除草剤ピラゾレートの水田土壌における分解

誌名	日本農薬学会誌
ISSN	03851559
著者名	山岡,剛 重松,由夫 安藤,満
発行元	日本農薬学会
巻/号	13巻4号
掲載ページ	p. 571-577
発行年月	1988年11月

J. Pesticide Sci. **13**, 571–577 (1988)

Original Article

Degradation of the Herbicide Pyrazolate in Rice Paddy Soils

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(Received January 5, 1988)

The degradation of pyrazolate was studied in soils under laboratory conditions by using ^{14}C-preparations labeled separately at the pyrazole and chlorinated benzene rings. Pyrazolate was hydrolyzed at the ester bond to give *p*-toluenesulfonic acid (PTSA) and the herbicidal entity, 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-hydroxypyrazole (DTP). The half-lives in two soils under flooded conditions were about 10 days. PTSA labeled with ^{14}C at the benzene ring was rapidly mineralized to CO_2, while DTP was relatively persistent in soils. DTP underwent oxidation at the 1- and 3-methyl groups, cleavage of the benzoyl bond, fission of the pyrazole and benzene rings, and was ultimately mineralized to CO_2.

INTRODUCTION

Pyrazolate, 4-(2,4-dichlorobenzoyl)-1,3-dimethylpyrazol-5-yl *p*-toluenesulfonate, is a herbicide used in paddy fields against various annual and perennial weeds.[1] Pyrazolate is hardly soluble in water, whose solubility in distilled water is 56 ppb at 25°C (M. Fujimoto: unpublished datum). Once dissolved in water, however, pyrazolate is readily hydrolyzed to *p*-toluenesulfonic acid (PTSA) and 4-(2,4-dichlorobenzoyl)-1, 3-dimethyl-5-hydroxypyrazole (destosyl pyrazolate; DTP).[2] Since DTP is the herbicidal entity of pyrazolate[1,3-6] soluble at 415 ppm in distilled water at 25°C (M. Fujimoto: unpublished datum), pyrazolate is a chemically release-controlled agent.[1,4,6]

Leaching behaviors of pyrazolate and DTP in soils have been reported previously.[7] DTP was adsorbed by soils, and most of the DTP adsorbed was released into water with successive desorption procedures, indicating that the adsorption is reversible. In paddy fields where a granular formulation of 10% pyrazolate was applied, both pyrazolate and DTP formed a treatment layer at the soil surface. They were hardly mobile by leaching and gradually dissipated by biodegradation.

The objective of this study was to identify the degradation products of pyrazolate and to determine the conversion rate of the parent compound and its major degradation products in paddy soils. Two different types of soil and two kinds of ^{14}C-pyrazolate along with a ^{14}C-PTSA were used. Studies were undertaken in flooded flask models and in pot plots where rice plants were grown until maturity so that the soil conditions could be simulated to those in paddy fields.

In Japan, granular formulations containing 4 to 10% of pyrazolate are usually applied at 30 kg/ha. When a 10% formulation is uniformly applied into the surface soil 10 cm deep at 30 kg/ha, the concentration of pyrazolate corresponds to 3 ppm. Dosages in this study were fitted for agricultural practice in the pot tests and doubled in the flask models.

MATERIALS AND METHODS

1. *Chemicals*

$^{14}C(P)$-Pyrazolate labeled at the 3rd position of the pyrazole ring and $^{14}C(B)$-pyrazolate

uniformly labeled at the chlorinated benzene ring were prepared by Yanai.[8] *p*-Toluenesulfonic acid uniformly labeled at the benzene ring (^{14}C-PTSA) was obtained from New England Nuclear (Boston, MA, USA). Specific activities in mCi/mmol: ^{14}C(P)-pyrazolate: 5.95, ^{14}C(B)-pyrazolate: 6.43, and ^{14}C-PTSA: 4.97, and the radiochemical purity based on thin-layer chromatography was more than 98%.

Among unlabeled chemicals, the following were synthesized for authentic standards in the Agricultural Chemicals Research Laboratories, Sankyo Co., Ltd.: pyrazolate, DTP, 4-(2,4-dichlorobenzoyl)-1, 3-dimethyl-5-methoxypyrazole [5-CH_3O-DTP], 4-(2, 4-dichlorobenzoyl)-5-hydroxy-3-methylpyrazole [1-H-DTP], 4-(2, 4-dichlorobenzoyl)-5-hydroxy-3-hydroxymethyl-1-methylpyrazole [3-CH_2OH-DTP], 4-(2, 4-dichlorobenzoyl)-5-hydroxy-1-methyl-3-pyrazolyl carboxylic acid [3-COOH-DTP], 1, 3-dimethyl-2-pyrazolin-5-one [1, 3-CH_3-PZO], 3-methyl-2-pyrazolin-5-one [3-CH_3-PZO], 1, 3-dimethyl-4-hydroxy-2-pyrazolin-5-one [1,3-CH_3-4-OH-PZO], 4-hydroxy-3-methyl-2-pyrazolin-5-one [3-CH_3-4-OH-PZO], 1,3-dimethylpyrazolin-4, 5-dione [1, 3-CH_3-4-OX-PZO] and 3-methylpyrazolin-4,5-dione [3-CH_3-4-OX-PZO]. 2,4-Dichlorobenzoic acid [2,4-DCBA], 2-chlorobenzoic acid [2-CBA] and 4-chlorobenzoic acid [4-CBA] were purchased.

2. Thin-layer Chromatography (TLC)

Precoated silica gel 60 F_{254} chromatoplates (20×20 cm, 0.25 mm thickness, Merck) were used. Solvent systems (A–E) and *Rf* values of authentic standards are listed in Table 1. Both 1,3-CH_3-4-OH-PZO and 3-CH_3-4-OH-PZO were auto-oxidized to 1,3-CH_3-4-OX-PZO and 3-CH_3-4-OX-PZO on TLC plates developed with each solvent system described above. They are not included in Table 1.

Radioactive spots on the TLC plates were examined with an Automatic TLC-Linear Analyzer (Berthold, LB-2832) and by autoradiography. Unlabeled compounds were visualized under UV light.

3. Soils

Soils were collected from rice paddy fields in Shiga (Azuchi) and Iwate (Morioka) prefectures and kept at 5°C in the dark. The soils were passed through a 2-mm sieve before use. Soil analysis data are summarized in Table 2.

4. Radioassay

Liquid scintillation counting (LSC) and combustion analysis were carried out according to the methods reported previously.[9]

5. Pot Experiments

Pot experiments were carried out in a green-

Table 1 *Rf* values of pyrazolate and its related compounds.

Compound	TLC solvent system				
	A	B	C	D	E
Pyrazolate	0.82	0.89	0.99	0.99	0.99
DTP	0.19	0.49	0.81	0.36	0.71
5-CH_3O-DTP	0.72	0.85	—	0.95	0.95
1-H-DTP	0.37	0.76	0.96	0.57	0.49
3-CH_2OH-DTP	0.07	0.61	0.71	0.28	0.67
3-COOH-DTP	0.05	0.71	0.89	0.34	0.67
1,3-CH_3-PZO	0.03	0.53	0.72	0.73	0.38
3-CH_3-PZO	0.12	0.67	0.81	0.55	0.34
1,3-CH_3-4-OX-PZO	0.63	0.88	0.91	0.92	0.70
3-CH_3-4-OX-PZO	0.56	0.88	0.88	0.89	0.43
2,4-DCBA	0.88	0.81	0.99	0.30	0.49
2-CBA	0.83	0.84	—	0.40	0.47
4-CBA	0.87	0.89	—	0.60	0.44

A: hexane/ethyl acetate/formic acid (10/10/1), B: 1-butanol/acetic acid/water (8/1/1), C: ethyl acetate/methyl ethyl ketone/formic acid/water (5/3/1/1), D: chloroform/methanol/water (65/25/4), E: benzene/ethanol/28% ammonium hydroxide (6/5/1).

Table 2 Analysis data of soils used.

Source	Origin	Texture	pH (H_2O)	Organic matter (%)	C. E. C. (meq/100 g)	Clay (%)	ACPA[a)]
Shiga	Alluvial	Light clay	5.8	3.1	13.1	29.2	850
Iwate	Volcanic ash	Sandy loam	5.6	8.9	26.6	29.7	3300

a) Adsorption coefficient of phosphoric acid.

house. Each soil sample was packed in a 1/5000 are Wagner pot (200 cm^2) about 15 cm deep, and water was filled to 3 cm above the soil surface. After the soil was allowed to settle for 2 weeks, two rice seedlings (cv. Nihonbare) at the 2-leaf stage were transplanted to each pot early in June. A week after planting, the water was removed from the pots, and 6 mg of either ^{14}C(P)- or ^{14}C(B)-pyrazolate in acetone (2 ml) was applied evenly on the soil surface. The applied amount corresponded to 3 kg/ha of the active ingredient. Each pot was again watered, and the plants were allowed to grow until maturity (4 months after application). Fertilizers were applied according to agricultural practice. Watering was moderated during the last month of cultivation so that the pots were kept under upland conditions for the period. Air temperature and relative humidity ranged from 23 to 28°C and 40 to 85%, respectively.

After harvest, soil masses were crushed into pieces and stirred thoroughly to mix all the layers. Root fragments were removed from the soils as completely as possible. The homogeneity of the soils was confirmed by measuring radioactivity with aliquots of samples.

Rice plants were cut about 5 cm above the soil surface and separated into root, straw and unhulled rice. About 150 mg of unhulled rice was combusted in an oxidizer for radioassay. Ten replications were averaged. Straws and roots were cut into pieces, and each sample (10 g) was homogenized and extracted with 70% acetone/water in a Polytron homogenizer. The extracts and residues were radioassayed.

6. *Time Course Study on Pyrazolate and PTSA in Flask Models*

Shiga soil (50 g) or Iwate soil (25 g on an oven-dry basis) was placed in a 500-ml Erlenmeyer flask to attain a soil layer about 1 cm thick. The soils were flooded with water upto 1 cm deep and preincubated at 25°C in the dark for 2 weeks. ^{14}C(P)- or ^{14}C(B)-pyrazolate dissolved in acetone (0.5 ml) was applied to each flask at a concentration of 6 ppm on a soil weight basis.

In order to examine the degradability of PTSA coexisting with DTP, ^{14}C-PTSA dissolved in water was applied along with unlabeled DTP in acetone (0.5 ml) at respective concentrations of 2.4 and 3.9 ppm (the ratio corresponds to that of the molecular weight of each compound).

During the incubation, moistened CO_2-free air was supplied over the water surface at 30 ml/min, and the effluent air was passed serially through a trap containing Amberlite XAD-4 (20 ml) and two traps containing 40-ml portions of 2 N NaOH to collect volatile radiocarbon.

The degradation rate of pyrazolate and the relative amounts of major degradation products were determined by extracting the samples treated with ^{14}C(B)-pyrazolate. Metabolites of PTSA were not examined, except for the $^{14}CO_2$ evolved.

7. *Extraction and Fractionation of Soil Samples*

Our preliminary experiments showed that pyrazolate in soils was readily extractable with neutral organic solvents such as acetone and methanol, but a quantitative recovery of DTP from soils required repeated extractions with organic solvents under acidic conditions. Pyrazolate was also hydrolyzed to some extent during the extraction under acidic conditions. The following extraction procedures were hence employed in this study.

Soil samples (100 g aliquots) were extracted

3 times with 300-ml portions of methanol–H_2O (5/1) in a Waring blender for 10 min (neutral extract) and then 3 times with 300-ml portions of methanol–H_2SO_4 (2/1) [0.5 N for the Shiga soil and 2 N for the Iwate soil] (acidic extract). The blended material was allowed to centrifugal separation, and each extract was concentrated with a rotary evaporator. The aqueous solution of the neutral extract was adjusted to pH 9 with 0.1 N NaOH and shaken with diethyl ether and then with ethyl acetate to extract organo-soluble radiocarbon. The resulting aqueous phase was combined to the aqueous solution of the acidic extract and shaken with diethyl ether and then with ethyl acetate. The residual soil was extracted 2 times with 200-ml portions of aqueous NaOH [0.5 N for the Shiga soil and 2 N for the Iwate soil] (basic extract). The basic extract was adjusted to pH 2 with 9 N H_2SO_4 and shaken with diethyl ether.

Each of the organo-soluble fractions was radioassayed and examined by TLC, while the aqueous phases were radioassayed. The residual soil was combusted for radioassay. Recoveries from the soils separately spiked at 6.0 ppm for pyrazolate, 3.9 ppm for DTP and 2.6 ppm for 2,4-DCBA were more than 96%.

8. Identification of Degradation Products

Radioactive compounds in the organo-soluble fractions were separated and identified by co-TLC with authentic standards. For further characterization, major products (DTP, 1-H-DTP and 2,4-DCBA) were derivatized after extraction with methanol from the corresponding gel regions of TLC: both DTP and 1-H-DTP were tosylated with tosyl chloride while 2,4-DCBA was methylated with diazomethane, after fortified with an authentic standard. The derivatives were subjected to TLC.

RESULTS AND DISCUSSION

1. Balance of Total Radioactivity in Pot Plots

Table 3 shows the distribution of radioactivity remaining in the pot plots to which ^{14}C(P)- or ^{14}C(B)-pyrazolate was applied. On harvest (4 months after application) 71 to 90% of the applied radioactivity was recovered: 66 to 83% in the soils and 4.7 to 6.9% in the rice plants.

In the plants, most of the radioactivity was localized in the roots, while the unhulled grain contained barely detectable radioactivity (Table 4). This finding is in accordance with the results that DTP was metabolized mainly in the roots of rice plants and that the majority of DTP and its metabolites were retained in the roots.[10]

Irrespective of the ^{14}C-preparations of pyrazolate and the types of soil, only small amounts of radiocarbon in the soils was extractable with aqueous methanol, and the remaining radiocarbon was efficiently released by extractions under acidic conditions. Unextractable residues in the soils accounted for 5.5 to 8.3% of the applied ^{14}C.

Radioactivity unaccounted for decreased in the order of ^{14}C(B)-pyrazolate/Shiga, ^{14}C(B)-

Table 3 Balance of radiocarbon in pot plots 4 months after treatment with ^{14}C(P)- or ^{14}C(B)-pyrazolate.

Plot	In soil				In plant	Total
	Solvent extract		Unextractable	Subtotal		
	MeOH & MeOH/H_2SO_4	Aq. NaOH				
^{14}C(P)-Pyrazolate						
Shiga soil	56.8	13.0	8.3	78.1	5.6	83.7
Iwate soil	68.6	8.6	5.5	82.7	6.9	89.6
^{14}C(B)-Pyrazolate						
Shiga soil	47.8	11.4	7.0	66.2	4.7	70.9
Iwate soil	60.7	9.3	6.8	76.8	4.9	81.7

% of the applied ^{14}C.

Table 4 Distribution of ^{14}C in rice plants.

Plot	Unhulled grain	Straw	Root
^{14}C(P)-Pyrazolate			
Shiga soil	1.6	24.1	74.3
Iwate soil	1.4	7.3	91.3
^{14}C(B)-Pyrazolate			
Shiga soil	1.2	28.7	70.1
Iwate soil	1.1	15.2	83.7

% of the total ^{14}C in rice plants.

pyrazolate/Iwate, ^{14}C(P)-pyrazolate/Shiga and ^{14}C(P)-pyrazolate/Iwate plots. The unaccounted radioactivity was probably due to the $^{14}CO_2$ evolved during the cultivation, as shown by the evidence described in section *3*.

2. Degradation Products in Pot Soils

Table 5 summarizes the relative amounts of the degradation products isolated from the soils 4 months after application of ^{14}C(P)- or ^{14}C(B)-pyrazolate to the pots. Unchanged pyrazolate was less than 1.4% of the total ^{14}C in the soils or less than 1.2% of the applied ^{14}C. At least ten degradation products were found in the organo-soluble fraction, among which DTP, 5-CH_3O-DTP, 1-H-DTP, 3-CH_2OH-DTP, 3-COOH-DTP and 2,4-DCBA were identified. DTP was a major product, amounting to 45 to 63% of the total ^{14}C in the soils or 35 to 52% of the applied ^{14}C. 2,4-DCBA was another major product which amounted to 6 to 8% of the total ^{14}C in the soils.

Table 5 Relative amounts of degradation products of ^{14}C(P)- and ^{14}C(B)-pyrazolate in soils 4 months after application to pot plots.

	^{14}C(P)-Pyrazolate		^{14}C(B)-Pyrazolate	
	Shiga soil	Iwate soil	Shiga soil	Iwate soil
Organo-soluble				
Pyrazolate	0.8	1.4	1.1	0.8
DTP	44.5	62.6	53.2	61.3
5-CH_3O-DTP	0.5	0.4	0.7	0.5
1-H-DTP	1.9	1.9	2.0	3.1
3-CH_2OH-DTP	1.5	1.7	0.6	0.3
3-COOH-DTP	0.9	0.6	0.9	0.5
2,4-DCBA	—	—	8.3	5.7
Others	6.7	4.3	4.1	2.7
Water-soluble	33.6	20.5	18.6	16.3
Bound residues	10.6	6.6	10.5	8.8
Total	100.0	100.0	100.0	100.0

% of the subtotal ^{14}C in soil shown in Table 3.

Neither 1,3-CH_3-4-OX-PZO, 3-CH_3-4-OX-PZO, 1,3-CH_3-PZO nor 3-CH_3-PZO was detected in the extracts of the soils treated with ^{14}C(P)-pyrazolate. No degradation products derived from the pyrazole moiety were identified. This may be due to rapid degradation of the pyrazole moiety into polar materials.

Neither 2-CBA nor 4-CBA was detected as a degradation product of ^{14}C(B)-pyrazolate, which suggests that any reductive dechlorination of pyrazolate and its degradation products is unlikely to occur under normal paddy conditions.

3. Degradation of Pyrazolate and PTSA in Flask Models

Pyrazolate degradation in the flooded flask models is shown in Fig. 1. The half-life of pyrazolate was about 10 days in both Shiga and Iwate soils, and 90% of the chemical degraded in 4 to 6 weeks. In the pyrazolate degradation the amount of DTP increased for 2 to 4 weeks, reaching about 60% of the applied ^{14}C, and then gradually decreased. The amount of 2,4-DCBA reached a plateau at the level of 7 to 9% of the applied ^{14}C in 6 weeks and then decreased.

Throughout the experiments on volatile products from the soils treated with either the ^{14}C-preparations of pyrazolate or ^{14}C-PTSA, no radioactivity was detected in the XAD trap, while alkali trapped radiocarbon, which was determined to be $^{14}CO_2$, increased with time.

Figure 2 shows the evolution of $^{14}CO_2$ from the Shiga and Iwate soils treated with ^{14}C(P)- and ^{14}C(B)-pyrazolate. The cumulative amount of $^{14}CO_2$ was 3.9 to 6.1% for ^{14}C(P)-pyrazolate and 6.8 to 10.7% for ^{14}C(B)-pyrazolate in 8 weeks of incubation. $^{14}CO_2$ was evolved in a greater amount from the Shiga soil than from the Iwate soil, irrespective of the ^{14}C-preparations. The results were in agreement with the finding that the unaccounted radioactivity

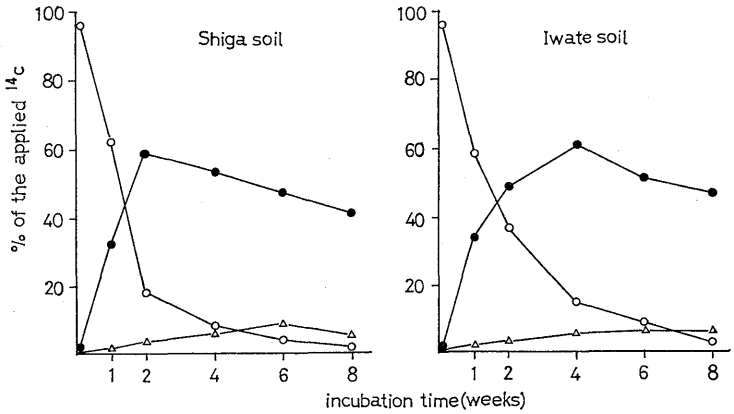

Fig. 1 Changes in amounts of pyrazolate, DTP and 2,4-DCBA in soils under flooded conditions (flask model).

○—○: pyrazolate, ●—●: DTP, △—△: 2,4-DCBA.

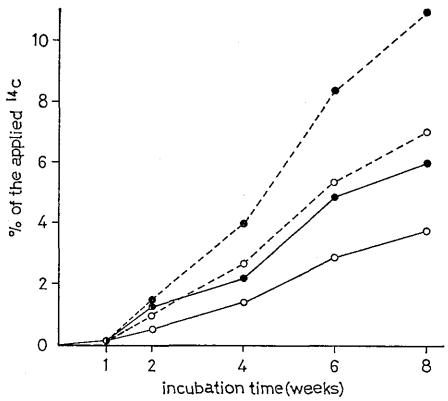

Fig. 2 Evolution of $^{14}CO_2$ from soils treated with ^{14}C-pyrazolate.

●···●: ^{14}C(B), Shiga soil, ○···○: ^{14}C(B), Iwate soil, ●—●: ^{14}C(P), Shiga soil, ○—○: ^{14}C(P), Iwate soil.

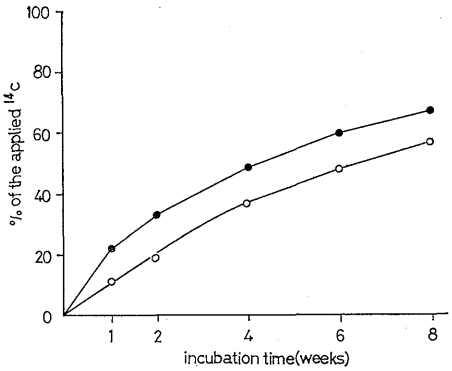

Fig. 3 Evolution of $^{14}CO_2$ from soils treated with ^{14}C-PTSA.

●—●: Shiga soil, ○—○: Iwate soil.

from the pot plots was the largest in the Shiga soil treated with ^{14}C(B)-pyrazolate and the smallest in the Iwate soil treated with ^{14}C(P)-pyrazolate, as described in section *1*.

As Fig. 3 shows, more than 55% of the applied ^{14}C was released as $^{14}CO_2$ from the ^{14}C-PTSA-treated soils in 8 weeks of incubation. The cumulative amount of $^{14}CO_2$ was larger in the Shiga soil than in the Iwate soil, as in the case of ^{14}C-pyrazolate.

4. *Metabolic Pathways*

Based on the identified products, the degradation routes of pyrazolate in the soils are summarized in Fig. 4. The first process was hydrolysis at the ester bond. The resulting PTSA was rapidly mineralized to CO_2. Although intermediates were not examined in this study, PTSA is known to be metabolized by soil microorganisms through oxidative desulfoxylation to 4-methylcatechol, followed by fission of the benzene ring to give propionaldehyde, pyruvic acid and formic acid.[11-14]

On the other hand, DTP was relatively persistent in the soils and the degradation

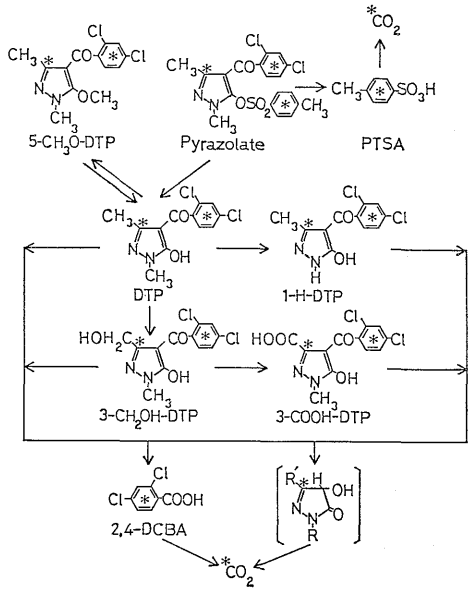

Fig. 4 Proposed degradation routes of pyrazolate in soils.

products were detected only to a limited extent. The degradation routes of DTP were demethylation of the 1-methyl group to 1-H-DTP, oxidation of the 3-methyl group to 3-CH_2OH-DTP and 3-COOH-DTP, and fission of the benzoyl bond to give 2,4-DCBA and the pyrazole moiety. A minor route involved methylation of the 5-hydroxy group to give 5-CH_3O-DTP. Both 2,4-DCBA and the pyrazole moiety were further broken down to polar materials and soil bound residues, and ultimately mineralized to CO_2. Although DTP is photodegradable in water,[15] the degradation in soil is apparently due to microbial metabolism, as supported by the information that DTP was metabolized by soil microorganisms, *Penicillium* spp. and the metabolites included all of the identified products described above (S. Kato, *et al.*, unpublished results).

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要　　約

除草剤ピラゾレートの水田土壌における分解

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中川昌之，石田三雄

ピラゾレートの土壌中での分解についてピラゾール環および塩素化ベンゼン環それぞれ別々に ^{14}C で標識した化合物を用いて室内条件で検討した．ピラゾレートはエステル結合の加水分解を受け，*p*-トルエンスルホン酸(PTSA) と除草活性の本体である 4-(2,4-ジクロロベンゾイル)-1,3-ジメチル-5-ヒドロキシピラゾール(DTP) を生成した．2種類の土壌中での湛水条件下での半減期は約10日であった．ベンゼン環を ^{14}C で標識した PTSA は土壌中で速やかに炭酸ガスにまで分解されたが DTP は徐々に分解された．DTP は1位と3位のメチル基の酸化，ベンゾイル結合の開裂，ピラゾール環およびベンゼン環の開裂を受け，最終的には炭酸ガスにまで分解された．