils. The procymidone residues ranged 0.005-0.017μg/g-raw in the vegetables grown in these fields, whereas the residues in strawberries were

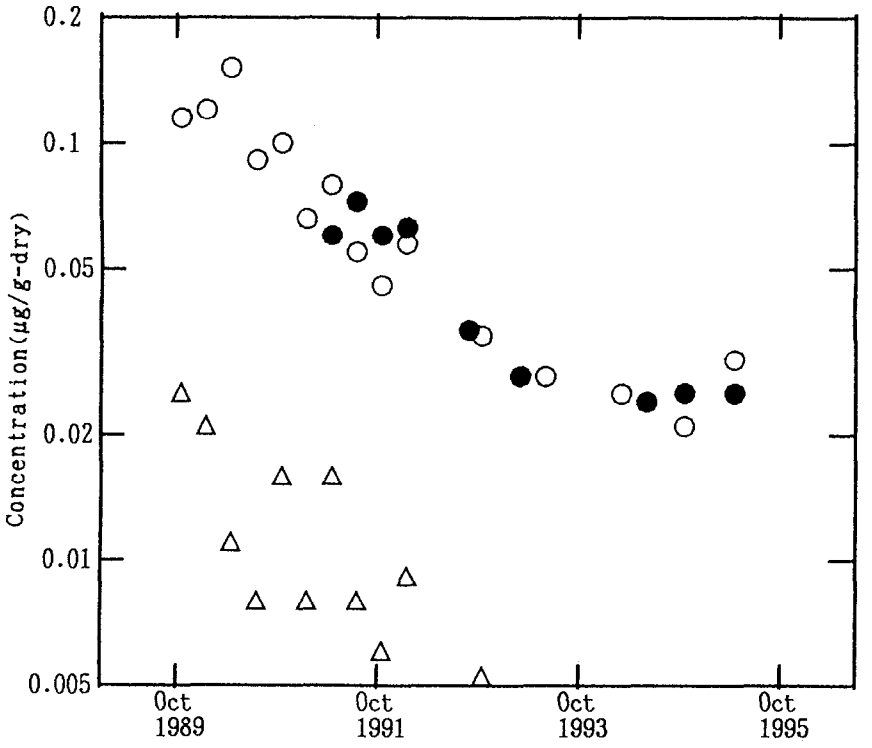

Figure 2. Persistence of procymidone in two agricluture fields
○, ● ; A1, B1 are in the greenhouses which had been fumed with procymidone
△ ; A2 is between the greenhouses.

Table 1. Procymidone concentrations in crops planted in the greenhouses where procymidone level in the soil ranged 0.06-0.14 μg/g-dry.

Crop	Concentration (μg/g-raw)				
	Fruit	Foriage	Root	Main root	Root hair
Strawberry(3times)	nd,nd,nd[a)]				
Spinach		0.005	0.018		
Radish		0.013	0.007		
Crown daisy		0.005	0.20		
Crown daisy		0.016		0.021	0.84
Japanese honeywort		0.017	0.036		
Komatsuna[b)]		0.010	0.009		

a) Not detected (<0.005μg/g-raw)
b) *Brassica Rapa*

Table 2. Uptake rates to crops of organochroline insecticides and procymidone

Crop	Article Pesiticide	Uptake rate (%) Lichtenstein(1970) DLD[a]	HCE[b]	γ-CD[c]	Suzuki(1973) α, β-BHC[d] γ, δ-BHC	DLD	END[e]	This study procymidone
Spinach					19 8 22 6	4	3	8
Radish root		10 11	20 18	3 3	6 5 7 2	4	9	10
Radish foliage					19 10 13 12	2		15

a) Dieldrin, b) Heptachlorepoxide, c) γ-Chlordane
d) Benzenehexachloride, e) Endrin

not detected. The uptake rates of organochlorine insecticides to spinash and radish (Lichtenstein et al. 1970; Suzuki et al. 1973) were tabulated with those of procymidone in Table 2. The uptake rates of procymidone were suggested to eqaul to the long-lived organochlorine insecticides. Remarkably, the root hair of crown daisy took up procymidone more than 5—fold of soil.

The persistence in soil and translocation rate to crops of procymidone suggested that procymidone falls under the category of long-lived organochlorine pesticides.

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