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Dymron Herbicide Residues in Paddy Soil and Channel Water

H. Nagami, S. Asanuma, N. Yajima, M. Usuda, M. Hirosawa, S. Shimizu

Japan Institute of Rural Medicine, 2241, Usuda, Usuda, Nagano, 384-0301, Japan

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Pesticide residues in the agricultural soil may persist for several years, presumably leading to the pesticide contamination of vegetables (Martijn et al. 1993; Tokyo Metropolis 2003; Nagami 1996). The breakdown of pesticides in the soil was often explained by the four-component model (Edwards 1966), and the fourth half-life is important to long term persistence. Long-term residue surveys were not reported on pesticides in Japan except for Nakamura (1990), Nagami (1996), and Nagami (1997). Also, the channel and river water of rice paddy areas in Japan may contain pesticides for rice production (Yamamoto 2003, Kibe et al. 2000, Okamura et al. 1999), and field soil contamination by pesticides in irrigation water is a great concern for organic production in Japan (Ministry of Agriculture, Forestry and Fisheries of Japan 2000).

The herbicide dymron (1-(α,α-dimethylbenzyl)-3-(4-methylphenyl)urea, $C_{17}H_{20}N_2O$) does good in suppressing the weeds of the family *Cyperaceae*, used for rice production widely in Japan. Its log(Pow) is 2.7, and the water solubility is 1.7 mg/L (The Royal Academy of Chemistry 1994). In this study, dymron residues were surveyed in three organic-rice fields in Nagano, Japan, and the persistence of these residues was followed up. Also, the channel water was monitored for dymron contamination and the potency of soil contamination by irrigation water was discussed.

MATERIALS AND METHODS

The analytical standard of dymron was supplied by Wako Pure Chemicals Inc. (Chuou, Ohsaka, Japan). It was dissolved in acetonitrile (MeCN) and diluted with H_2O/MeCN (60+40) for use as a working standard. Florisil-PR was also supplied by Wako Pure Chemicals Inc., and added with 10 v/w% of H_2O, shaken vigorously for 3 min, and left a few hours. Organic solvents and anhydrous Na_2S0_4 were of the grades for pesticide residue analysis.

The three fields (A, B, C) selected for this study are at the center of Saku-daira, Nagano, Japan, at lat. 36°11'N and long. 138°29'E, 700 meters above sea level. The normal temperature is 10°C and the normal amount of rainfall 920 mm/year in this region (Nagano Meteorological Observatory 1998). Fields A, B and C are triangular with their sides from 30 m to 50m. The soil of the fields is silt,

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Correspondence to: H. Nagami

Figure 1. Structure of dymron

and used for rice paddies once a year with pesticides before 1999 and in organic farming from 2000. Soil sampling began in Oct. 2001 on the three fields, done three times a year as a rule. The soil was collected between surface and 10 cm deep, with a core sampler, and removed gravel and plant pieces over 2 mm. The moisture content of the soil samples was measured as the weight loss rates by drying at 110°C. The results in three fields were from 30% to 60%.

Water samples were collected from the channel which supplies irrigation water to these fields and the nearby river, twice a week as a rule from late April to early August in 2002 and 2003. Along the upper streams of the channel and river, there exist a lot of rice paddies, the drainage of which may be contaminated with herbicides used on those fields.

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, and the residue was washed 3 times with 5 ml of acetone. The filtrate and washings were joined and added 50 ml of n-hexane and 100 mL of 10% NaCI aq, and shaken for 5 min. The lower layer was removed and the upper layer was washed 3 times with 50 ml of 10% NaCl aq. The washed solution was dehydrated with 20 g of anhydrous Na_2SO_4 and evaporated. The residue was dissolved with 2 mL of n-hexane, and the solution was loaded into a florisil column (10 v/w% hydrated, 2.5 g, 12 mmϕ). The column was eluted with 25 mL of diethylether/n-hexane (10+90) and 25 mL of diethylether/n-hexane (50+50), and the second fraction was evaporated. The residue was dissolved with 1.0 mL of H_2O/MeCN (60+40), and analyzed in liquid chromatography with a diode array detector (LC-DAD). The recovery rate and detection limit of dymron in the soil were 78±7% and 0.005 μg/g-dry, respectively.

A hundred milliliter of water sample was shaken with 30 mL of deithylether for 5 min. The upper layer was taken and evaporated. The residue was dissolved with 1.0 mL of H_2O/MeCN (60+40) and analyzed with LC-DAD. The recovery rate and detection limit of dymron were 93±5% and 0.1 μg/L, respectively.

LC-DAD analysis was carried out with the following instruments and under the following condition. Instrument; Shimazu LC-10AD, SIL-10AD, SPD-10A, Column; Nomura Chemicals Inc. (Seto, Aichi, Japan) Develosil Ph-HG-5 4 mmϕ x 150 mm, Mobile phase; H_2O: MeCN = 50: 50, 0.6 mL/min, Injection; 20 μL, Ultraviolet (UV) range; 205-300 nm. Quantify UV; 243 nm.

RESULTS AND DISCUSSION

Herbicide dymron residues were detected to the amount of 0.015 to 0.03 μg/g-

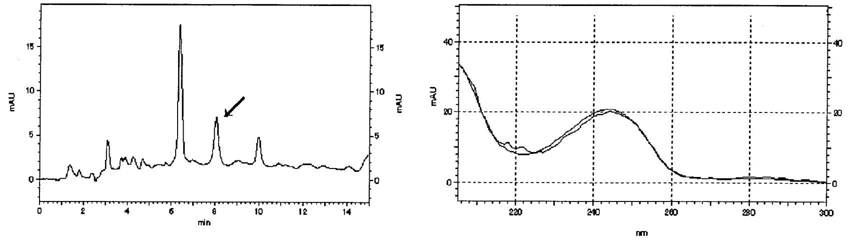

Figure 2. The UV-243nm chromatogram and UV spectrum of the soil sample detected herbicide dymron.

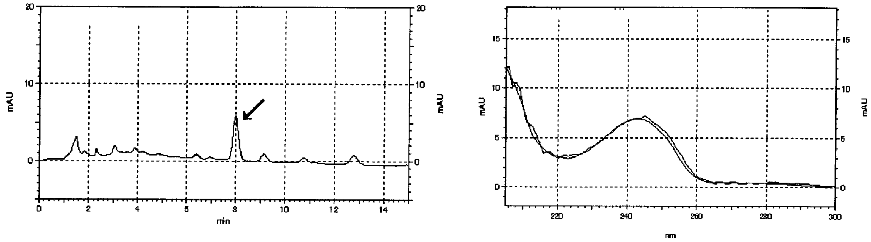

Figure 3. The UV-243nm chromatogram and UV spectrum of the water sample detected herbicide dymron.

dry from the soils of the three fields, and to the maximum amount of 3 μg/L from channel/river waters, respectively. The typical chromatograms of the soil and water samples detected the residues of dymron are presented in Figure 2 and 3, respectively. The UV 243nm chromatograms gave the isolated peaks at the retention time of dymron as in the left-hand, the UV-spectrum of which agreed well with dymron standard as the right-hand.

The dymron residues of the soil in the three fields seem to be due to herbicide uses before 1999. The breakdown of this was followed up for 1.5 years, and is presented in Table 1. The concentration in Field A did not decrease during this period. The data suggests that dymron has considerable persistence in the field soil. On the other hand, that of Fields B and C roughly halved from July to November in 2002. In this season, the farmer composted Fields B and C with an amount of 20 tons per hectare. With this fertilization, the

Table 1. Herbicide dymron residues in field soil, in Saku-daira, Nagano, Japan

Mon/Yr	Concentration (μg/g-dry)		
	Field A	Field B	Field C
Oct. 2001	0.016	0.028	0.015
Mar. 2002	0.015	0.030	0.015
Jul. 2002	-*	0.036	0.016
Nov. 2002	0.013	0.012	0.005
Mar. 2003	0.016	0.013	0.006

*; Not analyzed

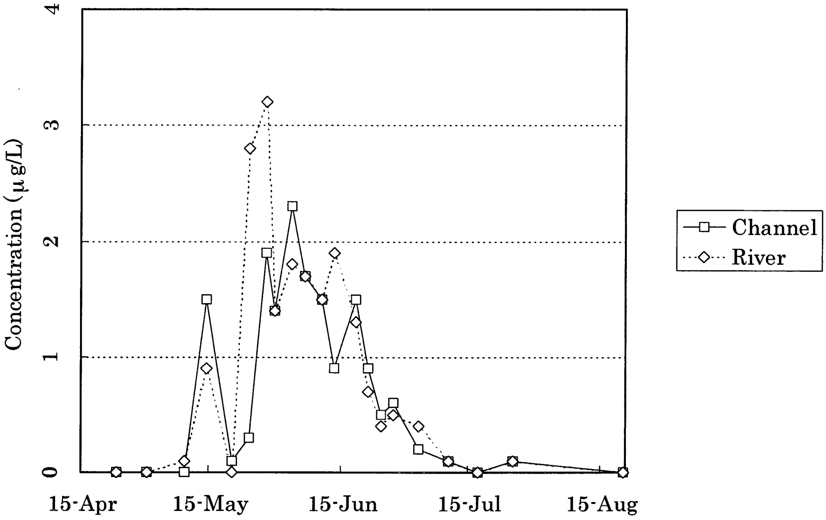

Figure 4. Dymron concentration in channel and river water in Saku-daira Nagano, Japan, in 2002

biodegradation of dymron may be accelerated in these fields.

Dymron was not detected from rice grown in Field B in 2001. But, if the plant hair root of which is used as crops (ex. ginseng) is grown in these fields, dymron may be accumulated and detected in crops (Nagami 1996).

The dymron concentration in the channel and river water was monitored in and around the period of herbicide spraying in 2002 and 2003, which is plotted in Figure 4. They reached about 3 μg/L in late May, remaining more than 1 μg/ L for about a month. The trend of the data in 2003 was the same as that of 2002.

Soil contamination by pesticides in the irrigation water is a grate concern for organic-rice production in Japan. We roughly estimate the potency of with our data as follows: Irrigation from late May to mid-June repeats about 20 times. The depth of water covering the field is controlled to be about 10 cm. Consequently, the dymron brought in this period is about 2 μg/L x 20 x 10 cm = 0.4 μg/cm^2-field. As log(Pow) of dymron is 2.7, the dymron brought by irrigation water is assumed to be absorbed to soil almost all. The plowed soil of these fields is about 20 cm in depth. The specific gravity of the soil is about 2 on a dry base. So, It seems to be increase about 0.4 / (20 x 2) = 10^{-2} μg/g-dry.

Kuwatsuka & Yamamoto (1998) summarized third half-lives of the pesticides in agricultural soil, and that of dymron is 49 days in rice paddy. According to this half-life, dymron contamination of rice paddy with the level of a few 10^{-2} μg/g-dry decrease to the level below detection limit by winter of the year. In Okayama, Japan, Okamura et al. (1999) detected dymron to an amount of a few tens μg/L in the river water around the Kojima Pond, where is not so plentiful as Saku-daira of our study. In this case, the contamination of field soil may reach a few 10^{-1} μg/g-dry by irrigation water, and it may be detected even in the next years.

In conclusion, herbicide dymron residues in field soils and channel water were detected and confirmed in liquid chromatography with a diode array detector. Dymron residues in the paddy soil may be persistent in Sakudaira, Nagano, Japan, but composting may accelerate the biodegradation of dymron. The channels and river water were contaminated with dymron, which could cause to irrigating field soil dymron detection in summer.

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