

Risk Assessment of Fenthion Oxide Derivatives in Aqueous Environment

Maiko TAHARA*, Reiji KUBOTA*, Kumiko SHIMIZU*, Naoki SUGIMOTO*, Tetsuji NISHIMURA*

* Division of Environmental Chemistry, National Institute of Health Sciences, Tokyo 158-8501 Japan

ABSTRACT

Fenthion (MPP), an organophosphorus pesticide, is widely used as an agricultural and household insecticide. The oxons are known to be the actual toxic forms of organophosphorus pesticides. Using an *in vitro* cytochrome P450 (CYP) metabolism system, MPP was metabolized to produce five metabolites: MPP sulfoxide, MPP sulfone, MPP oxon, MPP oxon sulfoxide and MPP oxon sulfone. MPP sulfoxide was the main product, while MPP oxon sulfone and the other metabolites were produced in small amounts. On the other hand, MPP was converted to MPP oxon sulfone by chlorination in a water purification system, raising the possibility of human exposure to MPP oxon sulfone through drinking water. MPP oxon sulfone showed the highest acute toxicity among MPP and its metabolites. In addition, MPP oxon sulfone was not metabolized by CYP3A4, the major CYP isomer in humans. It is important that MPP and its oxides are monitored and their health risk assessed to control drinking water safety because MPP was detected in river water.

Keywords: MPP, oxide derivative, risk assessment.

INTRODUCTION

Many chemicals from domestic wastewater, industrial effluent, agricultural run-off, and other sources flow into natural waters such as rivers. For this reason, it is relevant to consider that those pollutants could affect human health. In particular, the general public has a great concern for pesticides because of their adverse effects on human health. Therefore, numerous monitoring surveys of pesticides in natural water have been performed, and the detection data have been reported (Sancho *et al.*, 2004; Quintana *et al.*, 2001; Frenich *et al.*, 2001; Sabik *et al.*, 2000). In this study, we focused on fenthion (MPP), an insecticide from a class of organophosphorus pesticides, which is used in large amounts and has a high detection frequency. Organophosphorus pesticides may be converted to oxons, which are known to be their actual toxic derivatives (Eaton *et al.*, 2008; Casida and Quistad, 2004; Cox, 1994). Five oxide derivatives of MPP were determined including the side-chain oxidations and their oxons.

Concerns of the potential risk to human health of MPP have recently increased. We therefore sought to determine whether MPP could be biotransformed to oxon derivatives. Ingested chemicals are typically modified by the phase I oxidative reaction, of which the cytochrome P450 (CYP) proteins are the principal oxidative enzymes. CYP3A4 is found to be the major isomer in many organs (Denisov *et al.*, 2007; Guengerich, 1999). We examined and identified the *in vitro* metabolites of MPP mediated by human CYP3A4 and we also quantified the oxons.

Address correspondence to Tetsuji Nishimura, Division of Environmental Chemistry, National Institute of Health Sciences, Email: nishimur@nihs.go.jp

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In this study, we measured MPP and its oxides in river water. On the basis of the metabolic profile and from the knowledge of environmental exposure routes, we further discussed the possible acute toxicity from exposure to MPP oxide derivatives.

MATERIALS AND METHODS

Chemicals

Fenthion (*O,O*-dimethyl *O*-4-methylthio-*m*-tolyl phosphorothioate, MPP) and MPP sulfoxide were purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). MPP sulfone, MPP oxon, MPP oxon sulfoxide, and MPP oxon sulfone were purchased as 10 mg/L solutions in acetonitrile from Kanto Chemical Co., Inc. (Tokyo, Japan). Dichloromethane and acetone (pesticide residue analysis grade), acetonitrile and methanol (high performance liquid chromatography grade), and acetic acid were purchased from Wako Pure Chemical Industries, Ltd. The water used in the experiment was purified using a Milli-Q gradient A10 and Elix with EDS polisher water purification system (Millipore, Bedford, MA, USA). Microsomal enzyme solution and an NADPH regenerating system for the metabolic reaction were purchased from BD Biosciences (Woburn, MA, USA). The microsomal enzyme solution contained recombinant human CYP, human CYP reductase, and human cytochrome b₅, which were expressed from cDNA using baculovirus-infected insect cells.

Sampling procedure

River water samples were taken from the Naka River that flows through urban areas, Saitama and Tokyo, Japan. Sampling was performed twice a month from December 2007 to December 2008 in the riverside of Taniguchi Town, Misato City, Saitama Prefecture. A 2-liter glass bottle was washed twice with river water before the sample was placed and then the bottle was tightly covered so that air would not enter. The glass bottle containing the sample was kept at 4°C until the time of concentration and analysis which were done on the same day.

Pre-treatment of river water and GC/MS analysis

Analytes were extracted by solid-phase extraction (SPE) and were analyzed as previously reported (Tahara *et al.*, 2006). Two liters of river water samples were concentrated using a Sep-Pak Plus C18 SPE cartridge (Waters, Milford, MA, USA) with an automatic concentrator, Sep-Pak Concentrator Plus (Waters). The final volume used was 1 mL with dichloromethane for gas chromatography/mass spectrometry (GC/MS) analysis. The instrument was operated in selected-ion monitoring (SIM) mode. Two selected ions for each target compound were monitored for quantification and identification, and the retention times are summarized in Table 1.

Metabolic reaction

A 1 mM standard solution of pesticide was prepared in acetone and stored at -20°C. Working solutions were freshly prepared before use by diluting with acetonitrile. The reduction of MPP sulfoxide back to MPP by the cytosolic aldehyde oxidase enzyme was ruled out in this study. Each 0.5 mL reaction mixture contained 1.6 mM NADP⁺, 3.3 mM glucose-6-phosphate, 3.3 mM magnesium chloride, 0.01 mM pesticide, and 0.4 U/mL glucose-6-phosphate dehydrogenase in 100 mM potassium phosphate buffer (pH 7.4). After incubation at 37°C for 10 min, the microsome solution was added to make up

a 10 pmol CYP isomer. Reactions were stopped after 5, 10, 15, 20, 30, 40, 50 and 60 min by the addition of 250 μ L acetonitrile. And then they were centrifuged at 10,000 \times g for 3 min. The supernatant was analyzed by liquid chromatography/mass spectrometry (LC/MS).

Quantification using LC/MS analysis

Analysis by LC/MS was performed as previously reported (Tahara *et al.*, 2008a). The retention time and selected ions for each target compound were monitored for quantification and are summarized in Table 1.

Table 1 - Analysis of monitored ions and retention times of MPP and its oxides using GC/MS and LC/MS.

Compound	GC/MS			LC/MS	
	Retention time (min)	Quantitation ion (m/z)	Identification ion (m/z)	Retention time (min)	Quantitation ion (m/z)
MPP	16.0	278	125	18.3	279
MPP sulfoxide	23.0	125	278	13.3	295
MPP sulfone	23.3	310	125	16.9	311
MPP oxon	14.7	262	109	16.2	263
MPP oxon sulfoxide	21.3	263	109	4.0	279
MPP oxon sulfone	21.1	294	109	6.6	295

RESULTS AND DISCUSSION

MPP and its oxides in river water

MPP is widely used as a pest control agent for rice, leguminous plants, and fruit trees. As mentioned previously, the existence of MPP and its oxides in river water was studied. From the results of the GC/MS analysis for the period April to August, a peak was observed on the chromatogram which was recognized to be MPP with $m/z = 278$ at a retention time of 16 min (Fig. 1). The peaks of oxides were not detected in river water. The maximum concentration of MPP was 0.12 μ g/L on April (Fig. 2). As previously reported, insecticides and herbicides used in paddy fields become detectable in river water immediately after spraying (Tsuda *et al.*, 1998). Their concentrations show seasonal changes depending upon their usage.

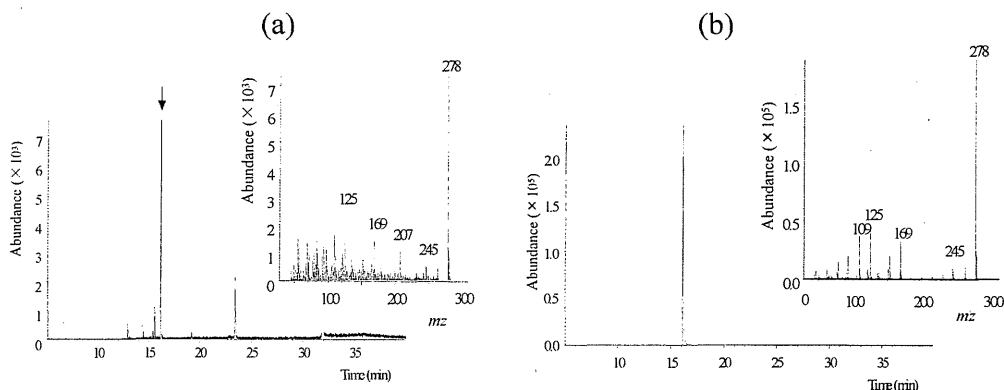


Fig. 1 - Ion chromatograms and mass spectra of MPP; (a) detected in river water, (b) 10 mg/L standard solution

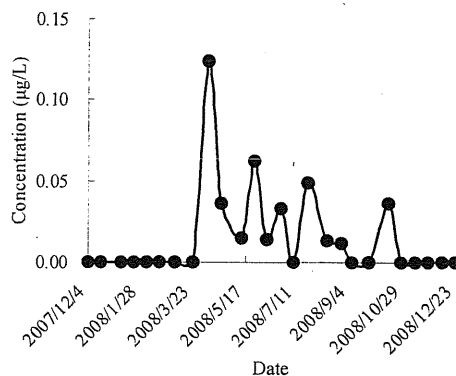


Fig. 2 - Detected concentration of MPP in river water sampled from Naka River in 2008

Metabolism of MPP by human CYP3A4

Among CYP isomers, CYP3A4 is found to have the largest quantity *in vivo*. In order to detect the metabolites of MPP and to help determine its potential risks to human health, MPP was allowed to react with human CYP 3A4. MPP sulfoxide was detected by LC/MS as the main metabolite, and four other metabolites (MPP sulfone, MPP oxon, MPP oxon sulfoxide and MPP oxon sulfone) were also detected at trace levels (Fig. 3). This metabolic reaction continued linearly for 10 min. Among the metabolites of MPP, we focused on the formation of oxon metabolites, which are known inhibitors of cholinesterase activity. The conversion rates of MPP to MPP oxon, MPP oxon sulfoxide and MPP oxon sulfone by CYP3A4 were 1.5, 0.52, and 0.02 nmol/min/nmol P450, respectively, calculated from the molarities at 10 min.

In addition, MPP was similarly metabolized by seven other CYP isomers: CYP1A2, CYP1B1, CYP2A6, CYP2C9, CYP2C19, CYP2D6 and CYP2E1. The major products of metabolism by these seven CYP isomers were MPP sulfoxide and MPP oxon. Trace amounts of MPP sulfone, MPP oxon sulfoxide, and MPP oxon sulfone were detected from CYP1A2 and CYP2C19.

Only small quantities of the bioactive derivatives, MPP oxon, MPP oxon sulfoxide and MPP oxon sulfone, were formed from the metabolism by any of the eight CYP isomers.

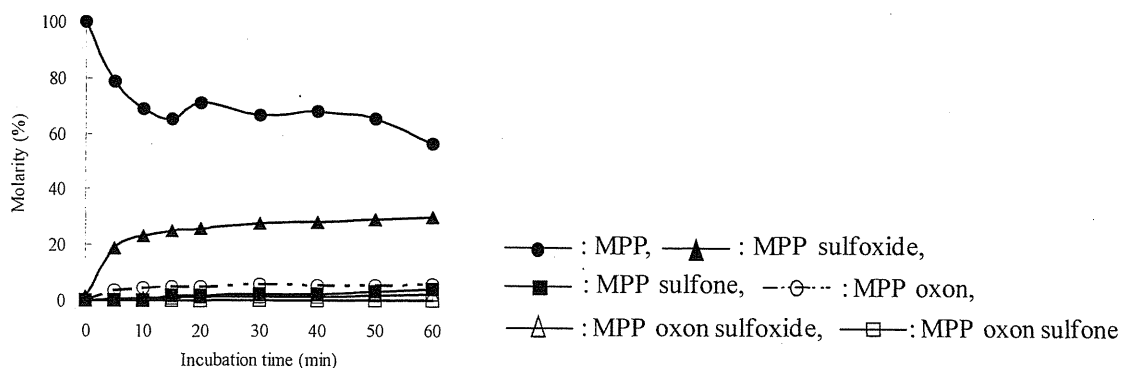


Fig. 3 - Formation of MPP metabolites by CYP3A4 up to an incubation time of 60 min. The molarity of MPP (10 µM) at the beginning of the reaction was defined as 100%.

Two major metabolites, MPP sulfoxide and MPP oxon were formed from MPP by some CYP and flavin-containing monooxygenase in the previously reported papers (Leoni *et al.*, 2008; Kitamura *et al.*, 2003). In their results, MPP sulfone and MPP oxon sulfone were not detected on chromatograms by HPLC/UV and GC/MS. Thus, we compared sensitivity on metabolites using GC/MS and LC/MS, and set the limit of detection of MPP sulfoxide, MPP sulfone, MPP oxon, MPP oxon sulfoxide and MPP oxon sulfone to 10, 2, 5, 50 and 20 µg/L for GC/MS and 0.02, 0.2, 0.05, 0.2 and 0.1 µg/L for LC/MS, respectively. Five compounds except MPP were able to be analyzed more effectively by LC/MS as compared with GC/MS. Since LC/MS had 10-500 times higher sensitivity in measurement of metabolites than GC/MS, it yielded satisfactory separation and it was used to analyze the metabolites. Therefore, traces of MPP sulfone, MPP oxon sulfoxide and MPP oxon sulfone were able to be detected.

Toxicity evaluation of MPP oxide derivatives

In water, MPP is gradually converted to MPP sulfoxide and then to traces of MPP oxon sulfoxide and MPP oxon sulfone (Tahara *et al.*, 2008a). Moreover, MPP has been thought to react with chlorine in the water purification process. The formation of four oxides, MPP sulfoxide, MPP sulfone, MPP oxon sulfoxide and MPP oxon sulfone, through chlorination process was observed, and after 24 hours, MPP was almost completely converted to MPP oxon sulfone (Tahara *et al.*, 2008a). The four MPP oxide derivatives have not received careful evaluation as toxic agents since they are not used as pesticides. Thus, the three MPP oxons were evaluated for toxicity by *in vitro* system using cholinesterase activity as an indicator (Tahara *et al.*, 2005). It was found out that MPP oxon sulfone has the most pronounced adverse effect followed by MPP oxon sulfoxide, and then MPP oxon. Consequently, human risk assessment for MPP must be done on the basis of the contributions of its oxides.

The stability of MPP oxon sulfone with CYP3A4 was examined next. The concentration of MPP oxon sulfone did not change for 60 min, which suggests that MPP oxon sulfone might accumulate and show toxicity without further *in vivo* modification. It was also found out that the oxidation of MPP to MPP oxon sulfone occurs more readily in the environment and in the water purification process than by *in vivo* metabolism.

The inhibition of cholinesterase activity was reported to be 280 times stronger with MPP oxon sulfone as compared with MPP (Tahara *et al.*, 2008b). Therefore, careful monitoring of MPP oxides in drinking water is required to evaluate the acute toxicity of MPP because human population could be exposed to MPP oxon sulfone through the drinking water and other aqueous environment.

CONCLUSIONS

In this study, the possible genesis of MPP oxide derivatives in the environment was investigated as well as their potential toxicity to humans in a cholinesterase assay. The *in vitro* metabolic profile of MPP from aqueous environment was observed to mimic *in vivo* metabolism. It was clarified that CYP3A4, one of the most common human oxidative enzymes, catalyzed the conversion of MPP to five oxide derivatives. In public health, characterizing metabolic pathways for widely used pesticides is of high significance, especially with organophosphorus oxons, which have shown acute toxicity.

Moreover, the behavior of MPP oxon sulfone using CYP3A4 was examined because it is the product of the chlorination of MPP in the water purification process and it displays the strongest acute toxicity. As a result, the concentration of MPP oxon sulfone did not change and no product peak was observed. In addition, MPP was detected from river water in the summer months and lower amounts found in the winter months. MPP has a potential risk to human health by its conversion to MPP oxon sulfone through the water purification process; the environmental conversion end point for organophosphorus pesticides is thought to be the same. As shown in this study, the careful monitoring of organophosphorus pesticides and their oxides in aqueous environment and in tap water is an important matter for health assessment from the viewpoint of controlling water purity and risk management.

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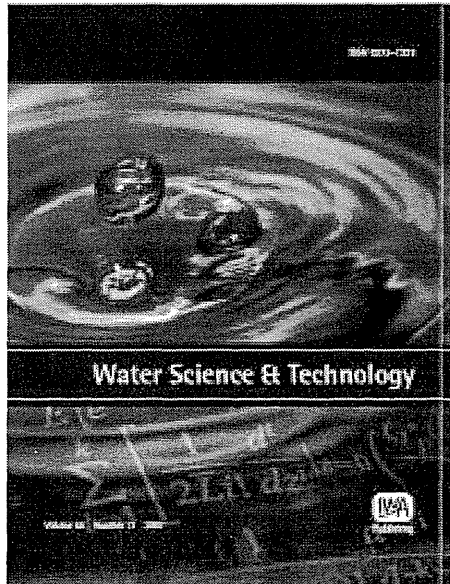
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Sensitivity analysis using a diffuse pollution hydrologic model to assess factors affecting pesticide concentrations in river water

Koji Tani, Yoshihiko Matsui, Kentaro Narita, Koichi Ohno and Taku Matsushita

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

Koji Tani
Yoshihiko Matsui (corresponding author)
Kentaro Narita
Koichi Ohno
Taku Matsushita
Graduate School of Engineering,
Hokkaido University,
N13W8,
Sapporo 060-8628,
Japan
E-mail: matsui@eng.hokudai.ac.jp

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 & Karpouzaz 2007). Some studies have suggested that the magnitude of the pesticide runoff differs depending on the solubility of the pesticides (Ueji & Inao 2001; 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 (Karpouzaz *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 gate 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-km² 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-km² 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

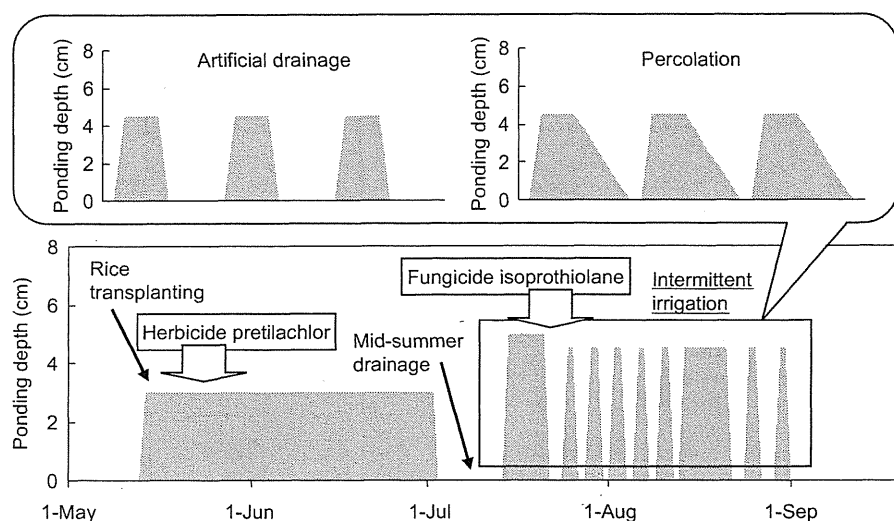


Figure 1 | Irrigation schedule and ponding depth of a rice paddy field with artificial drainage and percolation in the Kakkonda River basin.

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

	Water solubility (mg/L)	Adsorption coefficient, K_{oc} (mL/g)	Degradation rate constant in soil* (d^{-1})	Degradation rate constant in water* (d^{-1})
Isoprothiolane	54 [†]	1,230 [‡]	2.3×10^{-2} [‡]	2.3×10^{-2} [‡]
Pretilachlor	50 [†]	1,160 [§]	2.3×10^{-2} [‡]	4.9×10^{-2} [§]

*Calculated from half-life values by assuming first-order kinetics.

[†]Tomlin (2003).

[‡]Matsui et al. (2007).

[§]Food Safety Commission of Japan (2008).

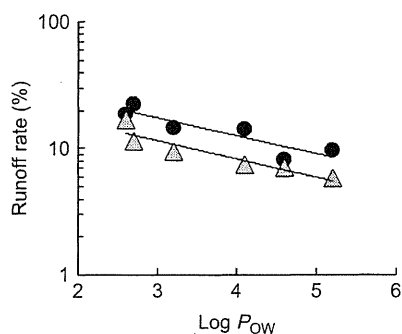


Figure 2 | Effect of $\log P_{ow}$ on pesticide runoff rates. Gray triangles indicate the simulation results. Black circles are the observed values from Nakano et al. (2004).

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 the 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

Table 2 | Properties of the pesticides in Figure 2

	$\log P_{ow}$	Water solubility (mg/L)	Adsorption coefficient, K_{oc} (mL/g) [†]	Degradation rate constant in soil [‡] (d^{-1})	Degradation rate constant in water [‡] (d^{-1})
Simetryn	2.6	400 [§]	290	$5.5 \times 10^{-3\ddagger}$	$5.5 \times 10^{-3\ddagger}$
Dymron	2.7	1.2 [§]	940 ^{**}	$1.4 \times 10^{-2\ddagger}$	$1.4 \times 10^{-2\ddagger\ddagger}$
Mefenacet	3.2	4 [§]	890 ^{**}	$1.8 \times 10^{-2\ddagger}$	$1.8 \times 10^{-2\ddagger}$
Pretilachlor	4.1	50 [§]	1,160 ^{††}	$2.3 \times 10^{-2\ddagger}$	$4.9 \times 10^{-2\ddagger\ddagger}$
Esprocarb	4.6	4.9 [§]	2,800 ^{**}	$1.4 \times 10^{-2\ddagger}$	$1.4 \times 10^{-2\ddagger\ddagger}$
Pyributicarb	5.2	0.32 [§]	3,500 ^{**}	$6.3 \times 10^{-2\ddagger}$	$6.3 \times 10^{-2\ddagger\ddagger}$

[†]Nakano et al. (2004).

[‡]Geometric means of reported values.

[‡]Calculated from half-life values by assuming first-order kinetics.

[§]Tomlin (2003).

^{||}Estimated by the PCKOCWIN model (US Environmental Protection Agency 2007).

[†]Estimated from the result of the BLOWIN3 model (Aronson et al. 2006).

^{**}Ministry of the Environment of Japan (2009).

^{††}Assumed the same value as the degradation-in-soil coefficient.

^{‡‡}Food Safety Commission of Japan (2008).

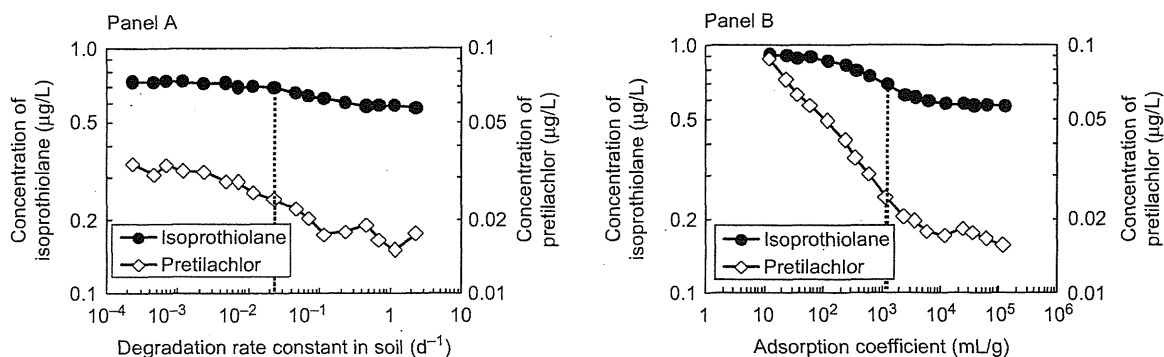


Figure 3 | Effect of pesticide degradability-in-soil (Panel A) and adsorbability (Panel B) on the average concentrations of the two pesticides in the river water 2 months after pesticide application on the paddy field. Vertical dotted lines indicate the actual values for the respective pesticides.

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

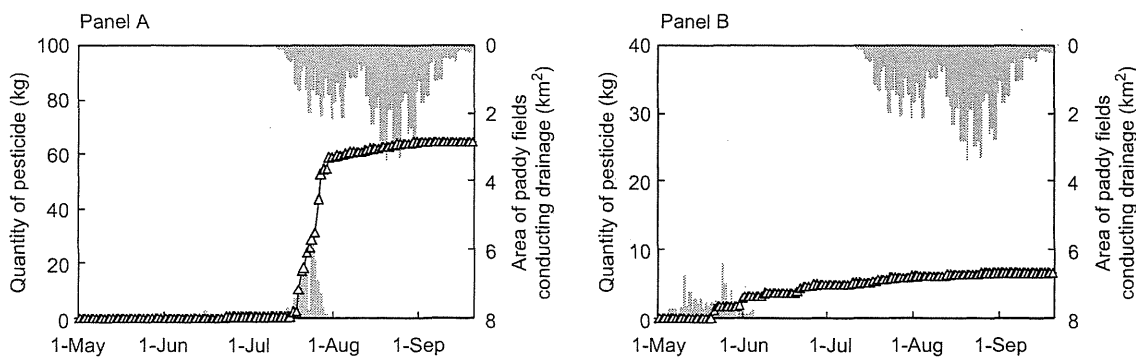


Figure 4 | Time-series runoff behavior of the fungicide isoprothiolane (Panel A) and the herbicide pretilachlor (Panel B) in 2004. Bars along the x-axis indicate the daily quantity of applied pesticide, and bars along the top axis indicate the total area of rice paddy fields conducting drainage in the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

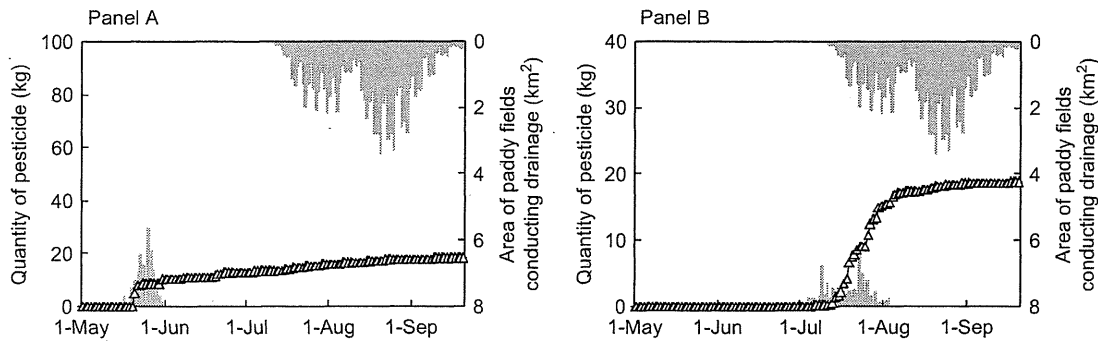


Figure 5 | Fictive time-series runoff behavior of isoprothiolane (Panel A) and pretilachlor (Panel B). Pesticide applications were interchanged; the fungicide isoprothiolane was applied in May prior to drainage, while the herbicide pretilachlor was applied in July at the time of drainage. Bars along 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).

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

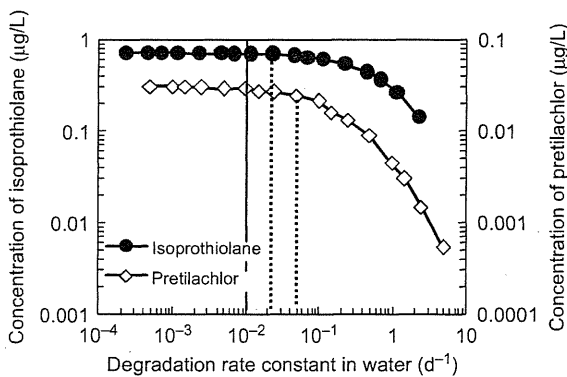


Figure 6 | Effect of pesticide degradability-in-water on the average pesticide concentrations. Vertical dotted lines indicate the actual values. Solid line indicates 10^{-2} d^{-1} .

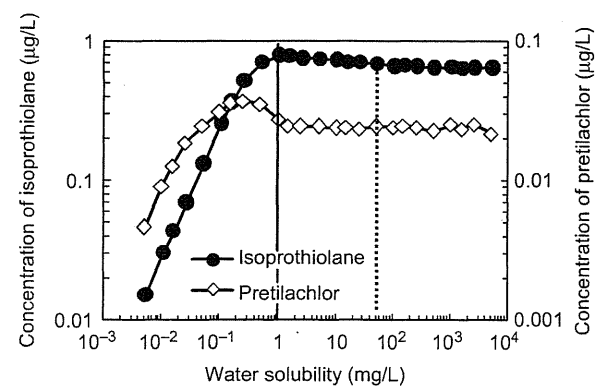


Figure 7 | Effect of pesticide water solubility on the average pesticide concentrations. Vertical dotted lines indicate the actual values. Solid line indicates 1 mg/L.

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

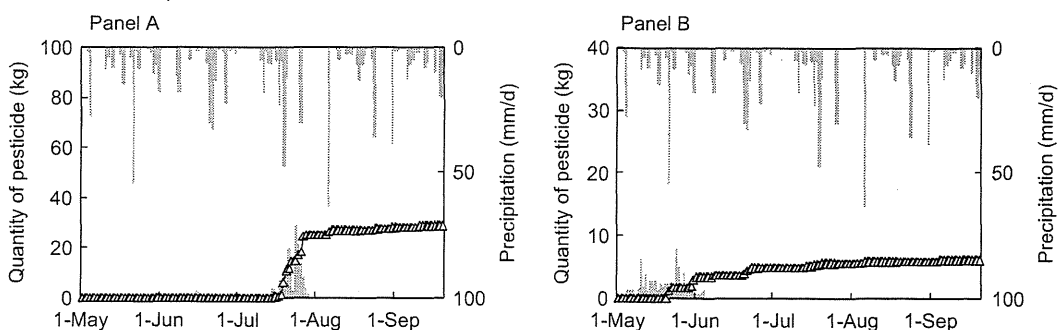


Figure 8 | Time-series runoff behavior of the fungicide isoprothiolane (Panel A) and the herbicide pretilachlor (Panel B) with percolation instead of artificial drainage during the intermittent irrigation period. Bars along the x-axis indicate the daily quantity of applied pesticide (in kg), and bars along the top axis indicate the amount of precipitation. Open triangles indicate the cumulative amount of pesticide runoff into the river.

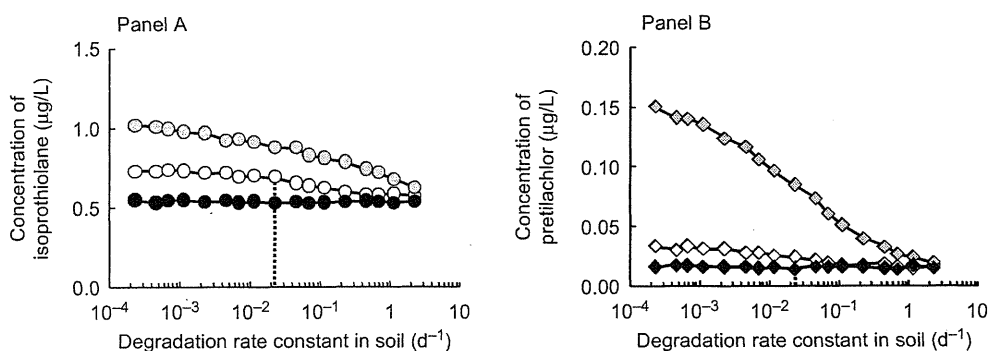


Figure 9 | Effect of the pesticide degradability-in-soil on the average concentrations of isoprothiolane (Panel A) and pretilachlor (Panel B) under the conditions of three adsorption coefficient values. Gray circles, white circles, and black circles indicate the results with the low, actual, and high adsorption coefficient values: 12.3 mL/g, 1230 mL/g, and 123 L/g, respectively, for isoprothiolane; 11.6 mL/g, 1160 mL/g, and 116 L/g, respectively, for pretilachlor.

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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Exposure assessment of metal intakes from drinking water relative to those from total diet in Japan

Koichi Ohno, Kohei Ishikawa, Yuki Kurosawa, Yoshihiko Matsui, Taku Matsushita and Yasumoto Magara

ABSTRACT

Daily intakes of 17 metals (boron, aluminium, chromium, manganese, nickel, copper, zinc, arsenic, selenium, molybdenum, cadmium, antimony, lead, uranium, magnesium, calcium, and iron) via drinking water and total diet were investigated in six cities in Japan. The daily metal intakes were estimated and compared with tolerable daily intake (TDI) values proposed by the WHO or Joint FAO/WHO Expert Committee on Food Additives for toxic metals and with recommended dietary allowances (RDAs) or adequate intake (AI) values proposed for essential metals by the Japanese Ministry of Health, Labour and Welfare. Among the 13 toxic metals, mean dietary intakes of 10 (except arsenic, selenium, and molybdenum) were less than 50% of TDI, suggesting that for these 10 metals the allocation of intake to drinking water in establishing guidelines or standards could possibly be increased from the normal allocation of 10–20% of TDI. For the 13 toxic metals, the contribution of drinking water to TDI was 2% or less in all six cities. Mean dietary intakes of the essential elements magnesium, calcium, and iron were less than the RDA or AI values. Drinking water did not contribute much to essential metal intake, accounting for less than 10% of RDA or AI.

Key words | dietary metal intake, drinking water quality, health risk assessment

Koichi Ohno (corresponding author)
Kohei Ishikawa
Yuki Kurosawa
Yoshihiko Matsui
Taku Matsushita
Graduate School of Engineering,
Hokkaido University,
N13W8,
Sapporo, Hokkaido 060-8628,
Japan
E-mail: ohnok@eng.hokudai.ac.jp;
k_ishikawa@eng.hokudai.ac.jp;
matsui@eng.hokudai.ac.jp;
taku-m@eng.hokudai.ac.jp

Yasumoto Magara
Center for Environmental Nano and Bio
Engineering,
Hokkaido University,
N13W8,
Sapporo, Hokkaido 060-8628,
Japan
E-mail: magara@eng.hokudai.ac.jp

INTRODUCTION

In the *Guidelines for Drinking-water Quality* of the World Health Organization (WHO), the guideline values for non-carcinogenic chemicals are derived from a certain percentage of tolerable daily intake (TDI). This percentage should be allocated on the basis of actual data on daily intakes from other sources such as food, air, and soil, but such data are not always available. As noted in the third edition of the guidelines (WHO 2004), when data on daily intake of the chemical are insufficient, the default allocation percentage to drinking water is 10% of TDI. In recent addenda to the guidelines, however, the allocation approach has changed twice. In the first addendum, the description of a specific percentage as the default allocation was changed to: "Where appropriate information is not available, values are applied that reflect the likely

contribution from water for various chemicals" (WHO 2006). The values generally vary from 10 to 80%, considering the exposure from all sources (WHO 2006). In the second addendum, the use of a default allocation value was re-established and the value was changed from 10 to 20% of TDI (WHO 2008). The second addendum stated that an allocation of 20% is still protective and that 10% was found to be excessively conservative (WHO 2008). The collection of chemical intake data from other sources such as food is becoming more crucial for the review and establishment of local drinking water quality standards that reflect actual exposures to chemicals.

Although numerous studies have measured daily metal intake from total diet (Biego *et al.* 1998; Bordajandi *et al.* 2004; Maitani 2004; Santos *et al.* 2004; Turconi *et al.* 2009),