An improved PADDY model including uptake by rice roots to predict pesticide behavior in paddy fields under nursery-box and submerged applications

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We developed an improved version of the PADDY model for predicting pesticide behavior in paddy fields, which includes pesticide uptake by rice roots. We applied the model to nursery-box and submerged pesticide applications. A paddy field was divided into root-zone and inter-plant areas, and paddy soil containing pesticides was vertically separated into three layers. Pesticide behavior was modeled with mass fractions of the pesticides in paddy water and the soil layers immediately after rice transplanting obtained from field experiments, and uptake by rice roots was described using the transpiration stream concentration factor. The improved model successfully simulated measured concentration changes in a paddy field, including rice plants, under nursery-box and submerged applications. The model evaluated the difference in the concentrations of nursery-box-applied pesticides between root-zone and inter-plant soil samples with several key parameters. Our study provides a useful solution for simulating the uptake of pesticides in soil by rice roots.

Keywords: environmental fate, paddy conditions, simulation model, plant uptake, nursery-box-applied granules.

Introduction

Paddy fields are major arable lands in Japan, and their area under rice cultivation was 1.48 million ha in 2016. Most paddy fields are treated with a wide variety of rice pesticides during the cropping season, and the pesticides can easily be transported to river systems via drainage canals due to spray drift, surface run-off or lateral seepage from paddy fields. Public concerns regarding the adverse effects of pesticides present in runoff on aquatic ecosystems and drinking water are increasing. In Japan, rice pesticides commonly used in paddy fields have been detected in rivers. The concentration and detection frequency of pesticides in rivers depend largely on pesticide behavior in paddy fields, which is affected by application amounts, frequency, and timing. Therefore, it is important to evaluate the behavior of rice pesticides in paddy water and soil in order to assess and manage the ecological risks of the pesticides in river systems.

Mathematical models are useful to supplement monitoring data and evaluate the environmental fate of pesticides. Recently, field-plot-scale models (e.g., PADDY and PCPF-1) have been developed to simulate the behavior of paddy rice pesticides in Japan. The original version of the PADDY model was developed and validated to simulate the behavior of paddy rice herbicides under submerged application. The latest version of the model includes a procedure for simulating the photosomerization and metabolism of the herbicide pyriminobac-methyl. Recently, nursery-box treatment, where a formulation containing a systemic fungicide and/or insecticide is applied to rice seedlings in nursery boxes before transplanting, has become popular in Japan for more effective and efficient plant protections during the early and middle growth stages of paddy rice. Some nursery-box-applied pesticides have been detected annually in river water by means of monitoring. These pesticides are taken up by rice roots and transported to the entire plant body. However, the PADDY model has not been validated with field experimental data for fungicides and insecticides used for nursery-box or submerged applications. The latest version of the PCPF-1 model was developed by adding a root-zone compartment to simulate the behavior of nursery-box-applied pesticides in paddy water and soil. However, no model has been developed for simulating pesticide transport and fate, including the uptake of the pesticides by rice roots under paddy conditions. Recently, high-density rice seedlings and sparse planting have become popular because they reduce costs and labor. However, concerns about less effective plant protections are increasing under these rice-cultivation methods. Therefore, it is important to evaluate the pesticide concentrations in rice plants for...
optimal protection against diseases and insect pests under various rice-cultivation methods.

The objective of this study was to develop and evaluate an improved PADDY model that includes pesticide uptake by rice roots under nursery-box and submerged applications. To validate the model, we compared the values calculated by the improved model with measured values from paddy field experiments.

**Theory, Materials, and Methods**

1. **Chemicals**
   
   Fipronil \([(\pm)-5\text{-}amino\text{-}1\text{-}(2,6\text{-}dichloro\text{-}a\text{-}a\text{-}a\text{-}trifluoro\text{-}p\text{-}tolyl)\text{-}4\text{-}trifluoromethylsulfinylpyrazole\text{-}3\text{-}carbonitrile}]\) is a phenylpyrazole insecticide used in the early and middle growing stages of paddy rice. The fungicide isoprothiolane (di-isopropyl 1,3-dithiolan-2-ylidenemalonate) is used to eradicate and prevent rice blast disease. These pesticides are available in granular formulations and are widely used for nursery-box applications in Japan. Isoprothiolane is also used for submerged or foliage application before rice heading or harvesting. In this study, we simulated the behavior of fipronil and isoprothiolane in paddy water, soil, and rice plants. The physicochemical properties of these pesticides\(^{16,18-21}\) are summarized in Table 1.

2. **Model description**
   
   The original PADDY model\(^{10,11}\) included (1) pesticide dissolution from granules into paddy water, (2) adsorption and desorption between surface soil and paddy water, (3) runoff and seepage, (4) leaching, (5) volatilization from paddy water to the atmosphere, and (6) degradation in paddy water and surface soil (Fig. 1). In this study, we considered the following situation to include pesticide uptake by rice roots under nursery-box application: Granular pesticides are applied to the soil surface in nursery boxes with rice seedlings just before transplanting, and the seedlings are transplanted into paddy fields by a rice-transplanting machine. Subsequently, the pesticides are buried in paddy soil near the seedlings. We made the following simplifying assumptions to determine pesticide distribution in paddy soil immediately after transplanting (Fig. 1): (1) the paddy field

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**Table 1. Physicochemical properties of isoprothiolane and fipronil**

| Parameter                              | Isoprothiolane\(^{18}\) | Fipronil\(^{16,19}\) |
|---------------------------------------|--------------------------|-----------------------|
| Molecular weight (g/mol)              | 290.39                   | 437.1                 |
| Water solubility (C\(_{sw}\), mg/L)   | 48.5 (20°C)              | 3.78 (20°C)           |
| Vapor pressure (Pa)                   | \(4.93\times10^{-4}\) (25°C) | <2\times10^{-6} (20°C) |
| Logarithmic \(n\)-octanol–water partition coefficient (log \(P_{ow}\)) | 2.80                     | 4.00                  |
| Equilibrium constants                 |                          |                       |
| Henry’s constant (dimensionless)      | \(1.2\times10^{-6}\) \(^{a}\) | \(1.0\times10^{-7}\) \(^{a}\) |
| Soil adsorption constant based on organic carbon (\(K_{oc}\), mL/g) | \(758\) (25°C)\(^{b}\) | \(1035\) (25°C)\(^{b}\) |
| Freundlich exponent (1/\(n\), dimensionless) | 0.98\(^{0}\)            | 1.0                   |
| Rate constants                        |                          |                       |
| Dissolution (\(k_{s}\), 1/day)        | \(1.0\times10^{-4}\) \(^{c}\) | \(5.0\times10^{-5}\) \(^{c}\) |
| Nursery-box-applied granules          |                         |                       |
| Submerged granules                    | \(1.0\times10^{-1}\) \(^{c}\) |                      |
| Adsorption (\(k_{ads}\), 1/day)       | \(1.2\times10^{-1}\) \(^{d}\) | \(2.3\times10^{-2}\) \(^{d}\) |
| Desorption (\(k_{des}\), 1/day)       | \(6.0\times10^{-2}\) \(^{d}\) | \(1.2\times10^{-2}\) \(^{d}\) |
| Volatilization (\(K_{L}\), m/day)     | \(2.1\times10^{-3}\) \(^{e}\) | \(1.4\times10^{-3}\) \(^{e}\) |
| Hydrolysis in water (\(k_{hydro}\), 1/day) | 0                       | 0                     |
| Photolysis in water (\(k_{photo}\), m²/kJ) | 0                       | \(7.8\times10^{-3}\) |
| Degradation in soil (\(k_{ds}\), 1/day) | 5.0\times10^{-3}         | 2.9\times10^{-2}      |

\(^{a}\) Calculated using the equation of Dilling (Ref. 20). \(^{b}\) Average value. \(^{c}\) Calibrated. \(^{d}\) Assumed to be equal to \(2\times k_{des}\). \(^{e}\) Estimated from \(C_{sw}\). \(^{f}\) Calculated by the method of Liss and Slater (Ref. 21).
is divided into the root-zone area to the total area of the field is defined as $f_{RZ/AT}$ (dimensionless).\(^{22}\) (2) paddy soil containing the granules is vertically separated into three layers: a 0.5 cm surface layer, a root-zone layer, and the interlayer between those two layers; and (3) when transplanting depth is $d_p$ (cm below soil surface), the root-zone layer ranges from $d_p-1$ to $d_p+1$ cm in depth.

2.1. Initial distribution of nursery-box-applied pesticides in the paddy field

If the granular pesticides are not present below the surface layer of the inter-plant area, their mass distribution immediately after transplanting can be expressed as follows:

For paddy water deposited on the soil surface,

$$M_{W,r} = f_W M_{app} \quad (1)$$

for the surface layer including root-zone and inter-plant areas,

$$M_{S,S,0} = f_s M_{app} \quad (2)$$

for the interlayer of the root-zone area,

$$M_{S,I,0} = (1 - f_w - f_s)(1 - f_r) M_{app} \quad (3)$$

and for the root-zone layer of the root-zone area,

$$M_{S,R,0} = (1 - f_w - f_s)f_r M_{app} \quad (4)$$

where

$M_{app}$=the amount of applied pesticide,

$M_{W,0}$=the initial amount of pesticide in paddy water,

$M_{S,S,0}$=the initial amount of pesticide in the surface soil layer,

$M_{S,I,0}$=the initial amount of pesticide in the interlayer of the root-zone area,

$M_{S,R,0}$=the initial amount of pesticide in the root-zone layer of the root-zone area,

$f_w$=the mass fraction of granules in paddy water,

$f_s$=the mass fraction of granules in the surface soil layer, and

$f_r$=the vertically distributed mass fraction of granules in the root-zone layer.

The $M$ values are expressed in milligrams, whereas the $f$ values are dimensionless. The initial mass distributions of the pesticides are used to determine the initial pesticide concentrations in the paddy field to solve the ordinary differential equations as described in Section 2.4.

2.2. Uptake of pesticides by rice roots

The transpiration stream concentration factor (TSCF, dimensionless) is the chemical concentration ratio between the transpiration stream in the xylem and soil water in the root zone. The TSCF was described by Briggs \(et al.\)\(^{23}\) and has been widely used as a descriptor of chemical uptake by plant roots. The mass flow to stem and leaf within the xylem ($N_{xylem}$, g/day) is expressed as

$$N_{xylem} = Q_{xylem} TSCF \cdot C_{W,RZ} \quad (5)$$

where

$Q_{xylem}$=the volumetric flow rate of the transpiration stream in the xylem (m$^3$/day), and

$C_{W,RZ}$=the pesticide concentration in soil water adjacent to the plant root zone (g/m$^3$).

We made the following assumptions for the chemical mass balance in paddy rice: (1) pesticides taken up by roots are instantaneously transported to the entire plant body and are distributed uniformly, (2) the exchange of pesticides between the plant body and air, photolysis on the plant surface, and degradation in the plant body are not considered, and (3) plant growth is approximated by an exponential function. Therefore, the chemical mass balance equation for the rice plant can be given as

$$\frac{dC_p}{dt} = \frac{A T_C}{m_p} TSCF \cdot C_{W,RZ} - \lambda_p C_p \quad (6)$$

where

$A$=the area of the paddy field (m$^2$),

$C_p$=the pesticide concentration in the plant (mg/kg on a fresh weight [FW] basis),

$T_C$=the fall in the paddy water level because of plant transpiration (= $Q_{TS}/A$, m/day),

$m_p$=the mass of the entire plant on a FW basis (kg), and

$\lambda_p$=the first-order plant growth rate constant (1/day).

2.3. Photolysis of fipronil in paddy water

In the UV-B range (280–315 nm), fipronil has a maximal absorption (6008 l/mole/cm) at 291 nm.\(^{24}\) Fipronil in water is degraded mainly by photolysis, with a half-life in distilled and natural water of 3.6–36.7 hr.\(^{19,25}\) To express mathematically the photolysis of fipronil in paddy water, we made the following assumptions: (1) photolysis results from UV-B irradiation, and (2) photolysis is a first-order reaction as a function of UV-B. Therefore, the mass balance equation in water can be given as

$$\frac{dC_W}{dt} = -k_{photo} \frac{dI_{UVB,W}}{dt} C_W \quad (7)$$

where

$k_{photo}$=the first-order photolysis rate constant in water (m$^2$/kL), and

$I_{UVB,W}$=the cumulative UV-B irradiance received by the water body (kJ/m$^2$).

The $I_{UVB,W}$ was calculated from cumulative UV-B irradiance above the rice plants (kJ/m$^2$) as reported previously.\(^{12}\)

2.4. Improved PADDY model

The water balance in a paddy field can be expressed as

$$A \frac{dh}{dt} = Q_{in} - Q_{out} + (P - ET_c) - Q_s - Q_h \quad (8)$$

where

$h$=the paddy water depth (m),

$Q_{in}$=the volumetric inflow (irrigation) rate (m$^3$/day),

$Q_{out}$=the volumetric outflow (overflow, drainage) rate (m$^3$/day),

$P$=the precipitation rate (m/day),

$ET_c$=the crop evapotranspiration rate (m/day),

$Q_s$=the volumetric flow rate of vertical percolation (m$^3$/day),
and

\[ Q_0 = \text{the volumetric flow rate of horizontal percolation (m}^3/\text{day).} \]

The \( ET_c \) was estimated from the reference crop evapotranspiration \( (ET_0, \text{m/day}) \) with a crop coefficient \( (K_c, \text{dimensionless})^{26} \):

\[ ET_c = ET_0 K_c \] (9)

The PADDY model simulates pesticide behavior in the surface and subsurface layers of a paddy field.\(^{10} \) The surface layer is composed of paddy water and surface soil compartments, which are assumed to be completely mixed systems. The thickness of the surface soil compartment was set at 0.5 cm, and the transport of pesticides into and out of this compartment with vertical percolation was not considered. If the pesticide concentration in irrigation water is equal to zero, then the chemical mass balance equations in the surface layer are as follows:

for the paddy water compartment,\(^{10} \)

\[
\frac{dC_w}{dt} = k_w(C_{ws} - C_w) - \frac{1}{Ah}(Q_{out} + Q_0 + Q_w)C_w
- k_{ads} \frac{dI_{uvbw}}{dt}C_w - k_{hydro}C_w - \frac{1}{h} \frac{dt}{dt}C_w
- k_{photo}C_{ws} - k_{ads}C_s
\]

and for the surface soil compartment,

\[
\frac{dC_s}{dt} = k_{ads}K_ifC_{ws}^{n_i} - k_{des}C_s - k_dC_s
\]

with \( C_s(t = 0) = \frac{M_{s,0}}{Adsp_o} \) (10)

where

\( C_w = \text{the pesticide concentration in water (mg/L),} \)
\( C_s = \text{the pesticide concentration in soil (mg/kg on a dry weight [DW] basis),} \)
\( k_w = \text{the dissolution rate constant (1/day),} \)
\( C_{ws} = \text{the water solubility of the pesticide (mg/L),} \)
\( d_s = \text{the thickness of the soil compartment (0.5 cm),} \)
\( p_o = \text{the bulk density of the soil (g/cm}^3), \)
\( k_{ads} = \text{the adsorption rate constant (1/day),} \)
\( k_{des} = \text{the desorption rate constant (1/day),} \)
\( K_i = \text{the Freundlich adsorption coefficient (cm}^2/\text{g),} \)
\( 1/n = \text{the Freundlich exponent (dimensionless),} \)
\( K_i = \text{the volatilization rate constant (m/day),} \)
\( k_{hydro} = \text{the first-order hydrolysis rate constant in water (1/day),} \)
\( k_d = \text{the first-order degradation rate constant in soil (1/day).} \)

For the dissolution of granules deposited on the soil surface,

\[
\frac{dM_w}{dt} = -Ahk_s(C_{ws} - C_w) \quad \text{with} \quad M_w(t = 0) = M_{w,0} \] (12)

When dissolution is completed \( (M_w = 0), \) \( k_s \) is set to zero in Eqs. (10) and (12).

The subsurface layer (including the interlayer and root-zone layer) is divided into segments composed of the pore water and soil compartments, which are assumed to be completely mixed systems with a thickness of 0.5 cm. The details of the compartment system in the subsurface layer have been reported.\(^{10} \) If the horizontal transport of pesticides in soil between root-zone and inter-plant areas is not considered and the downward rate of water percolation is constant, the chemical mass balance equations in the subsurface layer \( i \) are as follows:

for the pore water compartment,

\[
\frac{dC_{w,i}}{dt} = \frac{Q_v}{Adsp_i}TSCF \left(C_{w,j-1} - C_{w,i}\right)
- \frac{p_{hyd}}{\theta_{sat,i}}(k_{ads}K_iC_{w,j}^{n_i} - k_{des}C_{si})
- k_{hydro}C_{w,i} - \frac{T_{ci}}{n} \cdot TSCF \cdot C_{w,i}
\]

with \( C_{w,j}(t = 0) = 0 \) (13)

and for the soil compartment,

\[
\frac{dC_{s,i}}{dt} = k_{ads}K_ifC_{ws}^{n_i} - k_{des}C_{si} - k_dC_{si}
\]

with

\[
\begin{bmatrix}
0 \\
C_{s,j}(t = 0) = \frac{M_{s,i,0}}{f_{izone}Adsp_o} \\
\frac{M_{s,i,0}}{f_{izone}Adsp_o} \\
\frac{M_{s,i,0}}{f_{izone}Adsp_o}
\end{bmatrix}
\]

in the subsurface layer of the inter-plant area
in the interlayer of the root-zone area
in the root-zone layer of the root-zone area

where \( \theta_{sat} = \text{the volumetric saturated soil water content (= porosity, dimensionless),} \)

\( n = \text{the total number of subsurface layers where pesticides can be taken up by rice roots.} \)

If the pesticide uptake does not occur in the subsurface layer \( i \) because of the absence of rice roots, then \( T_{ci} = 0 \) in Eq. (13).

If the planting density of rice seedlings in the paddy field is constant, the chemical mass balance equation for the entire rice plant based on Eq. (6) is

\[
\frac{dC_p}{dt} = \frac{A}{m_p} \sum_{i=1}^{n} \left( \frac{T_{ci}}{n} \cdot TSCF \cdot C_{w,i} \right) - \lambda pC_p
\]

with \( C_p(t = 0) = 0 \) (15)

where the subscript \( j \) denotes the subsurface layer where pesticides can be taken up by rice roots.

These ordinary differential equations can be solved by a numerical solution\(^{10,11} \) with the initial pesticide concentration in each compartment derived from the initial mass distribution (Section 2.1); the solutions give the pesticide concentrations in the compartments of the surface and subsurface layers and in the entire rice plant as a function of time \( t \). A computer simulation program was developed with Visual Basic for Applications software (ver. 7.0) in Microsoft Excel 2010.
3. Validation of the improved PADDY model
A pesticide dissipation experiment was conducted in an experimental paddy field (500 m²) at the National Institute for Agro-Environmental Sciences (NIAES) in Tsukuba, Japan in 2008 and 2009. The soil texture was light clay with 1.8% w/w total carbon. Fuji-One Prince Granules (1.0% fipronil and 12.0% isoprothiolane) were used as a nursery-box-applied pesticide just before transplanting (May 12, 2008 and May 13, 2009), and the pesticide-treated rice seedlings were transplanted into the paddy field. The granular fungicide Fuji-One (12.0% isoprothiolane) was used for submerged application in the same field on July 1, 2008 and July 15, 2009. Intermittent irrigation management was used as the daily water management. At specified intervals, paddy water was collected from the field. Surface soil samples (3 cm deep) and rice plants were also collected in 2009. The concentrations of fipronil and isoprothiolane in each sample were determined. Daily UV-B irradiance values above the rice plants were estimated using the method of Kon et al.27) from daily solar irradiation observed by the NIAES in Tsukuba in 2008 and 2009 and the ratio of daily UV-B to daily solar irradiation. Experimental conditions, sampling, the analytical method, and the results are reported in detail in a separate paper.22)

Results and Discussion
1. Parameters for the uptake of pesticides by rice roots
To adequately estimate the uptake of residual pesticides in paddy soil by plants, the concentrations of pesticides in soil water need to be determined with more precision. Motoki et al.28) investigated the time-dependent increase in the soil adsorption coefficient (Kd, cm²/g) on five Japanese soils with different organic carbon contents and 27 pesticides with different physiochemical properties. In addition, they found that the time-dependent Kd values (Kd(t)) can be estimated from the Kd values obtained using the OECD method29) (i.e., the value of a 0-day incubation, Kd0):

\[ K_d(t) = K_{d,0} + 0.294K_{d,0}^{1.003} \sqrt{t} \]  

where t is the number of elapsed days after pesticide application. In this study, the Kd0 values of isoprothiolane and fipronil were calculated from the soil adsorption constant (Kf) shown in Table 1 and the total carbon content in paddy soil (1.8%); the time-dependent increase in the Freundlich adsorption coefficient (Kf) in Eqs. (10), (11), (13), and (14) was regarded as the Kd value calculated by Eq. (16).

Briggs et al.20) have reported that the TSCF is related to the n-octanol–water partition coefficient (Pow) of the pesticide for hydroponically grown barley plants:

\[ TSCF = 0.784\exp \left[ -\frac{\log P_{ow} - 1.78^2}{2.44} \right] \]  

Using the pressure chamber method, Hsu et al.30) found a similar equation for soybean plants:

\[ TSCF = 0.7\exp \left[ -\frac{\log P_{ow} - 3.07^2}{2.78} \right] \]  

The TSCF values of isoprothiolane were calculated to be 0.51 and 0.68 using Eqs. (17) and (18), respectively, and the corresponding values of fipronil were 0.10 and 0.51, respectively.

The Tc in Eqs. (13) and (15) can be estimated from the ETc by the following empirical equation as a function of the leaf area index (LAI),31) which is defined as the one-sided green leaf area per unit of ground surface area (m²/m²):

\[ T_c = ET_c\left[1 - \exp\left(-0.45LAI\right)\right] \]  

Figure 2 shows the changes in the ETc, Tc, and LAI in the experimental paddy field at the NIAES in 2009. The daily ETc was calculated using Eq. (9) with the Ke of 1.1 for the early experimental period and 1.2 for the late period30) from the daily ETc in Tsukuba (Tateno) near the NIAES, which was obtained from an agrometeorological database coupled with a crop model (MeteoCrop DB).32) The daily LAI was estimated by the Simulation Model for Rice-Weather relations (SIMRIW)33) with meteorological data (average daily temperature and daily solar irradiation) in 2009 for Tsukuba (Tateno), Japan,34) and the initial values of the seedlings (LAI = 0.08, developmental index = 0.2, and dry weight = 18 g/m² at a CO2 concentration of 350 ppm).35) The estimated Tc during the first 30 days after transplanting was small relative to the ETc (Fig. 2) because the plants were very small. The Tc then increased gradually with the increase of LAI and accounted for a large fraction of the ETc about 2 months later.

Fig. 2. Changes in crop evapotranspiration (ETc), transpiration (Tc), and the leaf area index of rice plants (LAI) in the experimental paddy plot in 2009.
Considering root growth by the time of pesticide application in the report by Oyanagi,23 who evaluated an average root depth of paddy rice at the late growth stage to be about 7 cm, we concluded that the soil layer where pesticides can be taken up by rice roots ranges from \( d_p \) to \( d_p + 2 \) cm for nursery-box application and from \( d_p \) to 10 cm in depth for submerged application.

2. Parameters of fipronil photolysis in paddy water

The photolytic half-life of fipronil in sterile natural water (0.95 mg/L) is reportedly 5.0 hr at 25°C under xenon arc lamp irradiation (33.14 W/m²; wavelength range, 300–400 nm).29 The ratio of cumulative irradiance in the UV-B region to that in the 300–400 nm range was estimated to be 0.015 with reference spectral irradiance data.30 From the above data, the first-order photolysis rate constant \( k_{\text{photo}} \) was estimated to be 0.078 m²/j. This value is comparable to that in the report by Thuyet et al.,25 who performed a lab-scale experiment under natural sunlight and estimated the \( k_{\text{photo}} \) of fipronil in paddy water to be 0.086 m²/j.

3. Parameters of initial distribution of nursery-box-applied pesticides in the paddy field

These parameters are shown in Table 2; the values were obtained from the results of field experiments in 2008 and 2009 and are reported in a separate paper.22 The ratio of the root-zone area to the total field area \( (f_{RZ\text{area}}) \) varied, probably because of differences in planting density and depth. We found that the root-zone area accounted for 10–15% of the total area of the experimental paddy field.22 Boulange et al.16 estimated the root-zone soil compartment to be 5 cm deep and to occupy 5% of the total paddy field area. Considering these results, we set the \( f_{RZ\text{area}} \) value at 0.1 in the model simulation. In general, a small fraction of the nursery-box-applied pesticides can be deposited on the soil surface during transplanting. Boulange et al.16 estimated that 6–14% of nursery-box-applied insecticides are lost through deposition into paddy water. In this study, the mass fraction of the granular pesticides in paddy water \( (f_g) \) was set at 0.03 in 2008 and 0 in 2009, because a small number of the granules were found on the soil surface just after transplanting in 2008 and hardly any granules were found in 2009.22 The mass fraction in the surface soil layer \( (f_s) \) was calibrated at 0.08 to secure the measured maximum concentrations of the pesticides found in an inter-plant soil sample 1 day after transplanting in 2009 (559 g/kg DW for isoprothiolane and 8.9 g/kg DW for fipronil).22 The vertically distributed mass fraction in the root zone layer \( (f_v) \) was calibrated at 0.8 to ensure the measured maximum concentrations of the pesticides in rice shoot samples in 2009 (13 mg/kg FW for isoprothiolane and 0.68 mg/kg FW for fipronil).22 The \( f_v \) value is reasonable because most of the granules were buried to a transplanting depth of about 3.5 cm around rice roots in 2009.22

4. Validation of the improved PADDY model

4.1. Sensitivity analysis of simulation results for nursery-box-applied pesticides

A conventional sensitivity analysis was performed to understand the relative importance of the input parameters used in the improved PADDY model for the nursery-box-applied pesticides. Sensitivity of the model output to one input parameter can be measured by the sensitivity ratio (SR)27 as follows:

\[
SR = \frac{(Y'-Y)Y}{(X'-X)X}
\]

where

- \( X \) = the standard value of an input parameter,
- \( X' \) = the value of the input parameter after changing \( X \),
- \( Y \) = the baseline value of the model output using standard values of the input parameters, and
- \( Y' \) = the value of the model output after changing the standard value of one input parameter.

The higher the absolute SR value calculated by Eq. (20), the more sensitive is the model output to the input parameters. The area ratio \( (f_{RZ\text{area}}) \) and the mass fractions \( f_o, f_s, \) and \( f_v \) for assessing the initial amount of the nursery-box-applied pesticides in paddy water and soil layers (Table 2) were included in the sensitivity analysis. In addition, the physicochemical properties of isoprothiolane and fipronil, i.e., the equilibrium constants \( (K_i) \), of a 0-day incubation and the TSCF) and the rate constants \( (k_o, k_{\text{photo}}, \text{and } k_{\text{alk}}) \), were included (Table 1). Sensitivity analysis was carried out independently for a +10% change of each input parameter value under the field conditions (i.e., water-balance component, UV-B irradiance, and transplanting depth) in 2008. Because the measured concentrations fluctuated greatly during the experimental period, the model outputs were set to be the average concentrations in paddy water, in a 0–3.5 cm soil layer (including the surface layer, interlayer, and root-zone layer), and in rice plants.

The SR values for isoprothiolane and fipronil applied to the improved PADDY model are shown in Fig. 3. There was not much difference in the results between these pesticides. The mass fractions in paddy water \( (f_g) \) and surface soil \( (f_s) \) were sensitive input parameters for simulating pesticide concentrations in paddy water. This result indicates that the concentrations in paddy water depend mainly on direct dissolution of the gran-
ules deposited on the soil surface and desorption from the surface soil layer. The output of the model was relatively sensitive to the Freundlich adsorption coefficient ($K_f$) for isoprothiolane ($SR = -0.34$), probably because isoprothiolane has low degradability in water and soil (Table 1), and therefore its concentration in paddy water depends largely on the $K_f$ value. The output of the model was also relatively sensitive to the photolysis rate constant ($k_{photo}$) for fipronil ($SR = -0.31$) because photolysis quickly reduces the fipronil concentration in paddy water.

The prediction of pesticide concentrations in the soil of the root-zone area was most sensitive to the area ratio ($f_{RZarea}$) ($SR = -0.90$). This result was expected considering the fact that the initial concentration in the root-zone area is calculated with the $f_{RZarea}$ under the initial conditions in Eq. (14). The simulation in soil of the inter-plant area was most sensitive to the mass fraction in the surface soil ($f_s$); pesticide mass in this area derives from the initial pesticide mass in the surface soil layer, which is fixed with the $f_s$ using Eq. (2).

The simulation of the concentration in rice plants was most sensitive to the mass fraction in the root-zone layer ($f_R$) and TSCF ($SR = 1.0$). The $K_f$ for both pesticides also significantly affected the results. These results can be explained as follows: The initial pesticide mass in the root-zone layer of the root-zone area is fixed with the $f_R$ using Eq. (4). The $K_f$ is important for evaluating the pesticide concentration in soil water in the root-zone layer, and the TSCF is required for estimation of the pesticide concentration in the xylem transpiration stream from its concentration in soil water in Eq. (15).

### 4.2. Validation for nursery-box-applied pesticides

The input parameters for isoprothiolane and fipronil used in the model simulation are shown in Table 1. The values of the dissolution rate constant from granules into paddy water were calibrated to ensure the initial increase in pesticide concentration in paddy water just after transplanting (Fig. 4). The values of the dissolution rate for nursery-box-applied isoprothiolane and fipronil were much lower than that for isoprothiolane under submerged application (Table 1). This difference is consistent with the nursery-box-applied granules being slow-release formulations and the granules for submerged application being conventional-release formulations. Isoprothiolane and fipronil were detected in the samples before transplanting in 2009 because of the presence of residue from the previous year’s use of the pesticides. Therefore, these data were used for the initial pesticide concentrations to solve the ordinary differential equations in Section 2.4.

The measured maximum concentrations of isoprothiolane and fipronil in paddy water were lower in 2009 (31.0 and 0.55 µg/L, respectively) than in 2008 (74.3 and 1.98 µg/L, respectively) (Fig. 4). The improved PADDY model successfully simulated the temporal patterns of the concentration changes in both years, with different $f_W$ values reflecting the differences in transplanting depth (2.5 cm in 2008 and 3.5 cm in 2009). The simulated concentrations were rather accurate (37–191% of the measured values) except for isoprothiolane after 14 days after transplanting in 2009 (about 10 times the measured values) (Fig. 4).

The measured concentrations of isoprothiolane and fipronil...
in the 0–3 cm soil samples from the root-zone area were 10–300 times those from the inter-plant area (Fig. 5). The improved PADDY model roughly simulated this difference. The simulated concentrations of isoprothiolane were in good agreement (within 200% of the measured concentrations) for 28 days after transplanting, whereas those of fipronil were one order of magnitude larger than the measured values. The model does not take into account horizontal pesticide transport in soil. Therefore, the difference was probably caused by the fipronil distribution in a smaller region near the granules due to its relatively low mobility in soil compared to that of isoprothiolane.22)

The \( \lambda_p \) in the early stage was estimated to be 0.13 (1/day) from the weight of rice shoots (Fig. 6). The measured concentrations in rice shoots peaked at 13 mg/kg FW for isoprothiolane and at 0.68 mg/kg FW for fipronil at 7 days after transplanting, and they then declined gradually (Fig. 6). The concentrations of isoprothiolane simulated with a TSCF of 0.51 using Eq. (17) agreed closely with the measured concentrations (by a factor of 1.1–4.8) for 28 days after transplanting, whereas fipronil concentrations tended to be underestimated with a TSCF of 0.10 using Eq. (17) (solid lines in Fig. 6). Fipronil concentrations simulated with a TSCF of 0.51 using Eq. (18) fit well with the measured values (dashed lines in Fig. 6). The results indicate that the accurate estimation of TSCF is required for the model simulation of the concentration in rice plants. Equations (17) and (18) were derived empirically from laboratory data for barley or soybean plants and different types of chemicals.23,30) Measured TSCF values vary greatly, particularly for very lipophilic chemicals. Because estimates of pesticide concentrations in rice shoots are most sensitive to the TSCF parameter, precise information about the TSCF values of paddy pesticides for rice is required for ac-

Fig. 4. Simulated and measured concentrations of nursery-box-applied pesticides in paddy water in 2008 and 2009. Upper graphs represent the UV-B irradiance estimated daily in Tsukuba during the field-experiment periods.

Fig. 5. Simulated and measured concentrations of nursery-box-applied pesticides in the 0–3 cm soil layers of root-zone and inter-plant areas in 2009.
curate simulation of their uptake by rice roots in paddy fields. Goodness of fit was assessed using the root-mean-square error (RMSE). In general, the lower the RMSE, the better the agreement is between measured and simulated data. The RMSE (%) values for isoprothiolane and fipronil in the simulation results were calculated (Table 3). In the root-zone and inter-plant soil samples under nursery-box application, the RMSE values of isoprothiolane were lower than those of fipronil. In rice plants, the RMSE of isoprothiolane (64.4%) calculated with the TSCF using Eq. (17) was lower than that (116.7%) calculated with the TSCF using Eq. (18), whereas the RMSE of fipronil (107.5%) with the TSCF using Eq. (17) was higher than that (68.4%) with the TSCF using Eq. (18). These data supported the simulation results mentioned previously.

4.3. Validation for isoprothiolane under submerged application
The simulation for submerged granular isoprothiolane was similar to that for granular rice herbicides under submerged applications. We assumed that all of the applied granules were deposited on the soil surface and that isoprothiolane dissolved directly from the granules into the paddy water. The measured and simulated changes in isoprothiolane concentrations are shown in Fig. 7. The simulated temporal patterns were similar to the measured ones in both years, although the model overestimated the concentrations. The simulated concentrations were less than 4.5 times the measured values during the first week after application. This was mainly because some granules may be captured by rice shoots in the active tillering stage or may drift outside the paddy field. In addition, the estimated distribution of isoprothiolane between paddy water and the surface soil layer in the simulation did not coincide with the experimental condition as a result of overrating the pesticide dissolution into paddy water or underrating the adsorption onto soil particles.

Table 3. Statistical analysis of the measured and simulated concentrations of the pesticides in the paddy field based on the root-mean-square error (RMSE)

| Application       | Sample       | Isoprothiolane | Fipronil |
|-------------------|--------------|----------------|----------|
|                   | 2008         | 2009           | 2008     | 2009     |
| Nursery box       | Paddy water  | 43.8           | 107.2    | 43.9     | 36.2     |
| Root-zone soil    | —            | 72.6           | —        | 237.0    |
| Inter-plant soil  | —            | 48.9           | —        | 193.8    |
| Rice plants       | Simulation 1 | —              | 64.4     | —        | 107.5    |
|                   | Simulation 2 | —              | 116.7    | —        | 68.4     |
| Submerged         | Paddy water  | 144.3          | 109.6    | —        | —        |
|                   | Soil         | 58.5           | —        | —        | —        |
| Rice plants       | Simulation 1 | —              | 22.6     | —        | —        |
|                   | Simulation 2 | —              | 37.1     | —        | —        |

a) Not analyzed. b) Calculated with transpiration stream concentration factor (TSCF) using Eq. (17). c) Calculated with TSCF using Eq. (18).
measured isoprothiolane concentrations in soil agreed by a factor of 0.5–2.4. The simulation also indicated that more than 80% of the total isoprothiolane mass in the 0–3 cm soil layer was distributed in the upper layer (0–1 cm) because the vertical percolation rate was very low (ca. 0.1 cm/day).

The $\lambda_P$ in the late stage was estimated to be 0.030 (1/day) based on the weight of the rice shoots (Fig. 8). The measured isoprothiolane concentrations in the rice shoots increased gradually and reached 0.51 mg/kg FW at 21 days after application. The improved PADDY model accurately simulated these changes. The isoprothiolane concentrations in this study were about one-tenth of those in a previous report (maximum of 4–7 mg/kg FW) because the simulated concentrations in the 3–10 cm soil layer, corresponding to the rice rhizosphere at the time of submerged application, were less than 1 mg/kg DW during the late experimental period (Fig. 8). Consequently, the concentration of isoprothiolane in the rice plants would be lower than the reported values.

**Conclusion**

In this study, we developed an improved PADDY model that includes the uptake of pesticides by rice roots under paddy field conditions. The model successfully simulated pesticide concentration changes in paddy water, soil, and rice plants under nursery-box and submerged applications. In particular, the model evaluated the difference in the concentrations of nursery-box-applied granular pesticides between root-zone and inter-plant soil samples by considering several key parameters: the ratio of the root-zone area to the total area of the paddy plot and the initial mass fractions of the pesticides in paddy water and soil layers. Our study provides a useful solution for simulating the uptake of residual pesticides in soil by rice roots. We anticipate that the improved PADDY model will be useful for evaluating whether pesticide concentrations in rice plants are effective against diseases and insect pests under various rice-cultivation methods.

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