Modelling of Atrazine Loss in Surface Runoff from Agricultural Watershed

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There have been growing concerns over the negative effect of pesticide usage on human health and environmental sustainability. It has been found out that atrazine, a widely used herbicide, threatens ecosystems. Its residues after application can be discharged into water bodies, and thus contaminate surface water and pose risks to public health. An integrated modelling system was developed to estimate atrazine losses through surface runoff. This model includes a distributed hydrological model, a pesticide adsorption model, relational databases, and a geographic information system. The proposed model can simulate atrazine losses due to runoff through the consideration of emission, degradation, adsorption, and movement of atrazine in dissolved and adsorbed phases at the top soil layer. A case study was carried out in the Auglaize-Blanchard Watershed. A comparison between observed and predicted data during May 1997 to April 1998 was conducted. The correlation coefficients are over 0.9 and the statistical significance level was approximately 5%, indicating a reasonable prediction accuracy. The modelling results provide useful decision support for water quality management.

Key words: atrazine, environment, pesticide, pollution, runoff, simulation, watershed

Introduction

Atrazine is a herbicide that selectively controls broadleaf (dicot) weeds, such as pigweed, cocklebur, and velvetleaf in fields of corn and sorghum. Since atrazine is cost efficient and can effectively reduce crop losses due to weed interference, it is one of the most widely used herbicides in the world. Its total average annual use is approximately 34,700 tonnes (active ingredient) in the United States (U.S. EPA 2002c). Atrazine can be well tolerated by actively growing corn and sorghum which absorb/metabolize and detoxify the herbicide. Corn (86%), sorghum (10%) and sugarcane (3%) are the main targets for the atrazine applica-
tions. Less than 1% of atrazine is applied to forestry, turf, and others (U.S. EPA 2002b).

The methods for atrazine application include jet/nozzle spraying and soil incorporation. After being applied to agricultural lands, the atrazine can transport to water bodies by being dissolved in runoff and/or adhering to eroded soil. The annual runoff losses of atrazine are approximately 5% of the initial application amount (Comfort and Roeth 1993). The level of atrazine loss through runoff is especially high in steep fields with fine soils that have low water permeability and low vegetation coverage.

Investigations for 50 and 123 midwestern streams were conducted by the U.S. Geological Survey (USGS) in periods of 1989 to 1990 and 1994 to 1995, respectively; and the maximum atrazine concentrations after runoff events reached 108 and 50 µg/L, respectively (USGS 2000). These concentrations greatly exceeded the maximum contaminant level (MCL) of 3 µg/L as regulated by the U.S. Environmental Protection Agency (U.S. EPA) in 1991 (U.S. EPA 2002a). In 1994, the U.S. Center for Disease Control and Prevention and nine midwestern states systematically monitored atrazine in a number of private wells throughout the upper Midwest (one well per 10 square miles). It was indicated that 0.1% of the wells had atrazine levels over 3 µg/L in Minnesota, and 0.2% over 3 µg/L in Wisconsin (Tetra Tech EM Inc. 2000).

Atrazine may cause a variety of acute and chronic toxic effects. Concerns about such adverse effects have been increasing (Mirgain et al. 1995; Graymore et al. 2001; Friedman 2002; Tappe et al. 2002; U.S. EPA 2002b,c). The recent assessments conducted by the U.S. EPA indicated that risk quotients exceeded the regulated criteria of direct chronic effects on mammals, birds, fish, and aquatic invertebrates as well as direct acute effects on non-target terrestrial and aquatic plants (U.S. EPA 2002b). For example, Hayes et al. (2002) found that 10 to 92% of male wild leopard frogs (*Rana pipiens*) in different regions of the United States showed gonadal abnormalities such as retarded development and hermaphroditism, due to their exposure to waterborne atrazine contamination.

Facing the adverse impacts from the application of atrazine, improvements in managing the related agricultural and soil conservation practices are desired. An effective decision support system is needed for facilitating such improvements, where simulation modelling plays a critical role for system forecasting. Many studies on modelling the fate and transport of pesticides have been conducted (Ehler et al. 1969; Hamaker 1975; Karickhoff 1981; Mahrt and Pan 1984; Mackay et al. 1986; Lewis et al. 1995; Chen et al. 2001a,b, Submitted for publication). Several rainfall-runoff models were developed and applied to pesticide-pollution problems. For example, CREAMS (Chemicals, Runoff, and Erosion from Agricultural Management System) was developed by the U.S. Department of Agriculture (Knisel 1980). This field-scale lumped model underestimated runoff volumes (Smith and Williams 1980; Clausen 1985). Opus, developed by Smith (1992), was an integrated agricultural hydrological model that could concurrently simulate water movement and
solute transport on the soil surface and within the root zone. However, the model has been tested merely under a limited scope of system conditions; discrepancies occurred on several occasions (Smith 1992; Ma 1998). AGNPS (Agricultural Nonpoint Source Pollution Model) was developed by the U.S. Department of Agriculture (Young et al. 1986, 1989) for simulating sediment, nutrient and pesticide losses from agricultural watersheds. It was generally used for estimating nitrogen and phosphorus losses after a single storm event. RZWQM (Root Zone Water Quality Model) is an integrated physical, chemical, and biological process model that simulates water and chemical movement, particularly in unsaturated zones (USDA 1995; Ma 1998). More recently, PeRM (Pesticide Runoff Model) was developed to predict runoff losses of pesticides from agricultural lands (Li et al. 2003a,b) Accepted for publication. PeRM was successfully used to estimate the loss of atrazine in the Kintore Creek Watershed, Ontario, Canada, during 1988 to 1992 (Li et al. 2003a,b).

Among the above studies were two model types: lumped and distributed hydrological models. The lumped models assumed the study watershed as a spatially homogeneous region (Ghadiri and Rose 1992). They were commonly used in the previous studies of pesticide transport. The distributed ones divided the watershed into multiple homogeneous units and routed up the flows with the horizontal and vertical interactions being reflected. Such a model type can incorporate the influences of the spatial variables (e.g., rainfall, topography, soil type, land use) within the simulation process (Engel et al. 1993). The distributed model usually has more advantages than the lumped one in reflecting the actual fate of pesticide transport and providing more accurate forecasting; however, few previous models developed specifically for simulating pesticide losses through runoff and also relied on the distributed methods. Furthermore, several important processes that contribute to pesticide losses through runoff desired further exploration. For example, the runoff wash-off of pesticide from plant canopy and surface residue may increase pesticide concentrations in the surface water. Moreover, emissions of pesticide (in gaseous state) from plant canopy and soil surface may reduce the losses through runoff. Ignoring these pathways could affect the modelling accuracy. Consequently, development of a pesticide loss modelling system that tackles all the related transport processes based on a distributed rainfall-runoff model is desired.

The objective of this study is to develop such a system. Many processes that affect pesticide transport will be taken into account. Especially, several processes that were not considered in the previous studies will be explored and combined into the modelling system, including snowmelt, wash-off and emission. In addition, techniques of Geographic Information System (GIS), such as terrain analysis, will be used to estimate several hydrological parameters, such as slope, aspect, contribution area, and runoff-flow direction, as well as manipulate the relevant database. The developed model will be applied to the Auglaize-Blanchard Watershed, U.S.A.
Methodology

Pesticide Runoff Model (PeRM)

The proposed model is an integration of a mathematical simulation model and a GIS, which accounts for the transport of pesticide and its spatial distributive characteristics. The simulation model consists of five modules: hydrology, wash-off, adsorption, concentration, and routing modules. To reflect the spatial distribution, the watershed is conceptually divided into a number of grid cells. Each cell can be treated as a unit for pesticide behaviour with inflows from and outflows to other grid cells. The spatial data from GIS and remote sensing (RS) studies, combined with related pesticide properties and soil characteristics, are combined into the grid system for modelling the pesticide losses. Finally, the modelling results are handled through the GIS and its database, and then presented graphically.

Hydrology module

A model developed by the U.S. Soil Conservation Service (SCS) was used to estimate runoff during rainfall events with a known precipitation depth. The volume of runoff \( Q \) depends on the volume of precipitation \( P \), snowmelt \( SM \), and the initial abstraction \( I \). The initial abstraction \( I \) is a fraction of total rainfall that does not appear as runoff (McCuen 1981):

\[
Q = \frac{(P + SM - I)^2}{(P + SM - I + S)}
\]

(1)

The initial abstraction, \( I \), is all losses before runoff begins. It includes water retained in surface depressions, water intercepted by vegetation, evaporation, and infiltration. This can be described as follows:

\[
I = 0.2S, S = 1000 \frac{Q}{CN} - 10
\]

(2)

where \( S \) is potential maximum retention after runoff begins, \( CN \) is SCS runoff curve number, which is an index representing the combined effects of soil hydrologic characteristics, land use and antecedent moisture conditions (McCuen 1981). It is a function of soil type, soil drainage properties, crop type, and management practice. Typically, specific curve numbers for a given rainfall event are determined by the sum of the rainfall totals for the previous 5 days, known as the 5-day antecedent moisture condition.

Snowmelt can be estimated on days when a snowpack exists and above freezing temperatures occur (Haith and Loehr 1979):

\[
SM = C_{sn}T_{ad}
\]

(3)

where \( C_{sn} \) is the degree-day snowmelt factor, which is the daily decrease of snow depth per degree day, and \( T_{ad} \) is the average daily temperature.
Wash-off module

During spray application, pesticides are always intercepted by the canopy, crop surface residue and soil surface. The losses due to advection or wind are negligible at the present stage. Pesticide residues on the soil surface may enhance pesticide movement in soil after soil incorporation. The fate of this part is considered in equation 17 in the module of pesticide concentration available for runoff. The interception part on canopy and the ground residue of crops will be washed off after rainfall and enter the top soil layers. A first-order rate equation was developed to describe the wash-off process of pesticides. This equation is used due to its ability to adequately predict observed wash-off data reported by Martin et al. (1978) and Willis et al. (1986). The change in pesticide content in wash-off water, $P_{wa}$, with respect to the cumulative volume of intercepted rainfall, $V_r$, is described as (Kenimer et al. 1989):

$$\frac{\partial P_{wa}}{\partial V_r} = -k_{waf} \cdot P_{wa}$$  \hspace{1cm} (4)

where $k_{waf}$ is the wash-off rate constant. Assuming that $P_{wa}$ is equal to $P_{wa0}$, the initial pesticide loading in wash-off water, when $V_r$ is equal to zero, and integrating yields:

$$\ln\left(\frac{P_{wa}}{P_{wa0}}\right) = -k_{waf} \cdot V_r$$  \hspace{1cm} (5)

The boundary conditions required to solve for $k_{waf}$ are obtained from Martin et al. (1978) as follows:

$$P_{wa} = P_{wa0} - W_{wa}, \quad V_r = 0.5$$  \hspace{1cm} (6)

$$P_{wa} = P_{wa0} - 2W_{wa}, \quad V_r = 3.5$$  \hspace{1cm} (7)

where $W_{wa}$ is the mass of pesticide washed from crop canopy or surface residue. Incorporating these conditions into equation 5 and solving for $k_{waf}$ results in a $k_{waf}$ value of 1.37. Rearranging yields:

$$P_{wa} = P_{wa0} \exp\left(-1.37V_r\right)$$  \hspace{1cm} (8)

The initial pesticide load in wash-off water is assumed to be composed of two parts: the initial pesticide load in wash-off water which comes from crop canopy ($W_{wa-c}$) and the initial pesticide load in wash-off water which is from ground residue of crops ($W_{wa-s}$). $W_{wa-c}$ is equal to the total pesticide application on the canopy minus the degradation and canopy emission as follows:

$$W_{wa-c} = W_{p-c} \cdot (LAI) \cdot \left[1 - \exp\left(-\ln2 \frac{t}{t_{1/2}}\right)\right] - FA_a \cdot F_p \cdot (LAI)$$  \hspace{1cm} (9)

where $W_{p-c}$ is the mass of pesticide spray application, $t_{1/2}$ is the half-life of pesticide in the soil, $t$ is the time period after pesticide application, $F$ is
volatilization flux of pesticide from canopy, \( A_a \) is the application area, \( f_p \) is the fraction of leaf area contacted by pesticide, and \( LAI \) is the leaf area index, which is defined as the one-sided area of leaves per unit ground area and can be estimated from RS data (Chen et al. 2001b, Submitted for publication).

The \( W_{wa-s} \) is equal to the initial pesticide spray application multiplied by the fraction of land area covered by the crop residue (\( R_{cr} \)) after deducting the degradation. The pesticide emission from the surface crop residue is considered negligible:

\[
W_{wa-s} = W_{p-c} R_{cr} \ln \left( 1 - \exp \left( - \frac{t}{t_{1/2}} \right) \right)
\]

Thus, the initial pesticide loading on soil cover is calculated as a function of the initial pesticide load on crop canopy and surface residue:

\[
P_{wa0} = W_{wa-c} + W_{wa-s}
\]

**Adsorption module**

The adsorption of pesticides by soil particles is a reversible process. In order to describe the adsorption/desorption processes, the Freundlich equation was used in some models like ARM (Donigian et al. 1977) or PLIERS (Kenimer et al. 1989). In CREAMS (Leonard et al. 1987) a constant partition coefficient was assumed between the adsorbed and the solution phase, which means that the active ingredient of pesticide reaches an instant equilibrium between the soil mass and the overland flow in the zone of interaction. The modified Freundlich equation was used in this study (Leonard et al. 1987). The pesticide concentration (\( C_r \)) in the solid phase is equal to the fraction of pesticides in runoff as follows:

\[
C_r = C_{aw} K_{ex} / (1 + K_e K_d)
\]

where \( C_{aw} \) is the runoff-available pesticide concentration in the surface soil layer in time \( t \) (days) after pesticide application, \( K_d \) is the soil/water partitioning coefficient, \( K_e \) is the pesticide equilibrium constant, and \( K_{ex} \) is the extraction coefficient. The partitioning of the available pesticide between the soluble and adsorbed phase can be determined by calculating the following soil/water partitioning coefficient \( K_{sw} \):

\[
K_d = a_{sg} K_{sw}(OM)
\]

where \( a_{sg} \) is an empirical constant, which equals 0.0058 (Sauer 1998), and \( OM \) is the percent organic matter.

Therefore, the soil/water partitioning coefficient (\( K_d \)) is a function of a pesticide property, organic carbon sorption coefficient, and a soil property, percent organic matter (\( OM \)). The constant \( a \) is calculated from two
equations that relate the partitioning coefficient to the organic carbon fraction in the soil, as well as the percent organic matter to the percent organic carbon (OC) (Novotny and Olem 1994):

\[ K_d \approx K_{sw} OC / 100 \]  
\[ OM \approx 1.67OC \]

In CREAMS, a functional relationship was developed to relate the extraction coefficient \( K_{ex} \) to the distribution coefficient \( K_d \) (Leonard et al. 1987):

\[ K_{ex} = \begin{cases} 
0.5, & \text{for } K_d \leq 1.0 \\
0.7 - 0.2K_d, & \text{for } 1.0 < K_d \leq 3.0 \\
0.1, & \text{for } K_d > 3.0 
\end{cases} \]  

**Pesticide available for runoff**

The total pesticide load on the soil is assumed to be composed of several parts: pesticide residue after soil incorporated application, intercepted pesticides by soil surface after spray application, pesticides washed off by rainfall from canopy and ground residue of crops. Under the assumption of a simple linear adsorption isotherm combined with an algorithm to estimate vertical movement of pesticide from the soil surface, the pesticide concentration available in the soil for runoff \( C_{av} \) is calculated by the following equation, which is modified based on that of Sauer (1998):

\[ C_{av} = \left[ W_{p-s} + P_{wa} + W_{p-c} \left( 1 - LAI - R_{cr} \right) \right] \left( 1 - F_t \right) \exp \left( - \frac{t}{t_{1/2}} \right) \]  

where \( W_{p-s} \) is the mass of soil-incorporated pesticide application, and \( F_t \) is the daily emission factor of pesticide. For atrazine, \( t_{1/2} \) is approximately equal to 60 days (Mackay et al. 1986). The residues left in soils due to the use of atrazine in the previous years were not considered here. The daily emission factors \( (F_t) \), generally defined as the ratio of emissions and the usage of the pesticide, can be obtained from the pesticide canopy emission model (Scholtz et al. 1997; Chen et al. 2001b).

**Pesticide routing module**

A mass balance technique, based on the continuity equation, was used to route pesticides. A mass balance of water, sediment and pesticides was performed on each cell during each time step. The mass balance technique is used because it reflects the continuity of the water, sediment and pesticides within the cells. Each cell’s pesticide inputs include those washed off of crop canopy and ground residue, as well as those that enter the cell from upslope sources in either dissolved or adsorbed form. The pesticide loads from these sources are then combined with those retained
since the last time step. The continuity equation for the pesticide runoff

\[ P_{in(i+1,t+1)} = P_{out(i,t)} = P_{cell(i,t)} + P_{in(i,t)} \]  

(18)

\[ P_{cell} = \frac{C_{av} Q}{N_{cell}} \]  

(19)

where \( P_{out(i,t)} \) is the amount of pesticide leaving a cell through runoff at the \( i \)th cell at time \( t \), \( P_{in(i,t)} \) is the sum of all pesticides entering a cell from other cells through runoff at the \( i \)th cell at time \( t \), \( P_{cell(i,t)} \) is the pesticide amount generated within a cell at the \( i \)th cell at time \( t \), and \( N_{cell} \) is the number of cells. The cell pesticide load is assumed to be evenly distributed throughout the “mixing zone,” the immediate soil surface which is able to supply pesticides to runoff water and sediment. The mixing zone is defined as the top 1 cm of the soil profile as suggested by other investigators (Donigian et al. 1977; Knisel 1980).

Integration with GIS

A watershed is usually composed of fields of different crops, soil types, and land slopes, leading to various ways for pesticide runoff. To reflect this spatial distribution, the watershed can be conceptually divided into a number of grid cells, with each of them being uniform with respect to crop species, soil type, hydrological conditions, and topological characteristics. Thus, each grid cell can be treated as a unit for pesticide behaviour with inflows from and outflows to other grid cells. A grid cell structure is a discrete representation of a terrain, based on identical square cells arranged in rows and columns. Grids are used to describe spatially distributed parameters. The number of grid cells in a watershed varies with the watershed’s size and the cells’ dimensions, but should be large enough to account for the watershed’s spatial variability. Output from a grid cell at the top of the watershed is routed to cells below it and/or to the stream channels, and finally to the watershed’s outlet. In each cell, the spatial data from GIS and RS combined with relative pesticide and soil properties data are input to the model for calculating the pesticide fate. After the specific calculating process, the final results will be managed through GIS and a database, and then presented graphically.

Thus, based on the grid-cell system, the modelling system was developed through an integration of the pesticide runoff simulation model and GIS. After inputting the digital feature layers and the related data from the database, the GIS can overlay these spatial data and calculate the necessary parameters for the pesticide runoff model (Chen et al. 2001a). For the conventional non-point source pollution model, all terrain input data must be coded in along with other soil and land-use data, which is a time-consuming process. In this study, several parameters, including cell numbers, cell connectivities, aspects (flow directions), land and channel slopes, slope lengths, slope shapes, and upslope contributing areas, were studied through terrain analysis techniques based on the digital elevation
model (DEM). The results were summarized and then exported to a database managed by computer interfaces. Many input parameters for the pesticide runoff model could then be estimated using a query function within the database; in addition, input files for the model could be organized in the database as well. After the input parameters and meteorological data were formatted for further simulation, the pesticide model would acquire the data from the database and then forecast pesticide runoff losses. The final results can be saved in the database and displayed graphically through the GIS combined with extensive spatial analysis.

Case Study

Overview of the Study Area

The Auglaize-Blanchard Watershed (Latitude: 40.49° ~ 41.28°, Longitude: -83.38° ~ -85.01°) is located in northern Ohio, U.S.A. (Fig. 1). It contains two adjacent sub-basins. The western portion is the Auglaize River Sub-basin and the eastern one is the Blanchard River Sub-basin. The length of the Auglaize River is 163 km, with the river basin covering an area of 6234 km². The Blanchard River extends 146 km, with its basin covering 1974 km².

The watershed comprises a flat lake plain in the centre, and sloping till plains around the edges. The USDA (1993) reported the average slope of 0.61 m/km for the Auglaize River and 0.17 m/km for the Blanchard River. Sand and gravel are present as discontinuous deposits in the river valleys as well as the western part of the basin. Annual precipitation between 1990

Fig. 1. The study area.
and 1998 in the Auglaize-Blanchard Watershed ranged from 853.4 mm (Paulding County) to 932.2 mm (Van Wert County). Rainfall peaks in May or June, while the lowest precipitation occurs in January or February.

In this watershed, about 75% of the land is for agricultural uses while 10% is for forest. The study area lies in the eastern U.S. Corn Belt (Hess 1995). The major crops are corn, soybeans, wheat, oats, and alfalfa (hay). Other agricultural land uses include pasture and forage crops (U.S. Department of the Interior and U.S. Geological Survey 2000).

An index of watershed indicators (IWI) proposed by the U.S. EPA (2002a) was utilized to describe the health of the aquatic resources in this watershed. The Auglaize River Basin scored 5 which represents the level of “more serious water quality problems” – “High Vulnerability” to stressors such as pollutant discharges. The Blanchard River basin got a score of 3, which indicates “less serious water quality problems” – “Low Vulnerability” to stressors. Non-point source pollutions including pesticide losses have been one of the most serious environmental problems in Ohio. Pesticide applications to crop lands are among the highest nationwide. The five most heavily applied agricultural pesticides are metolachlor, atrazine, cyanazine, acetochlor, and alachlor. Among them, atrazine, which is the target of this study, has been found in every stream and its pollution problem acquired more attention recently.

Data Collection and Analysis

The rainfall, snow, and temperature data are obtained from the dataset of NOAA (National Oceanic and Atmospheric Administration), NCDC (National Climatic Data Center) DAILY FSOD (U.S. NOAA 2003). Station 14825 at the Findlay Airport, Ohio, was selected for this study. Its data cover the period between 1990 and 1998.

Two outlets located in the area have been selected: Fort Jennings, the outlet at the centre of the watershed, and Defiance, the outlet of the entire watershed. The stream flow and atrazine concentration data for the Fort Jennings Outlet are available and are used to verify the proposed model. Data for the watershed outlet at Defiance are used to perform the simulation of atrazine loss in runoff. Runoff simulation was conducted to provide a basis for estimating atrazine loss. An accurate simulation of runoff volume would render reliability of atrazine-loss estimation.

The stream flow data came from the National Water Information System of USGS. Two stations located in the study area were selected: USGS Station 04186500 at Fort Jennings, Ohio, and USGS Station 04191500 at Defiance, Ohio. The monitoring dates ranged from 1990 to 2001 (Fig. 1). The information about the observed atrazine concentrations was acquired from the USGS Water Quality Sample Site at Fort Jennings. Eleven sets of the observed atrazine concentrations as obtained from monitoring programs during May 1997 and June 1998 were available for verifying the developed model.

The digital elevation model (DEM) data of the study area were obtained from the DEM STATUS GRAPHICS dataset of USGS. The
7.5-minute DEM data casts on the UTM projection system were referenced to the North American Datum of 1927 (NAD 27). These data were stored as profiles with a 30-metre square grid spacing along and between each profile.

The DEM data were used to generate basic hydrological inputs for the pesticide loss model. Several parameters were derived by using ArcView 3.1 GIS®. A grid of flow accumulation was produced and the flow directions were obtained (Fig. 2). Slope and aspect grids were also computed from the DEM based on terrain analysis and related hydrological methods (Chen et al. 2001a).

Gridded atrazine usage (1990 to 1998) in the United States was estimated from the data provided by the U.S. Geological Survey (USGS) Pesticide National Synthesis Project, while that in Canada was from Environment Canada (Li et al. 2003). The raw data of soil properties, such as bulk density, organic matter content, and soil hydrology group, were acquired from STATSGO - State Soil Geographic Data Base organized by USGS (USDA 1991). The data were in ARC/INFO coverage format, and were converted into a grid system. Information about land use, crop type, pesticide property, watershed boundary, and river drainage was collected from various sources. The physical and chemical properties of atrazine are shown in Table 1.

In this study, a 10 km × 10 km (or 1/12° × 1/8° latitude-longitude) grid system was created for the distributed modelling system. For each grid cell, the following parameters were acquired: latitude and longitude coordinates for each grid centroid, predominant soil type, soil bulk density, organic matter, land-use type, SCS curve number, total atrazine-application amount, atrazine-application efficiency, the first atrazine-application date (and percentage of application amount), and the second atrazine-application date (if any, as well as percentage of application amount).

![Fig. 2. Estimated surface flow directions of the Auglaize-Blanchard Watershed.](image-url)
Result Analysis

Many modelling parameters are imprecise, leading to uncertainties in the modelling results. Therefore, in addition to testing the modelling outputs against observation data, it is important to know sensitivity of the outputs to variations in the modelling inputs. Such information is useful for identifying critical factors in mitigating pesticide losses. Figure 3A shows the pesticide concentrations varying with different inputs. It indicates that the concentrations are most sensitive to variations in half-life of pesticide and soil organic matter content of soil. Pesticide application rate, which is pesticide application amount per unit area, has a significant effect on initial pesticide application amount, as well as application area rate, which is percentage of contacting area by pesticide to total application area. Generally, factors related to the pesticide losses include (a) half-life, (b) application area rate, (c) pesticide application rate, (d) emission factor, and (e) pesticide solubility, where (d) was defined in equation 17. These factors can be ranked in terms of the effect levels as follows: half-life > application area rate > pesticide application rate > emission factor > pesticide solubility (Fig. 3A); those related to the soil can be ranked as follows: organic matter content > bulk density > curve number > degree-day snowmelt factor (Fig. 3B), where the “curve number” and “degree-day snowmelt factor” were defined in equations 2 and 3, respectively.

Figure 3C shows the predicted runoff under different input factors related to the rainfall and snow. The value of the curve number is generally estimated from the hydrological conditions, which is the effect of land use, vegetation density, residue cover, and agricultural practices on infiltration and runoff (USDA 1986). The influences of curve number variations obtained under three types of hydrologic conditions, including good, fair, and poor hydrological conditions that are defined in Fig. 4, were compared. The influence of curve number variations on runoff prediction is more significant than that of the degree-day snowmelt factor. This means that the runoff is mainly caused by rainfall instead of snowmelt in the study area. Generally, the ranking in terms of the significance levels of the input factors is: curve number under poor hydrologic condition > curve

| Table 1. Physical and chemical properties of atrazine |
| Diffusivity in water (m²/day) | Solubility in water (µg/mL) | Half-life in soil (days) | Soil KOC (mL/g) |
| Sherwood et al. (1975) | 0.466 | 33 | USDA |
| Millette et al. (1994) | | | USDA |
| USDA (2001) | 60 | USDA |
| USDA (2001) | 100 | USDA |

number under fair hydrologic condition > curve number under good hydrologic condition > degree-day snowmelt factor (Fig. 4).

In the Great Lakes basins, atrazine is usually applied in May by spray and soil incorporation. A period between May 1997 (right after pesticide application) and June 1998 was selected for simulating the fate of atrazine in the Auglaize-Blanchard Watershed through the pesticide runoff model. Atrazine concentration (µg/L) in the river was used for analyzing the pollution conditions. The mass flux of atrazine could then be estimated based on the predicted concentrations and the total water discharge. The modelling results of runoff and atrazine concentration under different time scales were obtained and then compared with the observed data whenever they are available.

At the Fort Jennings Outlet

The model gives monthly water discharges at the Fort Jennings Outlet between May 1, 1997, and April 30, 1998 (Fig. 5A). The correlation between

Note: “Curve Number_Good”: value of curve number was estimated based on the good hydrological conditions, which indicates that the soil usually has a low runoff potential for that specific land-use, vegetation density, residue cover, and agricultural practices.

“Curve Number_Fair”: value of curve number was estimated based on the fair hydrological conditions, which indicates that the soil usually has a mediate runoff potential for that specific land-use, vegetation density, residue cover, and agricultural practices.

“Curve Number_Poor”: value of curve number was estimated based on the poor hydrological conditions, which indicates that the soil usually has a high runoff potential for that specific land-use, vegetation density, residue cover, and agricultural practices.

Fig. 3. Sensitivity of atrazine concentration to variations of input parameters.

Fig. 4. Sensitivity of runoff to variations of input parameters.
these two sets of data is given in Fig. 4B and the correlation coefficient is 0.95 (Fig. 5B). There was a statistically significant relationship between the predicted and the observed data with a significance level of 5%. The coefficient of determination ($r^2 = 0.90$) indicates that approximately 90% of the variation in the modelling outputs stem from the inputs. To further verify the model, the predicted daily water discharges were compared with the observed data at 11 selected days when the observed atrazine concentrations are available. Figure 6A shows that the predicted values match the observed ones well at the Fort Jennings Outlet. The mean absolute error is -0.41 m$^3$/s and the standard deviation is 0.71. The correlation between these two sets of data is demonstrated in Fig. 6B ($r = 0.98$). A statistically significant relationship exists between the predicted and observed data at a significance level of 5%.

The predicted daily atrazine concentrations at the Fort Jennings Outlet between May 1, 1997, and June 30, 1998, are given in Fig. 7. The concentra-
tions decreased significantly with time due to the natural attenuation, and were lower than the maximum allowable contaminant level of 3.0 µg/L as regulated in the water quality criteria (3745-1-34) under the “Safe Drinking Water Act” of Ohio (Ohio Environmental Protection Agency 2002).

Figure 8A shows the predicted and observed daily average concentrations of atrazine at the Fort Jennings Outlet for the 11 days. The correlation between these two sets of data is demonstrated in Fig. 8B. The predicted values well match the observed ones. The mean absolute error is 0.10 µg/L and the standard deviation is 0.16. The correlation coefficient is 0.94 with a 5% significance level, indicating a reasonable prediction accuracy (Fig. 8B).

Figure 7. Predicted daily atrazine concentrations at the Fort Jennings Outlet during May 1, 1997, to April 30, 1998.

Fig. 8. Verification of modelling results for daily mean atrazine concentrations at the Fort Jennings Outlet at 11 selected days during May 1997 to April 1998, where (A) is a comparison between predicted and observed discharges, and (B) is a scattered plot (correlation coefficient $r^2 = 0.89$; significance level = 5%).
At the Defiance Outlet

The predicted monthly water discharges at the Defiance Outlet between May 1997 and April 1998 are shown in Fig. 9A. The relation between the two sets of data is given in Fig. 9B, with a significance level of 5% ($r = 93$), indicating that the predicted data well matched the observed ones.

Figure 10 shows a comparison between the predicted and measured monthly runoffs as well as a historical record of monthly rainfalls. The predicted monthly runoff has a more significant correlation with the rainfall than the measured runoff. This indicates the existence of some difference between rainfall at the Findlay Weather Station (70 km straight distance away from Defiance) and that at the Defiance Outlet. Thus, the rainfall data obtained from the weather station can hardly represent varied conditions in the entire watershed; this could be a potential cause of the prediction errors.

Figure 11 shows the predicted daily average atrazine concentrations at the Defiance Outlet between May 1, 1997, and June 30, 1998. The concentrations decreased significantly with time. Atrazine concentrations in this period were all lower than the regulated 3.0 µg/L.

Figure 12 shows daily mass flux of atrazine at the Defiance Outlet between May 1, 1997, and April 30, 1998. Most of the atrazine mass was discharged in the spring (May 1 to June 30) and the highest flux was found on May 31, 1997. During this season, water discharge through the Defiance Outlet contributed 60% of the total pesticide loss. The total annual usage of this herbicide was 204.9 tonnes. According to the simulation results, approximately 7% of the total applied atrazine was removed from agricultural lands by surface runoff.

Fig. 9. Verification of modelling results for monthly runoff at the Defiance Outlet during May 1997 to April 1998, where (A) is a comparison between predicted and observed discharges, and (B) is a scattered plot (correlation coefficient $r^2 = 0.87$; significance level = 5%).
Fig. 10. Predicted versus observed monthly mean runoffs and monthly rainfalls at the Defiance Outlet.

Fig. 11. Predicted daily atrazine concentrations at the Defiance Outlet during May 1, 1997, to April 30, 1998.

Fig. 12. Predicted daily atrazine mass fluxes at the Defiance Outlet during May 1, 1997, to April 30, 1998.
Figure 13 shows the percentage of daily atrazine flux at the Defiance Outlet between May 1, 1997, and April 30, 1998, over the annual atrazine usage, as well as the daily precipitation data of Station 14825 at Findlay Airport, Ohio. A correlation between the precipitation and the pesticide loss could be found for the period of May to October 1997, indicating the importance of rainfall to the pesticide loss. A time lag is observed between the peak of pesticide loss and that of runoff, which results from the process of surface runoff transport. Based on the 30-year historical data, May and June have the highest monthly precipitation. Therefore, pesticide applied during this period is at the greatest risk of loss through runoff.

The differences between the observed and predicted values may be attributed to a number of factors, such as errors in the inputs (e.g., application rate, time of pesticide application, and rainfall intensity), and incorrect estimation of modelling parameters (e.g., emission factor and application efficiency). Obviously, rainfall intensity plays an important role in runoff generation. The rainfall data from the Findlay Weather Station may not be an accurate representation of the conditions in the entire watershed. This might be a main cause of the prediction errors.

Conclusions

(1) A pesticide runoff modelling system was developed to simulate the atrazine loss with surface runoff, based on a distributed rainfall-runoff model. Many processes that affect pesticide transport have been taken into account. In particular, several processes that were not considered in the previous studies have been explored and combined into the modelling system, including snowmelt, wash-off and emission.

(2) This model contains (a) a distributed hydrology module to calculate the volume of runoff, (b) a pesticide wash-off module to simulate the
pesticide wash-off from crop canopy and surface residue, (c) a pesticide adsorption module to describe the adsorption process in the mixing soil layer, (d) a pesticide concentration module to calculate the pesticide concentration in the soil, and (e) a pesticide routing module to route the pesticides during runoff using a continuity equation.

3) GIS techniques (e.g., terrain analysis) have been integrated within this system to estimate several hydrologic parameters, such as slope, aspect, contribution area, and runoff-flow direction, as well as to manipulate the relevant database. Pesticide losses in the entire study area can be predicted through additive and routing computations.

4) The developed modelling system has been applied to the Auglaize-Blanchard Watershed, Ohio, U.S.A. Atrazine, a widely used herbicide in the study area, was selected as the simulation target. The modelling outputs were verified through available observation data, which has demonstrated reasonable prediction accuracy. The results indicated that the modelling system provided an effective means for forecasting pesticide pollution in agricultural activities. The distributed properties of the related modelling modules, the consideration of emission and wash-off processes, and the integration of GIS provide the system with significant advantages.

5) Some prediction errors exist owing to the complex nature of the study area and uncertainties of the input data. Increasing the certainty of the data sets through further investigation and verification would help to enhance the credibility of the forecasting results.

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