Figure 3 Molecular structures of pesticides

pesticide application dates, places (grid cells), quantities of pesticide applied, irrigation and drainage schedules, degradation rate, and solid–water sorption coefficients in each compartment were created by the Monte Carlo method using available and published data by a procedure described elsewhere (Matsui *et al.*, 2005). A total of 2000 data sets for a pesticide, thiobencarb, were created, and a set of 2000 Monte Carlo simulations yielded a prediction of concentrations of the pesticide in river water (a prediction-of-pesticide pollutograph). For the other pesticides, the number of simulations for each pesticide was limited to 30 due to the time constraints imposed by the time that model calculation requires.

Predicting pesticide concentrations

Comparison of time-series pesticide concentrations as observed and as predicted

After the hydrological system parameters were calibrated, the hydrological and solute models were solved simultaneously by substituting the input data for the pesticide, giving the predicted concentrations of the pesticide in river water for the rice-cultivation seasons of 2000 and 2001. A total of 2000 data sets for thiobencarb were created, and a set of 2000 Monte Carlo simulations yielded a simulation predicting concentration of the pesticide in river water. Figure 4 shows the time variations in the predicted and observed thiobencarb concentrations for the Chikugo River basin in 2000 and 2001. Of the observed data points, 68% were in the range predicted with the 2000 data sets of the Monte Carlo inputs, and more than 40% were within the 1–99% range of the prediction. Although the pesticide-dusting dates and the quantity applied are influential factors for predictive accu-
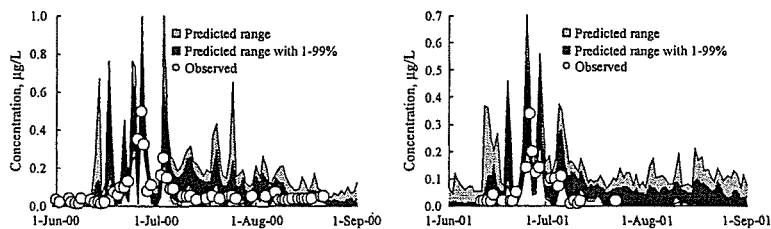

Figure 4 Predicted and observed thiobencarb concentrations in Chikugo River in 2000 and 2001

racy, our prediction was not based on precise data for the quantities used and dates of pesticide dusting by individual farmers. Moreover, the model calculations were conducted without optimizing the pesticide decomposition or sorption parameters. In the light of these limitations, we consider the thiobencarb pollutograph to be reasonably successful for a first estimate.

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Comparison of June–July-averaged concentrations as observed and as predicted

Figure 5 shows a comparison of predicted and observed concentrations of 13 pesticides for the June–July periods of 1999–2002, during which water sampling and pesticide concentration measurements were frequently conducted and pesticides were actually detected with high concentrations over the detection limits. Bars for concentrations indicate the arithmetic mean values of time-series concentrations predicted for June–July and of the arithmetic mean values of concentrations observed in June–July (the absence of a bar means the pesticide observation was not conducted for that year and for that pesticide). Water samples for pesticide concentration analysis were collected at 9 a.m., and the maximum number of the sampling events during the June–July periods was 43 times for two pesticides (mefenacet and bromobutide, both in June–July 2003). The concentration of one pesticide (dimethametryn) was measured just four times during June–July 1999. Some pesticides, such as pyrazolate, were not analysed at all. Therefore, the average values of observed pesticide concentrations may not necessarily represent the concentrations of the pesticides in the June–July period. On the other hand, the model calculation provides continuous outputs of time-varying concentrations and the predicted concentrations for the June–July periods are given as time-average values of the continuous outputs. Therefore, it may not be inappropriate to simply compare the observed values and the predicted values, in particular for pesticides for which the numbers of
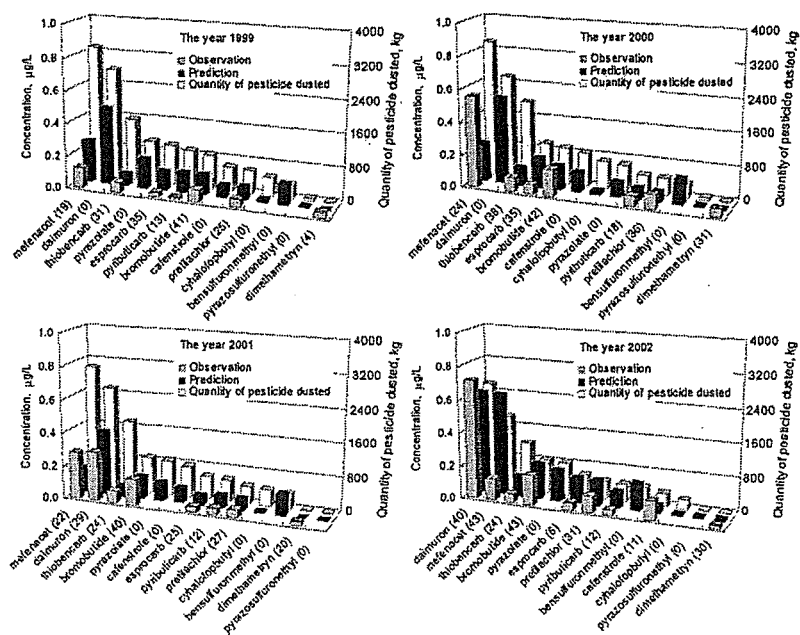

Figure 5 Comparison of June–July-averaged concentrations as observed and as predicted by the model (the numerical values in parentheses are the numbers of observations in June–July periods; the absence of a bar indicates no observed data)
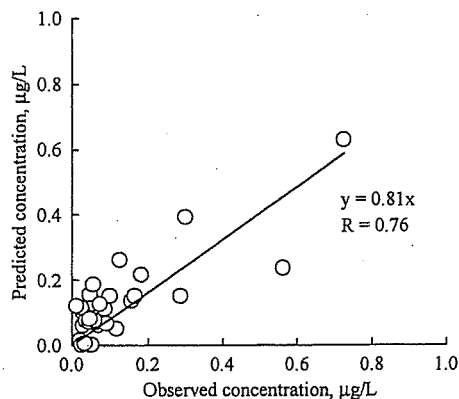
Figure 6 Comparison of observed and predicted pesticide concentrations (except mefenacet in June—July 2000)

sampling and observation were few. Nonetheless, the predicted concentrations were in fairly good agreement with the observed ones.

The figure also shows the quantity of each pesticide dusted in the target area in each year, which was estimated by the data of the annual sales of pesticide products obtained from the annual reports published by the Japan Plant Protection Association (2000, 2001, 2002, 2003). Pesticides that were dusted in large quantities did not necessarily lead to high concentrations in river water, as empirically known, and this empirical knowledge is validated by the model's prediction. Pesticide rankings by concentration, which could not be predicted solely by the quantity of pesticide dusted, are well predicted by the model.

For some pesticides, however, discrepancies still arise between observed and predicted concentrations, probably because the lack of available precise data leads to imprecise model input for quantities and dates of pesticide dusting, pesticide decomposition, and pesticide sorption. For example, prediction of a pesticide (mefenacet) far exceeded observation for the year 2002, although the model predictions for the years 1999—2001 were consistent with observations for those years. Further study is still needed to improve the prediction ability of the model. Excluding the data point for mefenacet in June—July 2002, the coefficient of correlation between predicted and observed concentration was R = 0.76 (see Figure 6).

A practical application of the model prediction is a screening-level analysis, in which pesticides to be monitored are selected and the monitoring schedule is determined for a catchment area where different pesticides are applied from year to year. The effectiveness of the screening-level analysis by the model prediction was examined for two pesticides, daimuron and cafenstrole. The predictions of 1999 and 2000 suggest daimuron concentrations to be 0.48 and 0.53 μg/L, respectively, which are the highest pesticide concentrations predicted by the model for those years (Figure 5). However, measurement of daimuron concentrations did not start until 2001. Daimuron concentrations observed in 2001 and 2002 (0.3 and 0.7 μg/L, respectively) were similar to the predicted values (0.39 and 0.63 μg/L, respectively). For the other pesticide, cafenstrole, concentrations were not measured until 2002, while the predicted concentrations for 1999, 2000, and 2001 were 0.07, 0.12, and 0.09 μg/L, respectively. The observed cafenstrole value for 2002 was 0.12 μg/L, similar to the concentrations predicted for the previous years (the predicted concentration for 2002 was 0.05 μg/L).

Conclusions

A basin-scale runoff model was developed to predict rice-farming pesticide concentrations in river water with imprecise model inputs for screening-level analysis, which can be used for selecting pesticides to be monitored and determining the monitoring schedule. Overall, the model successfully predicted pesticide concentrations within order-of-magnitude accuracy. The model outputs predicted the rankings of pesticides with respect to concentrations, which could be utilised to prioritise pesticides that require monitoring among numerous pesticides applied in the river basin.

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INVESTIGATING RICE-FARMING PESTICIDE CONCENTRATIONS IN RIVER WATER USING A BASIN-SCALE RUNOFF MODEL WITH UNCERTAIN INPUTS

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ABSTRACT. *In predicting time-series concentrations of pesticides in river water using diffuse pollution hydrological models, farming schedules (including pesticide application) and pesticide sorption/decomposition rates greatly affect prediction accuracy. For large, basin-scale catchments, precise acquisition of these data is not possible and substantial estimation uncertainty inevitably exists. This article presents the development of a basin-scale diffuse pollution hydrological model, a Monte Carlo method for creating input data, and its effectiveness in predicting the concentrations of paddy-farming pesticides in river water from a large catchment (1882 km^2). The Monte Carlo method created input data for numerous compartments of a paddy field in the basin model: the pesticide products, amounts and dates of pesticide application, rice varieties, rice seedling transplanting dates, time variation of water depth in rice paddies, and parameter values for pesticide decomposition and sorption. The model was calibrated with hydrological data only, without reference to observed pesticide concentration data. Results showed that the uncertainty bounds estimated for model outputs with Monte Carlo inputs encompassed observed data and that the model predictions were better with Monte Carlo inputs than with deterministic input. The Monte Carlo method provides a surrogate approach for obtaining precise data on individual farming schedules (including pesticide application dates), degradation rates, and sorption coefficients in each soil.*

Keywords. Agricultural chemicals, Herbicide, Pollutograph, Uncertainty, Water pollution.

Pesticides used in agriculture have the potential to enter hydrological catchment systems and contaminate river waters, which constitute the primary source of drinking water for many regions. It is important to predict and know which pesticides readily become entrained in runoff, the weather conditions that trigger pesticide runoff, and on a local scale, the fields from which the leached pesticides originate; from this information, it is possible to predict pesticide concentrations in river water. The predictions are valuable when used in screening-level analysis, providing order-of-magnitude accuracy with minimal investment of time and resources in water-quality monitoring for water treatment plants that take river water (Dabrowski et al., 2002). In Asian countries, the fate of rice-farming pesticides and their concentrations in river water are particularly important issues, because the rice-farming pesticides enter river water at higher rates than other pesticides used in upland fields. The rice-farming pesticides are applied directly on the ponding water of the paddy field and are more likely to con-

taminate river water by spillover during or after rainfall or drainage. Although annual pesticide consumption for upland fields is no less than that for the rice-paddy fields, most pesticides detected in the river water are those used in growing rice (Matsui et al., 2002).

Models have been designed to simulate pesticide transport in agricultural watersheds and changes in pesticide concentrations in river water. Mechanistic models, based on detailed physical and chemical descriptions of transport processes, have been used to simulate and predict the fate and transport of pesticides in watersheds, while statistical analyses are employed to interpret regional monitoring data for pesticide transport and to explain transport patterns observed at the watershed scale (Guo et al., 2004). To date, many mechanistic models have been designed and developed; most of them are designed for field-scale applications. For example, the field-scale Pesticide Root Zone Model (PRZM) has been used for pesticide regulatory assessment (Mullins et al., 1993). The validity of the field-scale models has been established under small-scale and edge-of-field conditions, where physical features, such as soil hydrological properties and slope, are relatively homogeneous (Mullins et al., 1993; Knisel, 1993). Therefore, extrapolation of the model results to runoff from larger and more heterogeneous watersheds and predictions of pesticide concentrations in river-basin water have had limited success (Solomon et al., 1996) because of spatial variabilities in land use, hydrological processes, and pesticide transport and reaction processes.

Hydrological diffuse pollution models (Borah and Bera, 2003, 2004), such as the Hydrologic Simulation Program-FORTRAN (HSPF; Johanson, 1983; Johanson et al., 1997) and the Soil and Water Assessment Tool (SWAT; Arnold et

al., 1998; Neitsch et al., 2002), were designed to simulate the movement of water and pollutants in river basins and thereby assess water quality. These are comprehensive models of watershed hydrology and water quality that allow the integrated simulation of runoff, sediments, nutrients, and pesticide transport with instream hydraulic and sediment interactions. Moore et al. (1988) applied HSPF to an 18-ha watershed planted in corn. Atrazine in runoff over a 13-month period was overestimated by 45%. Laroche et al. (1996) applied HSPF to a 78-ha watershed to simulate atrazine concentration at the outlet of the watershed. Simulated concentrations were in the same range as observed values and peak concentrations occurred simultaneously. Neitsch et al. (2002) applied the SWAT model to a 242 km² watershed to predict the daily pesticide concentration in river water, and demonstrated the ability of SWAT to realistically predict pesticide concentrations. They also discussed the reliability of the observed pesticide concentration data in the model calibration and validation processes. Unlike stream-flow, where the flow is measured hourly and 24 values are averaged to obtain the daily flow value, pesticide concentrations are measured at very low frequencies, such as one measurement per week or month for an instantaneous sample. Neitsch et al. (2002) stated that comparing an instantaneous grab sample with the daily average concentration calculated by the model could be invalid because the data are of two different kinds.

Although many models and their applications have been reported, few are designed to predict runoff of rice-farming pesticides from rice-paddy fields (Inao and Kitamura, 1999; Li and Migita, 1992). Moreover, very few studies have attempted to develop a model applicable to basin-scale catchments and able to predict rice-farming pesticide concentrations in river water (Matsui et al., 2002), probably due to the following reasons:

Since most agricultural land comprises upland fields in countries where simulation models are routinely used for environmental exposure assessment (i.e., in Europe and the U.S.), there is little need in those countries for a model to simulate transport and degradation of pesticides in rice-paddy fields with ponding water.

In addition, modeling and prediction requires accurate agricultural as well as hydrological, meteorological, and geographical data as input. Hydrological, meteorological, and geographical data are becoming obtainable and available as modeling inputs. For large target catchment areas, however, acquisition of precise data on farming schedules, including pesticide application dates, is a daunting task. Data acquisition becomes even more difficult when large numbers of farmers cultivate very small plots, as in Japan: the average farming scale in Japan is 1 ha (Census Statistics Office, 1997, 2002), much smaller than in other countries. Even though some statistical data or typical data are used, substantial uncertainty inevitably exists in the estimated data.

Moreover, many factors affect model input parameters related to the processes of pesticide sorption and decomposition. Without information on the reaction environment in a target river basin, it is impossible to quantify specific reaction rates. Generally, the reported values of input parameters are subject to different kinds of uncertainties (Dubus et al., 2003).

Finally, the models invariably require calibration and parameter estimation. For simulating pollutant transport, the hydrology of the system is calibrated and determined first, followed by pollutant transport when measured data are available. This calibration requirement precludes models from being applied to new pesticides. The differences in pesticide properties, regional pesticide usage, and other factors that result in surface-water contamination precludes the use of calibrated models for unmonitored river basins or unmonitored and new pesticides. Models that can accurately simulate new pesticides are needed, because new rice-farming pesticides are developed every few years (Japan Plant Protection Association, 1999-2001).

OBJECTIVES

The objective of the present study was to investigate the pesticide concentrations in river water that result from rice farming within an uncertainty analysis framework. A basin-scale runoff model was developed, the hydrologic component of the model was calibrated with daily river flow data, and 2000 different combinations of pesticide parameters were used in Monte Carlo iterations to consider uncertainties in the pesticide application practices, agricultural work schedules, and parameters for pesticide decomposition and sorption. The prediction accuracy of the model was evaluated using non-optimized pesticide parameters. The model was calibrated using hydrological data alone, without reference to observed pesticide concentration data. The prototypes of the model and a very primitive Monte Carlo approach were seen elsewhere (Matsui et al., 2002), but in this research the model structure has been advanced, it has been applied to a larger-size area, and the Monte Carlo approach has been applied widely.

MODEL DESCRIPTION

We developed a compartment model rather than using one of the models proposed elsewhere (Borah and Bera, 2003, 2004; Nakano et al., 2004), since the latter models do not account for the runoff from rice-paddy fields or were not designed for a large-scale catchment area and Monte Carlo inputs. In our model, a river basin is divided into a 1 km² grid of cells, and each grid cell consists of 12 compartments, as shown in figure 1:

- A river water compartment (R-compartment)
- A river bed compartment (S-compartment)
- A rice-paddy ponding compartment (W-compartment)
- Two rice-paddy soil compartments (X- and Y-compartments)
- A mountain compartment and its soil compartment (M- and N-compartments)
- A dry field compartment and its soil compartment (F- and G-compartments)
- Two deeper soil compartments (B- and C-compartments)
- An urban area compartment (U-compartment).

The area sizes of compartments are variable depending on the land cover of the grid cell composed of the compartments, by which heterogeneity of the watershed characteristics is incorporated.

The lateral movements of water and pesticides from all compartments except the C-compartment go into the R-compartment of the adjacent grid cell with the steepest slope among the eight surrounding grid cells, while the lateral
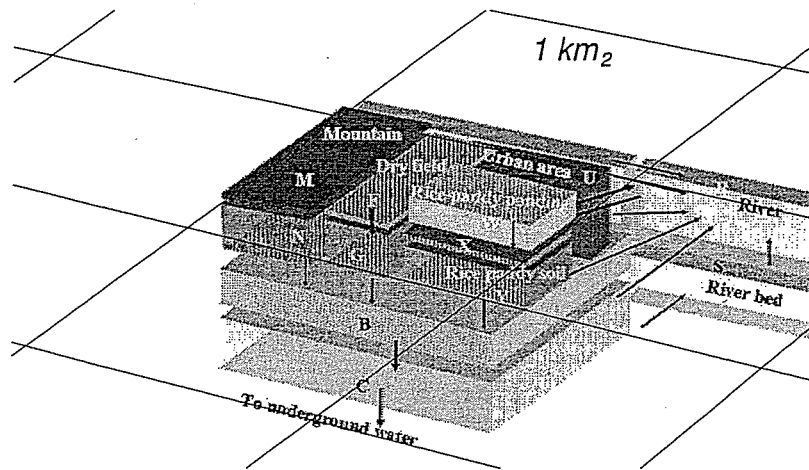
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Figure 1. Compartments in a 1 km^2 grid cell and flow directions.

movement from the C-compartment goes to the R-compartment via the S-compartment of the next grid cell. The irrigation water to the W-compartment is taken from the R-compartment of the same grid cell or neighboring grid cell when the flow rate in the R-compartment is insufficient to supply water for irrigation. The vertical flows from all compartments except the R-, S-, and C-compartments go to each lower compartment. The vertical flow from the C-compartment goes to the underground, which is assumed to not return to the river water. No vertical flows (no groundwater occurrences) were assumed for the R- and S-compartments.

Within a compartment, the solute concentration and water level were assumed to be uniform, and each is represented by a single variable. For example, rainwater that had reached a W-compartment was assumed to mix completely and uniformly with the pesticides therein. If a compartment consisted of multiple sub-elements (solids and water), a dynamic equilibrium existed between the dissolved and adsorbed fractions at the solid-water interface. The interfacial dynamics are usually described by a film model of mass transfer, and the incorporation of a film model makes the overall model descriptive but makes the model calibration too complex. Therefore, for a first estimate of the predictions in the present study, the interfacial phases were assumed to be in equilibrium at all times; sorption processes were considered to be instantaneous and were described by a single constant (a solid-water partition coefficient) in the linear equilibrium relationship. Solute movement in the soil is slow compared with the interfacial solute mass-transfer at the solid-water interface, and the interfacial solute mass-transfer may not be a rate-limiting step for overall solute movement. The assumption of all interfacial phases being in equilibrium could therefore be reasonable. Finally, once the concentration in one phase in a compartment was known, the concentration in the other phase could be calculated. The degradation of pesticides in water and soil are described by first-order reaction kinetics (Klaine et al., 1988).

The processes of pesticide uptake by plants and volatilization of pesticides into an atmospheric phase were not considered in this model, since the fractions of pesticide moved by these processes were assumed to be smaller than the fractions moved by decomposition, sorption, and runoff.

The loss due to the drift of pesticide was not accounted in the relevant compartments, because the target pesticide (thiobencarb) is in the form of granules whose drift is insignificant (Investigative Commission for Ecological Effect of Pesticide, 2002). Pesticides in the suspended-solid phase of water were not included in the model, because a study of the runoff characteristics of particulate pesticides from a paddy field revealed that the concentrations and the detection frequencies of pesticides in suspended solid phases were much lower than those in dissolved phases (Inoue et al., 2002).

A set of differential mass-balance equations describing the dynamics of a solute (pesticide) and water in each compartment was defined, based on the law of conservation (i.e., mass balance) for the solute and the water. For example, the mass balance of water in a rice-paddy ponding compartment (W-compartment) is given by:

$$A_{W,i} \frac{dh_{W,i}}{dt} =$$

$$Q_{in,W,i} - Q_{out,W,i} - Q_{V,W,i} - A_{W,i}E_{W,i} \qquad (1)$$

where $A_{W,i}$ is the area of the rice-paddy field (m^2), $h_{W,i}$ is water depth (m), t is time (d), $Q_{in,W,i}$ is the irrigation rate (flow rate of water into the rice-paddy field, m^3 d^{-1}), $Q_{out,W,i}$ is the drainage rate (flow rate of water out of the rice-paddy field, m^3 d^{-1}), $Q_{V,W,i}$ is the water loss due to percolation (m^3 d^{-1}), $E_{W,i}$ is the rate of evapotranspiration (m d^{-1}), and subscript i represents the grid number.

The solute balance is given as the product of concentration and water flow rate:

$$A_{W,i} \frac{dM_{W,i}}{dt} = C_{R,i}Q_{in,W,i} - C_{W,i}Q_{out,W,i}$$

$$- C_{W,i}Q_{V,W,i} - r_{W,i}h_{W,i}A_{W,i} + P_{D,i}A_{W,i} \qquad (2)$$

where $M_{W,i}$ is the mass of pesticide in rice-paddy water per unit of rice-paddy area (mg m^{-2}), $C_{W,i}$ is the concentration of a pesticide in rice-paddy water (mg m^{-3}), $C_{R,i}$ is the concentration of a pesticide in river water (mg m^{-3}), $r_{W,i}$ is the degradation rate of the pesticide in water (mg d^{-1} m^{-3}), and $P_{D,i}$ is the rate of pesticide application (mg d^{-1} m^{-2}). The

concentration in water phases such as $C_{W,i}$ and $C_{R,i}$ is given as the mass of pesticide divided by the volume of water. However, the concentration is given as the water solubility of the pesticide when the quantity of pesticide exceeds its water solubility limit. In that situation, the portion of pesticide over the solubility limit is considered to exist in the solid phase and is not subject to movement. For example, the pesticide concentration in rice-paddy ponding is given by:

$$C_{W,i} = \min\left(\frac{M_{W,i}}{h_{W,i}}, C_S\right) \qquad (3)$$

where C_S is the water solubility of a pesticide (mg m^{-3}). Water solubility and sorption characteristics of a pesticide may actually be altered by adjuvants, which are applied to modify the physical characteristics of the actual pesticide spray solutions. However, adjuvant effects are not considered in the model because no adjuvant data are presently available.

The rates of irrigation to and drainage from the W-compartment are described as functions of compartment water levels:

$$Q_{in,W,i} = A_{W,i} a_{in,W} \max(0, h_{0,W,i} - h_{W,i}) \qquad (4)$$

$$Q_{out,W,i} = A_{W,i} a_{out,W} \max(0, h_{W,i} - h_{0,W,i}) \qquad (5)$$

where $h_{0,W,i}$ is the desired water depth of rice-paddy ponding (m), and $a_{in,W}$ and $a_{out,W}$ are the irrigation and drainage rate coefficients of rice-paddy ponding (d^{-1}), respectively.

The water depth of rice-paddy ponding is artificially controlled at various levels according to the growth of rice. In the model, rice-paddy irrigation from and drainage to the river were adjusted so that the water depth of rice-paddy ponding was equal to the desired water depth. The flow rates of irrigation and drainage in the model were assumed to be proportional to the difference between the present water depth and the desired water depth. The desired water depth of the rice-paddy field ($h_{0,W,i}$) is a time-series model input that was determined according to published rice-farming schedules, as described later.

The vertical flow from a W-compartment depends on water depths in the W-compartment and the lower level X-compartment:

$$Q_{V,W,i} = a_{V,W} A_{W,i}$$

when $h_{W,i} > 0$ and $h_{X,i} < h_{0,X}$

$$Q_{V,W,i} = 0$$

when $h_{W,i} = 0$ or $h_{X,i} = h_{0,X}$ \qquad (6)

where $a_{V,W}$ is the infiltration rate coefficient of the rice-paddy field (m d^{-1}), $h_{X,i}$ is the water depth in the X-compartment (m), and $h_{0,X}$ is the depth of the X-compartment (m).

The rates of lateral surface flows from the M-, F-, and U-compartments were described by the Manning equation; for a U-compartment as an example:

$$Q_{H,U,i} = \frac{A_{U,i}}{B} h_{U,i} \frac{1}{n_{M,i}} h_{U,i}^{2/3} I_i^{1/2} \qquad (7)$$

where $Q_{H,U,i}$ is the lateral flow rate of a U-compartment (m^3 d^{-1}), $A_{U,i}$ is the area of a U-compartment (m^2), B is the side length of a grid cell (m), $h_{U,i}$ is the water depth of a U-compartment (m), $n_{M,i}$ is the Manning roughness coefficient (d m$^{-7/3}$), and I_i is the slope (dimensionless).

The rates of lateral interflow from the X-, Y-, N-, G-, B-, and C-compartments were described as functions of the water depth and the slope of the compartment; for a C-compartment as an example:

$$Q_{H,C,i} = a_{H,C} I_i \left(\frac{A_{C,i}}{B}\right) h_{C,i} \qquad (8)$$

where $Q_{H,C,i}$ is the lateral flow rate of a C-compartment (m^3 d^{-1}), $a_{H,C}$ is the lateral flow rate coefficient of a C-compartment (m d^{-1}), $A_{C,i}$ is the area of a C-compartment (m^2), and $h_{C,i}$ is the water depth in the C-compartment (m).

The rates of vertical interflows from the X-, Y-, M-, N-, F-, G-, B-, and C-compartments were described as a ratio of the relative water level to the compartment height, which is equivalent to the percentage of water content in the compartment; for a C-compartment as an example:

$$Q_{V,C,i} = a_{V,C} A_{C,i} \left(\frac{h_{C,i}}{h_{0,C}}\right) \qquad (9)$$

where $Q_{V,C,i}$ is the vertical flow rate of a C-compartment (m^3 d^{-1}), $a_{V,C}$ is the vertical flow rate coefficient of a C-compartment (m d^{-1}), and $h_{0,C}$ is the depth of the C-compartment (m).

The Manning equation was also used to describe the flow rate in the R-compartment:

$$Q_{R,i} = \frac{A_{R,i}}{L_R} h_{R,i} \frac{1}{n_{M,i}} h_{R,i}^{2/3} I_i^{1/2} \qquad (10)$$

where $Q_{R,i}$ is the river flow rate (m^3 d^{-1}), $A_{R,i}$ is the area of the river (m^2), L_R is the river length in a compartment (m), $h_{R,i}$ is the water depth of the R-compartment (m), and $n_{M,i}$ is the Manning roughness coefficient (d m$^{-7/3}$).

The flow rate coefficient of each type of compartment (e.g., $a_{V,Y}$) is assumed to be a single value regardless of which grid cell the compartment belongs to; a single value was thus assigned to each type of compartment throughout the grid. Therefore, the total number of the hydrologic parameters was reduced even though the target river basin was divided into numerous grid cells, simplifying the parameterization process and helping to solve the problem of the uniqueness of the parameters. The following problem is normally encountered in this type of distributed-parameter model: the sensitivity of the calculated river flow rate for a single parameter decreases with an increasing number of parameters, and a unique set of parameters cannot be found because the information that can be obtained by the measurement of river flow rates is usually not sufficiently differentiated to obtain a unique set of parameters. The scheme in which the hydrologic parameters are given, not to each compartment of each grid cell but to each type of compartment, increases the uniqueness of the hydrologic parameters. This scheme would enable the model to evaluate changes in land covers (e.g., rice field area); such condition can be simulated by changing the area of the compartments in each grid cell. However, if the hydrologic

condition of each type of compartment is changed, then the model probably needs hydrological re-calibration.

The hydrologic (water flow) model involves 23 parameters. The values of 13 parameters were given *a priori* or *a posteriori* by observation. The remaining 10 parameters were adjustable, and their values were searched for model simulation so as to give the best fit to the observed flow rates with the minimum error criterion of the Nash-Sutcliffe coefficient, E_{NS} (Nash and Sutcliffe, 1970):

$$E_{NS} = 1 - \frac{\sum\limits_{j=1}^{N} (Q_{obs,j} - Q_{cal,j})^2}{\sum\limits_{j=1}^{N} (Q_{obs,j} - Q_{ave})^2} \qquad (11)$$

where E_{NS} is the Nash-Sutcliffe coefficient, $Q_{obs,j}$ and $Q_{cal,j}$ are the daily observed and calculated flow rates ($m^3 s^{-1}$), respectively, Q_{ave} is the average observed flow rate ($m^3 s^{-1}$), and N is the number of data points. A Nash-Sutcliffe coefficient value can vary between $-\infty$ and 1, where a value of 1.0 indicates a perfect fit.

In addition to this best-fit criterion, the adjustable parameters were determined so that the hydrologic simulation did not yield any long-term water loss over years in the

C-compartment. The period for which the hydrological model was calibrated was the rice-cultivation season of the previous year of model predictions, and then model predictions of pesticide concentration as well as flow rate were performed for the subsequent years, by which the predictive capability of the model would be examined.

The equations are solved as a system of ordinary differential equations by Gear's stiff method (backward differentiation formulas) from the IMSL MATH/LIBRARY (Visual Fortran Versions 6.6, Compaq).

SITE DESCRIPTION

The model was applied to the upstream and midstream river basin of the Chikugo River of Kyushu Island, Japan (fig. 2). The upstream region of the river basin is mostly forest with a few rice-paddy fields (fig. 3). The midstream region consists mainly of agricultural land including rice-paddy fields. The target river basin includes rice-paddy fields (261 km^2) cultivated by 22,860 farmers (Fukuoka Prefecture, 2000; Kumamoto Prefecture, 2000; Oita Prefecture, 2000). Water samples were collected every weekday morning at approximately 9:00 a.m. by the Southern Fukuoka Water Supply Authority at the intake of a water purification plant,
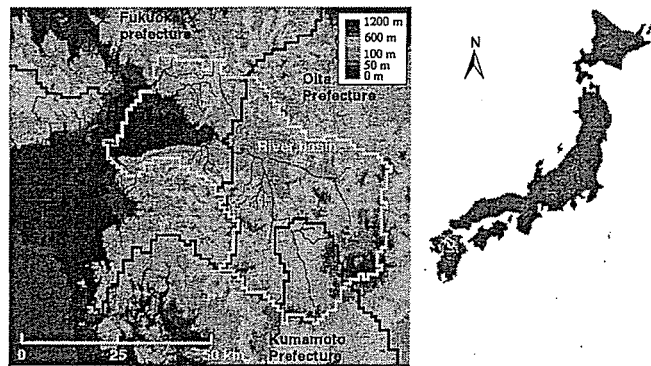

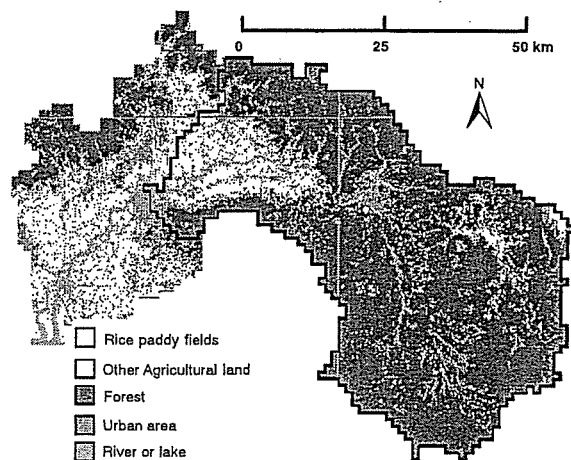Figure 2. Location of Chikugo River and the target river basin.

Figure 3. Land-use map for the river basin.

Table 1. Model parameters.

Symbol	Parameter	Value	Origin of the Data
$h_{0,X}$	Depth of X-compartment	0.01 m	
$h_{0,Y}$	Depth of Y-compartment	0.09 m	
$h_{0,G}$ and $h_{0,N}$	Depths of G- and N-compartments	0.1 m	
$h_{0,B}$	Depth of B-compartment	1.0 m	*a priori* judgment
$h_{0,C}$	Depth of C-compartment	5.0 m	
	River length in a grid cell	2 km	
	Porosity of soil	0.5	*a priori* judgment
	Soil particle density	2600 kg m^{-3}	(a typical value)
n_M	Manning roughness coefficient	$0.14 \times I^{0.25}$ s m$^{-7/3}$	A function of slope that is assumed from data in the literature[a]
$a_{V,U}$	Infiltration rate coefficient of urban area	0 m d^{-1}	*a priori* judgment (little permeability in urban area)
$a_{in,W}$	Irrigation rate coefficients of rice-paddy ponding	5.0 d^{-1}	Observed irrigation rate and paddy field structure
$a_{out,W}$	Drainage rate coefficients of rice-paddy ponding	2.0 d^{-1}	
$a_{V,W}$	Infiltration rate coefficient of rice-paddy field	0.01 m d^{-1}	Paddy field percolation rate (Ogata et al., 1978)
$a_{V,X}$	Vertical flow rate coefficient of X-compartment	0.01 m d^{-1}	
$a_{V,Y}$	Vertical flow rate coefficient of Y-compartment	0.04 m d^{-1}	
$a_{V,F}$ and $a_{V,G}$	Vertical flow rate coefficient of F- and G-compartment	0.6 m d^{-1}	
$a_{V,M}$ and $a_{V,N}$	Vertical flow rate coefficient of M- and N-compartment	0.13 m d^{-1}	
$a_{V,B}$	Vertical flow rate coefficient of B-compartment	0.035 m d^{-1}	
$a_{V,C}$	Vertical flow rate coefficient of C-compartment	0.2 m d^{-1}	Searching to give the best fit to observed river flow rates
$a_{H,Y}$	Lateral flow rate coefficient of Y-compartment	70 m d^{-1}	
$a_{H,G}$	Lateral flow rate coefficient of G-compartment	840 m d^{-1}	
$a_{H,N}$	Lateral flow rate coefficient of N-compartment	2500 m d^{-1}	
$a_{H,B}$	Lateral flow rate coefficient of B-compartment	1400 m d^{-1}	
$a_{H,C}$	Lateral flow rate coefficient of C-compartment	155 m d^{-1}	

[a] Chow, 1959; Marui, 1966; Japan Society of Civil Engineers, 1985; Murota, 1986.

about 50 km upstream from the river mouth. The water samples were analyzed for pesticide concentrations. Therefore, the target area of modeling and prediction was the catchment area upstream from the observation point of pesticide concentration (1882 km^2), as shown in figure 2. The target catchment area was divided into a 1 km^2 grid of 1882 grid cells. The catchment area comprised 22,584 compartments. A set of 22,584 equations was formulated to describe the movements of water in the river basin, and a set of 22,584 equations was formulated to describe the movements of a pesticide.

The model parameters are summarized in table 1. The vertical flow rate coefficients of the W- and X-compartments ($a_{V,W}$) were determined to be typical values of the percolation rate of water in rice-paddy fields, 0.01 m d^{-1} (Ogata et al., 1978). Irrigation and drainage rate coefficients of the rice-paddy field ($a_{in,W}$ and $a_{out,W}$) were determined to be 5 and 2 d^{-1}, respectively, based on the structure and dimension of outlets of some rice-paddy fields and on our measurement data for drainage flow rates from a rice-paddy field.

The altitudes of grid cells were determined from Geographic Information System (GIS) data (Geographical Survey Institute, 1999), and water flow directions among grid cells were tentatively determined based on the directions of the steepest gradients. The water flow directions were then amended based on information about tributary streams described in a 1:50,000 topographic map (Geographical Survey Institute, 2000). The GIS land cover data file (Geographical Survey Institute, 1990) was used to calculate the areas of the compartments (rice-paddy field, river, forest, upland field, and urban or town) in each grid cell. The file contains percentages of areas classified as 15 types of land cover as fractions of a 1 km^2 grid cell, and the 15 types of land

cover were re-classified into 5 (rice-paddy field, river, forest, upland field, and urban or town) in our model.

However, the available GIS data were obtained in 1990 and likely did not reflect the land utilization in the years 1999-2001 for the model prediction. Moreover, the GIS data may not be precise because variability and uncertainty may be introduced through the GIS data-acquisition process (Dubus et al., 2003; Burrough and McDonnell, 1998). The areas of rice-paddy fields, which are the most important land use in this research, were corrected using data books published by prefecture governments (Fukuoka Prefecture, 2000; Kumamoto Prefecture, 2000; Oita Prefecture, 2000). Information used included the areas of presently active rice-paddy fields and the curtailment percentages of rice-paddy areas due to compulsory production adjustment. Because the areas reduced by the compulsory production adjustment were usually used as upland fields, they were allocated as upland fields in the model input.

The time-series hydrological input for the model was precipitation after subtracting evapotranspiration. Radar-AMeDAS-analyzed precipitation datasets (Japan Meteorological Agency, 1999-2002a) were used for the input of precipitation data in each grid cell. The other meteorological data for each grid cell were estimated by interpolating the observed data for eight observation points located in or near the river basin (Japan Meteorological Agency, 1999-2002b), three-dimensionally accounting for altitudinal and areal variations (Japan Meteorological Agency, 2002; Seino, 1993). Then, the amount of evapotranspiration was estimated based on air temperature, wind velocity, duration of sunshine, and celestial declination in the meteorological data using the method of Brutsaert and Stricker (1979).
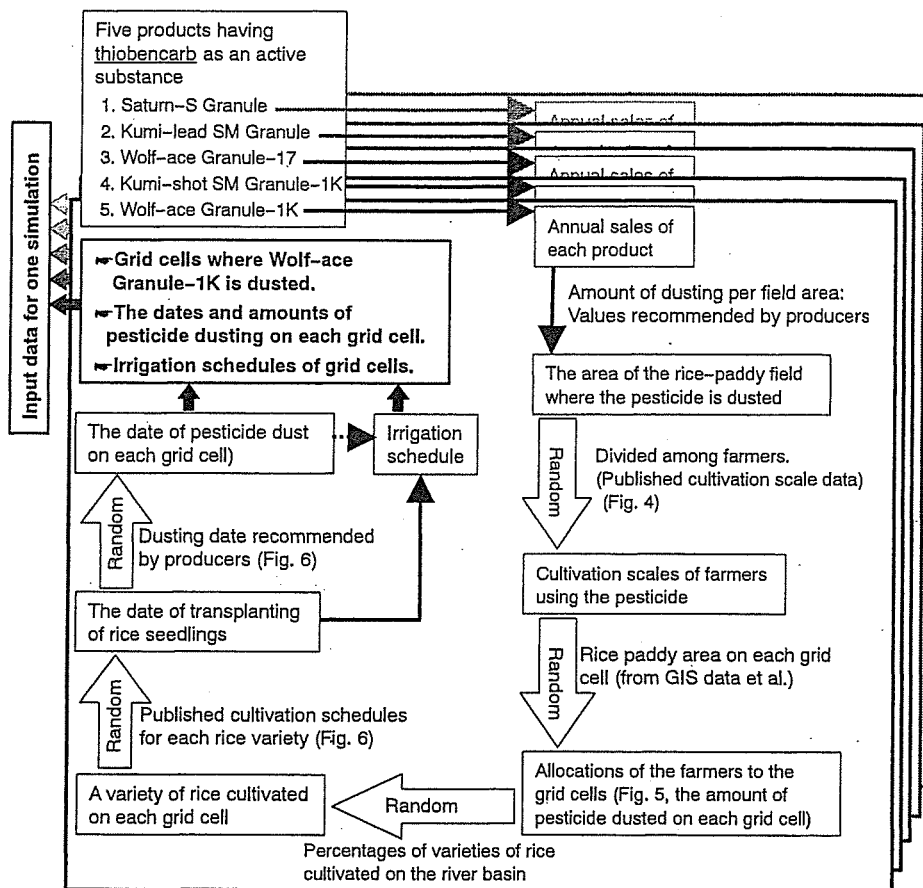
Figure 4. Flowchart for input data creation of agricultural work.

PESTICIDE APPLICATION DATA

MODEL INPUTS FOR PESTICIDE APPLICATION AND RICE FARMING

A pesticide (active ingredient thiobencarb) was selected for verifying the model predictions due to its detection in river water at high concentrations and frequency. Thiobencarb is included as an active substance in five commercial pesticide products on the market. Annual sales of each pesticide product were obtained from the annual reports published by the Japan Plant Protection Association, which state the annual sales of each commercial pesticide product sold in each prefecture in Japan (Japan Plant Protection Association, 1999-2001).

Pesticide application, irrigation, and drainage are the processes that most affect pesticide runoff among the numerous factors regarding agricultural work. Datasets of pesticide application dates, places (grid cells), amounts of pesticide applied, and irrigation and drainage schedules were created by the Monte Carlo method using available and published data by the following procedure, which is illustrated in figure 4:

Step 1: Each pesticide product has a recommended application rate per unit of field area (Japan Plant Protection Association, 1994); for example, the pesticide product Saturn-S Granule is applied once per year at a rate of 35 kg ha^{-1} (3.5 g m^{-2}). Therefore, the area of rice-paddy field where the pesticide product was applied could be estimated

from these data. For example, based on the amount of Saturn-S Granule sold in 2001 in Fukuoka Prefecture (2500 kg), the area of the corresponding rice-paddy field where that pesticide was applied was estimated as 71.4 ha.

Step 2: It is common practice, according to personal communication with an official in the local prefecture, that each farmer purchases and applies no more than one pesticide product on each rice-paddy field. Figure 5 shows the percentages of farmers in the cultivation area at each cultivation scale (Fukuoka Prefecture, 2000). Farmers who used a pesticide product and their cultivation scales were
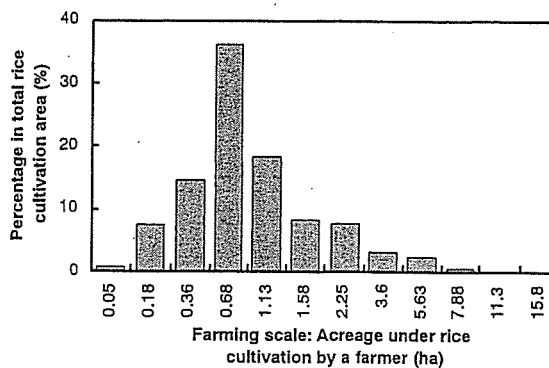

Figure 5. Farming scales in the river basin.

Table 2. An example of randomly selected farmers using pesticides that include thiobencarb as an active ingredient.

Scale of Farming (ha/individual)	Number of Farmers Using:				
	Saturn-S Granule	Kumi-lead SM Granule	Wolf-ace Granule-17	Kumi-shot SM Granule-1K	Wolf-ace Granule-1K
0.045	1	0	136	0	153
0.18	1	2	213	2	343
0.36	5	0	130	0	304
0.67	7	1	161	0	359
1.125	2	0	63	0	105
1.576	1	0	18	0	37
2.251	0	0	10	0	32
3.602	0	0	4	0	6
5.627	0	0	2	0	4
7.878	0	0	0	0	1
11.255	0	0	0	0	1
15.757	0	0	0	0	1

selected randomly using the data in figure 5 to define the selection probability (table 2).

Step 3: Allocations to the grid cells of the selected farmers using each pesticide product were also conducted randomly; the probability in selecting a grid cell for each farmer was the percentage rice-paddy field area of the grid cell to the total rice-paddy field area in the prefecture. When the rice-paddy field area in the grid cell selected for a farmer was larger than the area of rice-paddy field area possessed by the farmer, the remaining rice-paddy field area in the grid cell could be used for subsequent random selections for other farmers. When the area of rice-paddy field area possessed by a farmer was larger than the selected rice-paddy field area in a grid cell, such large-scale farming occupied adjacent grid cells. Figure 6 is an example allocation pattern of farmers using Wolf-ace Granule-1K, a pesticide having thiobencarb as an active ingredient.

Step 4: The dates of pesticide application are determined by each farmer, but application dates are recommended for each pesticide product by the pesticide manufacturers (Japan Plant Protection Association, 1994) based on the date of the transplantation of rice seedlings. For example, the manufacturer of Saturn-S Granule recommends its application to rice-paddy fields once between 15 and 26 days after the rice

seedlings are transplanted. The date for rice seedling transplantation depends on the variety of rice planted. The percentage of the total area planted with each rice variety was obtained from published data (Fukuoka Prefecture, 2000). Therefore, the rice variety planted in the rice-paddy fields of each grid cell was randomly selected based on this percentage as a selection probability. The date of rice seedling transplantation for each grid cell was then selected randomly from the rice-transplantation dates described for the selected rice variety in cultivation schedules (Mii Agricultural Co-operative, 2002; Niji Agricultural Co-operative, 2002; Chikuzen Asakura Agricultural Co-operative, 2002). We assumed that the selection probabilities of the dates for rice transplantation and pesticide application could be modeled by a triangular distribution, such as that shown in figure 7, and the dates were randomly selected after the variety of rice planted had been determined.

Step 5: Among the numerous tasks of rice farming, irrigation and drainage may most strongly affect pesticide runoff after application. The water depth in rice-paddy ponding is artificially controlled by irrigation and drainage according to the rice growth stage. In order to keep the water depth at a certain level during each stage of rice growth, the consumed water is supplemented or water is drained. Water consumed per day is the water requirement for a given depth, which reflects losses due to percolation and evapotranspiration. The irrigation and drainage tasks can be scheduled based on the seedling transplantation date because rice growth in the paddy field starts at transplantation. Figure 8
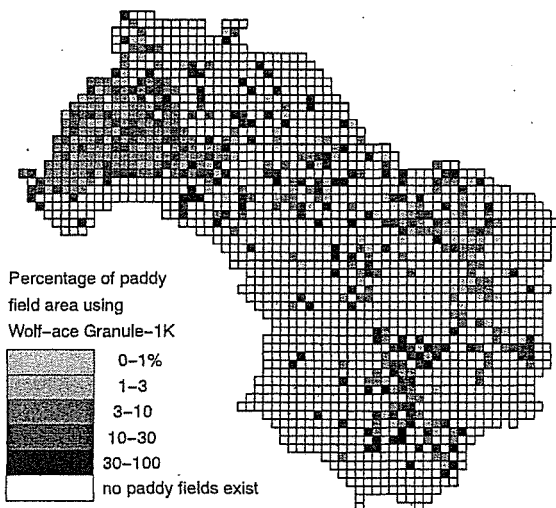

Percentage of paddy field area using Wolf-ace Granule-1K
- 0–1%
- 1–3
- 3–10
- 10–30
- 30–100
- no paddy fields exist

Figure 6. An example allocation pattern of paddy field area using Wolf-ace Granule-1K, a pesticide having thiobencarb as a active ingredient.
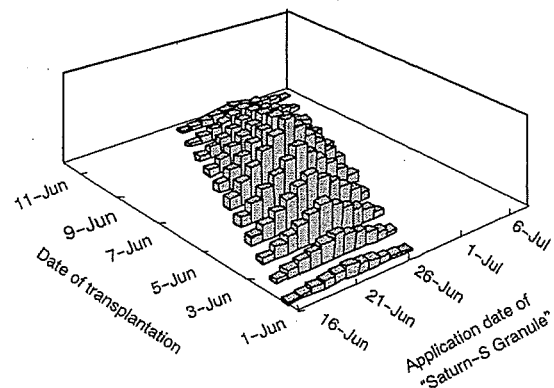

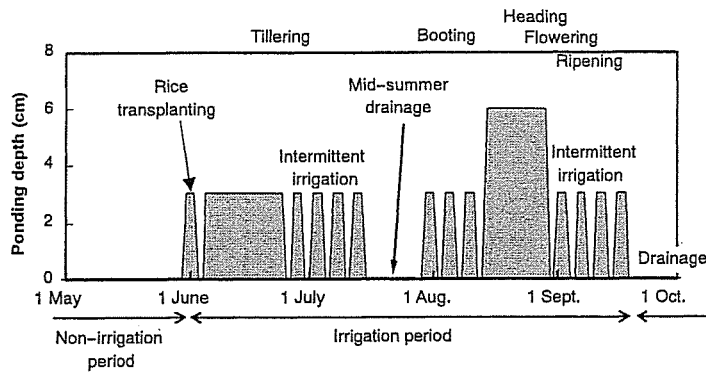Figure 7. Probability distribution of occurrences of farm activities.

Figure 8. Time variation of ponding depth in a rice-paddy field (pattern of irrigation) for rice variety 'Hinohikari.'

shows a pattern of desired water depth variation recommended for rice variety 'Hinohikari' by local governments (Mii Agricultural Co-operative, 2002; Niji Agricultural Co-operative, 2002; Chikuzen Asakura Agricultural Co-operative, 2002). Patterns of recommended desired water depth variation were obtained for each rice variety, and these were used to determine the input data for desired water depth. Therefore, the input data for desired water depth were determined after the variety of rice planted in the grid cell and the date of rice-seedling transplantation had been determined by the abovementioned procedure.

One dataset was created by executing steps 1 through 5 for the five pesticide products, and that dataset was used for one model simulation. A total of 2000 datasets for thiobencarb were created, and a set of 2000 Monte Carlo simulations yielded a prediction of concentrations of the pesticide in river water (a prediction of pesticide pollutograph).

For comparison with the model predictions based on Monte Carlo data creation, we also performed a model prediction with deterministic input, for which a single farming schedule for rice transplantation and pesticide application was used throughout the entire river basin. For example, the date of the highest bar in the histogram in figure 7 was used for the date of rice transplantation and pesticide application. The pesticides were assumed to be applied evenly throughout all rice-paddy fields in the river basin.

DEGRADATION RATE AND SOIL SORPTION COEFFICIENT OF PESTICIDES

Pesticides in soil and water phases are decomposed by chemical and biological reactions. Aerobic and anaerobic conditions, soil-sediment organic content, sufficient nutrients, and acclimation of the soil and aquatic microorganisms are factors that affect the decomposition process. However, due to the lack of information regarding the decomposition rate and the reaction environment, it is impossible to quantify specific decomposition rates in each place (each grid cell of the model). Although model parameters related to pesticide decomposition greatly influence predictions (Dubus and Brown, 2002), decomposition rates are subject to different kinds of uncertainties. Although some texts contain magnitudes of the microbiological decay and decomposition rates (or half-lives), the reported ranges in the rates are wide. This diversity of the reported rates is partly due to the variability of the reaction conditions (Dubus et al., 2003). Therefore, a

single reported value would not be appropriate to represent the decomposition rates in a whole area. Instead, all rate parameter uncertainties were assumed to be random and distributed within the range of reported values when several values were reported for each pesticide.

In our research, the first-order decay reaction was used as the model of the overall degradation of the pesticide (Klaine et al., 1988), and the degradation rate coefficients for the pesticide in a river water compartment (R-compartment) and a rice-paddy ponding compartment (W-compartment) in each grid-cell were randomly selected from values of uniform distribution in the log-scale (Soutter and Pannatier, 1996; Wolt et al., 2001; Warren-Hicks et al., 2002) that covered the value reported for degradation in water. The degradation coefficients for a rice-paddy soil compartment (X-compartment), mountain compartment (M-compartment), dry field compartment (F-compartment), and urban area compartment (U-compartment) in each grid-cell were selected in the same way using reported values for aerobic degradation in soil, whereas those of the remaining compartments, including rice-paddy soil compartments (Y-compartment) and deeper soil compartments (B- and C-compartments), were selected by using reported values for anaerobic conditions. The organic carbon content and the soil sorption coefficient of the pesticide were treated in the same way as the pesticide degradation rate.

The reported values for degradation rate and soil sorption coefficient are summarized in table 3 (Kanazawa, 1989; Cessna and Muir, 1991; British Crop Protection Council, 1994; Weber, 1994; Japan Plant Protection Association, 1994; Verschueren, 1996). Various values for organic carbon content in rice-paddy soils have been reported (Japan Plant Protection Association, 1993), and values were randomly selected from the range of 1.21% to 2.83% for each grid cell in a simulation. Then, the solid-water partition coefficient was given by (Lyman et al., 1990):

$$K_{OC} = \frac{100\,K}{f_{OC}} \qquad (12)$$

where K is the solid-water partition coefficient ($m^3\ kg^{-1}$), K_{OC} is the soil sorption coefficient ($m^3\ kg^{-1}$), and f_{OC} is the percentage of organic carbon content in the soil (dimensionless).

For comparison with this Monte Carlo approach, the model prediction with deterministic input was conducted using the average of reported values.

| | Water Solubility, C_S (mg L^{-1}) | Soil Sorption Coefficients, K_{OC} (μg adsorbed g^{-1} organic carbon) / (μg mL^{-1} solution) | Half-life in Soils (days) | | Half-life in Water (days) | Organic C Content (%) |
			Under Aerobic Conditions	Under Anaerobic Conditions		
Literature value	30 at 20°C	309, 900, 1043, 3170	12-21, 21, 40, 50, 80	180-240, 200	30	1.21 to 2.83
Monte Carlo input	30	309-3170	12-80	180-200	30	1.21 to 2.83
Deterministic input	30	990	31	190	30	1.9

RESULTS

HYDROLOGIC PARAMETER CALIBRATION

The hydrologic parameters of the model were successfully calibrated, fitting the data of observed river flow rates at six observation points taken by the Chikugo River Office with a Nash-Sutcliffe coefficient of 0.83, which indicates fairly good agreement. In addition to the Nash-Sutcliffe coefficient, the coefficient determination (R^2) was also calculated ($R^2 = 0.91$). The calibrated daily river flow for 1998 is graphed with measured river flow in figure 9. The Nash-Sutcliffe coefficients of the prediction years (1999, 2000, and 2001) were 0.63, 0.52, and 0.78, respectively, and the coefficient determinations were 0.82, 0.69, and 0.80, respectively. These values suggest that the predictions of flow rates for the years 1999, 2000, and 2001 were fairly good and the use of the hydrologic parameter values calibrated by the 1998 data was appropriate.

PESTICIDE CONCENTRATION PREDICTIONS

After the hydrological system parameters were calibrated, the hydrological and solute models were solved simultaneously by substituting the input data for the pesticide, and giving the predicted concentrations of the pesticide in river water for the rice-cultivation season of 1999-2001. In this way, the accuracy of the model was evaluated without optimizing the parameters for the pesticide. Although the model equations can give a time-series output with any time interval, they were programmed to give daily-average values since the model inputs are provided as daily amounts. Model-based predictions with the Monte Carlo inputs were obtained from model calculations with the 2000 datasets, and the prediction obtained with deterministic input was used for comparison.

Figure 10 shows the time course of variations in the predicted and observed thiobencarb concentrations (pollutograph). Of the observed data points, 68% were in the range
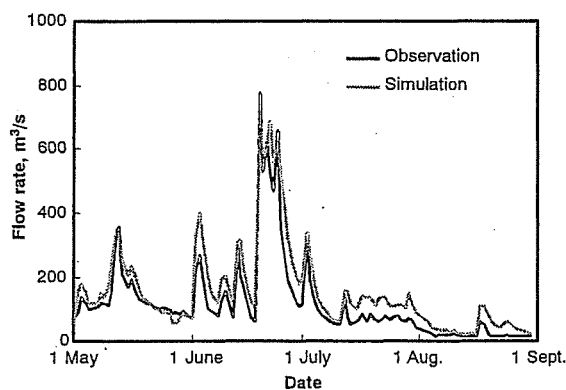

Figure 9. Observed flow rate and its best fit.

predicted with the 2000 data set of the Monte Carlo inputs, and more than 40% were within the 1% to 99% range of the prediction. Although the pesticide application dates and the amounts applied are influential factors for predictive accuracy, our prediction was not based on precise data for the amounts and dates of pesticide application by individual farmers. Moreover, the model calculations were conducted without optimizing the pesticide decomposition or sorption parameters. Water samples for the pesticide concentration measurements were collected at approximately 9:00 a.m., and consequently the observed data do not necessarily represent pesticide concentration of each observational day. In light of these limitations, we consider the model prediction for thiobencarb pollutograph to be reasonably successful, and for a first estimate of predictions, the approach seems to have merit.

In the range where the predicted concentrations were low, the model yielded a wider range of concentrations. Pesticide runoff at low concentrations probably occurs through soil and groundwater percolation, and therefore the concentrations depend on the values of pesticide decomposition and sorption parameters, which were randomly selected in each input dataset. On the other hand, high concentrations probably occurred by direct spillover from rice-paddy fields during or following rainfall or drainage. The concentrations of pesticides in direct runoff from paddy fields may not be affected by decomposition and sorption as much as those that result from percolation through soil. Therefore, high concentrations were predicted with narrower ranges of concentration distribution. Further study including sensitivity analysis of the model is planned for elucidating pesticide runoff phenomena in the model.

The Monte Carlo inputs yield a distribution of predicted concentrations for each date, and the ranges of distributions are presented in figure 10 as a function of date. The 50th percentile values of the concentration distributions predicted with the Monte Carlo inputs, as representative values of prediction with the Monte Carlo inputs, are compared with the prediction obtained with the deterministic input in figure 11. The prediction obtained with the deterministic input yielded a rather discrete concentration variation with incorrect concentration peaks, which did not always occur simultaneously with the observed peaks. The 50th percentile values of concentration ranges predicted with the Monte Carlo inputs were more successful in predicting the dates of concentration peaks and their heights. While the coefficient of determination between the observed concentrations and the concentrations predicted with the deterministic input was 0.21, the coefficient between the observed concentrations and the 50th percentile values predicted with the Monte Carlo inputs was 0.45. The Nash-Sutcliffe coefficient with the deterministic input was −1.36, while it was 0.2 with the Monte Carlo inputs. Therefore, the prediction using Monte Carlo inputs was better than that obtained with deterministic
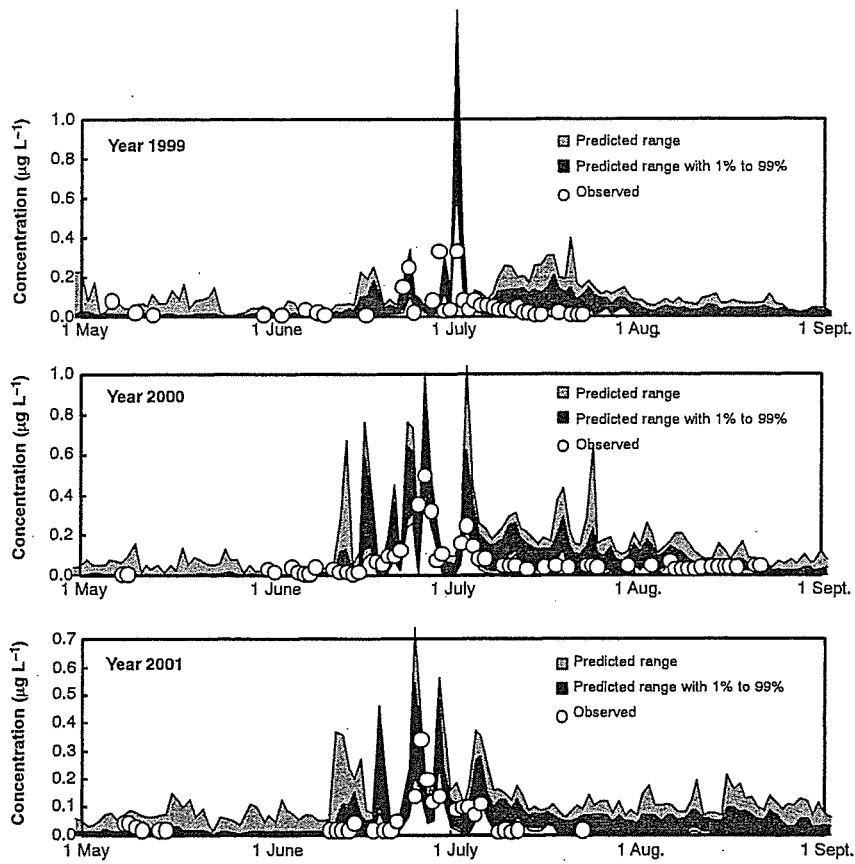
Figure 10. Comparison of concentrations observed and predicted by the model with Monte Carlo inputs.
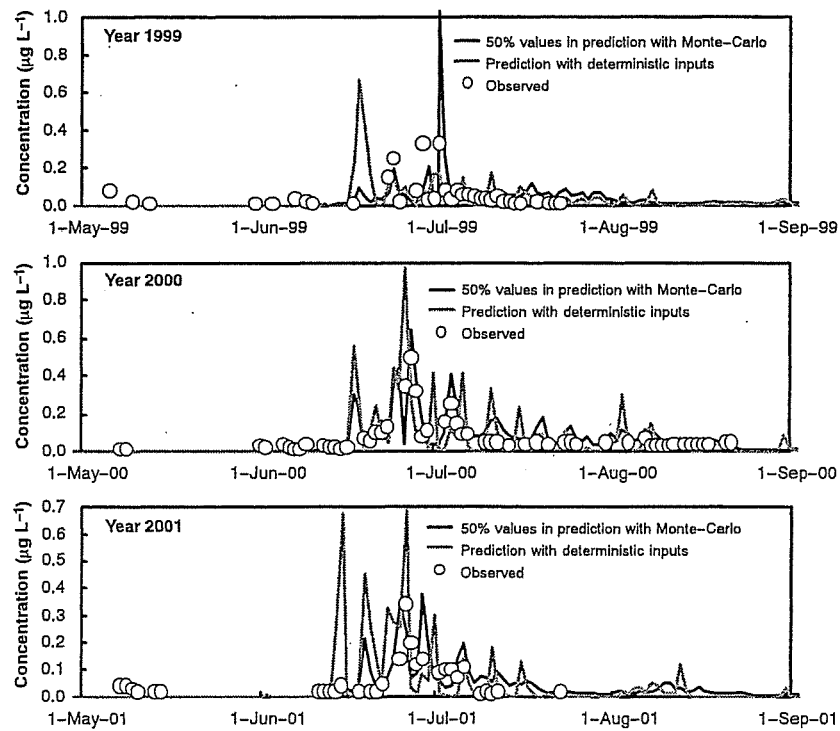

Figure 11. Comparison of concentrations predicted by the model with Monte Carlo inputs and deterministic inputs.

input. The coefficient of determination and the Nash-Sut-cliffe coefficient with the Monte Carlo inputs may still not be high, but that is because the predictions were conducted without any reference to observed pesticide concentration data and without any model parameter calibration for pesticide, by which we could investigate the predictability of true sense.

It should also be noted that the 50th percentile values of concentrations predicted with the Monte Carlo method did not coincide with the concentrations predicted with the deterministic input, although a median value was selected for each parameter from the range of reported values as a deterministic input. This result was actually contrary to our expectation. Although the reason for this result is not yet clear, it suggests that pesticide runoff from rice-paddy fields is affected synergistically and nonlinearly by timing of pesticide application, degradation and sorption, and spill-over of rice-paddy ponding water by rain or artificial drainage. Therefore, pesticide concentrations as a consequence of runoff cannot yet be predicted with model inputs using representative values (deterministic input).

The model was calibrated with hydrological data only, without reference to observed pesticide concentration data. The Monte Carlo method provided a surrogate approach for obtaining precise data on individual farming schedules (including pesticide application dates), degradation rates, and sorption coefficients in each soil. Therefore, once data for the quantities of pesticides applied in the river basin are available, the model should give a rough estimate of pesticide concentrations before the pesticide concentration observation. The model should be potentially useful for selecting new pesticides to be monitored and determining the monitoring schedule for river basins where different and new pesticides are applied from year to year.

CONCLUSIONS AND FUTURE RESEARCH NEEDS

In this article, we presented an application of the Monte Carlo method for creating input data for rice-paddy pesticides in a basin-scale diffuse pollution hydrological model. We showed its effectiveness when the model predicts the pesticide concentrations in the river water of a large catchment. The Monte Carlo method was used to account for uncertainties in input data: the names of the pesticide products applied, amounts and the dates of pesticide application, varieties of rice planted, dates of transplantation of rice seedlings, time-variation patterns of desired water depth of rice-paddy ponding, parameter values of pesticide decomposition, and parameter values of pesticide sorption.

However, these may not be the only sources of uncertainty in predicting pesticide concentrations. Other factors might affect prediction of pesticide concentrations, although their contributions are still largely unknown. In fact, 32% of observed data points were still outside the range predicted with the 2000 data set of the Monte Carlo inputs. Incorporation of the remaining uncertainty factors would decrease the percentage outside the predicted range and improve predictive accuracy. Among the remaining uncertainty factors, the uncertainty related not to model inputs but to the model itself still needs to be evaluated, and it should be evaluated particularly whether the model represents all the significant

processes for pesticide runoff and changes in pesticide concentrations in river water. The ability of the model to represent the significant processes will be examined when precise model inputs are used.

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Analysis of Active Oxon Forms of Nine Organophosphorus Pesticides in Water Samples Using Gas Chromatography with Mass Spectrometric Detection

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We established a method for the simultaneous quantitative analysis of nine organophosphorus pesticides (OPs) and their active oxon forms in water samples using gas chromatography with mass spectrometric detection with solid-phase extraction (SPE). In this method, the lower limit of detection for the nine oxons ranged from 0.5 to 20 ng/ml. Each calibration curve had good linearity, with correlation coefficients (R^2) greater than 0.991. In comparing three SPE cartridges, the recovery rate of these compounds extracted from water was highly reproducible using a cartridge of packed silica bonded with C_{18}. The limit of quantification ranged from 2.5 to 200 ng/ml at 500-fold concentrations. When the OPs were examined after chlorination treatment to simulate the water treatment process, they decomposed rapidly and were converted to their oxon forms as primary reaction products of chlorination. Under these established analytical conditions, the behavior of oxons formed in the environment and after water treatment can be determined accurately.

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INTRODUCTION

In recent decades, there have been several incidents involving various environmental pollutants which have drawn attention to their effects on human health. Among environmental pollutants, pesticides are commonly detected in river water and groundwater as the source of tap water,[1-5] giving rise to concerns about pesticide contamination of drinking water. Organophosphorus pesticides (OPs) of the thiono form with a P = S structure are used extensively. They are activated to the oxon form with a P = O structure by an oxidation reaction and are known to have adverse effects on living organisms through the inhibition of acethylcholinesterase.[6-10] Numerous papers have described the simultaneous detection of parent OP compounds.[1,11,12] However, there are few reports detailing the simultaneous analysis of their oxon forms. Furthermore, there were no standard methods for the analysis of oxons in the Water Quality Standard Guidelines of Japan.

Solid-phase extraction (SPE) is useful for the isolation of a wide spectrum of organic micropollutants in various fields, such as environmental sampling,[13] pharmaceuticals,[14] and food analysis.[15] The SPE extraction procedure is applied to carry out simultaneous extraction and concentration of pesticides in water samples.[16-20] The sorbents commonly used are C_{18} chemically bonded to slica, carbon black and polymeric resins, and styrene-divinylbenzene polymer. Gas chromatography with mass spectrometric detection (GC/MS) has been applied to detect a wide range of pesticides due to its superior sensitivity and specificity in identification and quantification.[5,15,19] The analysis employs electron-impact ionization using a full scan and selected characteristic ions for each compound. Our study focused on the combination of selective extraction and sensitive determination using SPE-GC/MS. We established an SPE method and employed GC/MS for the subsequent analysis of samples to detect parent OP compounds and their oxon forms in water samples.

OPs of the thiono form are converted to their respective oxon forms *via* oxidation, and we therefore investigated the influence of chlorination on the parent pesticides, since the compounds are exposed to chlorine during the water treatment process. Our goal is to examine the behavior of pesticides contaminating raw water under water treatment conditions. The nine OPs examined were isoxathion, isofenphos, EPN, chlorpyrifos, diazinon, tolclofos-methyl, fenitrothion (MEP), butamifos, and

prothiofos.

MATERIALS AND METHODS

Chemicals —— Butamifos, diazinon, diazinon oxon, EPN, EPN oxon, isofenphos, isofenphos oxon, isoxathion, isoxathion oxon, MEP, MEP oxon, prothiofos, and prothiofos oxon (pesticide residue analysis grade) were all purchased from Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Butamifos oxon, chlorpyrifos oxon, and tolclofos-methyl oxon (pesticide residue analysis grade) were obtained from Hayashi Pure Chemical Industries, Ltd. (Osaka, Japan), and chlorpyrifos and tolclofos-methyl were obtained from GL Sciences Inc. (Tokyo, Japan). EPA 525 Fortification Solution B containing phenanthrene-d_{10} used as an internal standard was supplied from Supelco (Bellefonte, PA, U.S.A.). Individual standard solutions were prepared in a volume of 1000 mg/l in acetone. A 0.1 mg/l solution of phenanthrene-d_{10} was prepared in dichloromethane as an internal standard. All standard solutions were stored at $-20°C$, and working solutions were prepared fresh for each use by diluting the standard stock solution.

Dichloromethane and acetone [pesticide residue polychlorinated biphenyl (PCB) analysis grade], methanol (HPLC grade), sodium hypochlorite solution, and L(+)-ascorbic acid sodium salt were purchased from Wako Pure Chemical Industries, Ltd. Laboratory water was purified with a Milli-Q gradient A10 Elix system with an EDS polisher (Millipore, Bedford, MA, U.S.A.).

GC/MS Analysis —— GC was carried out using an HP6890 Series Gas Chromatograph system (Hewlett Packard, Wilmington, DE, U.S.A.) with an HP6890 Series autosampler and split/splitless injector. The analytical column was a DB-5 fused-silica capillary column, 30 m × 0.25 mm i.d., 0.25 μm film thickness (J&W Scientific, Folsom, CA, U.S.A.). The oven temperature program was 70°C initial temperature for 2 min; ramped at 15°C/min to 190°C, 1.5°C/min to 220°C, and then 10°C/min to 290°C; and holding for 3 min at 290°C. The carrier gas (helium) flow was set at 1.2 ml/min. Pulsed splitless injection of a 2 μl volume was carried out at 250°C. MS was carried out using a 5973 Mass Selective Detector (Hewlett Packard) in electron-ionization mode with an ionization voltage of 70 eV and ion source temperature of 280°C. The instrument was operated in selected-ion monitoring (SIM) mode. Two selected ions for each compound were monitored for

identification and quantification and are summarized in Table 1.

Analytical Procedures —— The standard solutions were diluted with acetone to 50 ng/ml for diazinon oxon and tolclofos-methyl oxon, 100 ng/ml for isofenphos oxon and prothiofos oxon, 200 ng/ml for butamifos oxon, 500 ng/ml for EPN oxon and MEP oxon, 1000 ng/ml for chlorpyrifos oxon, and 2000 ng/ml for isoxathion oxon. A 250 μl aliquot of sodium ascorbic acid solution100 g/l was added to 500 ml of tap water to remove the chlorine and then was fortified with 50 μl of each solution. The fortified water samples were concentrated following the SPE method described below with each of three cartridges: Oasis HLB Plus Extraction Cartridge, Sep-Pak Plus PS-2, and Sep-Pak Plus C18 (Waters, Milford, MA, U.S.A.). The cartridges were equilibrated with dichloromethane 5 ml, methanol 5 ml, and water 5 ml, respectively. The extraction of water samples was carried out at a flow rate of approximately 10 ml/min. Air was then pulled though the cartridges for 10 min, followed by nitrogen gas for 20 min. The analytes were eluted from the cartridges with dichloromethane 5 ml. After evaporating the samples to less than 1 ml under a gentle nitrogen steam, the eluate was added to 50 μl of internal standard solution and adjusted to a final volume of 1.0 ml with dichloromethane for GC/MS analysis. The automatic concentrator used was a Sep-Pak Concentrator Plus (Waters).

Chlorination Processing —— Standard solutions of pesticides were added to purified water to make a final concentration of 10 ng/l. After dissolving the pesticides at room temperature, a 100 ml of the solution was collected as a sample at the start time. Subsequently, sodium hypochlorite solution was added to produce 1 mg/l of free chlorine. After mixing in an incubator at 20°C, a 100 ml sample of each solution was collected at reaction times of 0.5, 1, and 2 hr after the addition of the sodium hypochlorite solution. A 250 μl aliquot of sodium ascorbic acid 100 g/l was added to the sample solutions in order to eliminate chlorine. OPs and their by-products were extracted with SPE and then eluted with dichloromethane for GC/MS analysis.

RESULTS AND DISCUSSION

GC/MS Validation Study

We established the analytical conditions for detecting nine OPs and their oxon forms in GC/MS.

Table 1. Analytical SIM Conditions for GC/MS Analysis of Nine Parent OPs and their Oxons

Compound	Retention time[a] (min)	Quantitation ion (m/z)	Identification ion (m/z)
Butamifos	20.3	286	200
Chlorpyrifos	16.3	199	197
Daizinon	13.0	179	137
EPN	30.4	157	169
Isofenphos	18.2	213	121
Isoxathion	22.3	177	105
MEP	15.4	277	260
Prothiofos	20.7	309	267
Tolclofos-methyl	14.6	265	125
Butamifos oxon	18.8	244	216
Chlorpyrifos oxon	16.0	270	197
Daizinon oxon	12.6	273	137
EPN oxon	26.7	141	169
Isofenphos oxon	16.6	229	201
Isoxathion oxon	20.7	161	105
MEP oxon	14.1	244	109
Prothiofos oxon	18.1	162	139
Tolclofos-methyl oxon	14.0	249	109
Phenanthrene-d_{10}	12.9	188	—

a) On a DB-5 column.

The two monitored ions were selected based on their relative abundance in the MS spectrum, characteristic fragment ions, and lack of interference with nearby peaks. If the selected ions of the parent compound and its oxon were the same, we chose the next most relatively abundant ion. All compounds studied were separated with high sensitivity and selectivity in GC/MS on the DB-5 column. Retention times and selected ions are summarized in Table 1.

The quantitative analysis of oxon forms of the nine OPs was performed using GC/MS in the SIM mode under the conditions described above. For quantification, an internal standard solution was added to each sample. Standard curves showed good linearity, with correlation coefficients (R^2) greater than 0.991 for all oxons in the concentration ranges studied. The limit of detection (LOD) was calculated as 3-fold the standard deviation of the slope of the calibration curve. LOD values were 0.5 ng/ml for diazinon oxon and tolclofos-methyl oxon, 1.0 ng/ml for isofenphos oxon and prothiofos oxon, 2.0 ng/ml for butamifos oxon, 5.0 ng/ml for EPN oxon and MEP oxon, 10 ng/ml for chlorpyrifos oxon, and 20 ng/ml for isoxathion oxon. Correlation coefficients, concentration ranges, and LOD values of the nine oxons are summarized in Table 2. The LOD

values of the parent compounds were 0.5 ng/ml for tolclofos-methyl; 2.0 ng/ml for butamifos, chlorpyrifos, diazinon, EPN, MEP, isofenphos, and prothiofos; and 50 ng/ml for isoxathion. Under the present conditions, the nine oxons were analyzed with nearly equal sensitivity as the parent compounds.

Optimization of SPE

A recovery test was performed with tap water to determine the presence of matrix in water samples. Standard solutions in acetone were added at 5-fold the LOD levels to dechlorinated tap water. Recovery rates and relative standard deviations (RSDs) were assessed at 500-fold concentrations. Dechlorinated tap water 500 ml was used as the blank control. For quantification, an internal standard solution was added to all samples. Table 3 shows the level of the standard, mean recovery rates, and RSDs obtained for all compounds. Recovery rates were satisfactory with RSDs of less than 20%. The recovery test of isoxathion oxon was performed at 10-fold the LOD level because the recovery rate at 5-fold the LOD level was low. Butamifos oxon and EPN oxon had in low recovery rates for all SPE cartridges. The lowest results were obtained for EPN oxon. Recov-