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Original Article

Adsorption and Desorption of DTP, the Herbicidal Entity of Pyrazolate, by Soils and Vertical Mobility of Pyrazolate and DTP in Paddy Fields

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The adsorption-desorption of DTP [4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-hydroxypyrazole], a hydrolysate and herbicidal entity of pyrazolate, was studied with various types of soil. The adsorption isotherms of DTP fitted the empirical Freundlich equation. Although distribution coefficients (*Kd*) of DTP significantly varied among the test soils, the soils had a great adsorptive capacity for DTP. Most of DTP adsorbed by the soils was gradually and steadily desorbed into water. In paddy fields where a granular formulation of 10% pyrazolate was applied, both pyrazolate and DTP, forming a treatment layer at the soil surface, were hardly mobile by leaching and gradually dissipated through biodegradation.

INTRODUCTION

Pyrazolate, 4-(2,4-dichlorobenzoyl)-1,3-dimethylpyrazol-5-yl-*p*-toluenesulfonate, is a herbicide for control of both annual and perennial weeds in paddy fields.[1] In Japan, granular formulations containing 10% pyrazolate, and consisting of 4 to 8% pyrazolate with other suitable herbicide(s) have been developed. Such formulations are usually applied at 30 kg/ha.

Pyrazolate is hardly soluble in water, whose solubility in distilled water is 56 ppb at 25°C (Fujimoto, unpublished). Once dissolved in water, however, pyrazolate is rapidly hydrolyzed to give *p*-toluenesulfonic acid and 4-(2,4-dichlorobenzoyl)-1,3-dimethyl-5-hydroxypyrazole; *i.e.*, destosyl pyrazolate (DTP).[2] DTP is the herbicidal entity of pyrazolate,[1,3-5] with its solubility in distilled water being 415 ppm at 25°C (Fujimoto, unpublished). Accordingly, pyrazolate is a chemically release-controlled agent.

We have reported that chemical hydrolysis is a predominant factor for the transformation of pyrazolate in the aquatic environment over metabolism and sunlight photolysis.[2] The hydrolysates, DTP and *p*-toluenesulfonic acid, are metabolized in soil and by soil microorganisms.[1,6] In paddy water, DTP undergoes sunlight photodecomposition.[7] In each case, these compounds are ultimately mineralized to evolve CO_2 without accumulating any intermediates.

Adsorption and desorption of a herbicide by soil are important factors which control the fate of the chemical in paddy fields, persistence of its herbicidal activity, mobility and microbial degradability in soils.

This study deals with the adsorption and desorption of DTP by soils, and vertical mobility of pyrazolate and DTP in paddy fields.

MATERIALS AND METHODS

1. *Chemicals*

^{14}C-DTP labeled at the 3rd position of the pyrazole ring was synthesized by Yanai.[8]

Its specific activity was 2.40 mCi/mmol with a radiochemical purity of more than 98% as determined by thin-layer chromatography followed by autoradiography and liquid scintillation counting. Unlabeled DTP and pyrazolate synthesized in the Agricultural Chemicals Research Laboratories, Sankyo Co., Ltd. were purified through repeated crystallization. A granular formulation of 10% pyrazolate produced by the Yasugawa Factory, Sankyo Co., Ltd. was used for a study on the vertical mobility of pyrazolate and DTP in paddy fields. *N*-(Naphthyl)-3, 4, 5, 6-tetrachlorophthalimide supplied by Ube Industry Ltd. was used as an internal standard for gas chromatographic analysis of pyrazolate and DTP.

2. *Thin-layer Chromatography* (*TLC*)

Precoated silica gel 60 F_{254} chromatoplates (20×20 cm, 0.25 mm thickness, Merck) were used. Solvent systems used were A) benzene/ethanol (9/1) and B) 1-butanol/acetic acid/water (8/1/1). *Rf* values of DTP were 0.17 and 0.49 for systems A and B, respectively.

3. *Radioassay*

Radioactivity was counted with an Aloka LSC-673 liquid scintillation counter. The scintillation solution was composed of 8.0 g of PPO and 0.2 g of dimethyl-POPOP in a mixture of 500 ml each of ethanol and toluene.

4. *Soil Samples*

Ten types of soil listed in Table 1 were collected from the surface layer of rice paddy fields at agricultural experimental stations in various districts in Japan. The physicochemical properties of the soils were determined by the Laboratory of Soil Science of Tokyo University of Agriculture. The soil samples were air-dried, crushed and passed through a 2-mm sieve, followed by a 0.2-mm sieve prior to the adsorption study.

5. *Adsorption Study*

5.1 *Adsorption isotherms*

A stock solution of a mixture of labeled DTP (1.75×10^{-5} M) and unlabeled DTP (6.839×10^{-4} M) was prepared with distilled water. Working solutions ranging from 2.5 to 200 μg/ml (0.53 to 42.09 nCi/ml) were prepared from the stock solution. The soils used for adsorption isotherms were two alluvial soils (No. 1 and No. 9) and one volcanic ash soil (No. 7). A 20 ml portion of the working solution was mixed with 2.0 g of a soil (air-dried basis) and the mixture was shaken for 1 hr at 20±1°C to attain to an equilibrium. The mixture was centrifuged at 2500 rpm for 20 min, and aliquots of the supernatant were taken for radioassay.

5.2 *Distribution coefficients* (*Kd*)

A working solution of DTP (100 μg/ml) was prepared from the stock solution. Two grams

Table 1 Physicochemical properties of soils examined.

Soil No.	Origin	Soil texture	pH (H_2O)	Organic matter (%)	CEC (meq/100 g)	Clay (%)	Fe(o) (%)	Fe(d) (%)	Fe(o)/Fe(d)
1	Alluvial soil	Light clay	5.77	3.09	13.10	29.19	1.62	2.02	0.80
2	Alluvial soil	Light clay	6.64	1.33	24.63	25.07	1.27	1.74	0.73
3	Alluvial soil	Light clay	5.60	2.25	21.76	40.97	1.15	1.43	0.60
4	Volcanic ash soil	Sandy clay	5.56	8.88	26.57	29.72	2.30	3.67	0.63
5	Volcanic ash soil	Light clay	5.75	10.59	30.15	40.75	2.74	4.95	0.55
6	Alluvial soil	Clay loam	6.31	2.35	7.81	16.83	0.53	0.85	0.62
7	Volcanic ash soil	Heavy clay	6.47	15.67	44.91	51.70	2.29	3.36	0.68
8	Alluvial soil	Light clay	5.14	2.43	18.06	27.46	1.16	1.44	0.81
9	Alluvial soil	Clay loam	6.14	2.75	14.73	23.27	0.53	1.63	0.33
10	Alluvial soil	Clay loam	6.50	2.60	8.45	17.74	0.28	1.06	0.26

Soil No. is arranged in the order of the *Kd* values listed in Table 2.

Fe(o): determined by the TAMM method. Fe(d): determined by the Mehra-Jackson method.

Fe(o)/Fe(d): the ratio of amorphous iron oxide to amorphous and crystalline iron oxides.

of soil was shaken with 20 ml of the working solution. After shaking for 1 hr at 20±1°C the soil suspension was centrifuged and radioactivity in the supernatant was assayed. Distribution coefficients (*Kd*) were calculated from the ratio of the amount adsorbed to the equilibrium concentration in the ambient solution; *i.e.*,

$$Kd = \text{adsorbed amount } (\mu g/g)/\text{equilibrium concentration } (\mu g/ml)$$

5.3 Soil saturation and desorption

A saturation and desorption study was conducted with soils No. 1, No. 7 and No. 9 to evaluate the adsorption capacity for DTP and the features of desorption of DTP. A 20 ml portion of the working solution containing 100 μg/ml of DTP (21.04 nCi/ml) was shaken with 2.0 g of a soil for 1 hr at 20±1°C and the soil suspension was centrifuged at 2500 rpm for 20 min. Aliquots of the supernatant were radioassayed to determine the amount of DTP adsorbed. A fresh working solution was added to the soil precipitates to maintain a 100 ppm level. This procedure was repeated ten times within a day. After the repeated adsorption experiments, 10 ml of the supernatant was replaced with 10 ml of distilled water. The mixture was shaken for 1 hr, followed by centrifugation and 10 ml of the supernatant was replaced with 10 ml of distilled water. This procedure was repeated 31 times, and aliquots of the supernatant were radioassayed each time. Radiocarbon in the supernatant at the 15th and 30th desorptions was thoroughly extracted with dichloromethane after acidifying to pH 2 with 0.01 N HCl, and the extract was concentrated and subjected to TLC with authentic DTP.

6. Vertical Mobility of Pyrazolate and DTP in Paddy Fields

6.1 Experimental plots

A leaching study was conducted with a couple of outdoor plots (0.3 m^2, $50^l \times 60^w \times 50^h$ cm) made of reinforced concrete with a hole for drainage at the basal part of a wall. The plots were first filled with sand up to 15 cm from the bottom, then with an alluvial soil collected at a local paddy field up to 10 cm from the top and lastly with water full to the top. After the plots were allowed to settle for 2 weeks, the paddy water was adjusted to 4 cm deep and the granular formulation of 10% pyrazolate was applied at 30 kg/ha (0.9 g/plot) in the middle of June. The paddy water of each plot was drained daily to a 2-cm level up the soil surface, and then each plot was watered to maintain the former level. When it rained, the plots were covered with a tent. Both paddy water and soil were sampled from the plots 15 days after application. The paddy water (200 ml each) was pipetted and the soil was collected into iron borers (5.3 cm i.d.×20 cm length) at eight locations in each plot. After frozen in a freezer, the soil samples were taken out of the borers after slightly warmed, and the frozen soil columns were cut with a cleaver into vertical sections.

Field tests were carried out at rice paddy fields in various districts in Japan. From the beginning to the middle of May 1975, the granular formulation of 10% pyrazolate was applied at 30 to 40 kg/ha. Two to nine months after application, soil samples were collected from vertical sections 30 cm deep from the surface at five locations in each field (about 10a).

The soil samples in each section were thoroughly mixed before analysis of pyrazolate and DTP.

6.2 Analytical method

Pyrazolate and DTP in the paddy water was thoroughly extracted with dichloromethane after acidifying to pH 2. The extract was washed with 0.01 N NaOH to remove DTP, and the aqueous phase was acidified and shaken with dichloromethane to recover DTP. The soil samples were extracted and cleaned up according to the procedure shown in Fig. 1.

Pyrazolate and DTP, which was derivatized with tosyl chloride to pyrazolate, were determined by gas-liquid chromatography with a Hewlett-Packard 7625A equipped with ^{63}Ni 2 mCi ECD. Column: a spiral glass tube (3 mm i.d.×40 cm length) containing 80–100 mesh Gaschrom Q coated with 3% SP-2401. Temperature: injection port 240°C, column oven 215°C and detector 260°C. PR-5 gas: for both carrier (240 ml/min) and purge gas (4.2 ml/min). Pulse interval: 50 μsec.

Recoveries from the soils spiked at 0.5 to 3.0 ppm were 95 to 99% for pyrazolate, and

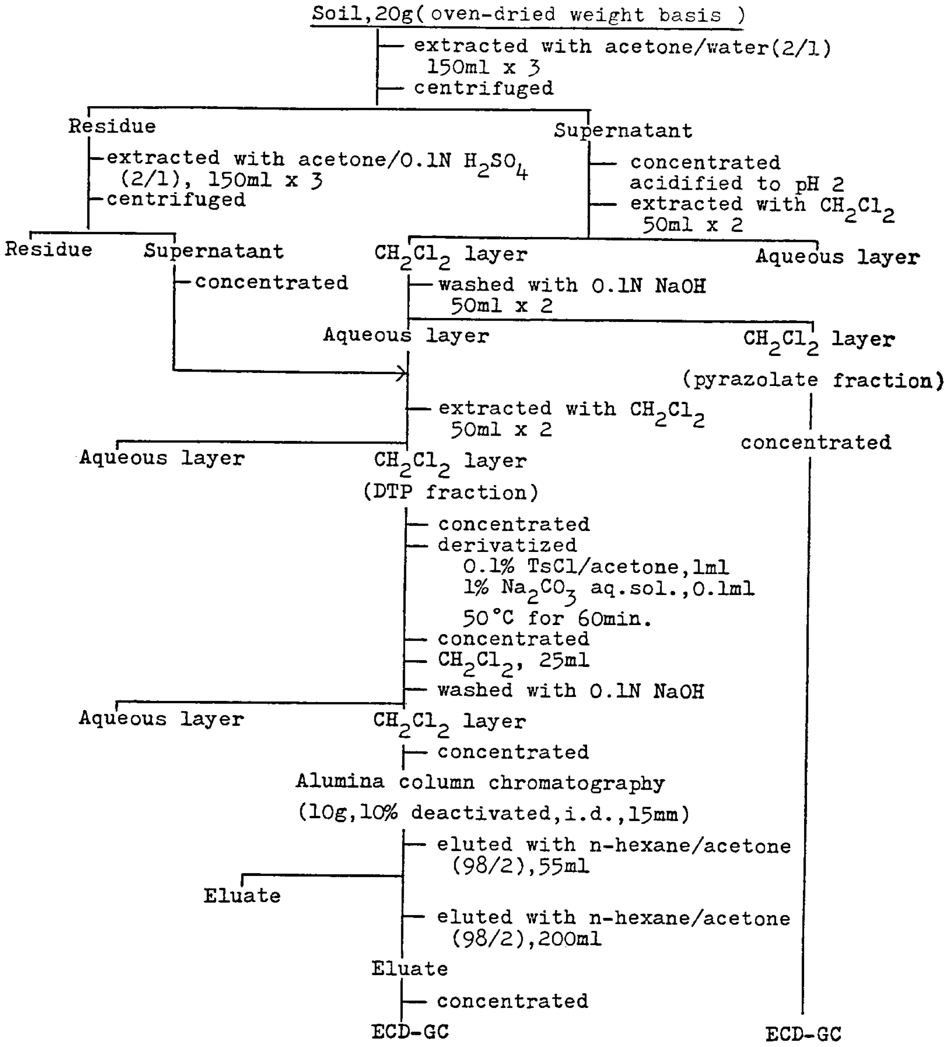

Fig. 1 Flow diagram of analytical method for pyrazolate and DTP residues in soils.

74 to 76% for DTP, and recoveries from the water more than 93% for both.

RESULTS

1. *Adsorption Isotherms and Distribution Coefficients* (*Kd*)

As Fig. 2 shows, the amount of DTP adsorbed by the soils against equilibrium concentrations was approximately linear on a logarithmic scale, so that the isotherms were expressed by the empirical Freundlich adsorption equation, which is

$$\log A = \log k + 1/n \log C$$

where, A is the amount of DTP adsorbed (μg/g), C is an equilibrium concentration (μg/ml), and k and $1/n$ are constants. The k values obtained from the isotherms were 2.85 for soil No. 9, 5.87 for No. 7 and 52.6 for No. 1. Values of $1/n$ were 1.15 for soil No. 7, 1.16 for

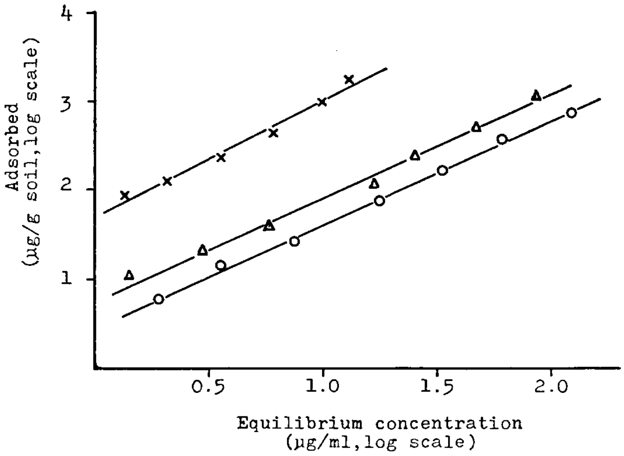

Fig. 2 Freundlich isotherms for the adsorption of DTP by soils.

×: Soil No. 1, △: Soil No. 7, ○: Soil No. 9.

No. 9 and 1.27 for No. 1. Since the $1/n$ values are close to 1, the adsorption isotherms are linear within the concentration range used.

As Table 2 shows, *Kd* values of the soils ranged from 4.1 to 95.7. The differences in the *Kd* values among the ten soils indicate that soil characteristics have a significant effect on DTP adsorption. No correlation was found, however, between the *Kd* values and the clay content ($r=0.0042$), the CEC ($r=-0.0780$) and the organic matter content ($r=-0.2561$) in the soils listed in Table 1. Since DTP is capable of forming metal complexes with cations of some metal species such as iron and aluminum,[1] correlation was examined between the *Kd* values and the content of free iron oxides in the soils. The correlation coefficients were 0.1822 for amorphous iron oxide (Fe(o)), −0.0259 for amorphous and crystalline iron oxides (Fe(d)) and 0.5476 for the ratio of Fe(o) to Fe(d). Thus, there was no correlation between the *Kd* values in Table 2 and each of the soil properties listed in Table 1. However, the relatively high correlation coefficient with the ratio of Fe(o) to Fe(d), which represents the activity of free iron oxides,[9] suggests that some type of metal oxides commonly distributed in soil is involved in DTP adsorption. No further effort was made to characterize the factors related to DTP adsorption.

Reports have shown that the amount of a herbicide adsorbed by soil highly correlates with organic matter content,[10,11] CEC[12] and clay content.[13,14] On the other hand, Saltzman *et al.*[15] reported that parathion adsorption by soil depends on a type of association between organic matter and mineral colloids. Hata *et al.*[16,17] reported that piperophos adsorption by soil varies depending on both the content and property of soil colloids. Hamaker & Thompson[18] reviewed the complexity of factors for adsorption of organic chemicals by soil and suggest that soil colloids such as clay minerals, clay-metal-organic matter complexes and hydrated metal oxides are involved in a soil's capacity to adsorb various organic compounds.

Table 2 Distribution coefficients (*Kd*) for the adsorption of DTP by various soils.

Soil No.	Distribution coefficient (*Kd*)
1	95.7
2	62.7
3	30.6
4	24.8
5	16.4
6	9.8
7	9.7
8	9.2
9	6.1
10	4.1

Initial concentration: 100 μg/ml.

These references and the results of correlation analyses described above indicated that clay-metal-organic matter complexes would influence the nature of the soil surface which is involved in DTP adsorption.

2. *Soil Saturation and Desorption*

Two alluvial soils with *Kd* values of 6.1 (soil No. 9) and 95.7 (soil No. 1) and one volcanic ash soil with a *Kd* value of 9.7 (soil No. 7) were used. The amount of DTP adsorbed was plotted against the number of repeated adsorptions in Fig. 3 (left). The amount of DTP adsorbed by the soils increased with repeated adsorptions for up to 10 times, and no soil reached saturation.

The features of DTP desorption from the soils are shown in Fig. 3 (right). DTP was gradually and steadily released into water, and a large portion of DTP was desorbed by successive extractions with water. The total DTP desorbed during the 31 desorptions amounted to 88% for soil No. 9, 83% for soil No. 7 and 60% for soil No. 1. The desorbed radiocarbon from each soil sample was identified as unchanged DTP.

3. *Vertical Mobility of Pyrazolate and DTP in Paddy Fields*

Table 3 shows the distributions of pyrazolate and DTP in the plots for the leaching test. The paddy water was drained by 2 cm daily for 15 days following the application of the granular formulation of 10% pyrazolate at 30 kg/ha (90 mg a.i./plot). The concentrations of both pyrazolate and DTP in the paddy water were very low compared with those in

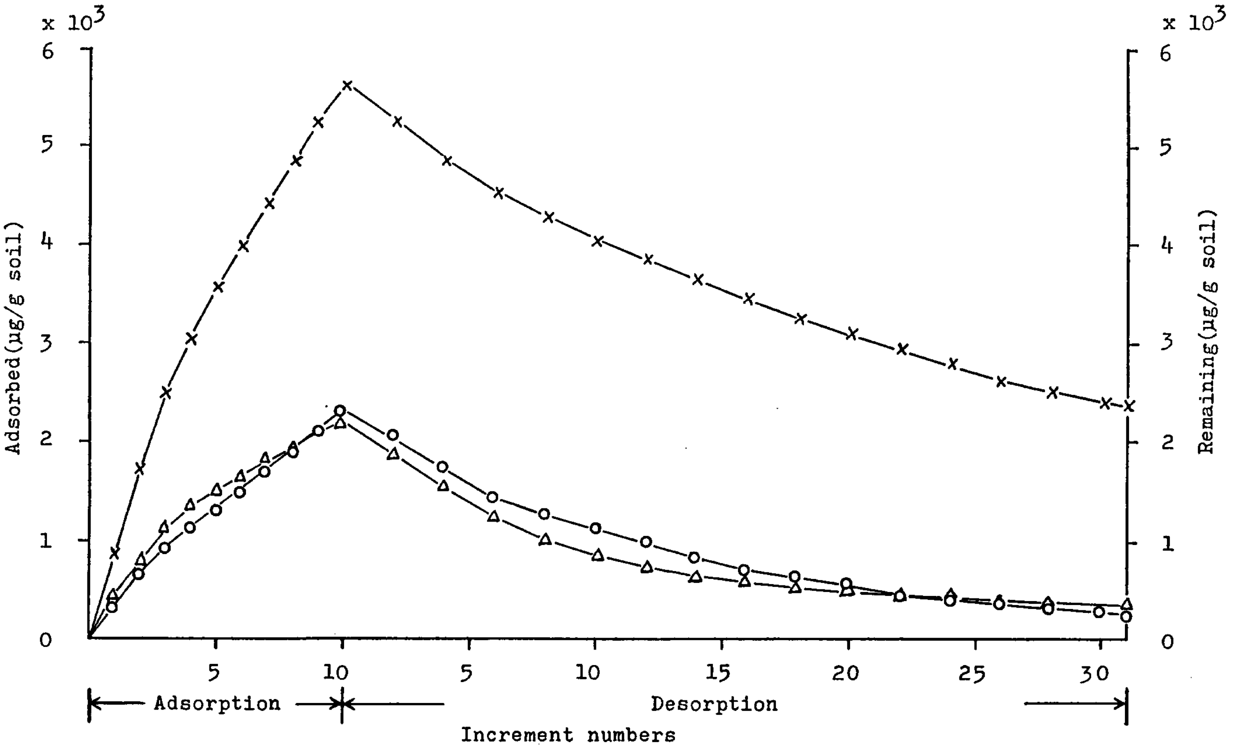

Fig. 3 Saturation of soils with DTP and desorption of DTP with water.
×: Soil No. 1, △: Soil No. 7, ○: Soil No. 9.

Table 3 Leaching of pyrazolate and DTP in paddy plot 15 days after application of pyrazolate.

Chemical	Pyrazolate	DTP
Paddy water	0.01	0.89
Soil		
0–5 (mm)	18.04[a]	8.78
5–15	0.43	0.46
15–25	n.d.[b]	n.d.
25–35	n.d.	n.d.

ppm.
[a] Theoretical value of the initial concentration in this layer of soil is 60 ppm.
[b] n.d.: not detected (<0.02 ppm).

the soil. The pyrazolate concentration in the water (0.01 ppm) was less than one-fifth the solubility in distilled water (0.056 ppm). Thus, the dissolution of pyrazolate from the granules into paddy water appears to be slower than hydrolysis of the dissolved chemical. Of both pyrazolate and DTP in the soil, the majority was retained at the surface layer (0–5 mm) and none was detected in the soil layers deeper than 15 mm. The results indicate that DTP as well as pyrazolate formed a treatment layer at the surface of paddy soil and were hardly mobile by leaching.

Tables 4 and 5 summarize the vertical distributions of pyrazolate and DTP in the paddy fields 2 to 9 months after the application of the pyrazolate formulation. Pyrazolate was detected only at the soil surface (0–5 cm). No DTP was detected in the soils deeper than 10 cm. The results, together with those of the leaching test described above, clearly show that both pyrazolate and DTP were moderately persistent in the environment and hardly mobile through soil layers.

DISCUSSION

The adsorption isotherms of DTP in the representative soils fitted the empirical Freundlich equation, and the data in Fig. 2 indicated that the amount of adsorbed DTP per g of soil varied significantly among the soils in a wide range of concentrations in the ambient solution. Indeed, the distribution coefficients (*Kd*) greatly varied among the ten types of soil, ranging from 95.7 to 4.1 at a concentra-

Table 4 Vertical distribution of pyrazolate and DTP in paddy soils (1).

District	Shiga					
Soil origin and texture	Alluvial, sandy loam					
Dosage (kg/ha)	30					
Days after application	58		98		129	
Chemical	Pyrazolate	DTP	Pyrazolate	DTP	Pyrazolate	DTP
Vertical section of soil						
0–5 (cm)	0.20	1.24	0.04	0.62	0.08	0.48
5–10	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
10–15	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
15–20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
20–30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

ppm, dry weight basis.
n.d.: not detected (<0.02 ppm).

Table 5 Vertical distribution of pyrazolate and DTP in paddy soils (2).

District	Miyazaki		Saga		Hyogo		Nagano	
Soil origin	Alluvial		Alluvial		Alluvial		Alluvial	
Soil texture	Clay loam		Silty clay		Clay loam		Sandy loam	
Dosage (kg/ha)	40		40		40		40	
Days after application	241		216		226		277	
Chemical	Pyrazolate	DTP	Pyrazolate	DTP	Pyrazolate	DTP	Pyrazolate	DTP
Vertical section of soil								
0–3 (cm)	n.d.	0.13	n.d.	0.23	0.20	0.58	0.25	0.40
3–10	n.d.	n.d.	n.d.	0.05	n.d.	0.08	n.d.	0.13
10–20	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.
20–30	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.

ppm, dry weight basis.
n.d.: not detected (<0.02 ppm).

tion of 100 μg/ml.

However, the soils were found capable to adsorb a large amount of DTP, and no saturation was achieved even after ten applications of 2 g soil/20 ml of 100 ppm solution. As shown in Fig. 3, the amount of DTP adsorbed by the soils increased with applications, and the adsorbed DTP was gradually and steadily desorbed into water, indicating the reversibility.

Accordingly, it is very likely that DTP in paddy fields is in a state of adsorption-desorption equilibrium which lies by far to the adsorption side, while unadsorbed part of the chemical is bioavailable to plants and microorganisms to undergo biodegradation. In fact, DTP as well as pyrazolate formed a treatment layer on the surface of soil in the paddy fields, were hardly mobile by leaching and gradually dissipated. The other hydrolysate of pyrazolate, *p*-toluenesulfonic acid, has been proved to undergo biodegradation in a paddy system so rapidly that the compound released from pyrazolate granules does not accumulate at all.[1]

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要約

ピラゾレートの除草活性本体DTPの土壌による吸着・脱着および水田におけるピラゾレートとDTPの垂直移動性

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ピラゾレートの加水分解産物で除草活性の本体であるDTP[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]の土壌による吸着・脱着について検討した．DTPの吸着等温線は経験的なフロイントリッヒの式に適合した．DTPの吸着分配定数（*Kd*）は土壌間で大きく異なったが，土壌のDTP吸着容量は総じて大であった．土壌に吸着されたDTPの大部分は少量ずつ，しかし着実に水に脱着された．ピラゾレート10%粒剤を散布した水田において，ピラゾレートおよびDTPは土壌表層で処理層を形成し，リーチングによってほとんど移動せず，生分解によって徐々に消失した．