EVALUATION OF THE ANNAGNPS MODEL FOR ATRAZINE PREDICTION IN NORTHEAST INDIANA

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ABSTRACT. *The Annualized Agricultural Nonpoint Source (AnnAGNPS) pollution model was developed for simulation of runoff, sediment, nutrient, and pesticide losses from ungauged agricultural watersheds. This article describes the first documented calibration and validation of AnnAGNPS for prediction of atrazine loading. Here, the model was applied to the 707 km^2 Cedar Creek watershed (CCW) and the 45 km^2 Matson Ditch sub-catchment (MDS), which are predominantly (>85%) agricultural, with major crops of corn and soybeans. Atrazine herbicide is of significant concern, as the St. Joseph River is the source of drinking water for the city of Fort Wayne, Indiana, with Cedar Creek being the main tributary. Major objectives were to evaluate the ability of AnnAGNPS to simulate runoff and atrazine concentrations in uncalibrated, calibrated, and validation modes. In an uncalibrated mode, flow discharge predictions by AnnAGNPS were satisfactory at the CCW scale but could be improved through calibration. Flow discharge for both CCW and MDS could be well matched with observed values during model calibration and validation. AnnAGNPS predictions of atrazine concentrations in runoff water were very poor, and it was impossible to improve the results through any type of calibration. Inspection of the model source code revealed a unit conversion error in the runoff value being input to the pesticide routine, which when corrected greatly improved the results. The corrected AnnAGNPS model code could be satisfactorily calibrated and validated for predictions of atrazine concentrations in the MDS, but not in the CCW where only coarse measured data were available.*

Keywords. *Agricultural runoff, Atrazine, Indiana, Modeling, Nonpoint-source pollution, Watershed.*

Like many other pesticides, the herbicide atrazine has played a substantial role in improving farmers' ability to improve crop yields, but it also has the potential to cause detrimental impacts to the environment and drinking water sources. The movement of pesticides from their intended application location to surface water and groundwater can potentially lead to the contamination of community sources of potable water. Variations in topography, climate, land use, and management in addition to the soil-plant-atmosphere processes and their interactions represent only a few of the issues that need to be considered in watershed assessments. Geographic information systems combined with mathematical models provide a means of simulating the complex processes and interactions between a multitude of variables, albeit through simplification. Analysis of the performance of these mathematical models under a variety of climates, soils, land covers, management practices, and scales is critical to determine their respective applicability and efficiency.

The AnnAGNPS model (Theurer and Cronshey, 1998; Bingner and Theurer, 2005; USDA-ARS, 2006), a continuous simulation enhancement of the AGNPS (Young et al., 1989) model, was developed by the USDA Agricultural Research Service (ARS) and Natural Resources Conservation Service (NRCS) to predict sediment and chemical delivery from ungauged agricultural watersheds up to 300,000 ha (Bosch et al., 2001). AnnAGNPS is a cell-based, batch-process computer program that utilizes an ArcView interface and routes runoff, sediment, nutrients, and pesticides from their origins in upland cells through a channel network to the outlet of the watershed (Bingner and Theurer, 2005). Batch processing allows the model to execute a series of programs that utilize predefined directories to enter the input and climate files and output selected files.

The climate data requirements for simulations include daily maximum and minimum temperature, precipitation, average daily dewpoint temperature and wind speed, and sky cover (Bingner and Theurer, 2005). Users have the option to input measured climate data by uploading the data into the AnnAGNPS input editor, or the Generation of weather Elements for Multiple applications (GEM) climate generation model (USDA-ARS, 2005) can be utilized to generate daily precipitation, maximum and minimum temperature, and solar radiation.

AnnAGNPS hydrology is based on a simple bookkeeping of inputs and outputs during the daily time steps where the input precipitation is divided into soil storage, evaporation, and plant uptake, with the remainder being identified as a mixture of shallow and overland flow that define runoff in the model (Bingner and Theurer, 2005). The hydrologic processes simulated in the model include interception evaporation, surface runoff, evapotranspiration, subsurface lateral flow, and subsurface drainage. Subsurface lateral flow and drainage are calculated using Darcy's and Hooghoudt's equations, respec-

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tively. Subsurface lateral flow and drainage are added to the reach at the same time as runoff and differ from baseflow in that baseflow is a slow return from groundwater and is not calculated in the model (Yuan et al., 2006). Runoff is predicted using the SCS curve number technique (USDA-SCS, 1986), and sheet and rill erosion is predicted with the Revised Universal Soil Loss Equation (RUSLE; Renard et al., 1997). Sediment transport in channels is computed using a modified Einstein equation, and the Bagnold (1966) equation is used to estimate sediment transport capacity of the flow (Bingner and Theurer, 2005). A constant time step procedure is used to calculate the soil moisture balance on a sub-daily time step for tillage and below-tillage composite soil layers (Bingner and Theurer, 2005). Sediment delivery ratios to the stream network are calculated using the Hydro-geomorphic Universal Soil Loss Equation (HUSLE; Theurer and Clarke, 1991). The amounts of organic carbon, nitrogen, and phosphorus in soluble and adsorbed forms in the soil, applied as fertilizer or manure, as well as components in plants and residues are estimated through a daily mass balance in each cell.

AnnAGNPS utilizes a modified version of Groundwater Loading Effects of Agricultural Management Systems (GLEAMS; Leonard et al., 1987) to simulate pesticides that are attached to clay particles and those in solution. GLEAMS is a daily time step model that calculates pesticide degradation, extraction into runoff, vertical flux, transport with sediment, evaporation, and plant uptake (Leonard et al., 1987). Pesticide applied to the field and its subsequent foliage washoff, transport in the soil profile, degradation, and the runoff of soluble and sediment-adsorbed fractions are calculated for each cell by a daily pesticide mass balance (Bosch et al., 2001; Bingner and Theurer, 2005).

Previous research has utilized the AnnAGNPS model for predicting hydrology and nutrient and sediment transport (Yuan et al., 2001, 2002, 2003; Suir, 1999; Suttles et al., 2003; Shrestha et al., 2006; Sarangi et al., 2007; Licciardello et al., 2007). However, application of the pesticide transport portion of the model has only been reported in one peer-reviewed journal article (Heathman et al., 2008) and one PhD dissertation (Tagert, 2006). Additionally, there have been no studies on calibration and validation of the pesticide routines in the model.

Suttles et al. (2003) conducted simulations with AnnAGNPS in the 333 km^2 (129 mi^2) Little River research watershed in south central Georgia and found that average annual runoff, sediment, and nutrient loads were all underpredicted in the upper part of the watershed. In the lower part of the watershed, predicted runoff was close to the observed value, but sediment and nutrients were overestimated. Suttles et al. (2003) concluded that the underpredictions in the upper part of the watershed were due to an overestimation of forested areas that caused an underestimation of runoff and, subsequently, of sediment and nutrients. Overprediction in the lower portion of the watershed likely resulted from not adequately quantifying the riparian and wetland areas there. Yuan et al. (2003) described application of AnnAGNPS to the Deep Hollow watershed in Mississippi to evaluate nitrogen loadings and reported poor predictions of monthly values. The poor predictions were attributed to the simplification of the nitrogen process in version 2.0 of the model. Nitrogen processes in the model have subsequently been refined in version 4.0 (Bingner et al., 2007).

Yuan et al. (2006) described enhancements to the AnnAGNPS model for simulation of subsurface flow and subsurface drainage and presented results of the model application to the Ohio Upper Auglaize watershed. Although validation was not possible due to use of only simulated climate, the subsurface flow and drainage enhancement reduced surface runoff by 16% to 23% for a variety of field management scenarios. In Ontario, Das et al. (2007) compared the performance of SWAT and AnnAGNPS for prediction of runoff and sediment loss from the Canagagigue Creek watershed, and Nash-Sutcliffe (1970) model efficiency (E_{NS}) values of 0.79 and 0.69 were achieved for monthly runoff predictions in the calibration and validation phases, respectively. For monthly sediment losses, model efficiency values for AnnAGNPS were 0.53 and 0.35 for the calibration and validation periods, respectively. Similarly, Parajuli et al. (2009) applied the AnnAGNPS and SWAT models to the Red Rock Creek and Goose Creek watersheds in south-central Kansas for prediction of flow, sediment, and total phosphorus. They found that AnnAGNPS calibrated and validated well for runoff prediction, with model efficiency values of 0.69 and 0.47, respectively. Model efficiencies for sediment predictions with AnnAGNPS were also good for calibration (0.60) and validation (0.64). Predictions of total phosphorus produced fair model efficiencies for calibration (0.32) but performed unsatisfactorily for validation (-2.38).

Heathman et al. (2008) applied the uncalibrated AnnAGNPS and SWAT models to the CCW to assess streamflow and atrazine losses and found that the uncalibrated AnnAGNPS produced poor predictions of both monthly streamflow and atrazine losses, with model efficiency values of 0.13 and -0.64, respectively. They also found that the AnnAGNPS-simulated atrazine concentrations were about 1/100th of the observed values. Similarly, Tagert (2006) had poor results when AnnAGNPS was applied to validate pesticide loading of atrazine and metolachlor from measured grab sample data in the 13,200 ha (32,600 acre) Upper Pearl River basin. With the exception of one substantial overprediction, her event-based results showed that the model underestimated loads for both atrazine and metolachlor. The model results also had poor correlation, with an R^2 of 0.09 for atrazine and 0.06 for metolachlor, when comparing measured and simulated loads. Although the model results were poor for both atrazine and metolachor, she concluded that low pesticide sampling intensity and few matching observed and simulated events were likely the causes for much of the deviation in the study.

In the present study, the AnnAGNPS pesticide transport routine was modified and the model was calibrated and validated to two watersheds draining to a major drinking water source in order to predict stream discharge and atrazine loading. This article describes the first documented calibration and validation of AnnAGNPS pesticide transport routines.

Background

The northeast Indiana city of Fort Wayne, like many other communities in the Midwest, is faced with seasonal contamination of its water supply by the herbicide atrazine, a restricted-use pesticide that is most often applied as a pre-emergence herbicide for corn. Fort Wayne draws its source water from the St. Joseph River. As a result, any con-

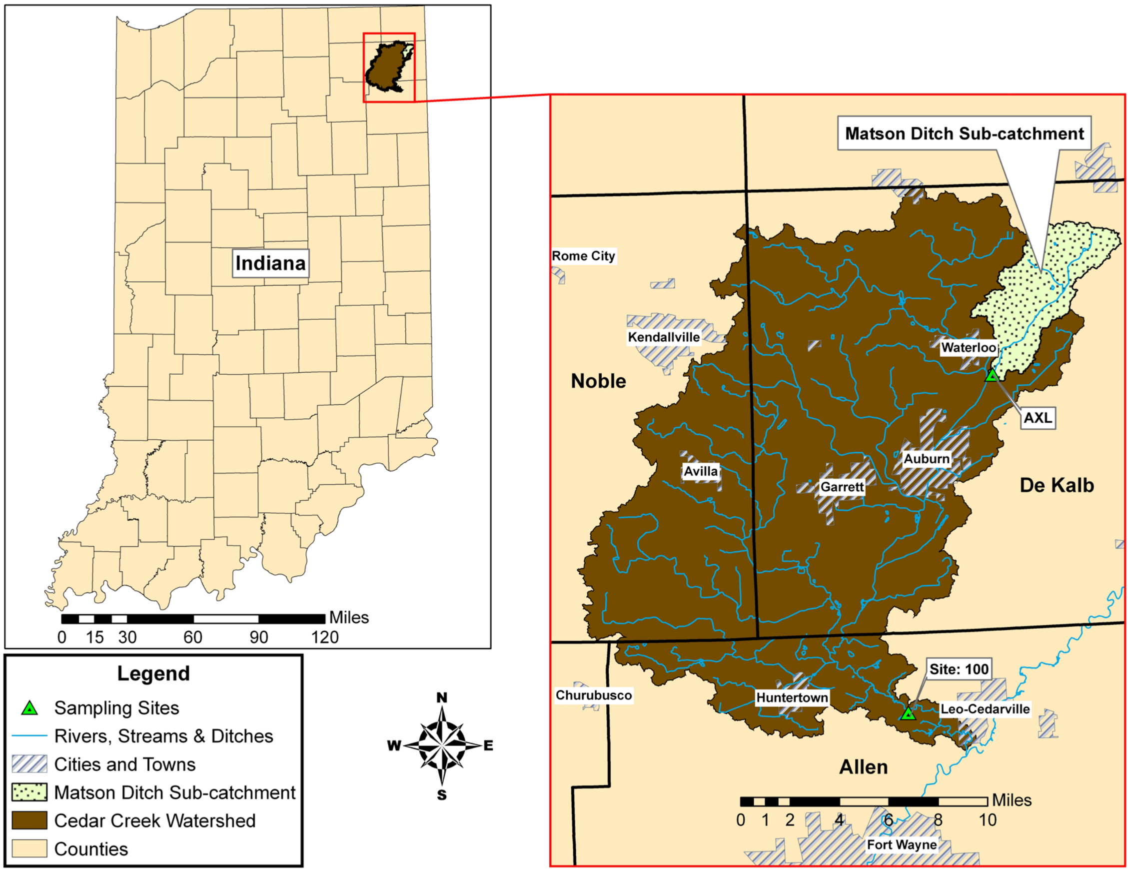

Figure 1. Cedar Creek watershed and Matson Ditch sub-catchment in northeast Indiana.

tamination of the source water of the St. Joseph River, upstream from Fort Wayne's intake, directly impacts the drinking water of approximately 250,000 residents. Risk analysis has identified the 707 km^2 Cedar Creek subwatershed of the St. Joseph River watershed and consequently the 45 km^2 Matson Ditch sub-catchment (MDS) of the Cedar Creek watershed (CCW) as potentially significant sources of the contamination (Vazquez-Amabile et al., 2006).

The largest tributary to the St. Joseph River is Cedar Creek, draining about 707 km^2 with drainage areas in DeKalb, Allen, and Noble Counties, Indiana (fig. 1). The CCW is located in the northeast Indiana portion (41° 4′ 48″ to 41° 56′ 24″ N and 84° 52′ 12″ to 85° 19′ 48″ W) of the St. Joseph River watershed. The CCW is comprised of two 11-digit hydrologic unit code watersheds, the Upper (04100003080) and Lower (04100003090) Cedar Creek. The Matson Ditch sub-catchment (MDS) of the CCW, located within DeKalb County, Indiana, drains approximately 45 km^2 of predominantly agricultural land in the northeast portion of the CCW (fig. 1). The topography of the CCW is generally flat to gently rolling with morainal hills composed of till or sand and gravel with local relief ranging from 30 to 60 m and many depressional areas that hold water after large rainfall events (SJRWI, 2005; Greeman, 1994). The CCW has an elevation minimum of 238 m and maximum of 326 m above sea level, with the lowest point located in Allen County near the confluence of Cedar Creek and the St. Joseph River.

Previous water quality modeling conducted in CCW with the Soil and Water Assessment Tool (SWAT) model has been reported by Larose (2005), Vazquez-Amabile et al. (2006), Larose et al. (2007), and Heathman et al. (2008). Larose (2005) calibrated and validated the SWAT model on daily and monthly hydrology and pesticide concentrations to assess the probability of exceeding the U.S. EPA drinking water standards. The calibrated SWAT model performed well in predicting both hydrology and atrazine pesticide loadings, with validation model efficiencies of 0.56 and 0.43, respectively. Vazquez-Amabile (2006) calibrated and validated the model to streamflow and atrazine concentration with satisfactory results for streamflow (E_{NS} = 0.64) and poor results for atrazine concentration (E_{NS} = -2.01).

Materials and Methods

Model Inputs

Topography of the CCW and MDS was determined using the National Elevation Dataset (NED) Digital Elevation Model (DEM) at a resolution of 1/3 arc-second with an elevation resolution of ±7 m to delineate the subwatershed slopes, stream network, and the watershed and subwatershed boundaries (USGS, 1999). The DEM was projected to Universal Transverse Mercator (UTM) NAD83, Zone 16 for the state of Indiana, re-sampled to an exact 10 m grid, and burned in at 1 m with the stream networks from the National Hydrography Dataset (NHD). The CCW was delineated using the TopAGNPS program (Garbrecht and Martz, 1999) within the AnnAGNPS ArcView interface (version 3.57 a2; USDA-ARS, 2006) using a critical source area (CSA) of 100 ha and minimum source channel length of 100 m. This CCW delin-

Table 1. Comparison of land cover classifications reported by the St. Joseph River Watershed Initiative (SJRWI) and those used in AnnAGNPS for the Cedar Creek watershed.

SJRWI Classification	AnnAGNPS Classification	% of Total Land Area	
		SJRWI	AnnAGNPS
Cropland	Corn and soybeans	51	62.8
CRP and other	Pasture, CRP, farmstead, and other	22	25.8
Forest	Forest	10	8.6
Urban	Urban	4	2.8
Wetlands	Water	13	<0.01
	Total:	100	100

eation resulted in a total area of 703.2 km^2 divided into 942 cells with an average area of about 75 ha. The MDS was included in this delineation with an outlet identified at the downstream end of reach 328 with a total area of 44.7 km^2. This CCW delineation (703.2 km^2) corresponded well with that of the U.S. Geological Survey (USGS), which identified CCW as 707.5 km^2, and MDS (44.7 km^2) corresponded well with Hogart (1975), who identified MDS as 45.07 km^2.

Spatial distribution of soils for AnnAGNPS cells in the CCW and MDS (Zuercher, 2007) was determined using the SSURGO spatial dataset. The dominant soils in the CCW are Blount (25% of the watershed), followed by Morley (16%), Pewamo (16%), and Glynwood (10%), with the remaining areas consisting of 41 other SSURGO soil series. Soil properties for the representative soils were retrieved in an AnnAGNPS input format using the National Soil Information System (NASIS) soil database. Due to a lack of soil data for muck soils and problems with how AnnAGNPS handles these, 56 AnnAGNPS cells (2765 ha) that were determined to have predominately muck soils were converted to Blount silt loam (BaB2), the predominant soil in the watershed.

A description of land cover in the CCW and MDS was determined from the USDA National Agricultural Statistics Service (USDA-NASS, 2001) Indiana Cropland Data Layer. The approximate scale of the 2001 imagery used was 1:100,000 with a ground resolution of 30 × 30 m. The Indiana Cropland Data Layer was converted from a raster file to an ESRI shapefile (ESRI, 1998) using ArcView. We evaluated the assigned land uses and determined that there was an overestimation of pasturelands and farmsteads and underestimation of soybeans, corn, and forest. A manual correction was conducted by overlaying the intersected land use and cover shapefile onto a color digital orthoquad (USDA-FSA-APFO, 2003) and the USDA National Agricultural Statistics Service (USDA-NASS, 2001) Indiana Cropland Data Layer in ArcView, and reclassifying the incorrectly assigned values. The corrected land cover was reasonably representative of the true condition, as shown in table 1 (SJRWI, 2005). For more detailed land classification maps, see Zuercher (2007).

Management Scenarios

Management operations were assigned to each classification of land cover in the CCW and MDS. For agricultural data, area-specific information on management activities collected for CCW during February 2005 was used as input for the model. Both the CCW and MDS are dominated by a corn-soybean rotation, with the majority of planting occurring between late April and the end of May (USDA-NASS, 2006) and corn planting starting before soybeans. Atrazine is

Table 2. Corn planting progress with subsequent atrazine application in Indiana for 2006.

Date (2006)	Cumulative Planted Area (%)	Incremental Change from Previous Application (%)	Atrazine Application (kg ha^{-1}) (1.46 kg ha^{-1} × % incremental change)	Cumulative Rate (kg ha^{-1})
April 17	3	3	0.04	0.04
April 24	9	6	0.09	0.13
May 1	33	24	0.35	0.48
May 8	52	19	0.28	0.76
May 15	74	22	0.32	1.08
May 22	77	3	0.04	1.12
May 30	89	12	0.18	1.30
June 5	100	11	0.16	1.46

the primary herbicide utilized for weed control on corn acreage in the watershed, with the majority applied as a pre-emergent spray. For this study, atrazine application was divided into eight applications with rates progressively increasing toward the peak corn planting time and then decreasing as the planting season tailed off. The number of atrazine applications was based on the number of crop reports available to determine planting progress during the corn planting season. The 2006 seasonal progress for corn planted in Indiana and the subsequent application rates can be found in table 2. For Indiana, the NASS Agricultural Chemical Database reported a seven-year average (1996 to 2002) of 1.01 atrazine applications per year, with an average application rate of 1.46 kg ha^{-1} (USDA-NASS, 2004).

DeKalb County, which contains the majority of the CCW and the entire MDS, had 28% of corn and 82% of soybeans in no-till systems during the 2004 crop year (ISDA, 2004). AnnAGNPS assigns land cover based on the dominant land cover for each cell; likewise, this study also utilized the dominant tillage practice for each crop cover. Due to the lack of accurate tillage practice spatial datasets and the fact that AnnAGNPS only utilizes the dominant management practice for each cell, this study utilized 100% conventional tillage for the corn rotation and 100% no-till for the soybean rotation. For this study, conventional tillage was modeled as post-harvest chisel plow tillage followed by pre-plant cultivator tillage.

We used two crop and three non-crop management schedules. The two crop management schedules included a corn and soybean rotation and a continuous alfalfa management, while the three non-crop management schedules were urban, fallow, and forest. The planting date was set to May 15 for corn and May 30 for soybeans. Harvest occurred on November 15 for corn and October 15 for soybeans. The alfalfa management consisted of a continuous cycle of hay re-growth and harvest with fall senescence. The RUSLE database in the AnnAGNPS input editor was utilized to populate the annual root mass, cover ratio, rainfall height, and surface residue cover parameters in the non-crop section of the AnnAGNPS input editor. The RUSLE identifiers used in this study were forest, fallow, and residential, with the latter used for urban areas.

For simulation in the CCW, daily precipitation and maximum and minimum air temperatures were obtained from the NOAA National Climate Data Center (NOAA-NCDC, 2007) for the Garrett Station (Coop ID 123207) located at 41° 20′ N, 85° 8′ W, elevation 265.2 m above sea level. This weather station is located within the CCW and contained the dataset from 1989 to 2006 required for the simulation periods of this study. Climate data for the MDS simulations were obtained from the USDA National Soil Erosion Research Laboratory (NSERL) Source Water Protection Initiative (SWPI) climate monitoring site for the time period of 2002-2006 at the sampling location AXL (41° 24′ 58″ N, 85° 0′ 18″ W). Other daily climate parameters were generated by processing the measured daily precipitation and the maximum and minimum air temperature data with the Complete_Climate program (USDA-ARS, 1999). A three-year period was used to initialize the soil moisture for the calibration and validation runs.

Observed Data

The observed stream discharge data for the CCW were obtained from the USGS for Cedar Creek gauge station 04180000 located near Cedarville, Indiana (41° 13′ 8″ N, 85° 4′ 35″ W) for January 1, 1989, to December 31, 2006. AnnAGNPS models quick-return shallow subsurface flow but not baseflow, which meant that stream discharge needed to be separated into its baseflow and direct runoff components. For this study, flow separation was done to achieve a baseflow percentage that matched the 48% baseflow reported by Beaty (1996). The daily stream discharge data were processed using the Eckhardt recursive digital filter method (Eckhardt, 2005) in the Web-based Hydrograph Analysis Tool (WHAT; Lim et al., 2005) with the filter parameter set to 0.980 and the baseflow index maximum (BFI_{max}) set to 0.627. The processed daily stream discharge data had a baseflow index of 0.480, which corresponded well with the measured baseflow contribution in table 3. The direct runoff portion of the daily stream discharge data was then averaged on a monthly basis to obtain results that would correspond to the monthly averaged output from AnnAGNPS.

Observed atrazine concentration data for the CCW were retrieved for May 1996 through October 2004 from the St. Joseph River Watershed Initiative (SJRWI) water quality database for Cedarville (site 100: 41° 13′ 8″ N, 85° 4′ 35″ W) in the form of grab samples that were taken approximately once every week. The data were only available for spring to fall months, not continuously for the year, and were averaged on a monthly basis. As the SJRWI did not measure flow discharge, the values were simple averages, not flow-weighted. Herbicides in the samples were analyzed by laboratory technicians at the Three Rivers Filtration Plant in Ft. Wayne, Indiana, using standard immunoassay (ELISA) kits manufactured by Abraxis, Warminster, Pa. (SJRWI, 2008).

The observed stream discharge data for the MDS were obtained from April 1, 2006, to December 31, 2006, from the USDA NSERL SWPI database. The discharge was directly measured using an ISCO 2150 AVF sensor with a 2108 AD converter to an ISCO 780 analog module (Lincoln, Neb.: Teledyne ISCO, Inc.; www.isco.com/products/products3.asp?PL=2021010). Like Cedar Creek discharge, the Matson Ditch stream data were processed using the Eckhardt recursive digital filter method (Eckhardt, 2005) in WHAT (Lim et al., 2005). Once baseflow separation was completed, the direct runoff portion of the daily stream discharge data was averaged on a monthly basis to obtain results that would correspond to the monthly averaged output from AnnAGNPS.

The observed atrazine data for Matson Ditch were obtained from the USDA NSERL SWPI AXL stream monitoring site for 2002-2006. In 2002, atrazine concentrations were determined by Great Lakes Analytical Laboratories in Ft. Wayne, Indiana, using U.S. EPA Method 525.2 modified NPD, a solid-liquid sample extraction followed by analysis with a gas chromatograph spectrometer system. In 2003-2006, atrazine concentrations were determined at the USDA-ARS NSERL in West Lafayette, Indiana, using modified U.S. EPA Method 525.2, in which the atrazine in the samples was preconcentrated by solid-phase microextraction (Rocha et al., 2008) and quantified by gas chromatography with mass spectrometry. Monthly atrazine concentrations used in this article were simple averages obtained by adding all daily sample values within a month and dividing the sum by the total number of days in the month. The ISCO 6712 automated samplers used were programmed to collect both a continuous daily sample (one bottle per day) as well as runoff event samples (up to a maximum of 20 bottles for an event). The continuous daily samples were composites of six 50 mL samples collected every 4 h (total of 300 mL per day); this composite sample concentration was used for days without an event. Event samples (initiated by an observed rising flow stage) were a composite of three 100 mL samples of ditch water collected every 30 min. On days with events, a simple average of all event composite sample atrazine concentrations within a day (midnight to midnight) was used to represent that day. Like the stream discharge, atrazine data were only available for spring to fall months, when the herbicide was most likely to be present.

Model Evaluation

AnnAGNPS simulation results were evaluated by examination of the mean, standard deviation (SD), root mean square error (RMSE), coefficient of determination (R^2), percent bias (PBIAS), and the Nash and Sutcliffe (1970) model efficiency coefficient (E_{NS}). A comparison of both mean and SD indicates whether the frequency distribution of the model results is similar to the measured frequency distribution. The RMSE is an estimate of the standard deviation associated with a simulated mean value. The R^2 value gauges the strength of the linear relationship between the observed and simulated values. The E_{NS} simulation coefficient indicates the consistency with which simulated values match observed values and how well the plot of observed versus simulated values fits the 1:1 line. The E_{NS} can range from $-\infty$ to +1, with 1 being a perfect agreement between the model and observed data and negative values indicating that the observed

Table 3. Cedar Creek streamflow characteristics.

USGS Station	Total Drainage Area (km^2)	Annual Mean Discharge Rate (m^3 s^{-1})	Annual Runoff (cm)	Annual Extreme Mean Discharge Rate (m^3 s^{-1})		Baseflow (% of total runoff)
				Maximum	Minimum	
Cedar Creek near Cedarville	699.3	7.2	32.6	13.7	2.4	48

data mean is a better predictor than the model (Santhi et al., 2001; Van Liew and Garbrecht, 2003; Moriasi et al., 2007). Simulation results in this study were considered to be satisfactory if $0.36 \leq E_{NS} \leq 0.75$ and good if $E_{NS} \geq 0.75$ (Van Liew and Garbrecht, 2003). Additionally, PBIAS, described by Gupta et al. (1999) and Moriasi et al. (2007), was calculated to assess model performance, as it indicates the average tendency of the simulated values to be greater or lesser than the corresponding observed values. Moriasi et al. (2007) provided general performance ratings for prediction of streamflow using PBIAS: very good ($0.0 \leq$ PBIAS < 10%), good (10% $\leq$ PBIAS < 15%), satisfactory (15% $\leq$ PBIAS < 25%), and unsatisfactory (PBIAS $\geq$ 25%). No PBIAS ratings were provided for pesticide constituent predictions in runoff water (Moriasi et al., 2007).

Calibration and Validation

Datasets were prepared using the AnnAGNPS version 3.57 a2 ArcView interface and input editor (Bingner and Theurer, 2005). The pollution loading model used for simulations in this study was version 4.00 a 023 (Bingner et al., 2007). Calibration of the AnnAGNPS model for stream discharge was done on a monthly basis for both the CCW and MDS. Model calibration was accomplished by comparing the baseflow-separated observed stream discharge values with those produced by the AnnAGNPS simulations. The statistics for E_{NS} and R^2 were evaluated to determine the model's efficiency and the proportion of variation in the observed discharge that is explained by the model output. Das et al. (2004) reported that the most sensitive AnnAGNPS parameters for runoff volume were the SCS runoff curve number (RCN) and precipitation, and to a lesser degree the Manning's "n" and hydraulic conductivity. Calibration of stream discharge was accomplished by adjusting the RCN and interception evaporation values. Calibration simulations were performed until the E_{NS} and R^2 values exceeded 0.5 and further changes to corresponding calibration parameters failed to improve the model's performance. The calibration period for the CCW flow was from January 1989 to December 1998, while the validation period was from January 1999 to December 2006. For the MDS, reliable flow data were only available for April to December 2006, so only calibration was possible.

Atrazine concentration calibration for the MDS and CCW was conducted after the stream discharge had been calibrated. Since there were no previous calibration studies for pesticides using the AnnAGNPS model, there was no information on the sensitivity of the model for any of the pesticide parameters. For this study, pesticide calibration was achieved by adjusting the percentage of pesticides applied to the soil and foliage and the percentage washoff from foliage. These parameters were chosen because they did not interfere with the stream discharge calibration and tended to be variable under different management and field conditions. Like the stream discharge calibrations, calibration of pesticide concentrations was completed when the E_{NS} and R^2 values exceeded 0.5 and further changes to corresponding calibration parameters failed to improve the model's performance. For the MDS, the atrazine calibration period was April to December 2006, whereas the validation period was June 2002 to October 2005. For the CCW, atrazine calibration was conducted from May 1996 to September 2000 and the validation period was April 2001 to October 2004.

Results and Discussion

Initial AnnAGNPS simulation results for the CCW, prior to calibration, are shown in table 4 and figure 2a. The stream discharge predictions showed satisfactory performance based upon the E_{NS} statistic (0.44) but unsatisfactory results based upon the PBIAS value of -30%. Mean comparison tests indicated that the predicted mean stream discharges were not significantly different from the observed. However, the time series data in figure 2a show a consistent overprediction in the months of July through January.

Cedar Creek Flow Calibration and Validation

Calibration of stream discharge in the CCW was conducted on a monthly basis for January 1, 1989, to December 31, 1998. While not significant ($\alpha = 0.05$), initial model simulations showed that modeled stream discharge tended toward overprediction. Thus, RCN values for agricultural land were decreased by 10% and the model was re-run. Results showed that a 10% reduction in RCN was not sufficient to reduce mean runoff to the observed level and also indicated that the default maximum and minimum rainfall interception values were likely too low. Bingner et al. (2006) had similar problems with AnnAGNPS modeling of the Auglaize River watershed in northwest Ohio.

At this point, RCN values for agricultural land were returned to the initial values, and the maximum and minimum interception evaporation values were increased. Interception evaporation is defined in the model as the portion of precipitation that does not infiltrate into the soil or become runoff, but is retained on exposed surfaces and in puddles and small depressions where it can evaporate (Bingner and Theurer, 2005). This process of increasing maximum and minimum interception evaporation values continued until the observed and predicted mean stream discharge values were nearly equal. The final value for minimum rainfall interception used in this study was 1.99 mm, and the maximum interception evaporation value was 5.08 mm. Although much higher than the default values of maximum (2.5 mm) and minimum (0.2 mm), the minimum is within the range observed by Savabi and Stott (1994) for various crop residues, and the maximum is well within the average value of 12.3 mm reported by Brye et al. (2000) for prairie residue. Savabi and Stott (1994) reported average rainfall interception values of 2.3, 2.0, and 1.8 mm for winter wheat, soybeans, and corn residue, respectively. The adoption of conservation tillage, which increases

Table 4. AnnAGNPS performance for Cedar Creek watershed monthly stream discharge.

Modeling Phase	Time Period	Mean[a] ($m^3\ s^{-1}$)		SD ($m^3\ s^{-1}$)		ENS	R^2	RMSE ($m^3\ s^{-1}$)	PBIAS (%)
		Simulated	Observed	Simulated	Observed				
Initial	1989-1998	5.34 a	4.24 a	5.98	4.61	0.44	0.71	3.3	-30
Calibration	1989-1998	3.86 a	4.24 a	4.87	4.61	0.65	0.70	2.7	9.1
Validation	1999-2006	3.63 a	4.15 a	5.15	4.62	0.46	0.60	3.4	19

[a] Means in the same row followed by the same letter are not significantly different in a simple t-test with $\alpha = 0.05$.

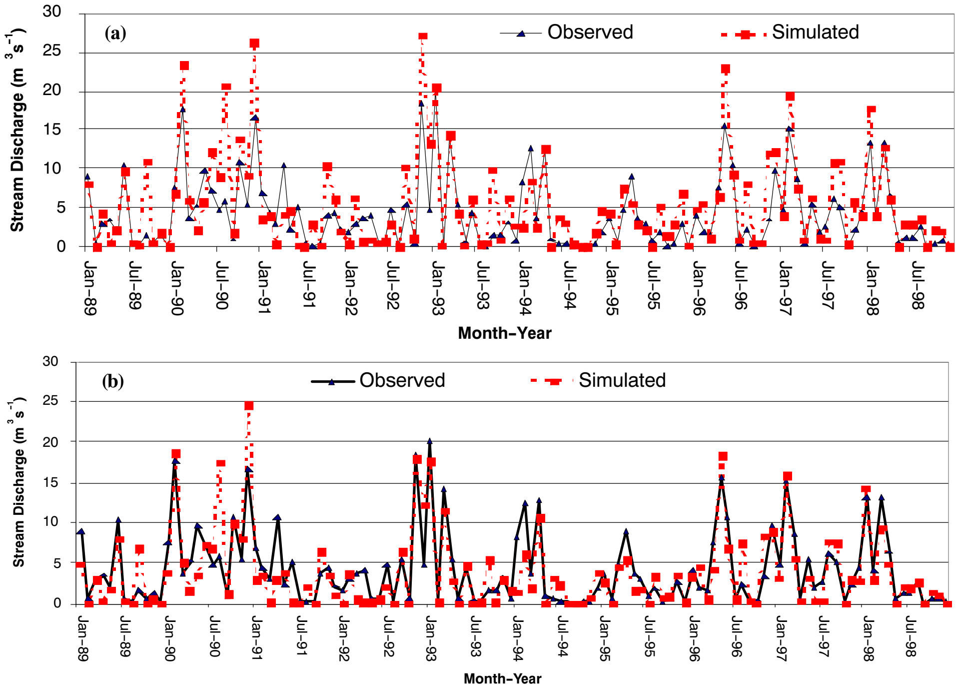

Figure 2. Observed and simulated monthly stream discharge versus time (a) before calibration and (b) after calibration for the Cedar Creek watershed.

residue, the implementation of CRP, and 10% forest in the CCW likely explain these elevated values. After modifying the interception values, RCN for agricultural land required additional adjustments. When they were increased by 10%, it resulted in an appreciable increase in prediction accuracy. However, stream discharge values for spring were overestimated, so early spring RCN values for agricultural land were returned to their original levels. Calibration of the model for stream discharge for the CCW was then considered to be complete.

Post-calibration simulations in the CCW showed major improvement in the PBIAS, E_{NS}, and mean discharge values (table 4). The time series data also appeared more reasonable, with far fewer overpredictions, minimal underpredictions, and greater accuracy during the July to January time period (fig. 2b).

The improvements in the summer months of July through September can be attributed to the increase in the maximum and minimum rainfall interception utilized during calibration. Since AnnAGNPS assumes that the actual evaporation on any given day's precipitation varies linearly between the maximum and minimum interception rates as a function of humidity (Bingner and Theurer, 2005), it is likely that the summer and fall months, with their higher average daily humidity, drastically limited interception evaporation when the default value was used.

Validation results from the calibrated model were satisfactory (table 4) but not as good as those obtained in the calibration period (E_{NS} reduced by 0.19, R^2 reduced by 0.10, and PBIAS increased by 10%), though this is to be expected. Overall, the simulated values were lower than the observed values, similar to that observed in the calibrated data. As was the case with the calibrated data, the values from January to June contained the majority of the underestimated values and those from July to December approached or exceeded the observed (fig. 3). This trend was likely associated with humidity, plant growth and seasonal patterns in the rainfall.

Matson Ditch Flow Calibration

Calibration of the model in the MDS involved two stages, one stage for stream discharge and the other for pesticide concentrations. Stream discharge and atrazine concentration

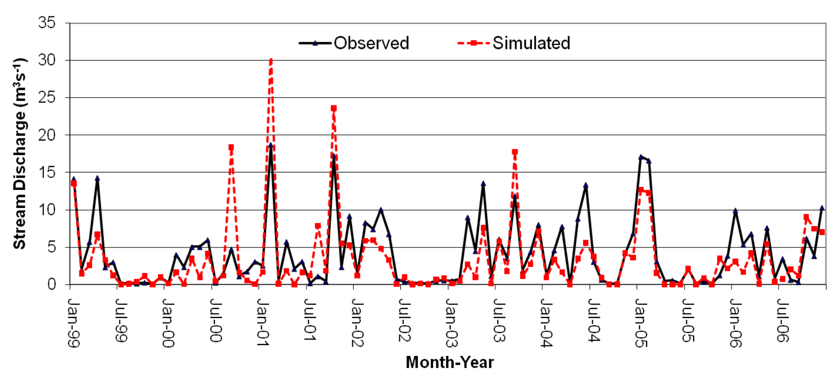

Figure 3. Validation period observed and simulated monthly stream discharge for Cedar Creek watershed.

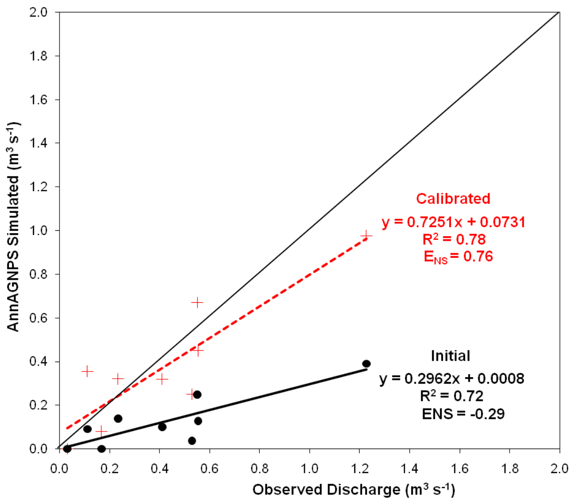

Figure 4. Simulated versus observed stream discharge before and after calibration for the Matson Ditch sub-catchment.

calibrations were performed on a monthly basis for the period of April 1, 2006 to December 31, 2006 in the MDS. The nine month calibration period was selected as it was the only time period when both atrazine concentrations and stream discharge data were directly measured. Utilization of a short calibration period likely limited the model's precision as it was not possible to select parameter values that could be calibrated over a wider range of climatic variation.

Similar to CCW, the calibration for Matson Ditch involved first adjusting the rainfall interception evaporation values and secondly adjusting the RCN for agricultural land. Initial results indicated that the model overpredicted stream discharge. Subsequently, the final rainfall interception minimum and maximum were reduced to 0.0508 mm and 1.016 mm respectively. The reduced rainfall interception values in the MDS were likely due to the lack of CRP and forest; as neither makes up 1% of the predominant land cover identified in the model and both have high rainfall interception rates (Gash et al., 1995; Clark, 1940). At this point, the RCN values were adjusted to improve the model's performance. Like the CCW, the MDS illustrated the same systematic differences in agricultural land RCN values with a 10% increase throughout the late spring to the end of winter and 10% decrease in early spring.

Calibration of the MDS was only completed for a nine month time period from April 2006 to December 2006. Due to the limited amount of accurate stream discharge data for the MDS, this short time period of data was the only workable option. Prior to calibration, results for MDS were unacceptable with significantly different ($\alpha = 0.05$) observed and simulated mean stream discharges as shown in table 5. In addition, the large PBIAS (71%) and negative E_{NS} value (−0.29) indicated that the model was not an adequate predictor of the observed values. The linear regression line showed that the overall model trend for simulated values was drastically below the observed values (fig. 4). The time series data in figure 5a show that the simulated stream discharge had

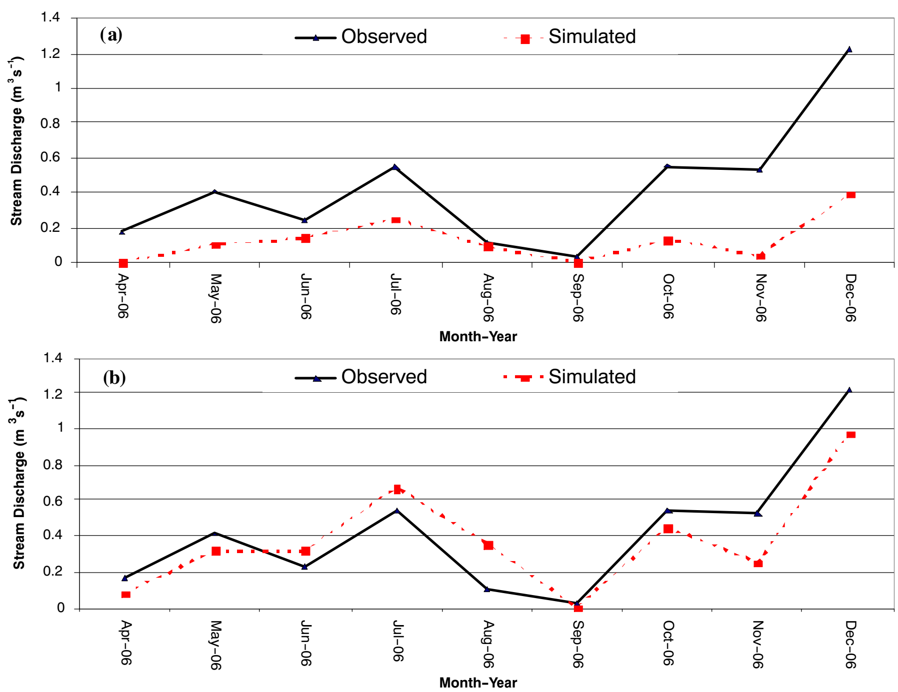

Figure 5. Observed and simulated monthly stream discharge (a) before calibration and (b) after calibration for the Matson Ditch sub-catchment.

Table 5. AnnAGNPS performance for Matson Ditch monthly stream discharge.

Modeling Phase	Time Period	Mean ($m^3 s^{-1}$)[a]		SD ($m^3 s^{-1}$)		ENS	R^2	RMSE ($m^3 s^{-1}$)	PBIAS (%)
		Simulated	Observed	Simulated	Observed				
Initial	2006	0.13 b	0.42 a	0.13	0.36	-0.29	0.72	0.39	71
Calibration	2006	0.38 a	0.42 a	0.30	0.36	0.76	0.78	0.17	10

[a] Means in the same row followed by the same letter are not significantly different in a simple t-test with $\alpha = 0.05$.

peaks and recessions in the same months as the measured values, but the magnitudes were greatly underestimated, and the differences in simulated and observed values grew as stream discharge increased. This trend was possibly due to an overestimation of infiltration and rainfall interception, although another reason may have been poor estimation of initial soil moisture conditions.

After calibration, the model statistical results greatly improved, with PBIAS decreasing to 10%, E_{NS} increasing to 0.76, and R^2 increasing to 0.78, and the mean stream discharge values were no longer significantly different (table 5). The linear regression equation in figure 4 illustrates that the observed values were still underestimated, but the extent to which this occurred was much more limited. Additionally, figure 4 shows that the model overpredicted when the observed monthly average discharges were below 0.3 $m^3 s^{-1}$ and underpredicted when they were above 0.3 $m^3 s^{-1}$. The time series stream discharge data (fig. 5b) demonstrated that the model overpredicted from June through August. Since this time period corresponds with increased crop cover, this pattern was likely related to the crop cover's interaction with precipitation. It is possible that the interception, evapotranspiration, and plant uptake were underestimated during this time period and overestimated from post-harvest to crop emergence. Interception evaporation likely played the largest role since it was reduced during calibration to obtain better model performance. As AnnAGNPS only allowed single maximum and minimum values throughout the entire simulation, it is likely that the calibrated value was actually below the true value during the crop growing season and above the true value when the field cover was reduced. Although this discrepancy existed, the model's hydrologic performance for MDS was considered satisfactory based on the overall statistical results.

Matson Ditch Atrazine Calibration and Validation

Calibration of atrazine concentrations was conducted for the time period of April 1, 2006, through October 31, 2006, as these were the only complete months of observed pesticide and streamflow data. Atrazine concentration calibration was achieved by adjusting the percentage of pesticides applied to the soil and foliage and the percentage of pesticide washoff from foliage. After the initial run of the calibrated stream discharge model, pesticide concentrations were unrealistically low (fig. 6). After exhaustively evaluating the inputs to the model with no improvement, concern was raised that the model pesticide routine was not functioning properly.

Correction to AnnAGNPS Model Code

A copy of the AnnAGNPS PL model version 4.00 a 023 source FORTRAN code was obtained from the model developers and analyzed for errors. Testing and evaluation revealed an error in line 1035 of Insitu_Routines/Insitu_Pesticides.f90. The original line read:

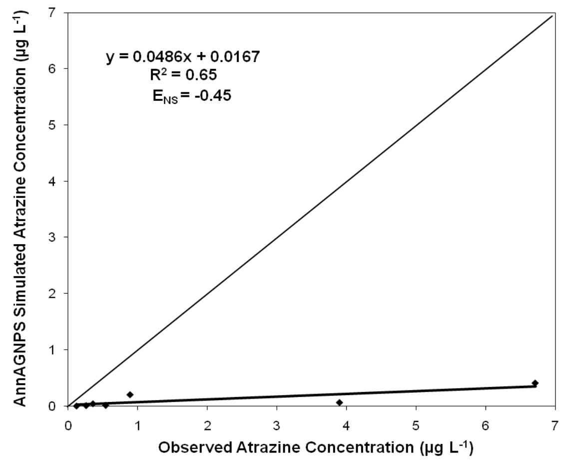

Figure 6. Observed and simulated monthly atrazine concentrations before calibration or code change for Matson Ditch sub-catchment.

```
rnof_H2O = cell_sur_rnof / ptcs%da_tot
```

where cell_sur_rnof is defined as surface unit area flow (mm), ptcs%da_tot is total drainage area of the cell (ha), and rnof_H2O is cell runoff (cm). The GLEAMS code in the model expects runoff to be in centimeters. To obtain this, the value for cell surface runoff needs to be in megagrams. In the corrected code, this is now calculated and given the value cell_sur_rnof_Mg. The corrected GLEAMS code sequence in AnnAGNPS now reads:

```
IF (ptcs%da_tot > 0.) THEN
rnof_H2O = cell_sur_rnoff_Mg / ptcs%da_tot ELSE
rnof_H2O = 0.
ENDIF
rnof_H2O = rnof_H2O / 100
```

Due to this error, input runoff depth for the pesticide calculations was drastically underestimated, helping to explain the original unrealistically low pesticide output values. This error and correction were reported to the AnnAGNPS model developers, and their response was that the evaluation was correct and an updated version of AnnAGNPS with this correction would be made available in the near future (R. Bingner, personal communication, 24 Oct. 2007). Simulations were re-run with the corrected model code, and the initial uncalibrated pesticide predictions were now much greater than those observed (table 6). A review of the latest publicly released version (AnnAGNPS 5.00) on 18 June 2010 revealed that this code change has been officially released.

The initial model output from the corrected model greatly overestimated the observed atrazine concentrations. As shown in table 6, the mean simulated value was approxi-

Table 6. AnnAGNPS performance for Matson Ditch monthly atrazine concentration with corrected code.

Modeling Phase	Time Period	Mean[a] (µg L^{-1})		SD (µg L^{-1})		ENS	R^2	RMSE (µg L^{-1})	PBIAS (%)
		Simulated	Observed	Simulated	Observed				
Initial	2006	63.3 a	1.91 b	88.4	2.77	-1540	0.33	100	-3200
Calibration	2006	2.04 a	1.91 a	2.69	2.77	0.93	0.93	0.69	-6.7
Validation	2002-2005	1.17 a	1.57 a	2.01	2.68	0.82	0.88	1.1	-25

[a] Means in the same row followed by the same letter are not significantly different in a simple t-test with α = 0.05.

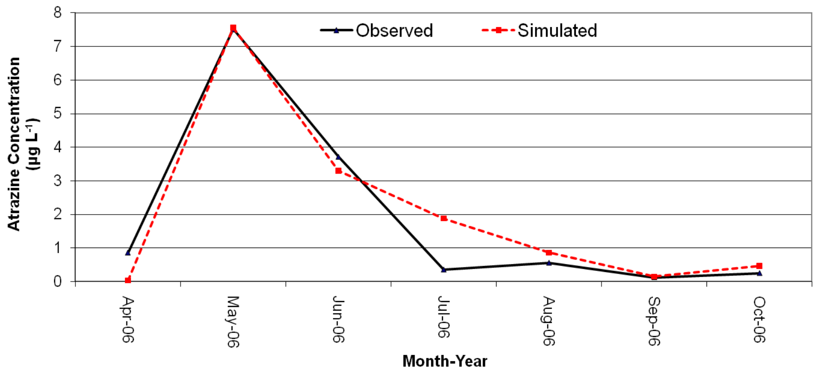

Figure 7. Calibration period observed and simulated monthly atrazine concentration for Matson Ditch sub-catchment in 2006.

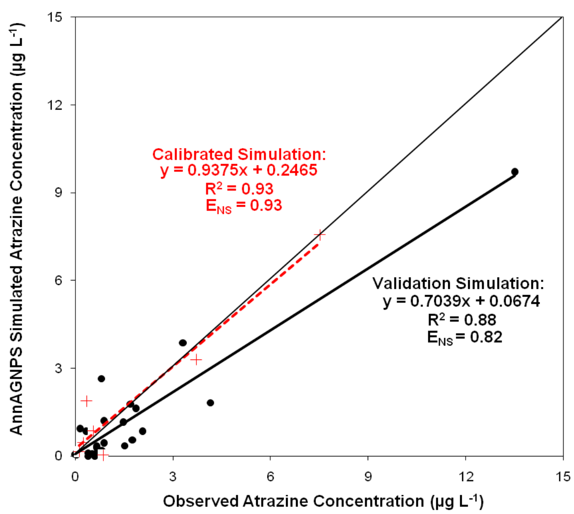

Figure 8. Simulated versus observed atrazine concentration for before and after calibration for Matson Ditch sub-catchment.

mately 33 times larger than the observed, PBIAS was −3200%, and the E_{NS} value was −1540. The model greatly overpredicted pesticide concentrations at application and moved nearer to the observed in September.

As a result, it was determined that more of the atrazine needed to be applied to the foliage since crop residue can act as foliage in AnnAGNPS (R. Bingner, personal communication, May 2007). Additional simulations confirmed that the model overpredicted when as little as 5% of the atrazine was soil applied. As a result, additional calibration runs proceeded with 100% of the atrazine applied to the foliage.

Final calibration of the model was accomplished with 100% of the atrazine applied to the foliage and the pesticide washoff fraction adjusted to 14% from 45%. The statistical results (table 6) indicated that the calibrated model had good performance in predicting atrazine concentrations for the very limited seven-month period studied here. With the exception of the month of July, the time series data (fig. 7) exhibited exceptional consistency, which revealed AnnAGNPS's ability to accurately predict atrazine degradation timing when the model was appropriately calibrated. The linear regression line in figure 8 was consistently near the 1:1 line, meaning that there was limited over- or underprediction by the model.

Although this calibration of the model showed good results, it is not really correct to apply 100% of the atrazine to the foliage. Although measured atrazine concentrations were not partitioned into attached and dissolved components, the percentage of attached atrazine was likely drastically overestimated in the model output. The calibrated pesticide model output showed roughly 12,000 times more attached than dissolved pesticide. Since atrazine is moderately soluble (33 mg L^{-1}), the concentration of dissolved pesticide should greatly exceed the sediment-attached fraction. The Mickelson et al. (2001) study of various tillage and incorporation techniques for pesticides near Boone, Iowa, reported that at least 95% of the total loss of atrazine recorded in the study was found in solution. Overall, this would suggest that the science in the pesticide model component may need updating or recoding.

Validation for monthly atrazine concentration values during 2002-2005 with the corrected and calibrated AnnAGNPS model showed very good results, with an E_{NS} of 0.82 and R^2 of 0.88, as shown in table 6. This is quite encouraging given the extremely limited calibration period. The linear regres-

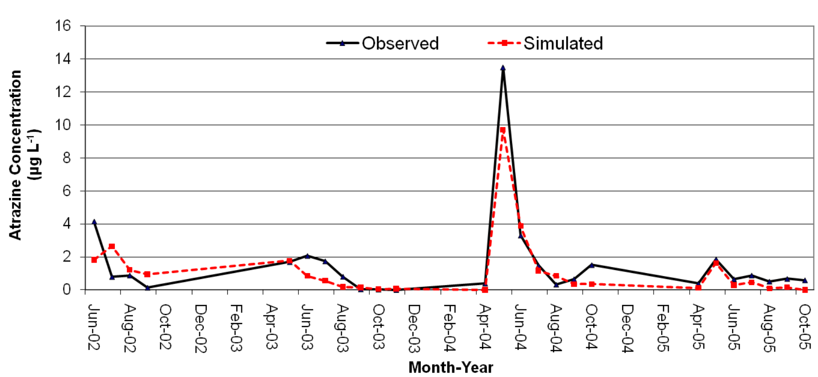

Figure 9. Validation period observed and simulated monthly atrazine concentration for Matson Ditch sub-catchment.

Table 7. Cedar Creek monthly atrazine concentration statistics.

Modeling Phase	Time Period	Mean[a] (μg L^{-1})		SD (μg L^{-1})		ENS	R^2	RMSE (μg L^{-1})	PBIAS (%)
		Simulated	Observed	Simulated	Observed				
Initial	1996-2000	20.6 a	1.25 b	33.2	1.59	-560	0.53	37.	-1600
Calibration	1996-2000	0.88 a	1.25 a	1.51	1.59	0.43	0.54	1.2	30
Validation	2001-2004	0.79 a	0.86 a	1.32	0.87	-0.09	0.53	0.89	8.7

[a] Means in the same row followed by the same letter are not significantly different in a simple t-test with $\alpha = 0.05$.

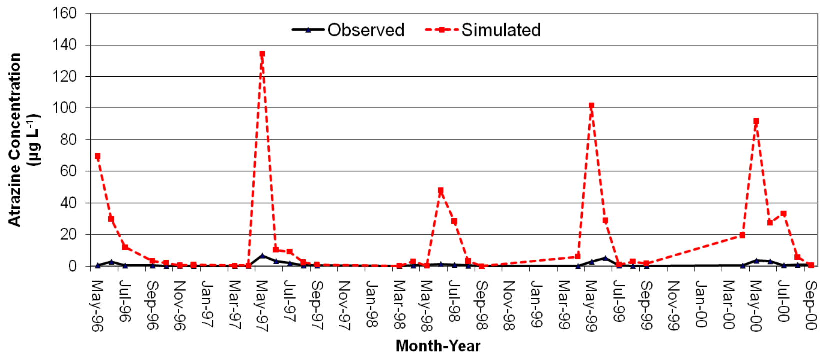

Figure 10. Observed and simulated monthly atrazine concentration before calibration for Cedar Creek watershed.

sion line on the 1:1 plot in figure 8 falls below the 1:1 line, which indicates that the model has an overall tendency to underpredict atrazine concentrations. The graph of time series data in figure 9 shows that simulated atrazine concentrations exhibited only slight seasonally consistent deviations from the observed concentration. The consistent deviations occurred during the months of June and July, where the model underpredicted for three of the four years. The lack of seasonal inconsistencies appears to indicate that the calibrated model may be applicable over a range of climatic and crop growth conditions.

Cedar Creek Atrazine Calibration and Validation

Calibration of the model for monthly average atrazine concentrations in the CCW was conducted from May 1996 through September 2000 for spring through fall months where both flow and atrazine data were available. Calibration was conducted using observed atrazine data from the SJRWI water quality database for site 100 (41° 13′ 8″ N, 85° 4′ 35″ W). Observed data were in the form of grab samples that were taken approximately once every week. Atrazine concentration calibration was achieved, in a similar fashion to that of the MDS, by adjusting the percentage of pesticides applied to the soil and foliage and percentage of pesticide washoff from foliage. Final calibration was achieved by adjusting the fraction of atrazine applied to the foliage to 100% and adjusting pesticide washoff fraction to 6.3% from 45%.

Utilizing the corrected code, the initial simulation with the model calibrated to CCW discharge produced poor results for prediction of atrazine concentration, with a PBIAS of −1600%, E_{NS} of −560, and R^2 of 0.53. These results were similar to those experienced in the simulations after the code correction and before calibration in the MDS, with simulated atrazine concentration being significantly overestimated. The simulated atrazine concentrations exceeded the observed concentration by approximately 17 times (table 7). The time series data (fig. 10) indicated that the model was able to predict the timing of the peaks but not their magnitude.

Statistical results (table 7) indicated that the calibrated model had sufficient performance in predicting atrazine concentrations for the five years of the simulation, with E_{NS} of 0.43 and R^2 of 0.54 (PBIAS was 30%). The mean simulated concentration for the calibration period was not significantly different from that of the observed values. The linear regression line in figure 11 is below the 1:1 line, illustrating that the model tended to underpredict atrazine concentration. In the time series data (fig. 12), the model underpredicted for four of the five years during the months of June through September. Similar to simulation in the MDS, the CCW simulations showed roughly 10,000 times more attached than dissolved atrazine.

Validation of the model for atrazine concentration in the CCW was conducted for the spring through fall months that had both atrazine and flow data during the four-year period from April 2001 to October 2004. Validation results for monthly values were poor, with an E_{NS} of −0.09 and R^2 of

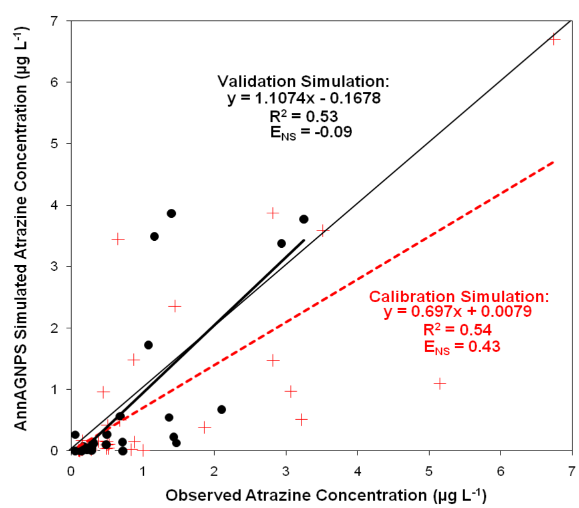

Figure 11. Simulated versus observed atrazine concentration for calibration and validation for Cedar Creek watershed.

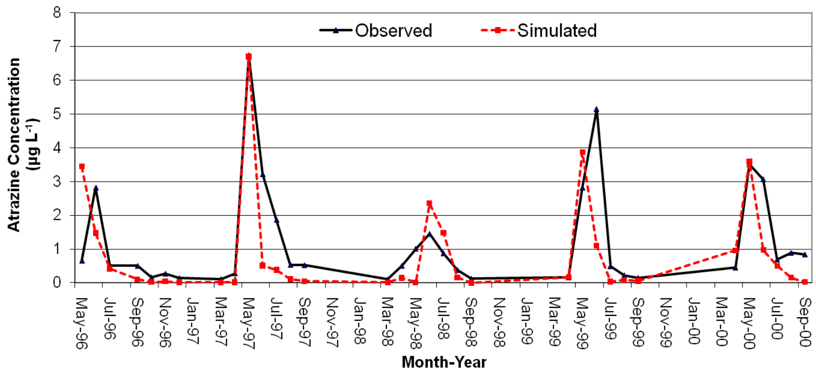

Figure 12. Calibration period observed and simulated monthly atrazine concentration for Cedar Creek watershed.

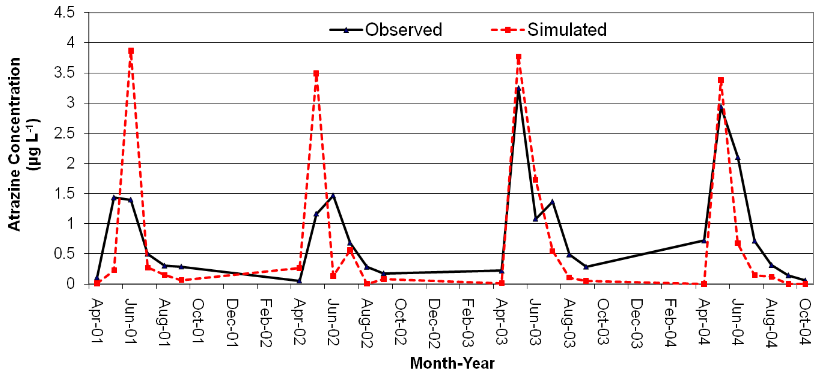

Figure 13. Validation period observed and simulated monthly atrazine concentration for Cedar Creek watershed.

0.53, although the PBIAS was quite low at only 8.7%. Although the E_{NS} was negative, the sample means were not significantly different (table 7). The linear regression line (fig. 12) is below the 1:1 line for observed values less than 1.56 μg L^{-1} and is above the line for values greater than 1.56 μg L^{-1}, meaning that the model tended to underpredict when concentrations were below 1.56 μg L^{-1} and overpredicted when they exceeded 1.56 μg L^{-1}. The time series data (fig. 13) show that the model greatly overpredicted the peak atrazine concentration in 2001 and 2002 and made reasonable predictions of the peaks in 2003 and 2004.

The source of the poor validation results could have been due to the coarse resolution of the sampling data utilized for calibration and validation. For the observed atrazine data, the time between grab samples for the SJRWI data ranged from 49 days to as little as one day with an average of nine days between samples for the nine years of available data. For the eight-year period from 1997 to 2004, the SJRWI sampling averaged less than one sample a week. Sampling frequency of the SJRWI data appeared more intensive when sampled atrazine concentrations were elevated. This likely increased the monthly average atrazine concentration, since there were more samples for events with high atrazine concentrations than for those with low atrazine concentrations. This sampling scheme and resulting data coarseness, although somewhat typical, likely deteriorated the ability to accurately calibrate the model.

Summary and Conclusions

The AnnAGNPS model hydrologic and pesticide routines were evaluated for their effectiveness at predicting stream discharge and atrazine concentrations in runoff water in the 707 km^2 CCW and the 45 km^2 MDS. A USGS 1/3 arc-second NED DEM, that was resampled to an exact 10 m grid and burned in at 1 m with the stream networks from NHD, was used to delineate the CCW into 942 cells that averaged 75 ha in size. Spatial soil data for both watersheds were obtained from SSURGO, while the soil physical properties originated from the National Soil Information System (NASIS) soil database. Dominant land use was determined by intersecting the delineated cells with the converted shapefile from the USDA NASS Indiana Cropland Data Layer. Management inputs such as the type of crops grown, tillage practices, fertilizers and pesticides used and the dates when field operations occurred came from the St. Joseph River Watershed Initiative (SJRWI) and the Soil and Water Conservation Districts (SWCD) of Allen, DeKalb, and Noble Counties.

The model was calibrated and validated against the best available data for each watershed. Hydrologic calibration simulations were performed from 1989 through 1996 for the CCW, with a resulting E_{NS} of 0.65, and in 2006 for the MDS, which resulted in an E_{NS} of 0.76. These results indicated that the model could be satisfactorily calibrated for discharge in both the MDS and CCW at watershed scale. Validation of the model calibrated to the CCW was done using independent data from 1997 to 2006, with a resulting E_{NS} of 0.46. Insufficient flow data were available for validation in the MDS. The satisfactory statistical results and evaluations of the flow time series graph indicated that model runoff predictions were reasonable.

Initial simulations of atrazine pesticide losses led to examination of the model source code, and ultimately correction of an error that had caused major underpredictions of atrazine losses. The original AnnAGNPS source code mistakenly routed runoff into the pesticide code as depth of runoff rather than mass. Corrections were made to the AnnAGNPS source code to properly route the runoff mass into the pesticide routine, and the corrected code was used for pesticide simulations in the MDS for 2002 through 2006. The results showed that calibration of the model to the MDS could produce very good results, with an E_{NS} of 0.93. However, calibration and validation for atrazine concentration was only possible by applying 100% of the atrazine to foliage, which is not realistic. Validation of the model was conducted from 2002 through 2005, and the resulting E_{NS} of 0.82 indicated that the model was capable of producing satisfactory predictions of atrazine concentrations in runoff in the MDS.

Calibration of AnnAGNPS for atrazine concentration in the CCW, utilizing the corrected model, for the time period of 1996 through 2000 produced satisfactory results, with an R^2 of 0.54 and E_{NS} of 0.43. However, like model simulations in the MDS, calibration was only possible by applying 100% of the atrazine to the foliage. Additionally, the washoff fraction had to be reduced to 6.3% from the default 45%. Validation of the model on independent data from 2001 to 2004 produced poorer results, with an R^2 of 0.53 and E_{NS} of −0.09. The poor validation results may be due, in part, to the coarse sampling resolution of the observed atrazine concentrations. Weekly grab samples increased uncertainty in the observed data by potentially failing to capture short high-concentration events. However, sampling intensity for this study was more frequent during high-flow events, which increased the likelihood that low concentrations in normal flow were not equally evaluated. Although the uncertainty with weekly grab samples is potentially high, it does not describe the drastic difference between the actual ground application of atrazine and the foliar application needed to calibrate the model.

Overall, this study found that the calibrated AnnAGNPS model produced satisfactory calibration and validation results for stream discharge. The study also revealed a number of problems within the pesticide routine of AnnAGNPS. Although reasonable predictions of atrazine concentrations were obtainable with calibration and validation using the corrected model in the MDS, several issues remain regarding the science in the model. In the CCW, validation and prediction were poor even though the calibration produced reasonable results.

Further review of the AnnAGNPS pesticide routine is needed to determine the cause of the underprediction of atrazine in solution and overprediction of total atrazine in runoff when atrazine is soil applied. Additionally, a sensitivity analysis is needed to determine why the model was relatively insensitive to RCN adjustments and quite sensitive to maximum and minimum interception evaporation adjustments in predicting runoff.

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