Original Article

Degradation and Adsorption of a Seed Fungicide Pefurazoate in Paddy Soil

Mitsuaki TAKENAKA, Shoji SAKAI,* Hitoshi NISHIDA,
Shuichiro KIMURA and Hiroshi HASE

*Ube Laboratory, Agrochemical Research Department, UBE Industries, Ltd.,
Kogushi Ube 755, Japan*

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Fate of the fungicide, pefurazoate (pent-4-enyl *N*-furfuryl-*N*-imidazol-1-ylcarbonyl-DL-homoalaninate, Healthied®) in flooded mineral and volcanic ash soils was investigated with ¹⁴C-labeled pefurazoate. ¹⁴C-Pefurazoate, when applied at 1 ppm, was quite easily degraded with a half-life of less than one week in both soils. Pent-4-enyl *N*-furfuryl-DL-homoalaninate, *N*-furfuryl-DL-homoalaninate, 1-[(*RS*)-1-carboxylato-propyl]-3-hydroxypyridinium, and *N*-(furan-2-ylcarbonyl)glycine were identified as major degradation products, amounting to less than 10% of the applied radioactivity. The radioactivity in the soil decreased due to the evolution of ¹⁴CO₂, which was an ultimate metabolite of pefurazoate. The Freundlich adsorption coefficient of pefurazoate was 16.3 in the mineral soil and 21.9 in the volcanic ash soil, suggesting pefurazoate was not adsorbed tightly by the soils.

INTRODUCTION

Pefurazoate (Healthied®, pent-4-enyl *N*-furfuryl-*N*-imidazol-1-ylcarbonyl-DL-homoalaninate) is a new fungicide developed by UBE Industries, Ltd. and Hokko Chemical Industry Co., Ltd. It is used for control of seed-borne pathogens of rice, e.g. *Gibberella fujikuroi*, *Cochliobolus miyabeanus*, and *Pyricularia oryzae*.¹⁾ Its antifungal action is considered to be the inhibition of ergosterol biosynthesis similar to that of the related azole fungicides.²⁾

Rice seeds disinfected with pefurazoate by soaking or spraying are cultured in nursery soil for three weeks, and the seedlings are transplanted in paddy fields. In this process pefurazoate may be transferred into paddy soil along with rice seeds.

In the present paper, the degradation and adsorption of pefurazoate in the soil were investigated.

MATERIALS AND METHODS

1. Chemicals

¹⁴C-Pefurazoate (Fig. 1) was synthesized from [methyl-¹⁴C]-2-aminomethylfuran (specific activity: 1.43 GBq/mmol, radiochemical purity: 98.5%) purchased from CEA as a starting ¹⁴C-labeled compound by three steps: A mixture of [methyl-¹⁴C]-2-aminomethylfuran (0.65 mmol), pent-4-enyl (*RS*)-2-bromobutanoate (1.95 mmol) and sodium carbonate (0.65 mmol) was refluxed in acetonitrile for 15 hr, and the crude product was purified to obtain pent-4-enyl *N*-¹⁴C-furfuryl-DL-homoalaninate (0.55 mmol) with a silica gel column. It was then stirred at room temperature for 6 hr with triethylamine (0.83 mmol) and trichloromethyl chloroformate (0.83 mmol) in toluene. The mixture was extracted with toluene after being quenched with water, and the toluene solution was treated at 65–70°C for 4 hr with triethylamine (0.98 mmol) and imidazole (1.95 mmol) to obtain ¹⁴C-pefurazoate (0.41 mmol).

The chemical structure of ¹⁴C-pefurazoate

* To whom all correspondence should be addressed.

Table 1 R_f values of pefurazoate and its degradation products by TLC.

No.	Solvent system	Volume ratio	Compounds								
			Pefurazoate	PFAB	FAB	HPB	FG	M-1	M-2	M-3	M-4
1	$\text{CHCl}_3/\text{EtOH}/28\%\text{NH}_4\text{OH}$	2:4:1	0.89	0.89	0.53	0.28	0.44	0.92	0.80	0.72	0.49
2	$n\text{-BuOH}/\text{AcOH}/\text{H}_2\text{O}$	5:1:1	0.79	0.62	0.32	0.20	0.49	—	—	—	—
3	$\text{AcOEt}/\text{MeOH}/\text{HCOOH}$	8:8:1	0.76	0.78	0.42	—	0.82	—	—	—	—
4	$\text{C}_6\text{H}_5\text{CH}_3/\text{AcOEt}$	1:5	0.32	0.59	0.00	0.00	0.01	—	—	—	—
5	$\text{AcOEt}/\text{MeOH}/\text{HCOOH}$	10:5:1	0.90	—	0.30	0.08	0.64	—	—	—	—
6	$n\text{-PrOH}/28\%\text{NH}_4\text{OH}$	2:1	0.81	—	—	0.04	—	—	—	—	—
7	$n\text{-C}_6\text{H}_{12}/\text{AcOEt}$	4:1	0.02	0.32	—	—	—	—	—	—	—

Fig. 1 Chemical structure of pefurazoate.

* labeled position.

was confirmed by EI-mass spectrometry (M-80A, Hitachi) [MS m/z : 347 (M^+), 252 (M^+ -imidazolylcarbonyl), 192 (M^+ -pentenyl butanoate), 83 (M^+ -pentenyl (N -imidazolylcarbonyl)homoalaninate)]. The radiochemical purity was more than 97% by TLC (silica gel plate, 60F₂₅₄, 20×20 cm, 0.25 mm thickness, Merck) with solvent systems 2 and 4 shown in Table 1.

Unlabeled authentic pefurazoate and four reference compounds (PFAB,* FAB,* HPB,*³⁾ FG*) were prepared as follows, and the chemical structures of them were confirmed by ^1H NMR (200 MHz, JASCO).

Pefurazoate was synthesized by the same method used in the synthesis of ^{14}C -pefurazoate [^1H NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$ ppm: 0.8 (3H, t , $J=7.2$ Hz, CH_2CH_3), 1.7–1.8 (2H, m , $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 2.0–2.2 (4H, m , CH_3CH_2 , $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 4.0 (1H, dd , $J=9.4$ Hz, 5.8 Hz, NCHCO), 4.2 (2H, t , $J=6.6$ Hz, $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 4.5 (1H, d , $J=16.4$ Hz, 2-furylmethyl), 4.7 (1H, d , $J=16.4$ Hz, 2-furylmethyl), 5.0–5.1 (2H, m , $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 5.8 (1H, m , $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 6.4

(2H, m , furan), 7.1 (1H, d , imidazole), 7.5 (1H, d , furan), 7.5 (1H, d , imidazole), 8.1 (1H, s , imidazole)].

PFAB: Furfurylamine was treated with methyl (RS)-2-bromobutanoate following the ester exchange with 4-pentenol [^1H NMR $\delta_{\text{TMS}}^{\text{CDCl}_3}$ ppm: 0.9 (3H, t , $J=7.2$ Hz, CH_2CH_3), 1.7–1.8 (4H, m , CH_2CH_3 , $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 1.9 (1H, s , NH), 2.1–2.2 (2H, m , $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 3.2 (1H, t , $J=6.4$ Hz, NCHCO), 3.8 (2H, d , $J=14.2$, 2-furylmethyl), 4.1 (2H, t , $J=6.6$ Hz, $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 5.0 (2H, m , $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 5.8 (1H, m , $\text{CH}_2\text{CHCH}_2\text{CH}_2\text{CH}_2\text{O}$), 6.2 (1H, d , furan), 6.3 (1H, dd , furan), 7.3 (1H, d , furan)].

FAB: Methyl N -furfuryl- DL -homoalaninate prepared by the above-mentioned route was hydrolyzed with alkali and neutralized with hydrochloric acid [^1H NMR $\delta_{\text{TMS}}^{\text{D}_2\text{O}}$ ppm: 1.0 (3H, t , $J=7.2$ Hz, CH_3CH_2), 1.9 (2H, m , CH_3CH_2), 3.6 (1H, t , $J=6.4$, $\text{CH}_3\text{CH}_2\text{CH}$), 4.3 (2H, d , 2-furylmethyl), 6.5 (1H, d , $J=3.6$, furan), 6.6 (1H, dd , furan), 7.6 (1H, d , $J=2.0$, furan)].

HPB: (RS)-1-(1-carboxylatopropyl)-3-hydroxypyridinium bromide prepared by the reaction of 3-hydroxypyridine with 2-bromobutanoic acid was treated with sodium hydroxide [^1H NMR $\delta_{\text{TMS}}^{\text{D}_2\text{O}}$ ppm: 0.9 (3H, t , $J=7.2$ Hz, CH_3CH_2), 2.1 (1H, m , CH_3CH_2), 2.4 (1H, m , CH_3CH_2), 4.8 (4H, dd , $\text{CH}_3\text{CH}_2\text{CHCO}$), 7.5 (1H, m , pyrimidine), 7.6 (1H, m , pyrimidine), 7.7 (1H, m , pyrimidine), 7.8 (1H, m , pyrimidine)].

FG: Ethyl N -(furan-2-ylcarbonyl)glycinate prepared by the reaction of furoyl chloride with ethyl glycinate was hydrolyzed with alkali and neutralized with hydrochloric acid

* PFAB, pent-4-enyl N -furfuryl- DL -homoalaninate; FAB, N -furfuryl- DL -homoalanine; HPB, 1-((RS)-1-carboxylatopropyl)-3-hydroxypyridinium; FG, N -(furan-2-ylcarbonyl)glycine

Table 2 Physicochemical properties of soil samples used.

Location	Parent material	Texture	Clay content(%)	Organic carbon(%)	Total nitrogen(%)	CEC (mEq/100g)	pH (H ₂ O)
Yamaguchi	Alluvial	SL	22.3	1.8	0.17	8.6	5.5
Ushiku	Volcanic ash	LiC	37.7	5.7	0.42	31.5	6.1

[¹H NMR $\delta_{\text{TMS}}^{\text{CD}_3\text{OD}}$ ppm: 4.1 (2H, s, NHCH₂-COOH), 6.6 (1H, d, furan), 7.1 (1H, dd, furan), 7.7 (1H, d, furan)].

2. Soil

The physicochemical properties of Yamaguchi and Ushiku paddy soils are shown in Table 2. Soil samples were air-dried and sieved under 2 mm. The soils were sterilized with an intermittent autoclave at 120°C and 2 atm for 30 min every day for three days.

3. Degradation Test

3.1 Unaerated condition

Air-dried soil (25 g dry weight) was preincubated in a 100-ml Erlenmeyer flask at 28°C for a week under a flooded condition with water 1 cm deep. After preincubation, 1 ml aqueous solution containing 25 μg ¹⁴C-pefurazoate (1.04×10^{-1} MBq, 1 ppm per soil) was injected into Yamaguchi and Ushiku soils and incubated at 28°C in the dark.

3.2 Aerated condition

This test was carried out to examine volatile compounds evolving during incubation. Air-dried soil was incubated aerated with a current of wet air (5 ml/min) by the same method as described in Unaerated Condition except for the use of an incubation apparatus.⁴⁾ Volatile ¹⁴C-compounds were trapped with two sequential bottles containing 10 ml of 10% NaOH aqueous solution. The solution was renewed every week. In this experiment, the recovery of the radioactivity from the soils was satisfactory (recovery ratio: 97.8% in the Yamaguchi soil and 92.3% in the Ushiku soil 8 weeks after application). ¹⁴CO₂ in the NaOH solution was determined from the radioactivity in the solution before and after treatment with 1 M BaCl₂ solution that was used to remove ¹⁴CO₂.

4. Analytical Method

Flooded water (flooded-water fraction) separated by centrifugation (10,000 rpm, 10 min) was lyophilized and dissolved with 3 ml of methanol.

The soil separated from the flooded water was shaken for 1 hr twice with 50 ml of 30% aqueous acetone solution. This extract (acetone-water-extractable fraction) was concentrated to dryness *in vacuo* below 40°C and dissolved with 3 ml of methanol.

The residues were subjected to refluxing for 2 hr with methanol. This extract (hot-methanol-extractable fraction) was concentrated *in vacuo* to 3 ml solution. The unextracted precipitate was classified as bound residue fraction.

Each fraction except the bound residue was analyzed by TLC. Individual solutions (10–100 μl) were spotted on silica gel plates and developed with solvent systems 1 and 4 as shown in Table 1. ¹⁴C-Compounds separated on the plates were detected by autoradiography (³H ARG film, Konica) and determined by liquid scintillation spectrometry (LSC, Tri-carb 2000 CA, Packard) with a Clear-Sol scintillator (Nakarai Chemical). The degradation products were identified by TLC co-chromatography with reference compounds.

Bound residue was extracted by shaking with 75 ml of 0.5 M NaOH solution for 18 hr at room temperature. The unextracted precipitate was classified as humin fraction. The extract was separated to two fractions by adjusting its pH to 1.0: The supernatant to a fulvic acid fraction and the precipitate to a humic acid fraction. The radioactivity in the supernatant fraction was determined by LSC and that in the total bound residue and the humin fraction was determined by LSC after treatment with an autocombustion system (ASC-113, Aloka). The radioactivity in the

humic acid fraction was calculated by subtracting the radioactivity in the fulvic acid and the humin fraction from that in the bound residue fraction.

5. Adsorption and Desorption Test^{5,6)}

5.1 Adsorption equilibrium time

Yamaguchi or Ushiku soil (2 g dry weight) was shaken reciprocally at 160 rounds/min in a polypropylene 100-ml centrifuging tube for 4, 24 and 48 hr at 25°C with 10 ml of 10^{-2} M CaCl_2 solution containing 25×10^{-6} M ^{14}C -pefurazoate (35.6 kBq, 43.1 ppm per soil) (solubility of pefurazoate in water: 1.25×10^{-3} M). The unadsorbed radioactivity in the supernatant, which was separated by centrifugation (19,000 g, 15 min) from the soil suspension, was determined by LSC. The concentration of pefurazoate in the equilibrium solution could be calculated from the measured radioactivity, since the result of TLC analysis of ^{14}C -compounds in the supernatant showed that most of pefurazoate in the supernatant remained undegraded (degradation ratio: 6.2% in the Yamaguchi soil and 5.8% in the Ushiku soil).

5.2 Adsorption and desorption coefficient

Soils were shaken with 10^{-2} M CaCl_2 solution containing pefurazoate at four different concentrations (0.345, 1.73, 8.63, 43.1 ppm per soil) for 24 hr by the same method as previously mentioned. After shaking, 8 ml of the supernatant obtained by centrifugation was removed and the radioactivity was determined. Subsequently to measure the desorption coefficient, 8 ml of fresh 10^{-2} M CaCl_2 solution was added to the soil suspension. After shaking for 24 hr, the desorbed radioactivity in the supernatant was determined. The concentration of pefurazoate in the desorption equilibrium solution was calculated from the measured radioactivity, since few degradation products were found in the desorbed solution. These tests were also carried out with sterilized soils in which pefurazoate was not degraded.

Freundlich adsorption coefficient (K_f) and adsorption exponent ($1/n$) were calculated with the following equation:

$$\log C_s = \log K_f + 1/n \log C_e$$

C_s : equilibrium concentration of

pefurazoate in the solid phase (ppm)
 $= (\text{added pefurazoate} - \text{pefurazoate in the equilibrium solution}) / \text{soil weight}$

C_e : equilibrium concentration of pefurazoate in the solution phase (ppm)

While K_f and $1/n$ of desorption were calculated, C_s was determined as follows:

$$C_s = (\text{adsorbed pefurazoate in the adsorption-equilibrium solution} + \text{unremoved pefurazoate in the adsorption-equilibrium solution} - \text{pefurazoate in the desorption-equilibrium solution}) / \text{soil weight}$$

RESULTS AND DISCUSSION

1. Degradation of Pefurazoate

1.1 Distribution of radioactivity (Fig. 2)

Total radioactivity remaining in the Yamaguchi soil gradually decreased to 36.9% of the dose after 14 weeks' incubation. The flooded-water fraction accounted for over 10% of the dose in the early period of incubation, and then it decreased to 2.0 and 0.2% after 6 and 14 weeks, respectively. In the acetone-water-extractable fraction, nearly 80% of the dose was recovered in the early period, but the recovery decreased to 11.3% after 14 weeks. The fate of this fraction corresponded with that of the total radioactivity. The hot-methanol-extractable fraction increased gradually to 12.3% (maximum) during the first four weeks. The radioactivity in the bound residue fraction increased to 21.4% during the first six weeks, but decreased to 18.8% during the last eight weeks.

Almost the same results were found in the Ushiku soil. However, there was a slight difference the radioactivity of the flooded-water fraction in the Ushiku soil was lower than that of it in the Yamaguchi soil during the first four weeks and that of the hot-methanol-extractable fraction was always lower.

1.2 Fate of pefurazoate and its degradation products (Table 3)

In the Yamaguchi soil pefurazoate was degraded to 51.7% during the first three days, but it gradually decreased to 13.9% during the following six weeks. Similarly in the Ushiku soil it decreased to 56.3% during the

Fig. 2 Distribution of radioactivity in paddy soil.

○: flooded-water, △: acetone-water, □: hot-methanol,
●: bound residue.

Table 3 Fate of pefurazoate and its degradation products.

(recovery ratio, %)

Soil	Detected compounds	Incubation period (day)				
		0	3	14	28	42
Yamaguchi	Pefurazoate	86.5	51.7	22.8	18.6	13.9
	PFAB	2.7	7.1	8.4	4.7	2.7
	FAB	1.6	8.8	12.1	7.5	2.7
	FG	0.6	0.5	0.8	0.6	0.5
	HPB	0.0	1.2	1.5	0.8	2.0
	M-1	<0.1	0.7	1.9	1.8	0.8
	M-2	1.0	4.2	6.8	5.4	2.7
	M-3	1.2	2.3	3.3	3.0	2.1
	M-4	1.6	0.8	1.3	1.1	0.8
	Others ^{a)}	6.6	15.9	11.8	7.2	7.1
	Bound residue	5.3	6.8	12.1	18.1	21.4
	Total	107.1	100.0	82.8	68.8	56.7
Ushiku	Perfurazoate	87.8	56.3	38.0	16.9	16.8
	PFAB	2.1	5.4	3.7	4.3	2.0
	FAB	0.7	5.4	6.7	2.7	1.0
	FG	0.4	0.4	0.8	0.7	0.4
	HPB	0.0	0.9	0.8	0.7	0.6
	M-1	0.0	1.6	1.5	1.7	0.9
	M-2	1.3	4.5	3.1	6.2	2.6
	M-3	0.2	2.1	1.7	3.2	1.4
	M-4	<0.1	0.8	0.7	1.6	0.6
	Others ^{a)}	6.7	11.9	6.0	6.2	5.2
	Bound residue	3.0	8.0	14.6	20.2	25.3
	Total	102.2	97.4	77.6	64.4	56.8

^{a)} Others contain many minor degradation products.

first three days and to 16.8% during the following six weeks. Thus, pefurazoate was easily degraded to half within a week, but the rate of degradation afterward was fairly slow.

Several degradation products were found by TLC in the flooded-water, acetone-water-extractable, and hot-methanol-extractable fractions. Of these major products, PFAB, FAB, HPB and FG were identified by TLC co-chromatography with several solvent systems as shown in Table 1, whereas other products (M-1, -2, -3 and -4) were failed to be identified. The accumulation ratio of each degradation product was less than 10% of the dose, being in the following order: PFAB, FAB, M-2 > M-3 > FG, HPB, M-1, M-4.

From these degradation products, a degradation pathway is proposed as in Fig. 3; The degradation of pefurazoate started with elimination of the azolylcarbonyl group to produce PFAB, or hydrolysis of ester and additional elimination to yield FAB *via* an unidentified intermediate. PFAB also released FAB, which then yielded FG and HPB. The former transformation was caused by the decarboxylation of ω and ω -1 carbons of the carboxylate moiety and the oxidation of furfuryl carbon.^{7,8)} The latter was by the condensation reaction between amine-nitrogen of FAB and the reactive position-5 carbon derived from cleavage of the bond between position-5 carbon and oxygen in the furan ring of FAB.

Unextractable bound residues (fulvic acid, humin and humic acid fractions) increased to 21.4% of the dose in the Yamaguchi soil and 25.3% in the Ushiku soil after 42 days' incubation. Of these fractions, fulvic acid, humin and humic acid fraction occupied 59.3%,

35.2% and 5.6%, respectively in the Yamaguchi soil, while in the Ushiku soil 40.6%, 56.6% and 2.8%, respectively. The ratio of organic ¹⁴C fractions (fulvic acid, humin and humic acid) found in the present study was quite different from that of the original soil organic carbon (fulvic acid: 42.6%, humin: 2.7%, humic acid: 54.7% in the Yamaguchi soil).⁹⁾

Under the unsterilized condition, the volatile ¹⁴C trapped with alkali solution amounted to 36.4% of the dose in the Yamaguchi soil and 30.9% in the Ushiku soil during eight weeks, and more than 95% of the trapped ¹⁴C-com-

Fig. 3 Proposed degradation pathway of pefurazoate in paddy soil.

Table 4 Volatile degradation products evolved from soil.

Treatment	Soil	Incubation period (week)				
		1	2	3	5	8
Unsterilized	Yamaguchi	5.0	11.2	15.5	22.4	36.4
	Ushiku	2.9	6.8	11.5	19.8	30.9
Sterilized	Yamaguchi	0.0	0.0	0.0	0.1	—
	Ushiku	0.1	0.2	0.3	0.5	—

(% of dose)

pounds consisted of $^{14}\text{CO}_2$. Under the sterilized condition, however, there was almost no trapped ^{14}C (less than 0.5% of the dose) in both soils as shown in Table 4. Thus, the microbial action was much involved in the degradation of pefurazoate.

2. Adsorption and Desorption

2.1 Adsorption equilibrium time

The adsorption amount during an additional 24-hr shaking increased to 0.6% in the Yamaguchi soil and 2.6% in the Ushiku soil under the unsterilized condition, while under the sterilized condition 3.8% in the Yamaguchi soil and 2.8% in the Ushiku soil. Thus, the adsorption equilibrium was attained during the first 24-hr shaking since there was only a slight increase of adsorption amount during the following 24-hr saking.

2.2 Freundlich constants

Adsorption and desorption equilibria of pefurazoate are shown in Tables 5 and 6.

The property of soil adsorption of pefurazoate was examined under the unsterilized and sterilized conditions since pefurazoate was

degraded only slightly (about 6% of the application) under the unsterilized condition.

Under both conditions, the correlation between the concentration of pefurazoate in the equilibrium solution and in the soil was high ($\gamma > 0.99$), therefore it was considered that pefurazoate was adsorbed in accordance with the Freundlich adsorption isotherm.

The Freundlich constants are shown in Table 7.

The Freundlich adsorption coefficient was 16.3 in the Yamaguchi soil and 21.9 in the Ushiku soil under the unsterilized condition, while under the sterilized condition 11.8 in the Yamaguchi soil and 17.5 in the Ushiku soil. The desorption coefficient was 21.1 in the Yamaguchi soil and 25.2 in the Ushiku soil under the unsterilized condition, while under the sterilized condition 21.4 in the Yamaguchi soil and 23.2 in the Ushiku soil. Thus the Freundlich adsorption coefficient was not much affected by soil sterilization. It was considered that soil sterilization had reduced the Freundlich adsorption coefficient by inducing soil organic matter acting as an ad-

Table 5 Adsorption equilibrium.

Treatment	Soil	Concentration of pefurazoate added to soil (ppm)	Equilibrium conc. of pefurazoate (ppm)		Adsorption ratio (K_d) ^{a)}
			Solution	Soil	
Unsterilized	Yamaguchi	0.0690	0.00845	0.300	35.5
		0.345	0.0465	1.49	32.0
		1.725	0.301	6.98	23.2
		8.625	2.43	30.1	12.4
	Ushiku	0.0690	0.00411	0.321	78.1
		0.345	0.0271	1.58	58.3
		1.725	0.210	7.38	35.1
		8.625	1.88	32.4	17.2
Sterilized	Yamaguchi	0.0690	0.0120	0.280	23.3
		0.345	0.0656	1.37	20.9
		1.725	0.430	6.34	14.7
		8.625	3.06	27.6	9.0
	Ushiku	0.0690	0.00755	0.301	39.9
		0.345	0.0435	1.47	33.8
		1.725	0.293	6.97	23.8
		8.625	2.22	31.3	14.1

^{a)} $K_d = (\text{concentration of pefurazoate in soil}) / (\text{concentration of pefurazoate in solution})$

Remark: Data are average of duplicates.

Table 6 Desorption equilibrium.

Treatment	Soil	Concentration of pefurazoate added to soil (ppm)	Equilibrium conc. of pefurazoate (ppm)		Adsorption ratio (K_d) ^{a)}
			Solution	Soil	
Unsterilized	Yamaguchi	0.0690	0.00525	0.283	53.9
		0.345	0.0301	1.38	45.8
		1.725	0.196	6.31	32.2
		8.625	1.43	25.5	17.8
	Ushiku	0.0690	0.00291	0.311	106.9
		0.345	0.0194	1.51	77.8
		1.725	0.154	6.85	44.5
		8.625	1.29	28.1	21.8
Sterilized	Yamaguchi	0.0690	0.00627	0.261	41.6
		0.345	0.0342	1.27	37.1
		1.725	0.191	5.84	30.6
		8.625	1.33	24.2	18.2
	Ushiku	0.0690	0.00463	0.286	61.8
		0.345	0.0271	1.39	51.3
		1.725	0.180	6.41	35.6
		8.625	1.33	27.2	20.5

^{a)} K_d = (concentration of pefurazoate in soil)/(concentration of pefurazoate in solution).

Remark: Data are average of duplicates.

Table 7 Freundlich constants.

Treatment	Soil	Adsorption		Desorption		ΔK (%) ^{c)}
		K_f ^{a)}	$1/n$ ^{b)}	K_f	$1/n$	
Unsterilized	Yamaguchi	16.3	0.813	21.1	0.803	29.4
	Ushiku	21.9	0.752	25.2	0.738	15.1
Sterilized	Yamaguchi	11.8	0.827	21.4	0.848	81.3
	Ushiku	17.5	0.815	23.2	0.803	32.6

^{a)} Freundlich adsorption or desorption coefficient.

^{b)} Adsorption or desorption exponent.

^{c)} Percentage change in the K_f values in going from adsorption to desorption.

sorbent to decompose, while it had raised the Freundlich adsorption coefficient by preventing pefurazoate from transforming into more hydrophilic compounds which were less adsorbed by the soil organic matter.

Pefurazoate was not tightly adsorbed compared with some marketed pesticides (paraquat, 202; linuron, 45.1; atrazine, 56.3)^{10,11)} in terms of Freundlich adsorption coefficient.

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要 約

水田土壌中における種子消毒剤ペフラゾエートの分解および吸着

竹中允章, 境 昭二, 西田 均
木村修一郎, 長谷 寛

水田土壌中におけるペフラゾエート（ベンタ-4-エニル=*N*-フルフリル-*N*-イミダゾール-1-イルカルボニル-DL-ホモアラニナート）の分解と土壌吸着性を、¹⁴C 標識ペフラゾエートを用いて調べた。ペフラゾエートの半減期は、鉍質および火山灰土壌いずれにおいても1週間以内であった。ペフラゾエート添加後6週間目には、添加したペフラゾエート由来の¹⁴Cは約56%が土壌に残留し、その他は炭酸ガスとして揮散した。主な分解生成物として、4-ペンテニル=*N*-フルフリル-DL-ホモアラニナート、*N*-フルフリル-DL-ホモアラニナート、1-[(*RS*)-1-カルボキシラートプロピル]-3-ヒドロキシピリジニウム、および *N*-(フラン-2-イルカルボニル) グリシンが同定された。これらはいずれも10%以下の集積率であった。ペフラゾエートの土壌吸着性は中程度で、フロインドリッヒの吸着定数は、鉍質土壌で16.3、火山灰土壌で21.9であった。