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Regular Article

Behavior of controlled-release pyrimisulfan in the soil and its herbicidal activity on *Echinochloa oryzicola* seedlings under various irrigation conditions

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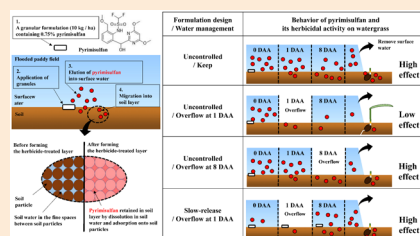
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 Supplementary material

Pyrimisulfan is a highly effective, water-soluble, and paddy herbicide used against various annual weeds, such as *Echinochloa* spp. Pyrimisulfan was released into surface water, and it migrated into soil water; it formed a herbicide-treated layer within seven days of the water-holding period upon the application of granules with uncontrolled formulation under the flooded condition. Although pyrimisulfan efficacy declined under overflow conditions before forming the herbicide-treated layer, the decrease in herbicidal activity was suppressed after layer formation. In addition to uncontrolled formulation, a controlled-release formulation was tested. Although time for the formation of the herbicide-treated layer increased, water fluctuation resistance improved. As a benchmark, the concentration of pyrimisulfan in soil water on the target date, after adsorption equilibrium, was 57.6 ppb. Although herbicidal activity generally decreases in soils with high organic carbon content, pyrimisulfan showed no loss of activity. This study provides fundamental insights into the mechanism of herbicide-treated layer formation.



Keywords: controlled-release, herbicide-treated layer, paddy field, paddy herbicide, pyrimisulfan.

Introduction

In rice cultivation, weed control in paddy fields is important for achieving stable yields. In particular, *Echinochloa* spp., one of the most troublesome weeds growing in paddies, has stimulated the development of effective herbicides in Japan.^{1–3)} Herbicides applied to flooded paddy fields form the so-called herbicide-treated layer.⁴⁾ Emerging seedlings of *Echinochloa* spp. absorb the active ingredient localized in the herbicide-treated layer through their roots and/or stems and die, whereas transplanted

rice seedlings avoid herbicide damage due to positional selectivity, as at the time of herbicide application, their absorptive root surfaces have already grown past the herbicide-treated layer, where the herbicidal active ingredient must be dissolved.^{4–9)} Indeed, previous studies have shown that the herbicidal activities of pyriftalid,⁵⁾ cafenstrole,^{6,7)} thienylchlor,⁸⁾ pretilachlor⁹⁾ and depend on the concentration of the active ingredient in the dissolved state. It should be noted that the above-mentioned previous study dissolved the active ingredient in acetone and mixed it into the soil, a procedure that differs substantially from actual application practices in paddy fields.

Generally, it is recommended that paddy fields are maintained in water holding conditions by blocking water inlets and outlets for seven days after herbicidal application to prevent herbicide off-site migration, which additionally contributes to the stabilization of the herbicide-treated layer.¹⁰⁾ However, the elution pattern from the formulation varies depending on the solubility of the active ingredient in water, whereby the period needed to form the herbicide-treated layer is expected to differ for each

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active ingredient. Therefore, a formulation design is required to optimize the elution pattern for each active ingredient, such that it enables the stable formation of the herbicide-treated layer within seven days of the water holding period. Thus, to date, formulations such as slow-release formulas using coating with a polymer,¹¹⁾ matrixing of wax^{12,13)} or loading with porous materials¹⁴⁾ have been developed for pesticides with high water solubility.

Pyrimisulfan (RS)-(2'-[(4,6-dimethoxypyrimidin-2-yl)(hydroxymethyl)-1,1-difluoro-6'-(methoxymethyl) methanesulfonanilide) was developed by Kumiai Chemical Industry Co., Ltd.²⁾ A case in point, pyrimisulfan is a herbicide with high solubility whose physical and chemical properties are summarized in Supplementary Table 1. At doses of 50–75 g a.i./ ha pyrimisulfan shows high efficacy against a wide range of annual weeds such as broadleaves weeds *e.g.* *Monochloa* spp., sedge weeds *e.g.*, *Scirpus* spp., and grass weeds *e.g.*, *Echinochloa* spp. A previous study showed that the efficacy of an uncontrolled formulation of this herbicide declined under overflow conditions compared with a slow-release formulation.¹⁵⁾ The slow-release formulation released an initial required amount, then slowed the release rate to maintain a target concentration over an extended period.¹⁶⁾ The initial elution was kept low to ensure stable effects when half the paddy water is replaced with fresh water a few days after application; furthermore, slow-release properties may also contribute to rice safety. However, the optimal elution pattern for forming a herbicide-treated layer during the water-holding period is not fully understood. By contrast, with an uncontrolled formulation, efficacy may not decline under overflow conditions once a herbicide-treated layer has formed and become sufficiently stable. In actual field applications of pyrimisulfan, overflow almost inevitably occurs owing to rainfall, unintended water flow from field edges, or forced drainage during operations such as mid-season drainage or methane gas release. Nevertheless, clarifying the pyrimisulfan concentration and duration required to properly form a herbicide-treated layer, as well as ensuring its stability after formation and resistance to runoff under overflow conditions, would support a soundly based formulation design. In this study, we used a granular formulation with two different elution patterns to evaluate the behavior of pyrimisulfan in paddy fields.

The herbicidal activity in the herbicide-treated layer was evaluated by removing the paddy surface water (surface water), assuming that the field surface was exposed after treatment. In addition to evaluating the required pyrimisulfan concentration and duration of elution, we also used soils with different properties, as soil organic matter content is another factor influencing the formation of the herbicide-treated layer.⁴⁾

Therefore, the objective of this study was to model the behavior of the active ingredient of pyrimisulfan in soil and surface water under simulated use conditions, and to clarify the mechanism underlying the formation of the herbicide-treated layer.

Materials and methods

1. Chemicals and formulations

Granules (10 kg/ha) containing 0.75% pyrimisulfan were prepared by the Chemical Research Institute of Kumiai Chemical Industry (Shizuoka, Japan), as shown in Table 1.

Formula P1, which released pyrimisulfan rapidly referred to as an uncontrolled formulation, was obtained by mixing pyrimisulfan with an anionic surfactant, pregelatinized starch, calcium carbonate, quartz, kaolinite, and water, and then granulating this mixture using an extruder MG-55 (Dulton Co., Ltd., Tokyo, Japan) through a 1.0 mm screen. In turn, formula P2, which released pyrimisulfan slowly referred to as a controlled-release formulation, was obtained by the same method as P1, except for using a cationic surfactant instead of an anionic one. Formulas P1 and P2 were dried by heating at 60°C and sieved through a 710 µm mesh. The elution of pyrimisulfan from P1 and P2 is shown in Supplementary Table 2 and Supplementary Fig. 1.

2. Quantification of pyrimisulfan

The P1 and P2 formulas were treated at 10 kg/ha in plastic containers flooded to a depth of 2 cm at 25°C, and water samples were collected over time and analyzed by high performance liquid chromatography (HPLC, LC2030; Shimadzu Co., Ltd., Kyoto, Japan), using an analytical column (CHEMCOBOND5-ODS-H 150 mm×3.0 mm; ChemcoPlus Co., Ltd., Osaka, Japan), an ultraviolet spectrophotometric detector that operated at 254 nm, and the analytical software LabSolutions, version 5.1117. The mobile phase (0.45 mL min⁻¹) was composed of ace-

Table 1. Formulation of granules P1 and P2

Formula No.		P1		P2	
Material	CAS No.	Purity (%)	Preparation (%)	Ratio (%)	Ratio (%)
Pyrimisulfan mixture ^a	221205-90-9	10.00	0.75	7.50	7.50
Cationic surfactant mixture ^b	107-64-2			0.00	10.00
Anionic surfactant	69669-44-9			0.50	0.00
Pregelatinized starch	9005-25-8			3.00	3.00
Calcium carbonate	471-34-1			26.60	18.10
Quartz/kaolinite	14808-60-7/1332-58-7			62.40	61.40
Total				100.00	100.00

^aPyrimisulfan mixture contained approximately 90% calcium carbonate. CAS No. was labeled for pyrimisulfan. ^bCationic surfactant mixture contained approximately 85% calcium carbonate. CAS No. was labeled for cationic surfactant.

tonitrile, methanol, and distilled water (15:40:45, v/v/v). The retention time for pyrimisulfan was 6.5 min.

Soils were collected from paddy fields located in Kikugawa (clay loam; organic carbon content: 5.8 g kg⁻¹; cation exchange capacity (CEC): 11.2 cmol (+) kg⁻¹), and Shiraiwa (clay loam; organic carbon content: 19.5 g kg⁻¹; CEC: 20.7 cmol (+) kg⁻¹), in Shizuoka Prefecture, Japan. These soil samples were sterilized by dry heat at 120°C for 6 hr. Air-dried and sieved (mesh size: 5 mm) paddy soil was placed in a plastic container, soaked in tap water, and mixed. The trial scales are shown in Supplementary Table 3.

After a few hours, the supernatant was discarded. The container was flooded to a depth of 2 cm from the soil surface.

After the granules were applied to the irrigation water, the level of the flooding water was maintained at the prescribed water depth and at 25°C, according to Supplementary Table 3, throughout the experiment. Regarding water management, “Keep” means continuously maintaining the prescribed water depth, while “Overflow” means discarding all the surface water at a predetermined time and then refilling to the prescribed water depth over a period of 6 hr. Previous reports indicate that using two or more inlets in a 1 ha field to apply 2 cm of irrigation requires 3 hr.¹⁷⁾ In this study, assuming only one inlet was available, we set the maximum time for applying 2 cm of water to 6 hr. On the prescribed days after granules application, flooding water was sampled as surface water and discarded. Then, after the container was tilted for 15 min to remove free water in soil, fractionated paddy soil samples were collected at depths of 0–1 and 1–2 cm.

The soil was centrifuged in double tubes at 3,500 × *g* for 30 min at 15°C to separate the plant available soil water (*i.e.*, soil water) between air-dry and permanent wilting point (pF 4.2). The amount of pyrimisulfan in surface water and soil water was determined by HPLC, using the method described above to assess elution rates. The same soil layer that was not centrifuged was extracted using 80% acetonitrile. The amount of pyrimisulfan in the extract from the moist soil layer after removal of soil water by centrifugation was determined by LC-MS/MS (ExionLCTM, Triple QUADTM 4500, AB SCIEX, Tokyo, Japan) with an analytical column (Kinetex C18, 2.6 μm, 100 × 4.6 mm, Phenomenex, Torrance, CA, U.S.A.), using distilled water containing 0.5% acetic acid (solvent A) and a mixture of acetonitrile containing 0.5% acetic acid (solvent B) as the mobile phase. The column temperature was maintained at 40°C and the flow rate was 0.5 mL min⁻¹ in a binary gradient mode with the following elution program: 0 min, 60:40 (A: B ratio (v/v)); 7 min, 25:75; 7.1 min, 10:90; 10 min, 10:90; 10.5 min, 60:40; 15 min, 60:40. The retention time for pyrimisulfan was 6.16 min. Mass detection was performed according to the following conditions: electrospray ionization (ESI negative); MRM scan mode *m/z* 418 (precursor ion) and *m/z* 304 (product ion); ion spray voltage, −3.5 kV; temperature, 600°C; gas 1, 50 arbitrary units; gas 2, 70 arbitrary units; declustering potential, −65 V; collision energy, −26 V; collision cell exit potential, −9 V. The limit of quantita-

tion for pyrimisulfan was 1 ppb and the recovery rate from the extracted soil samples exceeded 85%. Because the extracted soil contained soil water, the pyrimisulfan concentration in the soil was calculated by subtracting the amount of pyrimisulfan in the soil water. The total amount of pyrimisulfan in each fraction was calculated based on its concentration and weight, and the total amount of pyrimisulfan in the container was calculated. All experiments were conducted in triplicate.

The values of K_d and K_{oc} for pyrimisulfan were determined using the following equations¹⁸⁾ when soil water concentrations became statistically indistinguishable, or at 25 DAA.

$$K_d = \frac{(\text{concentration of pyrimisulfan in soil})}{(\text{concentration of pyrimisulfan in soil water})}$$

$$K_{oc} = K_d \times 100 / (\text{percentage of organic carbon})$$

3. Plant materials and bioassay

Dormancy-broken late watergrass (*Echinochloa oryzicola*) seeds (harvested from Life Science Research Institute, Kumiai Chemical Industry Co., Ltd. in 2018) were soaked in water for 15 hr at 27°C under dark conditions. Germinated seeds were transplanted to the sampled soil, which was not centrifuged, as described above, and grown in a growth chamber (PHC, MRT-350HT, Tokyo, Japan) at 25°C in a 12/12 hr light/dark cycle. Herbicidal activities were estimated by measuring seedling shoot elongation with a visual scale of 0 (no effect) to 100 (complete kill) at two weeks after treatment.¹⁵⁾ A visual rate of 80–89% indicated that weeds are not killed, but their growth is suppressed sufficiently to prevent yield reduction due to weed damage. In turn, a visual rate of 90% or higher indicated stronger weed growth suppression or wilting symptoms, visually demonstrating sufficient activity. The visual rate of 80% maximal inhibitory concentration (IC₈₀) was calculated by nonlinear regression analysis using JMP 19.0.1 (JMP Statistical Discovery LLC, Cary, NC, U.S.A.). Data were plotted using a log-logistic model.

$$Y = c / (1 + \exp(-a(X - b)))$$

where *Y* is herbicidal activity, *a* is the slope of the line, *b* is the necessary dose for 50% response, *c* is the limit, and *X* is the specific herbicide dose tested in each case.¹⁹⁾

Results and discussion

1. Behavior of pyrimisulfan as per formulation (Trial 1)

The time course of pyrimisulfan concentration in surface water, centrifuged soil water (soil water), soil, and the total amount of pyrimisulfan in the container for the uncontrolled granule P1 formula used on Kikugawa soil are shown in Fig. 1 and Supplementary Tables 4 and 5.

The total amount of pyrimisulfan measured in the container was 133 μg, indicating nearly 100% release from the 141 μg applied (Fig. 1B) 1 day after application (DAA). Pyrimisulfan concentration in surface water peaked at 1 DAA, then decrease (Fig. 1A). Meanwhile, pyrimisulfan concentration in the soil water at 0–1 cm soil depth gradually increased as it decreased in surface

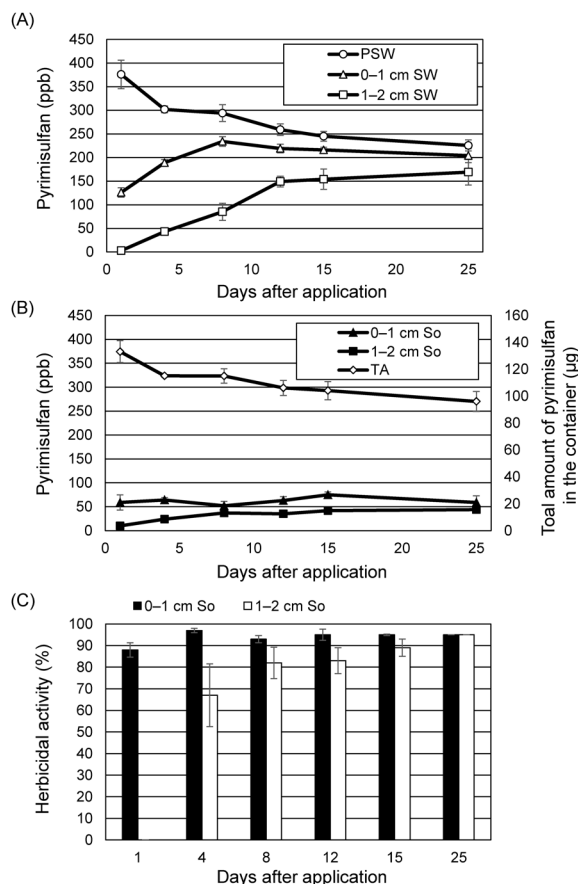


Fig. 1. Time course of pyrimisulfan concentration changes after P1 application to Kikugawa soil samples in water (A) and soil (B) and time course of the herbicidal activity in the soil (C). Surface water (○: PSW, paddy surface water), Soil water at 0–1 cm depth (△: 1 cm SW), soil water at 1–2 cm depth (□: 2 cm SW), soil after removal of soil water at 0–1 cm depth (▲: 1 cm So), soil after removal of soil water at 1–2 cm depth (■: 2 cm So), and total amount of pyrimisulfan in the container (◇: TA) are indicated. Herbicidal activity in the soil at 0–1 cm depth (black bar: 1 cm So) and at 1–2 cm depth (white bar: 2 cm So) are indicated. Data shown are means $\pm$ standard error ($n=3$).

water, reaching a maximum at 8DAA. Pyrimisulfan concentration in the soil after removal of soil water reached 59 ppb at 1 DAA and then remained at equilibrium (Fig. 1B). Herbicidal activity at a 0–1 cm soil depth showed a strong effect, with inhibition at 80% or greater, beginning 1 DAA (Fig. 1C). These results suggest that after P1 was applied to flooded paddy fields, pyrimisulfan was released from the formulation into the surface water, from where it migrated into the soil water in the fine spaces between soil particles, or was immediately adsorbed onto the soil. Fig. 1 shows that the formation of the herbicide-treated layer began at 1 DAA, with herbicidal activity observed in the 0–1 cm deep soil layer. After that, pyrimisulfan concentration in soil water at 0–1 cm depth reached equilibrium level at 4 DAA (Supplementary Table 4). In this study, “complete formation of the herbicide-treated layer” is defined as the point at which concentration equilibrium is reached; 4 DAA corresponds to that state at the 0–1 cm soil depth. Meanwhile, in the case of the

1–2 cm soil depth, pyrimisulfan concentration increased with a slight delay relative to its increase at 0–1 cm soil depth and reached equilibrium at 12 DAA in soil water (Fig. 1A and Supplementary Table 4), with a strong effect showing from 8 DAA (Fig. 1C). Specifically, pyrimisulfan concentration in the 1–2 cm deep soil layer reached approximately 37 ppb at 8 DAA and then plateaued (Supplementary Table 5). From both these datum and modeling-theory, concentration in the soil water in the 0–1 cm layer rapidly reach sufficient levels after treatment, establishing adsorption equilibrium early. In contrast, accumulation in the 1–2 cm soil layer is slower than in the 0–1 cm layer due to delayed downward migration (vertical percolation) from the upper layer.^{20,21)} This study used controlled containers and did not consider field-scale lateral transport (e.g., seepage/runoff, cracks, macropores). In future works, field-scale trials should account for these processes and verify concentration profiles with water-level dynamics, irrigation/drainage records, soil-crack observations and preferential-flow indicators.^{22,23)} As watergrass can germinate even at 2 cm soil depth,²⁴⁾ the delay in formation of the herbicide-treated layer in deep soil layers may reduce herbicidal activity. On the other hand, pyrimisulfan is absorbed not only through the roots but also from the basal parts of stems and leaves that contact shallow layers, so even individuals emerging from deeper layers may be affected *via* basal uptake.²⁵⁾ Future studies should assess how delayed development in the 1–2 cm layer influences residual efficacy and control failures under field conditions.

Previous studies have shown that herbicidal activity depends on the extent of dissolution of the active ingredient in soil water, *i.e.*, the actual concentration of active ingredient in soil water,^{4–9)} which is considered an essential component of the herbicide-treated layer. Consistent with previous reports, here, we observed the same tendency of pyrimisulfan concentration in soil water to strongly correlate with the strength of the herbicidal effect observed.

The total amount of pyrimisulfan in the container gradually decreased. Thus, for example, pyrimisulfan was 96 µg at 25 DAA, a 31.9% decrease relative to the theoretical amount (Supplementary Table 5). Similarly, a previous study showed that, owing to biodegradation, pyrimisulfan decreased by 50% and 74% at 12–13 and 26 DAA, respectively.²⁶⁾ It is not unlikely that, in this trial, the use of sterilized soil reduced pyrimisulfan biodegradation, potentially extending its half-life.

As for P2, approximately 10%–20% of pyrimisulfan was eluted into the surface water at 1 DAA, and its concentration gradually increased thereafter (Fig. 2A and Supplementary Table 6).

Pyrimisulfan in soil water increased as surface water increased and reached equilibrium at 12 DAA. A strong effect was shown at 4 and at 12 DAA in the 0–1 and in the 1–2 cm soil layers, respectively (Fig. 2C and Supplementary Table 7). According to Supplementary Table 6, 4 DAA marked the beginning, and 12 DAA marked the completed herbicide-treated layer formation in the 0–1 cm soil layer. As designed for the slow-release formulation, the onset of herbicidal activity and pyrimisulfan

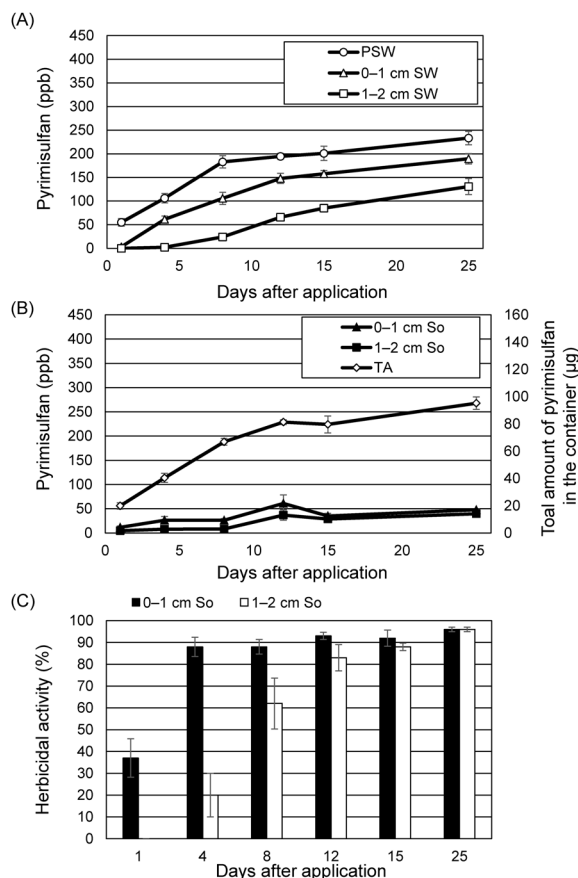


Fig. 2. Time course of pyrimisulfan concentration changes after P2 application to Kikugawa soil samples in water (A) and soil (B) and time course of herbicidal activity in the soil (C). Surface water (○: PSW, paddy surface water), soil water at 0–1 cm depth (△: 1 cm SW), soil water at 1–2 cm depth (□: 2 cm SW), soil after removal of soil water at 0–1 cm depth (▲: 1 cm So), soil after removal of soil water at 1–2 cm depth (■: 2 cm So), and total amount of pyrimisulfan in the container (◇: TA) are indicated. The herbicidal activity in the soil at 0–1 cm depth (black bar: 1 cm So) and at 1–2 cm depth (white bar: 2 cm So) are indicated. Data shown are means $\pm$ standard error ($n=3$).

concentration in the surface water and the soil water were slower in the P2-treated plots than those under the P1 treatment. Product designs such as slow-release formulas have been reported to stabilize herbicidal activity under overflow conditions,¹⁵⁾ or improve residual activity.¹²⁾ However, the onset of herbicidal activity has not been reported. In cases in which elution was excessively suppressed, the herbicide-treated layer may take a long time to form, which may adversely affect performance. The P2 treatment is considered to be at low risk because a previous study showed high herbicidal activity when pyrimisulfan concentration in the surface water was 15.6 ppb or greater.¹⁵⁾ In this study, surface water was removed to evaluate the herbicide-treated layer. However, after 7 day into the water holding period, pyrimisulfan concentrations above 15.6 ppb were commonly maintained in surface water (Fig. 2A), ensuring sufficient herbicidal activity.

The slow-release formula, which included a cationic surfac-

tant, was based on the patent.²⁷⁾ Although the mechanism controlling elution is not fully understood, P1 and P2 consist of calcium carbonate, which can acquire a negative surface charge in water²⁸⁾; the hydrophilic headgroups of cationic surfactant may adsorb onto the particle surfaces and form a hydrophobic barrier. Such a hydrophobic coating could physically impede the dissolution and release of pyrimisulfan.

2. Influence of overflow conditions on the concentration of pyrimisulfan as per formulation (Trial 2)

Fig. 3 shows the pyrimisulfan concentration trends in surface water. For P1 under non-overflow conditions, the concentration was 320 ppb at 1 DAA and gradually decreased to 228 ppb by 19 DAA (Fig. 3A).

Overflow at 1 DAA, pyrimisulfan concentration decreased to 32 ppb at 2 DAA and gradually increased up to 8 DAA, reaching a maximum of 66 ppb, and thereafter reached equilibrium (Supplementary Table 8). Overflow at 8 DAA, pyrimisulfan concentration decreased to 56 ppb at 9 DAA and rose to a peak of 87 ppb at 19 DAA. It did not reach equilibrium during the study. Because pyrimisulfan concentration in surface water under overflow conditions remained constant after a temporary decline, we think that pyrimisulfan in the herbicide-treated layer moved from soil water to surface water following the concentration gradient between the two. The difference in timing of equi-

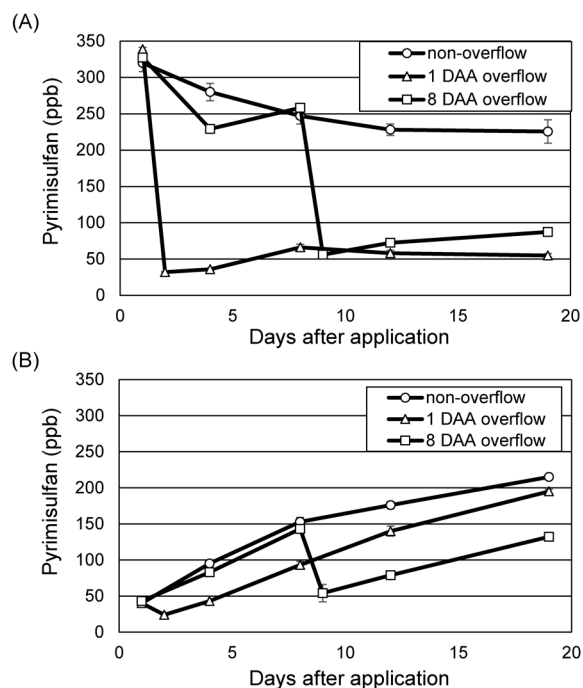


Fig. 3. Time course of pyrimisulfan concentration changes in surface water after application of P1 (A) and P2 (B) to Kikugawa soil samples under non-overflow (○: non-overflow), overflow at 1 DAA (surface water discarded and refilled at 1 DAA, △: 1 DAA overflow), overflow at 8 DAA (surface water discarded and refilled at 8 DAA, □: 8 DAA overflow). Data shown are means $\pm$ standard error ($n=3$). Pyrimisulfan concentrations in soil water and herbicidal efficacy are shown in Table 2.

Table 2. Pyrimisulfan concentration in soil water and herbicidal activity at 19 DAA

Formulation	Overflow	0–1 cm depth		1–2 cm depth	
		SW (ppb)	HA (%)	SW (ppb)	HA (%)
P1	—	224±6 a	95±0 a	209±4 a	94±1 a
	1 DAA	54±2 b	78±1 b	50±7 b	60±0 b
	8 DAA	103±10 c	93±2 a	102±6 c	83±3 c
P2	—	205±11 a	96±1 a	149±9 a	93±1 a
	1 DAA	176±7 a	95±0 a	127±7 a	77±9 a
	8 DAA	118±4 b	95±1 a	83±5 b	88±4 a

Approximately 10 kg/ha in plastic containers flooded to a depth of 2 cm at 25°C with soil. Overflow: Discarding all the surface water at a predetermined time and then refilling to the prescribed water depth over a period of 6 hr. DAA: Days after application. PSW: Pyrimisulfan concentration in surface water (paddy surface water). SW: Pyrimisulfan concentration in soil water. HA: Herbicidal activity as visually evaluated using a percentage scale from 0 (no effect) to 100 (completely killed). Standard error is shown ($n=3$). Different letters indicate significant differences between the overflow conditions within the formulation ($p=0.05$, Tukey's HSD).

librium likely reflects the amount of pyrimisulfan retained in the soil layer: the soil layer-held pyrimisulfan immediately before runoff was higher at 8 DAA than at 1 DAA (Fig. 1A). Pyrimisulfan concentrations in both surface and soil water, as well as herbicide activity at 19 DAA, were lower under overflow condition at 1 DAA than at 8 DAA (Table 2). This difference may be attributed to higher soil water concentrations during overflow at 8 DAA than at 1 DAA, which likely conferred greater overflow resistance.

As for P2, under non-overflow conditions, pyrimisulfan concentration in surface water was 40 ppb at 1 DAA and gradually increased to 215 ppb at 19 DAA (Fig. 3B).

Overflow at 1 DAA temporarily reduced the pyrimisulfan concentration to 24 ppb at 2 DAA, but subsequently increased and recovered to 195 ppb by 19 DAA (Supplementary Table 8). Overflow at 8 DAA caused pyrimisulfan concentrations to decline to 54 ppb at 9 DAA and then rise to 132 ppb at 19 DAA. Moreover, in soil water, overflow reduced pyrimisulfan concentrations more at 8 DAA than at 1 DAA (Table 2). However, herbicidal activity was not significantly affected at any soil depth.

These results suggest that, provided pyrimisulfan remains in a supply source such as a controlled-release formulation, a certain level of resistance to overflow is maintained in herbicidal activity.

3. Dependence of herbicidal activity on pyrimisulfan dose (Trial 3)

When P1 was applied at different dosages, pyrimisulfan concentration and herbicidal activity depended on the amount applied (Table 3).

High effects at 0–1 cm soil depth at 1 DAA required an application rate of 10 kg/ha at 4 cm water depth (161 ppb in surface water). Therefore, an initial elution of 161 ppb was required to begin the herbicide-treated layer formation period starting at 1 DAA, as with P1. Moreover, if the formulation was to be designed to achieve herbicide-treated layer formation after 7 day of the water holding period, pyrimisulfan concentration in surface water would require an application rate of 5 kg/ha at 4 cm water depth. This means that the 76 ppb in surface water at 1 DAA formed an herbicide-treated layer at 8 DAA. Therefore, desirable elution profiles can be established in this manner.

Table 3. Dose-dependency of herbicidal activity on pyrimisulfan concentration in surface water and soil water using P1.

Day after application	Dosage	Water-depth	Theoretical concentration	PSW (ppb)	0–1 cm depth		1–2 cm depth	
					SW (ppb)	HA (%)	SW (ppb)	HA (%)
1	10 kg/ha	2 cm	375 ppb	317±34	141±14	95±3	12±3	10±10
	10 kg/ha	4 cm	188 ppb	161±21	64±5	94±2	5±2	0±0
	5 kg/ha	4 cm	94 ppb	76±7	31±8	68±13	2±2	0±0
	2.5 kg/ha	4 cm	47 ppb	47±9	20±4	17±9	3±3	0±0
8	10 kg/ha	2 cm	375 ppb	276±9	216±14	96±2	146±20	95±2
	10 kg/ha	4 cm	188 ppb	156±5	115±4	95±0	62±5	91±5
	5 kg/ha	4 cm	94 ppb	79±4	58±3	94±1	33±7	74±10
	2.5 kg/ha	4 cm	47 ppb	52±6	33±4	78±1	19±2	33±7

PSW: Pyrimisulfan concentration in surface water (paddy surface water). SW: Pyrimisulfan concentration in the soil water. HA: Herbicidal activity as visually evaluated using a percentage scale from 0 (no effect) to 100 (completely killed). Standard error is shown ($n=3$).

4. Dose-response of pyrimisulfan in soil water

Herbicidal activity and pyrimisulfan concentration in soil water of the Kikugawa soil, as demonstrated in Trials 1–3, are shown in Supplementary Fig. 2.

When pyrimisulfan concentration in soil water was 57.6 ppb or higher, a high effect resulting in an inhibition rate of 80% was observed (Supplementary Table 9). Because the precision of the estimate was adequately supported by the standard error and the 95% confidence interval, the target value was retained at 57.6 ppb. However, because the empirical standard error of concentrations in soil water exceeded the uncertainty of the model estimate (SE: 3.7 ppb; one sided 95% confidence interval margin: 7.2 ppb), it may be necessary to adopt the upper bound of the 95% confidence interval (64.9 ppb) or more as safety margin. Thus, it is desirable to design a formulation that ensures that the pyrimisulfan concentration in soil water reaches a concentration of 57.6 ppb or greater by the target date.

5. Influence of soil physicochemical properties on herbicidal activity of the uncontrolled formulation (Trial 4)

Fig. 4 shows the changes in pyrimisulfan concentration in surface water, soil water, and in the soil, as well as the herbicidal activity of P1 in the Shiraiwa soil samples that had a higher organic carbon content than Kikugawa soil.

Shiraiwa soil samples exhibited lower pyrimisulfan concentrations in surface water and soil water (Fig. 4A and Supplementary Table 10) than Kikugawa soil samples (Fig. 1A and Supplementary Table 4), while showing a higher concentration of pyrimisulfan in the soil (Fig. 4B and Supplementary Table 11, Fig. 1B and Supplementary Table 5).

The soil adsorption distribution coefficient (K_d) at equilibrium was significantly higher in Shiraiwa soil than in Kikugawa soil, confirming that adsorption correlated with organic carbon content (Supplementary Table 11 and Supplementary Table 5). No significant differences in K_{oc} were observed between soils; the values matched $K_f^{ads}_{oc}$ values reported in the pesticide abstract (Supplementary Table 1), supporting the validity of the test. Pesticide adsorption correlates with organic carbon content in the soil and the adsorption capacity of organic compounds.²⁹⁾ Although variability exists due to the physicochemical properties of the soil and organic chemicals, this trend generally reflects the tendency of organic chemicals to adsorb onto soil particles.¹⁸⁾ Our results are consistent with this pattern. Previous reports indicate, in soils with low organic carbon content, the concentration of the active ingredient in soil water is higher and herbicidal activity greater.^{5,7)} In contrast, herbicidal activity was high in both soil layers in this trial (Fig. 4C and Supplementary Table 11). Because pyrimisulfan has low soil adsorption, its efficacy was less influenced by soil organic carbon content than that of other herbicides in previous studies.

The initial elution of 76 ppb established in Trial 3 is applicable to soils with low organic carbon content such as Kikugawa soil, but in soils with high content the concentration may fall below the target concentration due to adsorption by the soil, as ob-

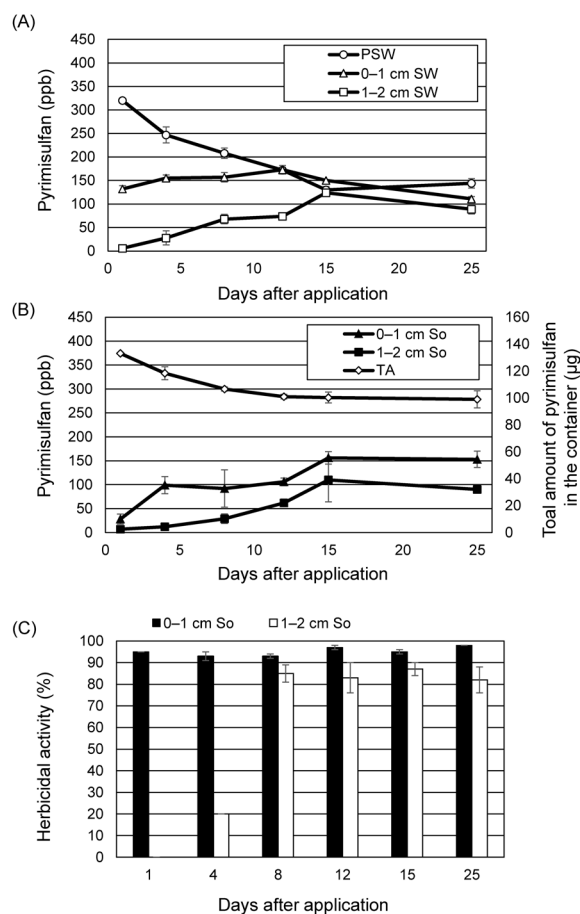


Fig. 4. Time course of pyrimisulfan concentration changes after P1 application to Shiraiwa soil in water (A) and soil (B); time course of the herbicidal activity in the soil (C). Surface water (○: PSW, paddy surface water), soil water at 0–1 cm depth (△: 1 cm SW), soil water at 1–2 cm depth (□: 2 cm SW), soil after removal of pore water by centrifugation at 0–1 cm depth (▲: 1 cm So), soil after removal of pore water by centrifugation at 1–2 cm depth (■: 2 cm So), and the total amount of pyrimisulfan in the container (◇: TA) are indicated by the corresponding symbols. The herbicidal activity in the soil at 0–1 cm depth (black bar: 1 cm So) and at 1–2 cm depth (white bar: 2 cm So) are indicated. Data shown means $\pm$ standard error ($n=3$).

served in this study (Supplementary Table 10 and Supplementary Table 4). Meanwhile, we set target values in the formulation guidelines of a “concentration in soil water of 57.6 ppb”. This target value refers to the concentration in soil water after adsorption equilibrium and can also be applied to soils with high organic carbon content.

Conclusions

Pyrimisulfan, which shows high water solubility, was almost completely eluted from P1, which was an uncontrolled formulation, at 1 DAA. Dissolved pyrimisulfan in surface water rapidly forms an herbicide-treated layer *via* migration in soil water and soil adsorption. The herbicide-treated layer was defined as the beginning of the formation period to begin showing a high effect against watergrass at 0–1 cm soil depth and as a completely

formed period to reach equilibrium with pyrimisulfan concentration in soil water and surface water. The P1 formulation showed the beginning of the herbicide-treated layer formation period at 1 DAA and the completed formation period at 4 DAA. Meanwhile, P2, designed as a slow-release formulation, showed a lower elution rate and a delayed formation period compared to P1. Under overflow conditions that drained all the surface water and then refilled it, P1 showed that the herbicidal activity and pyrimisulfan concentration in surface water and soil water decreased. In particular, overflow at 1 DAA was markedly affected compared to that at 8 DAA. After the completed herbicide-treated layer formation period, the amount of pyrimisulfan remaining in the herbicide-treated layer increased, causing herbicidal activity to stabilize. Despite a decline in concentration in surface water and soil water, the herbicidal activity of P2 was not significantly affected by each overflow condition. The controlled-release formulation such as P2 could show a high tolerance to overflow. An initial elution of 76 ppb was used as the benchmark to determine the desirable elution profile for the formulation. The pyrimisulfan concentration in soil water was determined at 57.6 ppb or higher by the target date. In addition to evaluating the formulation, we confirmed the impact of soil properties. Herbicidal activity generally correlates with soil organic carbon content; however, pyrimisulfan showed no reduction in activity even in high-organic-carbon soils. Soil adsorption reduces concentrations in surface and soil water, making initial elution dependent on organic carbon content, whereas concentration in the soil water reflects post-equilibrium levels and represents an intrinsic property of the active ingredient. This study aimed to model the behavior of the active ingredient in soil and surface water under simulated use conditions and to clarify the mechanism of the herbicide-treated layer formation. Further, this study provides fundamental insights into the formation mechanism of the herbicide-treated layer and proposes a formulation design to achieve the most stable efficacy.

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Electronic supplementary materials

The online version of this article contains supplementary material, which is available at <https://www.jstage.jst.go.jp/browse/jpestics/>

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