Original Article

Persistence of Isoprothiolane in Paddy Water and Rice Plants after Submerged Applications

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(Received March 18, 1982)

Persistence of isoprothiolane in paddy water and rice plants was studied by submerging its 12% granules at various stages of growth. The concentration in paddy water reached a maximum of 3-8 ppm within 1-3 days, and then decreased rapidly with a half life of 4 days. However, that in the plants changed more slowly so that the peak concentration was obtained 3-11 days after the application. The peak level in the shoots of plants was almost identical (4-8 ppm) when the granules were submerged. Therefore, the incorporated amount of the compound corresponds with the size of the plants. The compound then disappeared with a half life of about a month. However, the concentration in the shoots reduced more rapidly when dilution by new growth could accelerate it. After the panicles had headed, they progressively accumulated the compound. Their concentration was always lower than, but well related with, that in the other parts in which the compound was almost uniformly distributed. The residues in hulled rice and straws were nicely correlated with the number of days after application. These changes of isoprothiolane in rice plants should explain the residual effect against rice blast and planthoppers.

INTRODUCTION

Rice blast caused by *Pyricularia oryzae* Cav. is the most damaging disease in Japanese rice culture. A good blast controlling agent should minimize outbreaks of the disease. However, it is very difficult to prevent them completely since the fungal pathogen continuously attacks the plants throughout the season.¹⁾ Isoprothiolane (Fuji-one®, Diisopropyl 1,3-dithiolan-2-ylidenemalonate) exhibits a residual effectiveness against the blast, as well as against two major rice planthoppers, *Nilaparvata lugens* Stål and *Sogatella furcifera* Horváth, especially when its granules are directly applied into paddy water.^{2,3)}

Although various factors including soil adsorption lower the availability to the root system,⁴⁾ rice plants can absorb and easily translocate the compound acropetally.^{5,6)} There is no detailed study, however, on its persistence in paddy fields, which is one of the

most important characters for ensuring residual effectiveness. In the current report, the persistence of isoprothiolane in paddy water and rice plants after submerged applications at various stages of growth will be discussed.

MATERIALS AND METHODS

Isoprothiolane: A 12% granular formulation of isoprothiolane was used throughout the study.

Analysis: The compound in water and rice plants was extracted with benzene : acetone (1 : 1), cleaned up by partitioning and Florisil column chromatography and analyzed by gas chromatography as previously reported.⁷⁾

Field: The experimental field, which was located in Kawachi-Nagano, Osaka, was divided into 21 plots 5×5 m each with 1 m intervals between them. Rice plants, *Oryza sativa* (L.) cultivar. Tozan No. 38, were transplanted with a density of 25 hills/m² on June 23, 1977 and supplied with 50 kg/ha of ammonium

sulfate as a fertilizer and 30 kg/ha of X-52 (7% granules of chlomethoxynil) as a pre-emergence herbicide on June 25. Three plots were treated with 12% isoprothiolane granules at the rate of 40 kg/ha on July 1, 10, 26, August 5, 10 or 20. After the treatment, paddy water (100 ml) and rice plants (10 shoots) were randomly sampled, weighed and then stored at -20° until the analysis. Leaf blades, stems and panicles were separately analyzed if possible. Rice was harvested and threshed on November 1 and 18, respectively.

RESULTS AND DISCUSSION

1. Growth of Rice Plants

The fresh weight of the shoots of rice plants first increased logarithmically until August 25 to become 50 times as much as that (0.15 g/shoot) on July 1. Then it remained almost unchanged for about a month, but finally decreased gradually after September 29 probably due to drying (Fig. 1). During the drying, the shoots lost about 50% of their maximum weight so that weight at harvest was 4 g/shoot. Stems grew in a manner similar to that of the growth of the whole shoots. However, leaf blades gained their peak weight and started to lose it 2 weeks earlier than the other parts. The total weight of the shoots was attributable mainly to leaf blades in the

Fig. 1 Weight changes of the shoots and their parts of rice plants on paddy fields.

The rice plants were transplanted with a density of 25 hills/m² on June 23, harvested and threshed on November 1 and 18, respectively.

early stage of growth, then to stems after August 15, and finally to the panicles.

The panicles headed on September 5 when the logarithmic growth of leaves ended. They then continued to grow logarithmically until September 29. Even after the other parts began to dry, no dramatic loss of weight was observed in the panicles. Thus, this part finally became heavier than any other part of the rice plant shoot. Similar growth patterns have been obtained for other crops such as oat, *Avena sativa* (L.).⁸⁾

2. Isoprothiolane in Paddy Water

After the submerged applications, the compound concentration in paddy water reached a maximum of 3–7 ppm within 1–3 days. Thus, the compound in its granules seemed to be easily released into water. Probably due to various factors including soil adsorption,⁴⁾ biodegradation and photodecomposition, it then disappeared rapidly with a half life of 4 days so that its concentration became less than 0.1 ppm one month after the applications (Fig. 2). Whenever the compound was applied by submerging its granules, the concentration in paddy water showed a similar change.

Fig. 2 Concentration of isoprothiolane in paddy water after its granules containing 12% active ingredient were submerged at the rate of 40 kg/ha on July 1, 10, 26, August 5, 10 or 20.

Table 1 Residues of isoprothiolane in rice plants after submerged applications.

Sampling date	Isoplothiolane concentration (ppm)												
	Application date ^{a)}			July 1			July 10			July 26			
	Sampled portion	Stem	Leaf blade	Panicle	Whole shoot	Stem	Leaf blade	Panicle	Whole shoot	Stem	Leaf blade	Panicle	Whole shoot
July	2	— ^{b)}	—		1.98								
	4	7.57	5.60		6.47								
	6	—	—		5.59								
	8	—	—		4.37								
	13	—	—		—	—	—	—	2.97	—	—	—	—
	15	1.36	2.28		1.86	4.86	2.17	—	3.16	2.16	1.32	—	1.68
	17	—	—		—	5.19	3.50	—	4.04	—	—	—	—
	18	0.80	1.52		1.20	—	—	—	—	—	—	—	—
	20	—	—		—	2.12	3.33	—	2.71	—	—	—	—
	22	1.93	3.58		2.77	—	—	—	—	—	—	—	—
Aug.	26	—	—		—	1.87	5.45	—	3.84	2.16	1.32	—	1.68
	27	—	—		—	—	—	—	—	—	—	—	—
	31	1.49	4.40	—	3.04	2.01	3.79	—	2.91	—	—	—	—
	1	—	—		—	—	—	—	—	3.93	5.35	—	4.78
	3	—	—		—	1.08	0.11	—	0.48	2.43	5.38	—	4.19
	5	—	—		—	—	—	—	—	5.70	4.57	—	5.04
	6	—	—		—	—	—	—	—	—	—	—	—
	9	—	—		—	1.08	1.86	—	1.53	2.03	3.17	—	2.67
	10	0.44	1.03		0.74	—	—	—	—	—	—	—	—
	11	—	—		—	—	—	—	—	—	—	—	—
Nov.	12	—	—		—	—	—	—	—	—	—	—	—
	13	—	—		—	—	—	—	—	—	—	—	—
	16	—	—		—	—	—	—	—	1.62	3.03	—	2.21
	19	—	—		—	—	—	—	—	1.58	2.35	—	1.92
	20	—	—		—	—	—	—	—	—	—	—	—
	21	—	—		—	—	—	—	—	—	—	—	—
	25	—	—		—	—	—	—	—	—	—	—	—
	27	0.16	0.21	0.013	0.17	0.72	0.92	0.491	0.77	—	—	—	—
	30	—	—	—	—	—	—	—	—	—	—	—	—
	6	0.24	0.20	0.080	0.21	1.64	1.34	0.213	1.42	1.57	1.67	0.480	1.51
16	0.16	0.07	0.043	0.13	0.77	0.68	0.057	0.63	1.88	0.98	0.071	1.35	
29	0.17	0.13	0.137	0.15	0.60	0.23	0.376	0.47	1.27	0.73	0.079	0.92	
18	<0.03	<0.03	<0.006	<0.03	0.75	0.68	<0.006	0.31	2.32	1.33	0.013	0.84	

Table 1 (continued)

Sampling date	Application date	Isoplothiolane concentration (ppm)											
		Aug. 5				Aug. 10				Aug. 20			
		Stem	Leaf blade	Panicle	Whole shoot	Stem	Leaf blade	Panicle	Whole shoot	Stem	Leaf blade	Panicle	Whole shoot
July 2													
4													
6													
8													
13													
15													
17													
18													
20													
22													
26													
27													
31													
Aug. 1													
3													
5													
6		1.31	0.46		0.81								
9		2.01	1.52		1.74								
10		3.85	4.14		4.00								
11		—	—		—	1.92	0.11		0.97				
12		—	—		4.39	—	—		—				
13		—	—		—	—	—		4.02				
16		—	—		—	—	—		—				
19		2.48	3.80		2.90	—	—		—				
20		3.26	3.02		3.18	2.98	3.99		3.41				
21		—	—		—	—	—		—				
25		1.51	2.70	0.364	1.73	7.02	5.92	0.431	6.38	0.83	0.38		0.64
27		—	—	—	—	2.51	3.84	0.437	2.80	7.34	4.86	0.753	6.28
30		1.34	1.91	0.264	1.36	7.14	3.65	1.020	5.67	3.86	2.95	0.643	3.37
Sept. 6		2.75	3.66	0.880	2.82	4.89	7.24	1.000	5.11	2.06	2.90	0.374	2.19
16		2.66	2.12	0.109	2.09	4.15	3.56	0.165	3.10	6.43	3.83	1.410	5.29
29		0.38	2.22	0.224	0.79	3.45	2.69	0.358	2.47	4.79	4.82	0.679	4.07
Nov. 18		3.17	2.17	0.021	1.20	5.58	3.01	0.050	2.01	2.65	8.49	2.470	3.73
										6.25	5.66	0.136	2.61

a) Twelve % isoprothiolane granules were submerged into paddy water at the rate of 40 kg/ha on the indicated date.

b) Not determined.

a) Twelve % isoplothiolane granules were submerged into paddy water at the rate of 40 kg/ha on the indicated date.

b) Not determined.

3. Isoprothiolane in Rice Plants

The isoprothiolane concentrations in rice plants treated by submerging its granules are summarized in Table 1. The concentration in the shoots of rice plants progressively increased to reach a maximum of 4–7 ppm within 3–11 days. Since it then decreased gradually, the residual level at harvest ranged from less than 0.03 to 2.6 ppm, showing a correlation with the number of days between the applications and the harvest. The concentrations in leaf blades and stems showed a similar pattern to each other (Fig. 3), giving the peak concentrations 4–7 and 4–8 ppm, respectively (Table 1). This meant that the compound was uniformly distributed throughout the shoots of the plants. The increase of concentrations in the leaves after September 29 must be due to drying or the resulting loss of weight (Fig. 1).

During the logarithmic growth, the panicles progressively accumulated the compound to various peak concentrations ranging from 0.1 to 2 ppm (Table 1). Although the concentration in the panicles was much lower than that in other parts of the shoots, there existed a good relationship between concentrations in the panicles and in the leaf blades (Fig. 3), suggesting that the compound in leaves is mobile toward the panicles. This movement may contribute to the unique residual effective-

ness against panicle blast, which usually causes more crucial damage than leaf blast.²⁾

The acropetal movement of isoprothiolane in rice plants via the root system has occurred in the apoplast or as a mass flow from the root system to the leaves in the transpiration stream.⁵⁾ However, chemicals which have reached the leaves in the apoplast cannot be redistributed in plants in the same system.⁹⁾ Since movement from the leaves into other parts of the plants usually occurs in the symplast, the isoprothiolane accumulation in the panicles is a very interesting phenomenon especially since the compound in paddy water has become negligible.

After the panicles stopped growing on September 29, the concentration in them fluctuated and gradually reduced. The residue in the harvested panicles varied from less than 0.006 to 0.14 ppm, depending on that in other parts of the plants or the number of days between the applications and the harvest.

Isoprothiolane residues in rice straw and hulled rice are summarized in Table 2. There are again splendid relationships of isoprothiolane residues with intervals between the applications and the harvest (Fig. 4). The permissible residual limit in hulled rice is less than 2 ppm.

Even after the concentrations in the shoots started to decrease, the amount of the compound still continued to increase, although it soon reached a maximum of 7–50 $\mu\text{g}/\text{shoot}$ (Fig. 5). Here, an earlier application gave a smaller uptake by the plants. As shown in Table 1, however, the peak concentrations in the shoots were almost identical (4–8 ppm) whenever isoprothiolane granules were applied. These results suggest a possible relationship between the uptake and the size of the plants; indeed, there is good relationship between the peak amount of isoprothiolane in the shoots and their weight (Fig. 5). Since the half life seemed to be independent of the amounts, different peak amounts in the plants should result in different residual levels at harvest (Fig. 5).

Thus, isoprothiolane seems to be stable and persistent enough in rice plants to show a residual effectiveness against rice blast and planthoppers for more than a month.⁹⁾ How-

Fig. 3 Relationships among isoprothiolane concentrations in the rice leaf blades, stems and panicles on September 6.

Twelve % granules of isoprothiolane were submerged at the rate of 40 kg/ha on July 1, 10, 26, August 5, 10 or 20.

Table 2 Residues of isoprothiolane in hulled rice and straws.

Application date ^{a)}	Number of days between applications and harvest	Residue (ppm) in	
		Hulled rice	Rice straw
July	1	<0.006	<0.03
	10	<0.006	0.69
	66	0.013	1.65
Aug.	5	0.024	2.55
	10	0.040	4.05
	20	0.066	5.55

^{a)} Twelve % isoprothiolane granules were applied to paddy water at the rate of 40 kg/ha. Rice plants were harvested on November 1.

Fig. 4 Relationships of isoprothiolane residues in hulled rice and rice straw with the number of days between applications and harvest.

ever, the concentration in plants often decreases rapidly since dilution by new growth accelerates it. Such a situation has also been shown in investigations on the effect of isoprothiolane submerged at various stages of plant growth.³⁾ When the granules are applied in June or early July, an additional application is sometimes needed to ensure the control of such pests as rice blast and planthop-

Fig. 5 Changes of isoprothiolane amounts incorporated by the shoots of rice plants after the granules containing 12% active ingredient were submerged at the rate of 40 kg/ha on July 1, 10, 26, August 5, 10 or 20.

The dotted line indicates the mean weight ($\times 10^{-5}$) of a rice plants shoot.

pers throughout the season of rice culture.

ACKNOWLEDGEMENTS

The authors thank Misses S. Nagaoka and N. Michibata for their technical assistance throughout the study.

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要 約

水面施用したイソプロチオランの田面水および稲体中での消長

金内正俊, 内田又左衛門, 土屋勝夫
イソプロチオラン (フジワン®) 12% 粒剤を 40 kg/ha の割合で時期を変えて水面施用し, 田面水中および稲体中での消長をみた。田面水中濃度は, 施用時期にかかわらず 1~3 日で最高値 (3~8 ppm) となり, その後速やかに消失した (半減期 4 日)。稲体中濃度はより緩やかに変化し, 3~11 日で最高値 (4~8 ppm) となった。稲体中最高濃度が施用時期にかかわらずほぼ同一レベルになったことは, 吸収量が稲の大きさと相関していたことになる。稲体内に吸収されたイソプロチオランは, その後半減期 1 カ月で減少したが, 早期施用の場合には新たな生育による希釈のためか, より速い濃度減少もみられた。葉身部と葉鞘部では濃度消長はおおむね一致し, イソプロチオランが茎葉部に均一に分布することを示唆した。しかし, 穂部では常にこれより低く推移し, 玄米中残留も <0.006~0.066 ppm と低かった。玄米中の残留値は, 稲わらのそれと同様に, 施用から収穫までの期間が長くなるほど低くなっていた。このようなイソプロチオランの消長は, そのイモチやウンカに対する持続効果との関連できわめて重要な知見といえよう。