Sensitivity analysis using a diffuse pollution hydrologic model to assess factors affecting pesticide concentrations in river water

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ABSTRACT

We quantitatively evaluated the factors that affect the concentrations of rice-farming pesticides (an herbicide and a fungicide) in river water by a sensitivity analysis using a diffuse pollution hydrologic model. Pesticide degradation and adsorption in paddy soil affected concentrations of the herbicide pretilachlor but did not affect concentrations of the fungicide isoprothiolane. We attributed this difference to the timing of pesticide application in relation to irrigation and drainage of the rice paddy fields. The herbicide was applied more than a month before water drainage of the fields and runoff was gradual over a long period of time, whereas the fungicide was applied shortly before drainage and runoff was rapid. However, the effects of degradability-in-water on the herbicide and fungicide concentrations were similar, with concentrations decreasing only when the rate constant of degradation in water was large. We also evaluated the effects of intermittent irrigation methods (irrigation/artificial drainage or irrigation/percolation) on pesticide concentrations in river water. The runoff of the fungicide, which is applied near or in the period of intermittent irrigation, notably decreased when the method of irrigation/artificial drainage was changed to irrigation/percolation. In a sensitivity analysis evaluating the synergy effect of degradation and adsorbability in soil, the degradation rate constant in soil greatly affected pesticide concentration when the adsorption coefficient was small but did not affect pesticide concentration when the adsorption coefficient was large. The pesticide concentration in the river water substantially decreased when either or both the degradation rate constant in soil and adsorption coefficient was large.

Key words | adsorption, degradation, isoprothiolane, pollutograph, pretilachlor

INTRODUCTION

Although global attention is now being paid to their health hazards, pesticides are still necessary for agriculture to improve production efficiency and reduce labor requirements. Various kinds of pesticides are applied to rice paddy fields, particularly in countries where rice is a staple food. Rice cropping on paddy fields requires a large amount of fresh natural water, which is discharged to the river by artificial drainage or percolates into the ground. In Japan, about two-thirds of water use is for agricultural purposes, and about 90% of this water is used for rice cropping (Ministry of Land, Infrastructure, Transport and Tourism, Japan 2006). Pesticides applied to paddy fields enter environmental waters more easily than pesticides applied to upland fields because paddy water is discharged directly into rivers and lakes. Therefore, pesticides applied to rice paddy fields have a greater potential to contaminate river
water, some of which is the source of drinking water. It is therefore important to understand how the pesticides applied to paddy fields influence the pesticide concentrations in river water.

On dry fields, half-life in soil and soil/water adsorption coefficient are considered to be two key environmental fate properties for pesticides (Chen et al. 2002), but runoff of rice-farming pesticides applied directly onto ponded paddy water is influenced by properties such as water solubility, the adsorbability to soil (the soil–water partitioning coefficient normalized for the organic carbon content, $K_{OC}$), and half-lives for pesticide degradation in soil and water (Iwakuma et al. 1993; Sudo et al. 2002; Capri & Karpouzas 2007). Some studies have suggested that the magnitude of the pesticide runoff differs depending on the solubility of the pesticides (Ueji & Inao 2000; Ebise & Inoue 2002), whereas other studies have indicated a correlation between sorption behaviors of pesticides and their loss (Fajardo et al. 2000). Correlations to $K_{OC}$ and water solubility (WS) could be taken to indicate the same phenomena because pesticides with high $K_{OC}$ are mostly low in WS and vice versa (Lyman et al. 1990). Although $K_{OC}$ and WS are essentially different pesticide properties, these two properties are not generally evaluated separately when assessing pesticide concentrations in runoff. Runoff rates are reported to be well correlated with another sorption-related parameter, the octanol–water partition coefficient, log $P_{OW}$, rather than with the water solubility of herbicides (Nakano et al. 2004). Watanabe et al. (2007) reported that $K_{OC}$ seems to be a stronger indicator of the aquatic fate of an herbicide compared to WS, suggesting that sorption rather than dissolution is the key phenomenon driving rice-farming pesticide runoff. However, the effects of $K_{OC}$ and WS on pesticide runoff have not been separately and quantitatively analyzed, nor have the effects of half-lives for degradation in soil and water been analyzed.

Irrigation–water management practices strongly influence rice pesticide runoff, and consequently the runoff quantity and pesticide concentration in the runoff water could be decreased by improving management practices (Miao et al. 2003; Christen et al. 2006; Numabe & Nagahora 2006). For minimizing the risk of high pesticide loads entering surface water bodies, prolongation of paddy closure after pesticide application has been studied as a useful strategy (Karpouzas et al. 2006). The fate and transport of three herbicides in rice production using different water management practices have been studied, and results have indicated an advantage of increasing the water holding period and the excess water storage depth in reducing runoff of pesticides from paddy plots over the practice of overflow drainage (Vu et al. 2006; Watanabe et al. 2007; Phong et al. 2008). The practice of intermittent irrigation with a shallow water depth and a high drainage rate to maintain a high excess water storage depth and increase the water holding period saved irrigation water and prevented herbicide runoff, whereas the practice of continuous irrigation and overflow resulted in significant losses of water as well as herbicides (Inao et al. 2008).

Rice pesticide concentrations are also of concern downstream, after their discharge from paddy fields, where river water may be taken as a source of drinking water. Pesticide concentrations in river water are considered to be changed through a complex system affected by various factors, including geographic and hydrologic elements, agricultural practices, and the physicochemical and biologic properties of the pesticides (Matsui et al. 2002, 2005). It is therefore difficult to evaluate the individual effects of these factors on pesticide concentrations in downstream regions of river systems merely by field observations or experiments; modeling and simulation are useful tools in this regard. In this study, we evaluated the factors that affect the concentrations of pesticides (an herbicide and a fungicide) in river water by a sensitivity analysis using a diffuse pollution hydrologic model.

**MATERIALS AND METHODS**

**Model river basin and pesticide diffuse pollution model**

The Kakkonda River, Iwate, Japan, which has a 191-km$^2$ catchment area consisting mainly of forest and rice paddy fields, was selected as a model river for conducting the sensitivity analysis. Details of the diffuse pollution hydrologic model are described elsewhere (Matsui et al. 2006a), but briefly in the model the river basin was divided into a grid of 1-km$^2$ cells. Each cell was subdivided into...
compartments including a river water compartment and several rice paddy ponding compartments representing the rice paddy fields of each farmer in the river basin. It is assumed that applied pesticides reach the paddy fields (the loss due to the drift of pesticide, the effect of application mode, the effect of spray formulation, and the effect of adjuvants were not accounted). In the compartment consisting of solids and water, an instantaneous equilibrium was assumed between the dissolved and adsorbed fractions at the solid–water interface, and the equilibrium relationship was described by the adsorption coefficient $K_{OC}$. Pesticide degradations in soil and water were each described by first-order reaction kinetics with a degradation rate constant. A set of differential mass-balance equations was defined to describe the dynamics of pesticide and water in each compartment based on mass conservations for the pesticide and water. This model was first applied to predict the concentrations of paddy-farming pesticides in river water from a large catchment (1,882 km², Matsui et al. 2006a). Although the model was calibrated with hydrologic data only, 68% of the observed concentration data were in the range of model prediction with the Monte Carlo inputs: the Monte Carlo method was applied to account for the uncertainty in the model inputs relating to farming work schedules and pesticide adsorption/degradation rates in the large catchment. The model predicted pesticide concentrations within an order-of magnitude accuracy, and the pesticide rankings according to the predicted concentration roughly agreed with those observed (Matsui et al. 2006b). By using improved model inputs after collecting precise information on farming work schedules of the farmers within the catchment area and obtaining pesticide adsorption/degradation rates for rice paddy soils in the river basin, the model’s capability to reproduce observations of rice farming pesticide concentrations in river water was further verified (Matsui et al. 2007).

**Farming data and target pesticides**

For the sensitivity analysis, the model used precise data of agricultural activity, such as the places where pesticide was applied and the irrigation schedule, so that the effects of each factor on pesticide concentration in river water in a river basin could be clearly evaluated. The farming data of the rice paddy fields in the river basin, including the irrigation and pesticide application dates and the quantity of pesticide applied for each paddy field for all 372 farmers in the catchment area, were obtained by courtesy of the farmers in the catchment area and compiled into a database for input to the model. The target pesticides were the herbicide pretilachlor and the fungicide isoprothiolane, which are popular pesticides in rice cropping in the river basin. The herbicide (67 kg) was applied in the middle or end of May 2004, within 0.5 or 1 month after transplanting the seedlings, and the fungicide (153 kg) was applied around July 2004, about 1.5 months before harvest (see Figure 1). For water management, a water level of a few centimeters was maintained from May to June, after which the water was drained. In August and September, paddy fields were irrigated and drained intermittently to rehydrate and oxygenate the soil, respectively. The characteristics of the pesticides are listed in Table 1.

**RESULTS AND DISCUSSION**

**Effects of pesticide degradation in the soil, adsorption, and application period**

Sensitivity analysis was applied to the diffuse pollution hydrologic model, which is capable of predicting the pesticide concentrations in river water (Matsui et al. 2006a,b, 2007). Before using the sensitivity analysis, the model was verified with the data of Nakano et al. (2004) who reported that the runoff rates of six herbicides in the Kozakura River, Japan, were well correlated with log $P_{OW}$, as shown in Figure 2. We conducted model simulations of the same six herbicides in the Kakkonda River with the model input values for the pesticide characteristics (Table 2). The trend in the relationship between the pesticide runoff rate and the log $P_{OW}$ (the logarithm of the octanol–water partition coefficient) obtained by our model simulation for the Kakkonda River was similar to the trend observed in the Kozakura River, although our pesticide runoff rate values were lower. These lower values for the Kakkonda River could be a result of runoff rate dependency on the length of the river in relation to the catchment area as the catchment area of the Kakkonda River (191 km²) is
much larger than that of the Kozakura River (15.4 km²).
Because the trend was the same for the two rivers, we performed a sensitivity analysis of the model simulation to provide quantitative information on pesticide concentration in river water in relation to pesticide characteristics.

In the sensitivity analysis, model simulations were conducted in which the adsorption coefficient and the degradation rate constant in soil were varied through a range of 0.01 to 100 times their actual values to determine the effects of pesticide degradation and adsorption: the range of the variations in the adsorption coefficient and the degradation rate constant in soil and were determined to cover actual values of pesticides (Tomlin 2003). The sensitivity of the pesticide degradability in soil affecting the pesticide concentration in river water was different for the two pesticides (see Figure 3A). Although an increasing the degradation rate constant in soil reduced the concentration of the herbicide in river water, the effect on the fungicide was not as noticeable. Increasing the degradation rate constant in soil by a factor of 100 (from the default values of $2.3 \times 10^{-2} \text{ d}^{-1}$ for the fungicide and the herbicide; see the dotted line in Figure 3A and Table 1) decreased the herbicide concentration in the river water by about 30% and the fungicide concentration by 20%.

Decreasing the degradation rate constant in soil by a factor of 100 increased the herbicide concentration by about 40%, while the fungicide concentration scarcely changed.

The adsorbability affected the concentration of the herbicide in river water but had little effect on the concentration of the fungicide (Figure 3B). The effects of the pesticide adsorbability were greater than those of the pesticide degradability on the concentrations of both the herbicide and the fungicide. Runoff behavior can be assessed by a time-series analysis. The fungicide was applied

Table 1 | Default values of the model input

<table>
<thead>
<tr>
<th>Compound</th>
<th>Water solubility (mg/L)</th>
<th>Adsorption coefficient, $K_{OC}$ (mL/g)</th>
<th>Degradation rate constant in soil (d⁻¹)</th>
<th>Degradation rate constant in water (d⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isoprothiolane</td>
<td>54†</td>
<td>1,230‡</td>
<td>$2.3 \times 10^{-2}$‡</td>
<td>$2.3 \times 10^{-2}$‡</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>50†</td>
<td>1,160§</td>
<td>$2.3 \times 10^{-2}$†</td>
<td>$4.9 \times 10^{-2}$§</td>
</tr>
</tbody>
</table>

†Calculated from half-life values by assuming first-order kinetics.
‡Tomlin (2003).
§Matsui et al. (2007).
in July and ran off rapidly over a short period of time during artificial drainage of the rice paddy fields (Figure 4A). About 65 kg (42%) of the 153 kg of fungicide applied to the rice paddy fields flowed into the river soon after its application. In contrast, the herbicide was applied in May, more than one month before any drainage of the rice paddy fields (Figure 4B). The herbicide ran off slowly, and only 7 kg (10%) of the 67 kg of applied herbicide flowed into the river, indicating that more of the herbicide is degraded by or adsorbed to the paddy soil than the fungicide. This difference in runoff characteristics is a result of the different application periods for the herbicide and fungicide.

To further confirm this result, model simulations were conducted with the assumption that the fungicide isoprothiolane was applied in May prior to drainage, while the herbicide pretilachlor was applied in July at the time of drainage. By interchanging these application periods, the simulation showed that the total runoff of isoprothiolane decreased from 65 kg (42%) to 19 kg (12%), and the total runoff of pretilachlor increased from 7 kg (10%) to 19 kg (28%) (Figure 5). Not only the quantity of pesticide runoff but also the runoff patterns changed. In this model simulation, pretilachlor rapidly flowed into the river because the rice paddy fields were being drained at the time of herbicide application. The runoff pattern of pretilachlor in this model simulation (Figure 5B) and the runoff pattern of the fungicide isoprothiolane in the original model simulation (Figure 4A) were similar. Therefore, the effects of the degradability-in-soil and the adsorbability on the pesticide runoff are primarily dependent on the pesticide application period and corresponding water management of rice paddy fields.

Pesticide degradation in water and water solubility

The effect of pesticide degradation-in-water on pesticide concentration was evaluated by varying their degradation rate constant in water through a range of 0.01 to 100 times their default values (2.3 \times 10^{-2} \text{ d}^{-1} for the fungicide and 4.9 \times 10^{-2} \text{ d}^{-1} for the herbicide; see Table 1) in the model simulations. Increasing the degradation rate constant in water decreased the runoff rate of the fungicide isoprothiolane and increased the runoff rate of the herbicide pretilachlor.

### Table 2 | Properties of the pesticides in Figure 2

<table>
<thead>
<tr>
<th></th>
<th>Log ( P_{OW} )</th>
<th>Water solubility (mg/L)</th>
<th>Adsorption coefficient, ( K_{OC} ) (mL/g)#</th>
<th>Degradation rate constant in soil( ^{\dagger} ) (d^{-1})</th>
<th>Degradation rate constant in water( ^{\ddagger} ) (d^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simetryn</td>
<td>2.6</td>
<td>400§</td>
<td>290#</td>
<td>5.5 \times 10^{-3}#</td>
<td>5.5 \times 10^{-3}#</td>
</tr>
<tr>
<td>Dymron</td>
<td>2.7</td>
<td>1.2§</td>
<td>940##</td>
<td>1.4 \times 10^{-2}##</td>
<td>1.4 \times 10^{-2}##</td>
</tr>
<tr>
<td>Mefenacet</td>
<td>3.2</td>
<td>4§</td>
<td>890##</td>
<td>1.8 \times 10^{-2}##</td>
<td>1.8 \times 10^{-2}##</td>
</tr>
<tr>
<td>Pretilachlor</td>
<td>4.1</td>
<td>50§</td>
<td>1,160##‡‡</td>
<td>2.3 \times 10^{-2}‡‡</td>
<td>4.9 \times 10^{-2}‡‡</td>
</tr>
<tr>
<td>Esprocarb</td>
<td>4.6</td>
<td>4.9§</td>
<td>2,800##‡‡</td>
<td>1.4 \times 10^{-2}‡‡</td>
<td>1.4 \times 10^{-2}‡‡</td>
</tr>
<tr>
<td>Pyributicarb</td>
<td>5.2</td>
<td>0.32§</td>
<td>3,500##‡‡</td>
<td>6.3 \times 10^{-2}‡‡</td>
<td>6.3 \times 10^{-2}‡‡</td>
</tr>
</tbody>
</table>

\( ^{\dagger} \) Geometric means of reported values.
\( ^{\ddagger} \) Calculated from half-life values by assuming first-order kinetics.
\( ^{\#} \) Estimated by the PCOCWIN model (US Environmental Protection Agency 2007).
\( ^{\#\#} \) Estimated from the result of the BIOWIN3 model (Aronson et al. 2006).
\( ^{\#\#\#\#} \) Assumed the same value as the degradation-in-soil coefficient.
water decreased the fungicide concentration only when the degradation rate constant in water was greater than about $10^{-2}$ d$^{-1}$ (Figure 6). This trend was also seen for the herbicide, indicating that pesticide degradation in water is similar regardless of whether an herbicide or fungicide is used and irrespective of application periods. When the pesticide degradation rate constant in water was less than approximately $10^{-2}$ d$^{-1}$ (indicated by the solid line in Figure 6), the pesticide concentration remained unchanged regardless of pesticide degradation rate constant. This suggests that pesticides applied to rice paddy fields experience minimal degradation in the ponded water of the paddy field, in runoff, or in the river when their degradation rate constant in water is less than approximately $10^{-2}$ d$^{-1}$.

The effect of water solubility on pesticide behavior was evaluated by varying the value of water solubility through a range of $10^{-4}$ to 100 times their default values (54 mg/L for the fungicide and 50 mg/L for the herbicide; see Table 1) in model simulations. Although the effect of water solubility on herbicide concentration was less than that on fungicide concentration, both herbicide and fungicide concentrations showed a similar trend (Figure 7). A decrease in water solubility decreased the fungicide concentration only when water solubility was less than approximately 1 mg/L.

Pesticide concentrations in the river were only minimally affected by water solubility greater than approximately 1 mg/L (solid line in Figure 7), suggesting that above this level pesticides are in the dissolved form and therefore are more likely to run off the fields. In contrast, the pesticide applied on rice paddy fields could remain mostly in the undissolved form in the paddy field when water solubility is less than about 1 mg/L. This would result in lower concentrations in the river.

Figure 3 | Effect of pesticide degradability-in-soil (Panel A) and adsorbability (Panel B) on the average concentrations of the two pesticides in the river water 2 months after pesticide application on the paddy field. Vertical dotted lines indicate the actual values for the respective pesticides.

Figure 4 | Time-series runoff behavior of the fungicide isoprothiolane (Panel A) and the herbicide pretillachlor (Panel B) in 2004. Bars along the x-axis indicate the daily quantity of applied pesticide, and bars along the top axis indicate the total area of rice paddy fields conducting drainage in the model catchment. Open triangles indicate the cumulative amount of pesticide runoff into the river.
in greater pesticide degradation because runoff of the undissolved fraction could be delayed.

In an earlier study of pesticide outflow from rice paddy fields, the pesticide runoff rate was strongly correlated with water solubility (Maru 1990). Water solubility affects pesticide runoff, but highly soluble compounds tend to have low adsorbability (low adsorption coefficients in soil) and vice versa (i.e. the soil adsorption coefficient and water solubility are related (Lyman et al. 1990)); hence, both water solubility and adsorbability are correlated with pesticide runoff (Watanabe et al. 2007). However, the mechanisms by which water solubility and adsorbability affect pesticide runoff are basically different. Pesticides with low water solubility exist in soil in an undissolved form and are less likely to be transported as run off, whereas pesticides with high adsorbability are adsorbed on the soil phase and would not, therefore, be transported with drainage water. Although the correlation between water solubility and concentration has been noted for pesticides (Maru 1990; Nakano et al. 2004; Watanabe et al. 2007), our sensitivity analyses suggest that the correlation includes a component involving adsorbability and pesticide concentration, in particular for pesticides with water solubility greater than 1 mg/L.

Irrigation/artificial drainage and irrigation/percolation

Some rice paddy fields have well-drained soil. In these cases, during intermittent irrigation periods, farmers may shut off the water intake from irrigation canals and allow the water level to recede by percolation instead of artificial drainage (Figure 1). Percolation would be expected to result

Figure 5 | Fictive time-series runoff behavior of isoprothiolane (Panel A) and pretilachlor (Panel B). Pesticide applications were interchanged; the fungicide isoprothiolane was applied in May prior to drainage, while the herbicide pretilachlor was applied in July at the time of drainage. Bars along the x-axis indicate the daily quantity of applied pesticide (in kg), and bars along the top axis indicate the total area of rice paddy fields conducting drainage in the model catchment. Open triangles indicate the cumulative amount of pesticide runoff into the river (in kg).

Figure 6 | Effect of pesticide degradability-in-water on the average pesticide concentrations. Vertical dotted lines indicate the actual values. Solid line indicates $10^{-2} \text{ d}^{-1}$.

Figure 7 | Effect of pesticide water solubility on the average pesticide concentrations. Vertical dotted lines indicate the actual values. Solid line indicates 1 mg/L.
in a decrease in pesticide concentrations in river water compared to artificial drainage. According to studies on pesticide runoff from paddy plots, a prolonged water-holding period by paddy closure after pesticide application effectively reduces pesticide discharge (Karpouzas et al. 2006; Vu et al. 2006). However, this agricultural practice may not always be effective because rainfall, and in particular the heavy rainfalls that occur during the Asian monsoons, including in Japan, may cause spillover of paddy-ponding water to the rivers.

For the fungicide isoprothiolane and the herbicide pretilachlor, model simulations were conducted where percolation instead of artificial drainage were practiced during the intermittent irrigation period. The other model simulation conditions were the same as those of Figure 4, and therefore the effect of percolation/artificial drainage could be compared. As comparing Figure 8A with Figure 4A, the model simulation revealed that percolation instead of artificial drainage resulted in a decrease in the total amount of fungicide runoff, from 65 kg to 30 kg. However, no substantial change in herbicide runoff (Figures 8B and 4B). The result of fungicide suggests that 35 kg of the 153 kg applied to rice paddy fields flows to the river during artificial drainage of the fields and about 30 kg can potentially flow to the river from spillover caused by precipitation. Precipitation of 47 mm on July 19 and 30 mm on July 26 could have resulted in pesticide spillover as almost all of the runoff of the pesticides occurred during this short period of time. As reported elsewhere (Sudo et al. 2002; Phong et al. 2008), pesticide runoff from spillover is dependent on the frequency and intensity of precipitation and the height of the paddy water outlet to accommodate the excess precipitation without spilling over. Therefore, the quantity of runoff and the concentration of a fungicide in river water should vary depending on the structure of the paddy and the amount of precipitation, although in our sensitivity analyses using model simulations the concentration of the fungicide in the river water decreased by about one-third when intermittent irrigation was combined with percolation.

The results of the sensitivity analyses shown in Figure 3 were based on simulations of artificial drainage in intermittent irrigation periods. We then conducted similar sensitivity analyses for percolation in intermittent irrigation periods. The effect of the degradability in soil on the fungicide concentration did not change; the overall concentrations were merely shifted downward (data not shown). Changing the drainage practice did not alter the effect of the adsorbability on the fungicide concentration. Even with percolation, the majority of the fungicide runoff occurred through spillover of paddy water, with soil permeation only slightly affecting total runoff. The effect of the degradability in soil, therefore, on fungicide concentrations was not particularly large.

Synergetic effects of pesticide degradability and adsorbability

We carried out a sensitivity analysis of the effects of the degradability-in-soil on the concentrations of pretilachlor and isoprothiolane in the river water. The value of the degradation rate constant in soil was changed under the three conditions of adsorption coefficients and the two
drainage practices. As shown in Figure 9, with a low pesticide adsorbability to soil (adsorption coefficients of 12.3 mL/g for the fungicide and 11.6 mL/g for the herbicide, which are 0.01 times the default values; see Table 1), the concentrations of the pesticides increased as the degradation rate constant in soil decreased. With a high pesticide adsorbability (123 L/g for the fungicide and 116 L/g for the herbicide), concentrations were not affected by degradability. We interpret this as pesticides with high adsorbability existing mostly in soil, which minimizes the potential pesticide loads to river water regardless of their degree of degradability.

When the pesticide degradation rate constant in soil was high (degradation rate constants were increased to 2.3 d\(^{-1}\) for both pesticides, 100 times the default value), the effect of adsorption decreased, suggesting that pesticide loads are minimal when either adsorbability or degradability are high. When the pesticide adsorbability in soil was low, pesticide concentrations were decreased with the increase in the degradation rate constant in soil. The concentration of the herbicide was more affected by the degradation rate constant compared to the fungicide because fungicides are removed with drainage water and spillover by rain within a short time after application. The effect of the degradability on the fungicide concentration was more prominent with percolation compared to artificial drainage. Fungicides with low soil adsorbability may permeate underground or flow by lateral water seepage/leakage through the ridge of paddy fields to adjacent drainage canals, which suggests that percolation may not be effective in preventing fungicide runoff when soil adsorbability is low.

Overall, concentrations of pesticides were highest with the simultaneous condition of low adsorption coefficients and low degradation constants. The pesticide degradability in soil affected the pesticide concentration only when the pesticide adsorbability was low.

**CONCLUSIONS**

(1) The rice pesticide concentrations in downstream river water differed according to the application period of the pesticide and the irrigation schedule. When the pesticide is applied more than a month before the paddy fields are drained (as in the case of herbicide application), the pesticide runs off slowly, and the pesticide concentration in river water is affected by the degradability and adsorbability in soil. In contrast, when pesticides are applied just prior to intermittent irrigation and artificial drainage (as in the case of fungicide application), the pesticide runs off rapidly, and neither the degradability nor the adsorbability has a notable effect on the pesticide concentration in the river water. Therefore, even if pesticides have similar characteristics, pesticide concentrations vary greatly in river water depending upon the application timing.

(2) Only degradation rate constant in-water larger than approximately 10\(^{-2}\) d\(^{-1}\) and water solubility values less than 1 mg/L influenced pesticide concentrations.

(3) The total runoff quantity of fungicides, which were applied shortly before the start of artificial drainage of
the paddy fields, was partly depressed by using percolation rather than artificial drainage; fungicide still entered the river via spillover of paddy field water during rain events. Therefore, the effect of soil adsorbability on fungicide concentrations was not large, regardless of whether artificial drainage or percolation was used during intermittent irrigation.

(4) The concentrations of pesticides decreased when either the degradation rate constant in soil or the adsorption coefficient was large. The concentrations of pesticides greatly increased when both the degradation rate constant in soil and adsorption coefficients were small.

We obtained these findings from the sensitivity analysis, but further observations are needed for their confirmation.

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REFERENCES


