**Introduction**

Rice production is one of the major non-point sources of pesticide pollution in Japan because more than half of all arable land is paddy fields, from which pesticides can easily be transported to rivers. Public concerns regarding the adverse effects of pesticides in runoff on aquatic ecosystems and drinking water are increasing. In 2003, the Ministry of the Environment of Japan imposed a new pesticide registration scheme concerning ecological risk in an aquatic environment based on concepts adopted in the EU and the USA. In this scheme, the acute effect concentration in the assessment species (i.e., fish, Daphnia, or algae) is compared with the predicted environmental concentration calculated using environmental models based on the standard scenario of the pesticide use.\(^1\)

Recently, mathematical models (e.g., PADDY\(^2,3\)) and PCPF-\(^1,4–6\)) have been developed to simulate the transport and fate of paddy rice pesticides in Japan; however, these models do not consider metabolites derived from the parent compound by hydrolysis, photolysis, or microbial degradation. The RICEWQ model, developed in the EU and the USA, is the only one that considers metabolites under paddy conditions.\(^7\) The metabolites of some pesticides, such as organophosphorus insecticides, may be more toxic to aquatic organisms than the parent compound. Therefore, for ecological risk assessment it is necessary to evaluate the exposure of aquatic organisms not only to the parent compound but also to its metabolites.

PADDY\(^2,3\)) is used to predict pesticide behavior in paddies. The objective of this study was to develop and evaluate an improved PADDY-based model that includes photoisomerization and metabolic pathways and applied to the herbicide pyriminobac-methyl. Isomerization of pyriminobac-methyl in paddy water by sunlight was modeled as a reversible first-order reaction between the (\(E\))- and (\(Z\))-isomers in response to UV-B irradiation. The formation and degradation of its main metabolites in flooded soil were expressed as consecutive first-order reactions. The model was validated by comparing calculated values with measured values from paddy lysimeter and field experiments. The improved PADDY model successfully simulated changes in the concentrations of pyriminobac-methyl and its metabolites over time under paddy conditions. ©Pesticide Science Society of Japan

**Keywords:** environmental fate, paddy conditions, simulation model, pyriminobac-methyl, photoisomerization, metabolite.

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**Improved PADDY model including photoisomerization and metabolic pathways for predicting pesticide behavior in paddy fields: Application to the herbicide pyriminobac-methyl**

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An improved simulation model for predicting pesticide behavior in paddy fields based on PADDY was developed to include photoisomerization and metabolic pathways and applied to the herbicide pyriminobac-methyl. Isomerization of pyriminobac-methyl in paddy water by sunlight was modeled as a reversible first-order reaction between the (\(E\))- and (\(Z\))-isomers in response to UV-B irradiation. The formation and degradation of its main metabolites in flooded soil were expressed as consecutive first-order reactions. The model was validated by comparing calculated values with measured values from paddy lysimeter and field experiments. The improved PADDY model successfully simulated changes in the concentrations of pyriminobac-methyl and its metabolites over time under paddy conditions. ©Pesticide Science Society of Japan

**Keywords:** environmental fate, paddy conditions, simulation model, pyriminobac-methyl, photoisomerization, metabolite.

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major fate process in water, and the primary process is \((E)/(Z)\) geometrical isomerization.\(^8,9\) In paddy soil under flooded conditions, the main metabolites of \(I\) and \(II\) are methyl 2-(4-hydroxy-6-methoxy-2-pyrimidinylxoy)-6-(E)-(1-methoxyimino-ethyl)benzoate (III) and methyl 2-(4-hydroxy-6-methoxy-2-pyrimidinylxoy)-6-(Z)-(1-methoxyiminoethyl) benzoate (IV), respectively, derived by microbial degradation.\(^10\) In this study, the behaviors of compounds \(I\)–IV in paddy water and soil were selected for simulation. The proposed main metabolic pathways and physicochemical properties of these compounds are shown in Fig. 1 and Table 1.

2. Photoisomerization in paddy water

2.1. Theory

To express mathematically the photoisomerization process of pyriminobac-methyl in paddy water, we made the following assumptions: (1) the isomerization reaction occurs as a result of UV-B (wavelength of 280–315 nm) irradiation, and (2) isomerization is a reversible first-order reaction between \(I\) and \(II\) as a function of UV-B. Therefore, the mass balance equation

\[
\text{Photoisomerization} \quad \text{in paddy water} \quad \text{Fig. 1. Proposed main pathways of pyriminobac-methyl in water and soil.}
\]

<table>
<thead>
<tr>
<th>Parameter</th>
<th>I</th>
<th>II</th>
<th>III</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Molecular weight ((MW, \text{g mol}^{-1}))</td>
<td>361.4</td>
<td>361.4</td>
<td>347.3</td>
<td>347.3</td>
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<tr>
<td>Water solubility ((C_{sw}, \text{mg l}^{-1}))</td>
<td>9.25</td>
<td>175</td>
<td>171</td>
<td>412</td>
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<tr>
<td>Vapor pressure (Pa)</td>
<td>(3.50 \times 10^{-5})</td>
<td>(2.68 \times 10^{-5})</td>
<td>(8.49 \times 10^{-8} a)</td>
<td>(8.49 \times 10^{-8} a)</td>
</tr>
<tr>
<td>Equilibrium constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Henry’s constant (dimensionless)</td>
<td>(5.5 \times 10^{-7} b)</td>
<td>(2.2 \times 10^{-8} b)</td>
<td>(7.0 \times 10^{-11} b)</td>
<td>(2.9 \times 10^{-11} b)</td>
</tr>
<tr>
<td>Soil adsorption constant based on organic carbon ((K_{oc}, \text{ml g}^{-1}))</td>
<td>741 (^c)</td>
<td>372 (^c)</td>
<td>258 (^d)</td>
<td>159 (^d)</td>
</tr>
<tr>
<td>Freundlich exponent (1/n)</td>
<td>0.86 (^d)</td>
<td>0.86 (^d)</td>
<td>1.0</td>
<td>1.0</td>
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<tr>
<td>Rate constants</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Dissolution ((k_d, \text{day}^{-1}))</td>
<td>(2.6 \times 10^{-2})</td>
<td>(2.4 \times 10^{-4})</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Adsorption ((k_{ads}, \text{day}^{-1}))</td>
<td>(8.4 \times 10^{-2} c)</td>
<td>(1.8 \times 10^{-1} c)</td>
<td>(1.8 \times 10^{-1} c)</td>
<td>(3.2 \times 10^{-1} c)</td>
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<tr>
<td>Desorption ((k_{des}, \text{day}^{-1}))</td>
<td>(4.2 \times 10^{-2} f)</td>
<td>(9.2 \times 10^{-2} f)</td>
<td>(9.0 \times 10^{-2} f)</td>
<td>(1.6 \times 10^{-1} f)</td>
</tr>
<tr>
<td>Volatilization ((K_v, \text{m day}^{-1}))</td>
<td>(8.9 \times 10^{-5} g)</td>
<td>(3.6 \times 10^{-6} g)</td>
<td>(1.1 \times 10^{-5} g)</td>
<td>(4.7 \times 10^{-5} g)</td>
</tr>
<tr>
<td>Degradation in water ((k_{d, w}, \text{day}^{-1}))</td>
<td>(3.1 \times 10^{-3})</td>
<td>(3.7 \times 10^{-3})</td>
<td>(6.9 \times 10^{-5})</td>
<td>(6.9 \times 10^{-5})</td>
</tr>
<tr>
<td>Formation fraction in water ((f_{aw}))</td>
<td>–</td>
<td>–</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Degradation in soil ((k_{d, s}, \text{day}^{-1}))</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volcanic soil</td>
<td>(5.2 \times 10^{-3})</td>
<td>(9.1 \times 10^{-3})</td>
<td>(1.4 \times 10^{-2})</td>
<td>(2.2 \times 10^{-2})</td>
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<tr>
<td>Diluvial soil</td>
<td>(3.5 \times 10^{-1})</td>
<td>(2.0 \times 10^{-1})</td>
<td>(4.1 \times 10^{-2})</td>
<td>(2.6 \times 10^{-2})</td>
</tr>
<tr>
<td>Formation fraction in soil ((f_{as}))</td>
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<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Volcanic soil</td>
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<td>–</td>
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<td>0.98</td>
</tr>
<tr>
<td>Diluvial soil</td>
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<td>–</td>
<td>0.75</td>
<td>0.77</td>
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<tr>
<td>Photoisomerization in water ((k_{pho, w}, \text{m}^2 \text{kJ}^{-1}))</td>
<td>(1.5 \times 10^{-1})</td>
<td>(1.1 \times 10^{-1})</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

\(^a\) Calculated with EPI Suite ver. 4.0.\(^11\) \(^b\) Calculated using the Dilling equation.\(^12\) \(^c\) Average for 5 soils.\(^13\) \(^d\) Calculated by the Kenaga and Goring equations.\(^14\) \(^e\) Assumed to be equal to 2\(k_{d, w}\) \(^f\) Calculated from \(C_{sw}\) \(^g\) Calculated by the Liss & Slater method.\(^15\)
of I and II in water can be given by:
\[
\frac{dC_{E,W}}{dt}_{UVB} = -\frac{dC_{Z,W}}{dt}_{UVB} = -k_{photo,E}C_{E,W} + k_{photo,Z}C_{Z,W}
\]

(1)

Where the subscripts E, Z and W denote I, II, and the water compartment, respectively, and

- \(C_W\) = pesticide concentration in water (mg l\(^{-1}\))
- \(I_{UVB,W}\) = cumulative UV-B irradiance received by the water body (kJ m\(^{-2}\))
- \(k_{photo}\) = first-order rate constant of photoisomerization (m\(^2\) kJ\(^{-1}\)).

Equation 1 can be rewritten by applying the chain rule for the differentiation of composite functions as:
\[
\frac{dC_{E,W}}{dt} = -\frac{dC_{Z,W}}{dt} = -k_{photo,E} \frac{dI_{UVB,W}}{dt} C_{E,W} + k_{photo,Z} \frac{dI_{UVB,W}}{dt} C_{Z,W}
\]

2. Net UV-B irradiation (\(I_{UVB,h}\), kJ m\(^{-2}\)) at a water depth of \(h\) (m) can be expressed by taking into account the fraction of irradiation intercepted by the rice crop (\(f_{crop}\)) and the fraction reflected from the water's surface (ref) and using the Lambert-Beer law as:
\[
I_{UVB,h} = I_{UVB,f_{crop}}(1-ref)\exp(-\alpha_{UVB}h)
\]

3. Formation and degradation of metabolites in soil

3.1. Theory

On the basis of the proposed pathways in soil (Fig. 1), the formation and degradation processes of III and IV were expressed as consecutive first-order reactions\(^{1,2}\):
\[
\frac{dC_{ME,S}}{dt} = f_{d,E}k_{d,E}C_{E,S} \frac{MW_{ME}}{MW_{E}} - k_{d,E}C_{ME,S}
\]

\[
\frac{dC_{MZ,S}}{dt} = f_{d,M}k_{d,M}C_{Z,S} \frac{MW_{MZ}}{MW_{Z}} - k_{d,M}C_{MZ,S}
\]

(6)

(7)

Where the subscripts ME, MZ, and S denote III, IV, and the soil solid compartment, respectively, and

- \(C_E\) = pesticide concentration in soil (mg kg\(^{-1}\))
- \(f_{d}\) = formation fraction from a parent into a metabolite in soil (–)
- \(k_{d}\) = first-order degradation rate constant in soil (day\(^{-1}\))
- \(MW\) = molecular weight (g mol\(^{-1}\)).

The formation fraction is the ratio of the amount of substance transformed from a precursor into a degradation product, and can be directly estimated as a free parameter in fitting equation 6 or 7 to measured data by the nonlinear least-squares method.\(^{19}\)

3.2. Soil degradation experiment

A soil degradation experiment\(^{10}\) was conducted with Habikino and Ushiku soils (Table 2). The soil samples were passed through a 2-mm sieve, and then samples weighing 20 to 30 g were placed in 100-ml Erlenmeyer flasks, covered with water up to 1.5 cm deep, and incubated at 30°C in the dark for 12 days. The pre-incubated soils were then treated with I or II labeled with \(^{14}\)C at the benzene ring (radiochemical purity: >99.0%) at a concentration of ca. 0.15 mg kg\(^{-1}\) on a dry weight basis, and incubated at 30°C in the dark for 56 days (Habikino soil) or 335 days (Ushiku soil). At specified intervals, the incubated soil was extracted with aqueous acetone at 80°C and then partitioned into ethyl acetate. Ethyl acetate extracts were examined by thin-layer chromatography and radioassayed by liquid scintillation counting. Rate constants and formation fractions for each pathway (Fig. 1) were calculated as described in Section 2.2.

4. Improvements of PADDY model

The PADDY model was originally developed to predict pesticide concentrations in water and soil in a paddy field.\(^{3,4}\) Pesticide transport processes and fate in the paddy field included in the model were (1) pesticide dissolution from granules into paddy water, (2) adsorption and desorption between paddy water and surface soil, (3) runoff and seepage loss, (4) leaching, (5) volatilization from paddy water to atmosphere, and (6) sedimentation reported by Kon et al.\(^{18}\) Photoisomerization rates of I and II were calculated by the nonlinear least-squares method with Microsoft Excel Add-In software.\(^{19}\)
In this study, we improved the PADDY model by including photoisomerization between I and II, the transport, formation and degradation processes of III and IV (Fig. 2).

The water balance in a paddy field can be expressed as:

$$\frac{dA}{dt} = Q_{in} - Q_{out} + A(P - E - T) - Q_v - Q_h$$  \hspace{1cm} (8)

Where
- $A$ = area of the paddy field (m$^2$)
- $Q_{in}$ = irrigation rate (m$^3$ day$^{-1}$)
- $Q_{out}$ = outflow rate (m$^3$ day$^{-1}$)
- $P$ = precipitation (m day$^{-1}$)
- $E$ = evaporation rate (m day$^{-1}$)
- $T$ = transpiration rate (m day$^{-1}$)
- $Q_v$ = vertical percolation rate (m$^3$ day$^{-1}$)
- $Q_h$ = horizontal percolation rate (m$^3$ day$^{-1}$).

The PADDY simulates pesticide behavior at the surface and subsurface layers in a paddy field. The surface layer is composed of paddy water and surface soil compartments assumed to be completely mixed systems. The thickness of the surface soil compartment was set at 5 mm; therefore, the transport of pesticides into and out of the surface soil compartment with vertical percolation was not considered. If the pesticide concentration in the irrigation water is equal to zero, then the chemical mass balance equations at the surface layer are as follows:

For the paddy water compartment,

$$Ah \frac{dC_{E,W}}{dt} = Ahk_{s,E}(C_{w,E} - C_{E,W}) - (Q_{out} + Q_i + Q_h)C_{E,W}$$

$$- Adp_1(k_{ads,E}K_{f,E}C_{w,E}^{\text{ads,E}} - k_{des,E})C_{E,S}$$

$$- K_{E,W}AC_{E,W}$$

$$- Ah\left(k_{photo,E} \frac{dI_{UVB,W}}{dt} + k_{div,E}\right)C_{E,W}$$

$$+ Ahk_{photo,E} \frac{dI_{UVB,W}}{dt} C_{Z,W}$$

$$- AC_{E,W} \frac{dh}{dt}$$  \hspace{1cm} (9)

For the surface soil compartment,

$$Ah \frac{dC_{Z,W}}{dt} = Ahk_{s,Z}(C_{s,E} - C_{Z,W}) - (Q_{out} + Q_i + Q_h)C_{Z,W}$$

$$- Adp_1(k_{ads,Z}K_{f,Z}C_{s,E}^{\text{ads,Z}} - k_{des,Z})C_{Z,S}$$

$$- K_{Z,W}AC_{Z,W}$$

$$- Ah\left(k_{photo,Z} \frac{dI_{UVB,W}}{dt} + k_{div,Z}\right)C_{Z,W}$$

$$+ Ahk_{photo,Z} \frac{dI_{UVB,W}}{dt} C_{E,W}$$

$$- AC_{Z,W} \frac{dh}{dt}$$  \hspace{1cm} (10)

For the paddy water compartment,

$$Ah \frac{dC_{ME,W}}{dt} = -(Q_{out} + Q_i + Q_h)C_{ME,W}$$

$$- Adp_1(k_{ads,ME}K_{f,ME}C_{ME,W}^{\text{ads,ME}} - k_{des,ME})C_{ME,S}$$

$$- K_{ME,W}AC_{ME,W}$$

$$+ Ah\left(f_{div,ME}k_{div,ME}C_{E,W} \frac{MW_{ME}}{MW_E} - k_{div,ME}C_{ME,W}\right)$$

$$- AC_{ME,W} \frac{dh}{dt}$$  \hspace{1cm} (11)
where $C_{ws}$ = water solubility of the pesticide (mg l$^{-1}$)

$k_f$ =  first-order degradation rate constant (day$^{-1}$)

$d$ = thickness of the surface soil compartment (m)

$\rho_b$ = bulk density of the soil (g cm$^{-3}$)

$k_{ads}$ = adsorption rate constant (day$^{-1}$)

$k_{des}$ = desorption rate constant (day$^{-1}$)

$K_f$ = Freundlich adsorption coefficient (cm$^3$  g$^{-1}$)

$1/n$ = Freundlich exponent (~)

$K_L$ = volatilization rate constant (m day$^{-1}$)

$k_{dw}$ = first-order degradation rate constant in water (day$^{-1}$)

$f_{dw}$ = formation fraction from a parent into a metabolite in water (~).

For dissolution of the granule formulation,

$$\frac{dm_E}{dt} = -Ahk_{f,E}(C_{ws,E} - C_{E,W})$$

$$\frac{dm_z}{dt} = -Ahk_{f,Z}(C_{ws,Z} - C_{Z,W})$$

Where $m$ = amount of the pesticide in the granule formulation (mg).

When dissolution of the pesticide from the granule is completed ($m=0$), $k_f$ is set to zero in equations 9 and 10.

The subsurface layer is divided into segments composed of the pore water and soil compartments assumed to be completely mixed systems with a thickness of 5 mm. Details of the compartment system and chemical mass balance equations at the subsurface layer were reported previously.21

These ordinary differential equations can be solved by techniques reported previously,2,3 and the solutions give the pesticide concentrations in the compartments in the surface and subsurface layers as a function of time $t$. A computer simulation program was developed with Visual Basic for Applications software in Microsoft Excel.

5. Experiments for model validation

5.1. Paddy lysimeter experiments

Paddy lysimeter experiments were conducted outdoors at the Life Science Research Institute in Kakegawa. Lysimeters (1 m x 1 m x 1 m deep) were packed from top to bottom with a soil layer (60 cm), a sand layer (15 cm), and a gravel layer (15 cm). Two types of soil (Kikugawa and Tochigi) were used for this study (Table 2). At 8 days after rice transplanting, so-called “1 kg granules” containing 0.3% of pyriminobac-methyl were applied uniformly at a rate of 10 kg ha$^{-1}$ under flooded conditions. The experiment was performed with intermittent irrigation management and without percolation of paddy water. The water depth was kept at 5 cm during the experiment. At specified intervals, paddy water was sampled at 2-3 cm below the water surface from four spots on the diagonal lines of the lysimeters, and the composite sample was analyzed for I and II. Daily UV-B was estimated from daily solar irradiation observed in Shizuoka, as described in Section 2.2.

5.2. Pesticide residues in soil

Experiments to determine pesticide residues in soil were conducted in two paddy fields, one at the Osaka Prefectural Agricultural and Forestry Research Center in Habikino, Osaka, and the other at the Japan Association for Advancement of Phyto-Regulators in Ushiku, Ibaraki (Table 2). The area of the fields in Habikino and Ushiku was 40 and 21 m$^2$, respectively. At 28 days (Habikino) or 25 days (Ushiku) after rice transplanting, so-called “1 kg granules” containing 0.3% of pyriminobac-methyl were applied uniformly at a rate of 10 kg ha$^{-1}$ under flooded conditions. The experiment was performed with intermittent irrigation management, and the water depth was kept at ca. 5 cm during the experiment. At specified intervals, soil samples from the surface to 10 cm depth were collected at 5-8 random spots in the fields, and the composite sample was analyzed for I-IV. Daily UV-B was estimated from daily solar irradiation observed in Osaka and Tsukuba, as described in Section 2.2.
5.3. Field dissipation experiment

A pesticide dissipation experiment was conducted in a paddy field (40 m²) at the National Institute for Agro-Environmental Sciences (NIAES) in Tsukuba. The soil characteristics are listed in Table 2. At 7 days after transplanting the rice plants (12 May 1997), Prosper-A One Kilo Granule 36 (azimsulfuron 0.06%, bensulfuron-methyl 0.30%, mefenacet 4.5%, and pyriminobac-methyl 0.30%) was applied uniformly at the rate of 10 kg ha⁻¹ under flooded conditions. The experiment was performed with intermittent irrigation management. At specified intervals, paddy water and surface soil of 10 cm deep were sampled, and the concentrations of I and II were quantified. Details of the experimental conditions, sampling, and analytical method were the same as reported previously.¹¹

Results and Discussion

1. Parameters of pyriminobac-methyl and its metabolites

1.1. Photoisomerization in water

Figure 3 shows the changes of I and II in water exposed to sunlight obtained from the measurement of the photoisomerization rate. \((E)/(Z)\) isomerization reached approximate equilibrium after 4.5 hr. The kinetic analysis showed that the \((E)/(Z)\) ratio in the photostationary state \((k_{\text{photo},E}/k_{\text{photo},Z})\) was about 1/1.35, and the reaction rates of I and II \((k_{\text{photo},E} \text{ and } k_{\text{photo},Z})\) as a function of UV-B irradiation were 0.15 and 0.11 m²kJ⁻¹, respectively. Another photodegradation study using a xenon arc lamp with various UV filters found that irradiation at 280–320 nm was the main contributor to photoisomerization,⁵ therefore, it is reasonable to express photoisomerization as a function of UV-B irradiation.

The fraction of irradiation intercepted by the rice crop \(f_{\text{crop}}\) was assumed to be zero because of the small rice canopy at the time of herbicide application in the outdoor experiments. In general, the fraction reflected by the water’s surface \(f_{\text{ref}}\) is small (0.06–0.08); therefore, \(f_{\text{ref}}\) was set at 0.06. The attenuation coefficient \(a_{\text{UVB}}\) was assumed to be constant with the average values of \(C_{\text{CHL}}, C_{\text{DOC}}, \text{ and } C_{\text{SED}}\) in paddy water, which were assumed to be 0.001, 5, and 10 mg L⁻¹, respectively, at 1–4 weeks after transplanting, corresponding to the timing of herbicide application in the experiment.

![Fig. 3. Photoisomerization of I and II in water. (○), (△): measured; (--), (-----): simulated.](image)

1.2. Formation and degradation of metabolites in soil

Figure 4 shows the changes of \(^{14}\text{C}\) distribution in I and III, or in II and IV in Habikino soil treated with I or II. Kinetic analysis based on the product distribution showed that the formation and degradation of III and IV in the two soils followed consecutive first-order reactions, as expressed by Eqs. 6 and 7.¹⁹,²⁰ The parent compounds of I and II had decreased exponentially to 7.2 and 19.9% of the applied \(^{14}\text{C}\), respectively, at 7 days after treatment. The metabolites of III and IV increased rapidly and peaked at 71.4 at 7 days and 69.7% of the applied \(^{14}\text{C}\) at 14 days, respectively, and then decreased gradually. Similar patterns of these compounds were observed in Ushiku soil, but the decrease of I and II and the increase of III and IV were slower than in Habikino soil. The reaction rates and formation fractions obtained for each pathway are shown in Table 1. The formation fractions from I into III \((f_{\text{III,AB}})\) and from II into IV \((f_{\text{IV,AB}})\) in Habikino soil were 0.75 and 0.77, respectively, and the corresponding values in Ushiku soil were 1.0 and 0.98, respectively; therefore III and IV were the major metabolites in soil transformed from I and II, respectively.

![Fig. 4. Distribution of radioactivity in Habikino soil treated with I (A) or II (B). (○), (△): measured; (--), (-----): simulated.](image)

2. Validation of the improved PADDY model

2.1. Paddy lysimeter experiments

The measured concentrations of I and II in paddy water increased immediately after herbicide application and then decreased gradually (Fig. 5). The maximum concentrations of I and II in paddy water for Kikugawa soil were 0.031 at 3 hr and 0.014 mg L⁻¹ at 3 days, respectively, and the corresponding values for Tochigi soil were 0.023 at 3 hr and 0.009
mg l$^{-1}$ at 1 day, respectively.

The concentration changes in paddy water simulated by the improved PADDY model with and without consideration of photoisomerization are shown in Fig. 5. Simulation without consideration of photoisomerization overestimated the concentration of I and underestimated the concentration of II at all time points because the rapid transformation from I to II by photoisomerization immediately after herbicide application described in Section 1.1 was not reflected in the simulation. Good agreement between the simulated and observed concentrations was obtained by considering photoisomerization because the improved model successfully simulated the rapid degradation of I and the increase of II during the first week after herbicide application. However, the concentration of II was overestimated in the early time period probably because the setup for the estimated attenuation coefficient ($\alpha_{UVB}$) in paddy water did not coincide with the experimental condition as a result of overrating the efficiency of the photoisomerization reaction in the simulation. Goodness of fit was assessed using the statistical index of root mean square error (RMSE).26,27)

$$\text{RMSE} = \frac{100}{\bar{O}} \sqrt{\frac{1}{n} \sum_{i=1}^{n} (P_i - O_i)^2}$$  \hspace{1cm} (19)

Where $P_i$ and $O_i$ are the predicted and observed values, respectively, $\bar{O}$ is the mean of the observed values and $n$ is the number of observations. In general, the lower the RMSE, the higher is the agreement between observed and predicted data. RMSE values of I with consideration of photoisomerization were lower than those without considering photoisomerization (Table 3). On the other hand, the RMSE values of II with consideration of photoisomerization were higher than those without considering photoisomerization due to the large margin of error between observed and predicted data on days 1 and 3. In analysis excluding the data on days 1 and 3, the RMSE values of II with consideration of photoisomerization were 44.9 and 76.7% for Kikugawa and Tochigi soil, respectively. Consequently, an acceptable agreement was obtained in the simulation by the improved PADDY model except for overestimation of the concentration of II in the early time period.

2.2. Pesticide residues in soil

The measured and simulated concentrations of I–IV in the 0–10 cm soil layer are shown in Fig. 6. The improved PADDY model successfully simulated the measured concentration changes of I and II in the 0–10 cm soil layer. I and II disappeared faster in Habikino soil than in Ushiku soil. This result is explained by the soil degradation study results, because the degradation rate constants of I and II in Habikino soil were much larger than those in Ushiku soil (Table 1). The measured concentration of I in Habikino soil peaked at 0.014 mg

![Fig. 5. Concentrations of I and II simulated with (—) and without (-----) consideration of isomerization, and measured concentrations (○) in the surface water of the paddy lysimeters. (A) Kikugawa soil; (B) Tochigi soil.](image)

<table>
<thead>
<tr>
<th>Soil</th>
<th>RMSE of I (%)</th>
<th>RMSE of II (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Previous$^{a)}$</td>
<td>Improved$^{b)}$</td>
</tr>
<tr>
<td>Kikugawa</td>
<td>70.4</td>
<td>28.6</td>
</tr>
<tr>
<td>Tochigi</td>
<td>99.2</td>
<td>15.0</td>
</tr>
</tbody>
</table>

$^{a)}$Simulation without consideration of photoisomerization.

$^{b)}$Simulation with consideration of photoisomerization.
kg\(^{-1}\) immediately after application and then quickly decreased to less than the detection limit of 0.005 mg kg\(^{-1}\) after 7 days. \(\text{II} \) was not detected (<0.005 mg kg\(^{-1}\)) during the experiment. In contrast, the concentrations of \(\text{I} \) and \(\text{II} \) in Ushiku soil peaked at 0.058 at 3 hr and 0.015 mg kg\(^{-1}\) at 3 days, respectively, and then decreased gradually.

Figure 7 shows the simulated distribution of \(\text{I} \) and \(\text{II} \) in the upper soil layer of 0–3 cm in the two fields. The average vertical percolation rate was ca. 5 mm day\(^{-1}\) in the two fields. The simulated results showed that most of \(\text{I} \) and \(\text{II} \) were distributed in the 0–1 cm soil layer and that leaching losses below 3 cm depth were less than 0.1% of the applied mass in the two fields because \(\text{I} \) and \(\text{II} \) have relatively high soil adsorption constants \(K_{oc}\), as shown in Table 1. The residual mass of \(\text{I} \) and \(\text{II} \) in Ushiku soil was larger than in Habikino soil, explained by the strong adsorption of \(\text{I} \) and \(\text{II} \) to organic carbon in Ushiku soil, which has higher organic carbon content than Habikino soil (Table 2). Moreover, the difference in the degradation rate of \(\text{I} \) and \(\text{II} \) of the two soils also affected the behavior, as mentioned previously.

In the two study fields, metabolites \(\text{III} \) and \(\text{IV} \) were not detected (<0.005 mg kg\(^{-1}\)) during the experiment. The simulated peak concentrations of \(\text{III} \) and \(\text{IV} \) in Habikino soil were 0.0039 and 0.0038 mg kg\(^{-1}\), respectively, and the corresponding value in Ushiku soil was 0.0023 mg kg\(^{-1}\). These results are also in agreement with the measured results.

### 2.3. Field dissipation experiment

Daily evapotranspiration \((E+T)\) was estimated by the FAO Penman-Monteith method\(^{29}\) with meteorological data observed by NIAES in Tsukuba and the value of the crop coefficient for the initial stage \((K_{c ini}=1.1)\) obtained from the literature.\(^{29}\) Daily UV-B was obtained from data from the Aerological Observatory, Japan Meteorological Agency,\(^{30}\) near NIAES. The average vertical percolation rate was 3 mm day\(^{-1}\) during the experiment. Daily precipitation, estimated daily outflow, water depth in the field, and daily UV-B irradiation are shown in Fig. 8. Simulated water depth agreed well with the trend in the measured values.

Figure 9 shows the measured and simulated changes in \(\text{I} \) and \(\text{II} \) in the paddy field in Tsukuba. Measured dissipation
patterns in the paddy water were similar to those in the paddy lysimeter study. In the 0–2.5 cm soil layer, peak concentrations of I and II were 0.050 and 0.015 mg kg$^{-1}$, respectively, 3 days after application; the concentrations then decreased gradually. I and II were not detected (<0.001 mg kg$^{-1}$) in either the 2.5–5 or 5–10 cm soil layers during the experiment.

The improved PADDY model simulated with acceptable accuracy the dissipation of I and II in paddy water and the 0–2.5 cm soil layer (Fig. 9). The RMSE values of I and II in paddy water were 63.3 and 164.8%, respectively, and the corresponding values in the 0–2.5 cm soil layer were 91.8 and 55.3%, respectively. The simulated peak concentrations of I and II in the 2.5–5 and 5–10 cm soil layers were less than 0.00001 mg kg$^{-1}$. These results are in agreement with the measured results.

**Conclusion**

The improved PADDY model, including photoisomerization and the metabolic pathways of herbicide pyriminobac-methyl, is a useful tool for predicting pesticide concentrations in paddy fields. Although additional validation of the model with another pesticide having the main metabolites detected frequently under paddy conditions is necessary, we anticipate that this model can be used to assess exposure to pesticides and their main metabolites.

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**References**