Predicting pesticide concentrations in river water with a hydrologically calibrated basin-scale runoff model


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Abstract Hydrological diffuse pollution models require calibration before they can be used to make accurate long-term predictions for a range of hydrological and meteorological conditions. As such, the applicability of the models to the dispersion of new pesticides is limited due to the lack of calibration data. In this study, the performance of a GIS-based basin-scale runoff model for predicting the concentrations of paddy-farming pesticides in river water was examined when calibrated using hydrological data alone, without optimization based on empirical pesticide concentration data. The prediction accuracy on a daily or hourly scale was somewhat unsatisfactory due to inevitable compromises concerning rice farming schedules. However, the month-averaged pesticide concentrations were satisfactorily accurate; more than 50% of predicted values were between half and twice the observed values, considering the deficiencies of the input data, particularly for pesticide usage, which may include up to 60% error.

Keywords Hydrograph; modeling; pesticide; pollutograph; runoff

Introduction Pesticides used in agriculture have the potential to enter hydrological catchment systems and contaminate rivers, which constitute the primary source of drinking water for many regions. There are several possible routes for pesticides to enter surface runoff, and knowledge of the dispersion of pesticides in river basins is critical to risk assessment and management decisions. The transport of pesticides in hydrological systems involves complex phenomena that are influenced by many processes, and there are many factors that affect the contamination potential of pesticides in river water. For example, soil type, pesticide type, and rainfall characteristics all influence the timing and severity of pesticide runoff. It is important to know which pesticides readily become entrained in runoff, the weather conditions that trigger pesticide runoff, and on a local scale, the field from which the leached pesticides originate.

Hydrological diffuse pollution models are designed to simulate the movement of water and pollutants in river basins and thereby assess water quality. Simulation of the effects of pesticide application in watersheds is an important tool that can be used as a screening level analysis for the exposure assessment of pesticide runoff, providing order-of-magnitude accuracy with minimal investment in time and resources. The models used invariably have required calibration and optimization. For simulating pollutant transport, the hydrology of the system was calibrated and determined first, followed by pollutant transport when measured data were available. This calibration requirement precludes these models from being applied to new pesticides. However, the application of models that has been reported involves parameter calibration and optimization. Laroche et al. (1996) applied the Hydrologic Simulation Program-FORTRAN (HSPF) (Johanson, 1983; Johanson et al., 1997) to a 78 ha watershed. Variations in atrazine concentration were simulated before and after degradation, and equilibrium parameters of the pesticide were optimized using
measured data. The use of optimized parameters resulted in only a slight improvement of the fit to the observed data. This result suggests the unimportance of the calibration and optimization routine.

The objective of this research was to develop and verify a GIS-based basin-scale runoff model that can be used to predict the concentration of paddy-farming pesticides in river water. Paddy-farming pesticides (simetryn, pretilachlor, thiobencarb, butachlor, and mefenacet) were observed at high concentrations as a result of direct irrigation intake and subsequent drainage. The prediction accuracy of the model was evaluated when used with non-optimized pesticide parameters; the model was calibrated using hydrological data alone without reference to observed pesticide concentration data.

Model description

Model concept
A river basin is divided into a grid of 1 km × 1 km compartments. Each compartment consists of eight zones: a river water zone (R-zone), a river bottom zone (S-zone), a paddy field water zone (W-zone), a paddy field bottom zone (X-zone), a land surface zone (A-zone), a subsurface zone (B-zone), an inter-flow zone (C-zone), and a base-flow zone (D-zone), as shown in Figure 1. A set of differential mass-balance equations describing the dynamics of a solute (pesticide) and water in each zone are defined, based on the law of conservation for the solute and the water. The equations are solved as a system of ordinary differential equations by Gear’s stiff method (backward differentiation formulae) from the IMSL MATH/LIBRARY. A hydrology (water flow) model describes water flow, and a solute model describes pollutant transport and transformation. For solute movement between zones, advection and diffusion are considered, and within a zone, the water level and solute concentration are assumed to be uniform, each represented by a single variable. For example, rainfall is assumed to mix completely and uniformly with pesticides in the paddy field water zone (W-zone). If a zone consists of multiple sub-elements, such as solid-solid and soil-water, a dynamic equilibrium exists between the dissolved and adsorbed fractions at the soil-water interface. These phases are assumed to be in equilibrium at all times; sorption processes are considered to be instantaneous and are described by a single constant (solid-water partition coefficient) of the linear equilibrium relationship. Hence, once the concentration in one phase is known, the concentration in the other phase can be calculated.

Figure 1 Model concept showing flow pathways
The degradation of pesticides in each zone is described by first-order kinetics. The processes of pesticide uptake by plants and evaporation of pesticide into an atmospheric phase are not considered in this model.

**Hydrologic system parameters**

The vertical flows from the W-, X-, A-, B-, and C-zones are directed toward each lower zone and the flow rates are assumed to be proportional to the water level in each zone. The rates of lateral water flow from X-, A-, B-, and C-zones are also described as a function of the water level of the zone and the slope of the zone. The lateral movements from the R-, X-, A- and B-zones are directed toward the R-zone of the next compartment, while the lateral movement from the C-zone is directed toward the R-zone via the S-zone of the next compartment. The Manning equation is employed to describe the flow rate in the R-zone. The coefficients of lateral and vertical flow rates in all zones are assumed to be at a proportionality relation; once the vertical flow rate coefficient has been determined, the lateral flow rate coefficient can be calculated. The flow rate coefficients of the R-, X-, B-, and C-zones are each assumed to be single values across all compartments. However, the hydrologic parameters of the A-zone were identified for each land-use type (mountain and forest, dry farm field, and town). The flow rate coefficient of the A-zone of each compartment is dependent on the land coverage of the compartment, and is given as an area-averaged value of the proportion of three land-use types. Land-use coverage data is available from Geographic-Information-System (GIS) data (The Geographical Survey Institute, 1990). As the hydrologic parameters for the A-zone in each compartment are given according to the proportions of land coverage, the total number of hydrologic parameters is reduced, thus minimizing the level of uncertainty in determining model parameter values, which is a typical problem in this type of distributed-parameter modeling.

The water depth of a paddy field is artificially controlled at various levels according to the growth of rice and the weather condition. Paddy irrigation and drainage into the river are conducted such that the objective water depth is maintained. The flow rate of irrigation and drainage in the model is assumed to be proportional to the difference between the present water depth and the objective water depth.

**Site description**

The model was applied to the Oirase River Basin (main stream length 70 km, total basin area 844 km²) in order to examine its prediction accuracy. The composition of the river basin is 54% mountains and 17% agricultural land. The agricultural land is comprised primarily of rice paddy fields (92 km²), with the remainder farmlands (53 km²), worked by 3,400 and 4,100 farmers, respectively. Although annual pesticide consumption for the remainder farmlands is 2.5 times that for the rice paddy fields, the only pesticides detected in the river water are those for rice paddy use. Therefore, the target pesticides in this research are 5 rice-farming herbicides that have been detected in the river and have been used in large quantities in the river basin area. The concentrations of pesticides in the river water were measured weekly, 3.5 km upstream from the river mouth, during 1995 and 1996. The river flow rate was observed 16.5 km upstream of the intake. The whole area of the river basin was divided into the 1 km-square grid, as shown in Figure 2. The altitude of each compartment was determined from GIS data (The Geographical Survey Institute, 1999), and water flow directions between compartments was determined based on the direction of the steepest gradient. The river basin was divided into 667 compartments (4,670 zones), and a set of 9,338 equations was solved to describe the movements of water and pesticides in the river basin.
Marketing information regarding the sale of commercial pesticide products was used to estimate the amount of herbicide dusting in each compartment. The target river basin consists of five administrative districts and each district has an agricultural cooperative that sells pesticides with a market share of 50% or more. Questionnaires were sent out to each agricultural cooperative and data concerning the volume of annual sales for each pesticide were collected. The annual usage of each pesticide for each administrative district was estimated based on these data. The data collected, however, is considered to include a margin of error of about 50% due to the existence of other pesticide marketing routes. More accurate information is difficult to obtain without conducting a comprehensive and detailed survey.

Rice cultivation schedule

Among the numerous tasks of rice farming, pesticide dusting a irrigation/drainage are the processes that most affect pesticide runoff, and these tasks can be scheduled relating to the transplantation of rice seedlings. In general, the transplant season continues for several weeks, and each herbicide has a recommended dusting period based on the transplantation schedule. These schedules are not synchronized between farms, precluding the use of a single schedule for the river basin. However, modeling the schedule of each farm is not a feasible approach. In this case, due to the large scale of the study area, it is possible to consider agricultural tasks as random events within a defined period of time. Here, we assumed that the frequency of the transplant events in the river basin can be modeled by a triangular distribution. For example, about 14% of farms are assumed to transplant rice seedlings on the 14th of May, as shown in Figure 3. The herbicide dusting period is then defined based on the rice seedling transplant time for each herbicide; i.e. if a paddy was transplanted on the 14th of May, herbicide dusting would be conducted according to a triangular frequency distribution for each herbicide (e.g. for simetryn, between 3rd and 13th of June). Therefore, working days for simetryn dusting are distributed over 21 days (between 30th of May and
19th of June), and 21 pesticide dusting schedules are created. A schedule was randomly assigned to a compartment in the river basin. Runoff events and pesticide concentration in the river are dependent on the pesticide dusting schedule. Therefore, the model prediction results are affected by allocation patterns of pesticide dusting schedules, even if they are allocated randomly in the river basin. A total of 5 allocation patterns for each pesticide were created and provided as simulation input. The model calculations with the 5 input patterns were averaged to yield the prediction. This is an approach similar to the Monte Carlo Method.

Irrigation and drainage
Water management for rice cultivation depends on the growth of rice. Herbicide dusting and ambient temperature also affect the schedule of irrigation and drainage. For example, after herbicide dusting, irrigation and drainage are halted for 4 days. Water depth is controlled depending on the ambient temperature as well as rice growth. An irrigation pattern recommended by the regional body governing the river basin was used to define the input data for water depth and irrigation rate.

Degradation rate and solid-water partition coefficient of pesticide
Pesticide in the soil and in water is decomposed by biochemical reactions, chemical oxidation-reduction, hydrolysis, and photochemical transformation. There are many factors that affect the decomposition process. Due to the lack of information regarding the reaction environment, however, it is not possible to quantify specific degradation rates. The only reliable information available is the half-lives in soil and in water. In this study, a first-order decay reaction was used as the model for the overall degradation of pesticide. The degradation rate coefficient for each pesticide in the W-zone and R-zone was determined from the reported half-life of the pesticide in water, whereas the coefficient in the other zones was taken from the reported half-life in soil (Verschueren, 1996). A value taken from the literature (Verschueren, 1996) was used for the solid-water partition coefficient in all zones and all compartments.
Hydrological inputs

Input parameter evaluation

The time-series input for the model is precipitation after subtracting evapotranspiration. The meteorological data for each compartment were estimated by interpolating the observed data for eight observation points three-dimensionally, accounting for altitudinal and areal variations. First, the amount of evapotranspiration was estimated based on air temperature, wind velocity, duration of sunshine, and celestial declination by the method of Brutsaert and Stricker (1979), which was chosen from 5 candidates because it produced the median result. The resultant hydrological input from precipitation is taken as the combination of rainfall and snowmelt; at air temperatures below a critical value, precipitation occurs as snow, which then melts as the temperature increases and contributes to the hydrological input. Rainfall and snowmelt are precisely estimated using a temperature index method (Ikebuchi et al., 1984, 1985), which describes the complex phenomena of snowmelt in terms of a heat budget.

Hydrologic system parameters

The hydrologic (water flow) model involves seven parameters; the vertical flow ra coefficients of the X-, B-, and C-zones, and the three land-use types for the A-zone, and the ratio of vertical/lateral flow rate coefficients. The values of the parameters were searched so as to give the best fit to the observed river flow rate. Besides this best fit criterion, the parameters were determined to give no annual long-term water loss in the C-zone. The period for which the model was calibrated was 1995 to 1997. Figure 4 is a comparison of the observed and calculated hydrographs; the hydrologic parameters of the model were successfully calibrated, fitting the observed stream flow data to within 45%.

Predicting the pesticide concentration

After the hydrological system parameters were calibrated, the hydrological and solute models were solved simultaneously by substituting solute input data (pesticide dusting), giving the predicted concentrations of the 5 pesticides in river water for the 1995 and 1996 period. In this way, the accuracy of the model without optimizing the pesticide parameters was evaluated. Figure 5 shows the results for simetryn. Even without optimizing pesticide parameters, the model yielded simetryn concentrations that are close to the observed values, however the peaks in the observed and predicted concentrations do not always occur simultaneously. This disagreement is thought to be due to the low observation sample rate or the inaccuracy of pesticide dusting period data. Pesticide concentration in the river water was measured once per week at a predetermined time. Under such circumstances, the measured concentration is unlikely to represent a peak concentration. Furthermore,
the pesticide dusting period and the dusting mass are important factors in predicting the concentration. However, farming events including pesticide dusting obviously occur through an individual farmer’s activity within a recommended interval in a large study area, and it is impossible to pursue individual farming schedules. In light of these limitations, we consider the model prediction for simetryn to be reasonably successful. The accuracy of the results for pretiaclov was similar, however the results for thiobencarb, butachlor, and mefenacet were less accurate. In these less successful cases, peak heights and peak timing were both in error, probably due to the poor estimation of annual pesticide usage. A better estimation for pesticide sales will improve the prediction. However, we feel that modeling on a daily or hourly scale will be extremely difficult, requiring precise farming schedule data for individual farmers. The prediction of month-averaged concentration is then a realistic and practical goal. Figure 6 summarizes the prediction performance for month-averaged concentration. More than 50% of predicted values fell in between half and twice the observed concentration. This is considered to be satisfactory considering the deficiencies of the input data, particularly for pesticide usage, which may include up to 50% error.

Conclusions

A model for the prediction of rice-paddy-farming pesticide concentrations in river water based on GIS data was developed. The model involved dividing the target area into zones, in this case a river basin of 844 km², divided into 4,670 zones; and a set of 9,338 differential equations was solved to give the concentration of pesticides in the river. Hydrological input data and system parameters were obtained from observed hydrological and meteorological data. Pesticide dusting (loading) data were obtained from market data for pesticide sales, and system parameters for pesticide degradation and sorption were extracted from literature. The prediction accuracy of the model was tested when calibrated with only hydrological data, without reference to observed pesticide concentration data. The model prediction is shown to be satisfactorily accurate regarding month-averaged pesticide concentrations, with more than 50% of predicted figures falling between half and twice the observed values; however the prediction accuracy is limited due to significant errors in input data concerning pesticide dusting volume and farming schedules. The time-series prediction accuracy of this model could not be assessed based on the data acquired in this study, requiring a higher field-sampling rate.
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