Thenylchlor Concentration in Soil Water and its Herbicidal Activity

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Abstract: The herbicidal activity of soil applied thenylchlor [2-chloro-*N*-(3-methoxy-2-thienyl) methyl-2', 6'-dimethylacetanilide] on *Echinochloa crus-galli* Beauv. var. *formosensis* Ohwi was more remarkable in Ryugasaki paddy soil than in Yawara paddy soil. The soil applied with thenylchlor solution was separated into centrifuged-soil and plant available soil water by centrifugation. The amount of thenylchlor in the soil water was greater in Ryugasaki soil than in Yawara soil, whereas the amount in the fresh-soil and the centrifuged-soil were found greater in the latter. The growth of *E. crus-galli* in thenylchlor solution directly prepared was suppressed so that it was similar to that in the soil water from soils previously applied with the herbicide. The metabolites of thenylchlor in soil had no herbicidal activity on the weed. It was suggested that the herbicidal activity of thenylchlor applied to soil was dominated by the concentration in plant available soil water.

Key words: Thenylchlor, concentration in soil water, herbicidal activity, adsorption in soil, *Echinochloa crus-galli*.

Introduction

Thenylchlor [2-chloro-*N*-(3-methoxy-2-thienyl) methyl-2', 6'-dimethyl acetanilide]

(NSK-850) is a newly developed α -chloro-acetamide herbicide for annual and perennial paddy weeds and selectively controls the weeds when applied to the transplanted rice paddy fields^{4~7}. The downward mobility of thenylchlor in soil was relatively slight but was affected by the soil characteristics⁵. It is well-known that the adsorption in soil and activity of an herbicide on plant growth is influenced by the characteristics of the soil, but there has been little information generated on the relationship between herbicidal activity and the performance in soil. Our previous studies^{10~13} revealed that the herbicidal activity of butachlor [*N*-(butoxymethyl)-2-chloro-2', 6'-diethylacetanilide], pretilachlor [2-chloro-2', 6'-diethyl-*N*-(2-propoxyethyl) acetanilide], mefenacet [2-benzothiazol-2-yloxy)-*N*-methylacetanilide] and metolachlor [2-chloro-2'-ethyl-*N*-(2-methoxy-1-methylethyl)-6'-methylacetanilide] was well correlated with the concentration of water-soluble ingredients in soil, and suggested that herbicidal activity of soil applied herbicide was dependent on the concentration in soil water. In these studies, however, the water-soluble ingredient was extracted with added water from the herbicide-applied soil. Hence, it could not be determined whether the soluble ingredient in water extracts is contained in the soil water itself, especially in plant available soil water².

The objective of the present study was to clarify the relationship between the concentration of thenylchlor in plant available soil water and its herbicidal activity.

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Materials and Methods

Soils and thenylchlor application

Soils were collected from paddy fields located in Yawara and Ryugasaki, Ibaraki prefecture, Japan¹⁰⁾. Two hundred grams of air-dried soil was put into 500 ml of aqueous thenylchlor solution containing 0.1% acetone at various designated concentrations (Table 1), and vigorously stirred with the thenylchlor solution in a beaker. The prepared-soil was then placed in a plastic pot (5 cm in diameter and 4 cm in height) with holes in the bottom, and allowed to stand for several hours to reach maximum water capacity (63.8% for Yawara and 49.5% for Ryugasaki soil) by remov-

ing the gravitational water, hereinafter referred to as fresh-soil.

Extraction and determination of thenylchlor in soil

The soil applied with thenylchlor solution was centrifuged with double tubes at $13,000 \times g$ for 40 min to separate it into a solution which collected in the bottom of the outer tube and the soil remaining in the inner tube using the modified method of Seto⁸⁾ (Fig. 1); the soil water (40.1% for Yawara soil and 36.8% for Ryugasaki soil) was generally considered as plant available water²⁾ (the former and the latter was hereafter abbreviated as available soil water and centrifuged-soil, respectively). After the

Fig. 1. Scheme for determination of thenylchlor content in soil and soil water.

centrifugation, the water contained in the centrifuged-soil, most of which was considered hygroscopic water, was 23.7% for Yawara soil and 12.7% for Ryugasaki soil. Thenylchlor extracted from the soil water was prepared for gas chromatographic (GC) analysis in a similar method to that used for metolachlor¹³⁾. Thenylchlor in the centrifuged-soil was extracted with acetone, the acetone solution was concentrated and then extracted with *n*-hexane. The amount of thenylchlor was determined by GC (HP 5890) with N-P FID using a glass column packed with 2% OV-101 on 100-120 mesh chromosorb W operating at 245°C. The carrier gas was nitrogen at 25 ml/min, the air flow rate at 100 ml/min and hydrogen flow rate at 3.5 ml/min, respectively. The detector and injection port was held at 270°C. The detectable limit of thenylchlor was 0.008 ppm, and the recoveries from the centrifuged-soil and the soil water were over 90%.

Plant materials and bioassay

Seeds of *E. crus-galli* were soaked in distilled water at 28°C for one day. Effect of thenylchlor and the metabolites of thenylchlor, reported by Hirao *et al.*¹⁾, 2-chloro-2', 6'-dimethylacetanilide (M-1), *N*-(3-methoxy-2-thienyl) methyl-2', 6'-dimethylacetanilide (M-2), 2-hydroxy-*N*-(3-methoxy-2-thienyl) methyl-2', 6'-dimethylacetanilide (M-3), and 2', 6'-dimethylacetanilide (M-4) in soil¹⁾, on the growth of *E. crus-galli* was examined in soil culture, soil water culture and

water culture. In soil culture, the germinated seeds were planted and covered with the soil to which thenylchlor had earlier been applied in the plastic pot as described above. In water culture, the germinated seeds were placed in 3 ml solution of thenylchlor or the proposed metabolites at various designated concentrations with 0.1% acetone in a vial (2 cm in diameter and 4 cm in height). In soil water culture, the weed was grown in the soil water centrifuged as available soil water from the soil previously applied with thenylchlor solution, and the bioassay was carried out in the same way as that in water culture. The plants in the vial were placed in an incubator (25°C, 14 hr-illumination at 4 Klux) for 3 days, and the shoot length was measured.

Three replications were made of all treatments.

Results

Table 1 shows the growth of *E. crus-galli* and the amount of thenylchlor actually contained in fresh-soil, centrifuged-soil and available soil water. The growth of *E. crus-galli* was suppressed more remarkably in Ryugasaki soil than in Yawara soil applied with the aqueous solution of thenylchlor at 0.3 and 1.0 nmol/ml in soil culture. The amount of thenylchlor in available soil water was much greater in Ryugasaki soil than in Yawara soil, whereas in both the fresh- and the centrifuged-soil it was less in the Ryugasaki than in the Yawara soil. The result

Table 1. Growth of *E. crus-galli* and amount of thenylchlor in Yawara and Ryugasaki paddy soils applied with various concentrations of solution.

Concentration applied (nmol/ml)	Amount of thenylchlor determined						Plant growth	
	Fresh-soil (nmol/ml)		Centrifuged-soil (nmol/ml)		Available soil water (nmol/ml)		Shoot length (% of control)	
	Y*	R*	Y*	R*	Y*	R*	Y*	R*
0.1	0.399	0.197	0.645	0.331	ND**	ND**	101.5	99.8
0.3	0.538	0.307	0.847	0.509	0.018	0.041	85.3	56.8
1.0	1.481	1.192	2.296	1.986	0.043	0.119	66.4	35.9
3.0	7.414	4.973	11.368	8.277	0.237	0.570	25.4	25.6

* Y: Yawara paddy soil, R: Ryugasaki paddy soil.

** ND: not detected.

Fig. 2. Growth of *E. crus-galli* in available soil water and in distilled water containing thenylchlor and the proposed metabolites at various concentrations.

demonstrated that the greater herbicidal activity in Ryugasaki soil coincided with the higher amount of the herbicide in soil water but not with the amount in the fresh- or the centrifuged-soil. This indicated that the herbicidal activity essentially reflected the herbicidal concentration in available soil water but not that in fresh-soil and centrifuged-soil.

The growth of *E. crus-galli* in the thenylchlor solution directly prepared was suppressed to a similar extent to that in the available soil water from Ryugasaki and Yawara soil previously applied with the herbicide (Fig. 2). None of the proposed metabolites of thenylchlor showed herbicidal activity. Thus the herbicidal activity of soil applied thenylchlor appeared to be dependent on the concentration in available soil water but not on the amount in the fresh-soil.

Discussion

With respect to the relationship between the performance of soil applied herbicide in soil and herbicidal activity, it has demonstrated that herbicidal activity was closely related to the amount of water-soluble ingredient^{3, 9-13}. In these studies, however, it was not clear whether the ingredient was actually contained in the soil water, especially in the plant available water in soil. Here, the amount of thenylchlor in soil water was directly separated by centrifugation from soil previously applied with the herbicide,

and it was found that the greater herbicidal activity of thenylchlor in Ryugasaki soil than in Yawara soil was correlated well to its higher concentration in the plant available soil water from the former but not to the amount in the fresh-soil, in which the plant actually grew.

It thus appears that the herbicidal activity of soil applied thenylchlor is substantially induced by the quantity of herbicide in plant available soil water. Comparing Ryugasaki soil with Yawara soil, a good correlation was noted between the greater herbicidal activity and the higher concentration in plant available soil water in the former. Given the relationship between the herbicide adsorption in soil and the soil characteristics, it is generally accepted that the amount of adsorption is largely influenced by soil organic matter. Consequently, a tentative conclusions might be that herbicidal activity of soil applied herbicide is induced by its concentration in plant available soil water, and that its concentration in soil water is dominated by its adsorption in and desorption from the soil, both of which are influenced by soil organic matter. Further studies on other herbicides differing in chemical structure and herbicidal properties are necessary to confirm the relationship between herbicidal activity of soil applied herbicide and its concentration in plant available soil water.

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テニルクロールの殺草活性と土壌水中濃度

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摘 要

竜ヶ崎、谷和原水田土壌およびヒメタイヌビエ (*Echinochloa crus-galli* Beauv. var. *formosensis* Ohwi) を供試し、土壌に施用したテニルクロール[2-chloro-N-(3-methoxy-2-thienyl) methyl-2', 6'-dimethylacetanilide] の殺草活性と土壌水分中濃度の関連について検討した。

本剤の水溶液を処理した土壌(新鮮土壌)を二重の遠心管を用いた遠心分離法により有効水と想定される土壌水と残さ土壌(遠心分離土壌)とに分別し、新鮮土壌における本剤の存在量を土壌水と遠心分離

土壌とに分けて測定した(Fig. 1)。土壌水中濃度は、谷和原土壌に比べ、竜ヶ崎土壌が高かったが、新鮮土壌および遠心分離土壌における存在量は竜ヶ崎土壌に比べて谷和原土壌が高かった(Table 1)。また谷和原水田土壌に比べ竜ヶ崎水田土壌に施用した場合に本剤の殺草活性が高く、殺草活性と土壌水中濃度は密接に関連していたが、新鮮土壌および遠心分離土壌に含まれている量とは関連がなかった。なお、本剤を施用した土壌から採取した土壌水と蒸留水を用いて直接調製した本剤の水溶液を用いた生物検定における殺草活性が一致した(Fig. 2)。

以上の結果から土壌に施用したテニルクロールの殺草性は、土壌に存在する有効水中濃度に依存して発現するものと思われる。

キーワード: テニルクロール, 土壌水中濃度, 殺草活性, 土壌吸着, ヒメタイヌビエ

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