

Modeling Pesticide Runoff from Small Watersheds Through Field-Scale Management Practices: Minnesota Watershed Case Study with Chlorpyrifos

Authors: Gali, Rohith K., Cryer, Steven A., Poletika, Nicholas N., and Dande, Praveen K.

Source: Air, Soil and Water Research, 9(1)

Published By: SAGE Publishing

URL: <https://doi.org/10.1177/ASWR.S32777>

BioOne Complete (complete.BioOne.org) is a full-text database of 200 subscribed and open-access titles in the biological, ecological, and environmental sciences published by nonprofit societies, associations, museums, institutions, and presses.

Your use of this PDF, the BioOne Complete website, and all posted and associated content indicates your acceptance of BioOne's Terms of Use, available at www.bioone.org/terms-of-use.

Usage of BioOne Complete content is strictly limited to personal, educational, and non - commercial use. Commercial inquiries or rights and permissions requests should be directed to the individual publisher as copyright holder.

BioOne sees sustainable scholarly publishing as an inherently collaborative enterprise connecting authors, nonprofit publishers, academic institutions, research libraries, and research funders in the common goal of maximizing access to critical research.

Modeling Pesticide Runoff from Small Watersheds Through Field-Scale Management Practices: Minnesota Watershed Case Study with Chlorpyrifos

Rohith K. Gali¹, Steven A. Cryer², Nicholas N. Poletika³ and Praveen K. Dande⁴

¹Waterborne Environmental, Champaign, IL, USA. ²Dow AgroSciences LLC, Indianapolis, IN, USA. ³Risk Analysis Solutions, LLC, Carmel, IN, USA. ⁴Technosoft Corporation, Southfield, MI, USA.

ABSTRACT: Experimental studies of pesticide fate in surface runoff offer only a snapshot of the near semi-infinite parameter combinations that can and do occur in the environment, and mechanistic modeling is often used to supplement the often limited number of experimental observations. However, what has been lacking in pesticide surface runoff modeling is the impact of field-scale best management practices (BMPs) on the concentrations of pesticides found at the watershed outlet. A novel application of melding three agricultural models together was used to address field-scale BMPs and off-target pesticide environmental concentrations at the watershed scale resulting from agricultural surface runoff. These models were the pesticide root zone model [PRZM, an edge-of-field runoff and leaching model sanctioned by the US Environmental Protection Agency (USEPA)]; the United States Department of Agriculture-Agricultural Research Service watershed scale model, the soil and water assessment tool (SWAT); and the academic model, the vegetated filter strip model (VFSMOD). Watershed models such as SWAT, using high-resolution local input data, are capable of predicting watershed behavior but are limited when addressing field-scale BMPs. A unique method to approximate a small watershed as a linear combination of sub-basins and fields [hydrologic response units (HRUs)] is presented. Water, sediment, and pesticide runoff for each HRU are simulated using the USEPA field model PRZM. Daily edge-of-field PRZM predictions for pesticides in runoff water and eroded sediment are coupled with VFSMOD to address the effectiveness of a maintained vegetated filter strip (VFS) across the growing season in reducing pesticide loadings and water quality at the watershed outlet. Daily chlorpyrifos (CHP, insecticide) concentrations simulated for the Seven Mile Creek Watershed, MN, using the above modeling approach resulted in a spectrum of concentrations reported by the MN Department of Natural Resources. Simulated VFS effectiveness when used across all pesticide-treated fields ranged between 22% and 100% reductions in CHP mass across all runoff-producing events.

KEYWORDS: PRZM, SWAT, VFSMOD, BMPs, pesticide runoff modeling, chlorpyrifos

CITATION: Gali et al. Modeling Pesticide Runoff from Small Watersheds Through Field-Scale Management Practices: Minnesota Watershed Case Study with Chlorpyrifos. *Air, Soil and Water Research* 2016;9:113–122 doi:10.4137/ASWR.S32777.

TYPE: Original Research

RECEIVED: May 31, 2016. **RESUBMITTED:** August 15, 2016. **ACCEPTED FOR PUBLICATION:** August 28, 2016.

ACADEMIC EDITOR: Carlos Alberto Martinez-Huitle, Editor in Chief

PEER REVIEW: Five peer reviewers contributed to the peer review report. Reviewers' reports totaled 1408 words, excluding any confidential comments to the academic editor.

FUNDING: Authors disclose no external funding sources.

COMPETING INTERESTS: Authors disclose no potential conflicts of interest.

COPYRIGHT: © the authors, publisher and licensee Libertas Academica Limited. This is an open-access article distributed under the terms of the Creative Commons CC-BY-NC 3.0 License.

CORRESPONDENCE: sacryer@dow.com

Paper subject to independent expert single-blind peer review. All editorial decisions made by independent academic editor. Upon submission manuscript was subject to anti-plagiarism scanning. Prior to publication all authors have given signed confirmation of agreement to article publication and compliance with all applicable ethical and legal requirements, including the accuracy of author and contributor information, disclosure of competing interests and funding sources, compliance with ethical requirements relating to human and animal study participants, and compliance with any copyright requirements of third parties. This journal is a member of the Committee on Publication Ethics (COPE).

Provenance: the authors were invited to submit this paper.

Published by Libertas Academica. Learn more about this journal.

Introduction

Simulations of pesticide runoff (dissolved in water or entrained/adsorbed to sediment) from watersheds are an area of active research. Regulatory bodies such as the US Environmental Protection Agency (USEPA) often use field studies and field-scale environmental fate simulation models to approximate anticipated environmental concentrations in aquatic habitat and surface sources of drinking water. From a practical standpoint, any required management practice can only be targeted to individual fields within a watershed through product labeling since different fields often have different owners. Objectives for this work are to develop a novel approach to estimate environmental concentrations in pesticide runoff and watershed management (at the field scale) that can be used to predict the impact with and without management practices. The United States Department of Agriculture-Agricultural Research Service (USDA-ARS) soil and water assessment tool (SWAT)^{1,2} is used to parameterize unique sub-basins and fields within the watershed. The USEPA pesticide

root zone model (PRZM)^{3,4} is used to simulate edge-of-field runoff for these fields that map into the watershed boundary, and the impact of pesticide reduction/removal through a vegetative filter strip is simulated using the vegetative filter strip model (VFSMOD).^{5,6} These processes are linked and automated using a customized programmable interface.

There are limited field-edge models that have been used at the watershed level to address the impact of best management practices (BMPs) on the watershed at large. PRZM is a dissipation model developed and used by the USEPA to predict reasonable (daily) edge-of-field runoff predictions for agricultural scenarios. This model has been used concurrently at the watershed level by addressing edge-of-field estimates for pesticide, water, and sediment transport for every agricultural field that occurs within the watershed. A case study for the insecticide chlorpyrifos (CHP) runoff from a Minnesota watershed is provided, along with an insight into the impact that watershed scale and watershed subdivision have when mapping the watershed to a series of unique fields for approximating watershed behavior.

Materials and Methods

Pesticide runoff management tool. The pesticide runoff management tool (PRMT) is a conceptual system that brings together three mechanistic models (SWAT, PRZM, and VFSSMOD) to approximate pesticide losses in runoff (water and sediment) and the impact of vegetative filter strips on pesticide removal from surface runoff (Fig. 1). PRMT operates on a daily time step and simulates runoff, erosion, and pesticide loss over crop growing seasons for watersheds dominated by croplands with little/no stream network (ie, does not simulate pesticide routing mechanisms in streams). SWAT defines the watershed boundary, sub-basins within the watershed, and smaller unique areas known as hydrologic response units (HRUs). PRZM is used to simulate transport processes in HRUs, and VFSSMOD is applied to a grassed filter strip width delimited by the length of a stream reach associated with each sub-basin within the watershed. Details of each component in the PRMT are described next.

Soil and water assessment tool. SWAT is a deterministic, watershed-scale model developed by the USDA-ARS and Texas A&M AgriLife Research. SWAT predicts the impact of conservation practices and land use changes on surface and ground-water quality^{1,2} and is capable of simulating the impact to water quality resulting from long-term crop management changes. SWAT is parameterized by spatial and temporal data (land use, soil, topography, and meteorology) to estimate watershed hydrology, erosion, and chemical yields. SWAT partitions a watershed into sub-basins, and each sub-basin is further discretized into unique HRUs, making SWAT computationally efficient in modeling river basin-scale watersheds (Fig. 2). An HRU is a unique combination of land use, soil, and slope in each sub-basin.

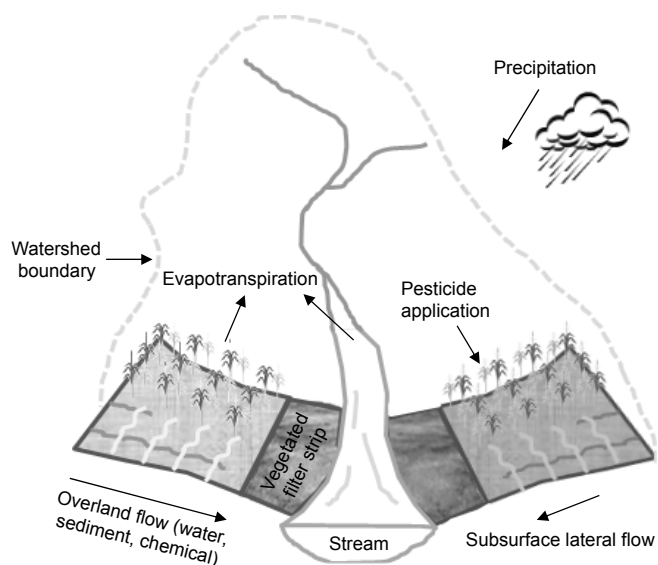


Figure 1. Hydrologic and chemical components simulated within a watershed by PRMT.

Pesticide root zone model. PRZM is a one-dimensional, field-scale, compartmental model developed by the USEPA to simulate pesticide fate and transport in surface soil and the crop root zone.^{3,4,7} PRZM has the capability to simulate hydrology, chemical volatility, fate and transport in soil, and soil temperature. Pesticide transport characteristics in surface runoff and lateral flow are the only mechanisms currently used and summarized in PRMT.

PRZM calculates surface runoff using the USDA NRCS Curve Number method⁸ and three methods for soil erosion: MUSLE,⁹ MUST, and MUSS.⁷ The pesticide fate and transport in the soil surface zone are tracked in dissolved, adsorbed, and vapor phases. Fate and transport processes include surface runoff, erosion, pesticide decay/transformation, volatilization, foliar wash off, advection, dispersion, uptake by plants, and sorption within the soil environment.

Every HRU within a sub-basin is simulated by PRMT as a unique field using PRZM. PRZM generates daily runoff, sediment yield, and pesticide in runoff and eroded sediment. Thus, PRZM runoff results for every HRU are summed to obtain an area-weighted average for each sub-basin. This approach allows for parameters known to impact runoff such as field slope, soil type, and cropping to represent hydrology and pesticide transport approximations. Actual geospatial field locations and sizes (eg, polygons) are not used to define a field boundary. Thousands to tens of thousands of unique HRUs are generated depending upon the associated data layers, watershed size, and the number of sub-basins the watershed is discretized into. For the case study provided, the number of HRUs (and thus PRZM simulations) ranged from 2000 to 6000, depending on the number of discretizing sub-basins selected in SWAT (discussed later). Also, subsurface and deep draining flows were excluded from the modeling results presented. This is appropriate given the physicochemical properties of CHP, which are indicative of a molecule of little to no vertical movement through the soil profile. This assumption would have to be relaxed for more water soluble pesticides.

Vegetative filter strip model. VFSSMOD is a field-scale, runoff event model developed by the Department of Biological and Agricultural Engineering, North Carolina State University (and now maintained by the Department of Agricultural and Biological Engineering at University of Florida). VFSSMOD can be used to design vegetative filter strips (VFSs) and evaluate strip performance on runoff reduction and sediment trapping efficiency at field scale.⁵ VFSSMOD has recently been used for season long VFS effectiveness.¹⁰ An empirical extension of VFSSMOD uses infiltration, sediment trapping, clay content in sediment, and a pesticide phase distribution parameter to calculate pesticide trapping efficiency.¹¹

For VFSSMOD parameterization, the width of the sub-basin is taken as the approximate width of the VFS. However, watershed discretization by SWAT often yields irregularly shaped sub-basins. In PRMT, the irregularly shaped sub-basins

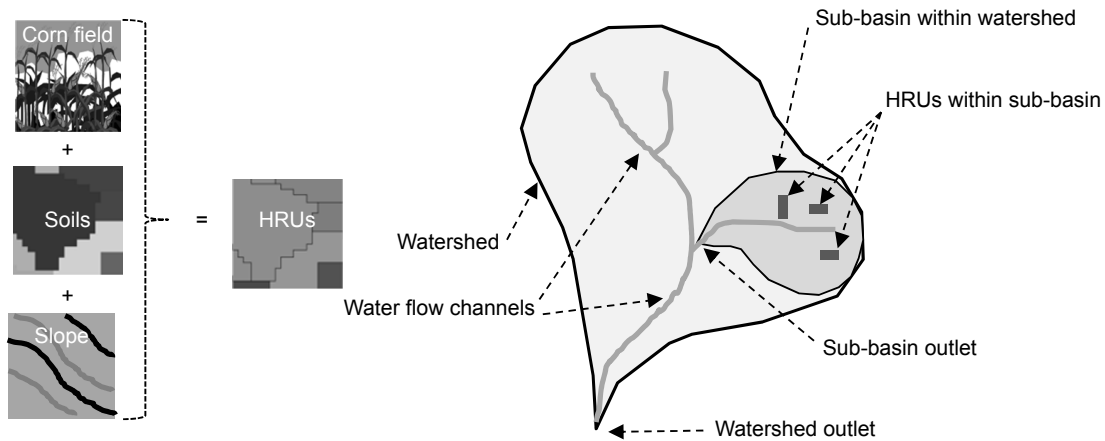


Figure 2. Breakdown of watershed into sub-basins, where each sub-basin is further discretized into a unique combination of HRUs where each HRU is a unique combination of slope, soil type and cropping.

were converted to a rectangular-shaped agricultural field by assuming that the length of reach in a sub-basin to be the width of agricultural field and VFS (Fig. 3). The length of the rectangular-shaped agricultural field is calculated by dividing the area of the sub-basin by the length of reach/width of the agricultural field.

The graphical user interface (GUI) for PRMT has user-defined cell prompts for other parameters required by PRZM and VFSMOD (eg, length of the buffer, attributes of the buffer vegetation, and so on). Currently for VFSMOD execution, all buffers are assumed a constant slope (linear) from the field edge (user supplied input). A summary of the VFSMOD parameters used to define the filter strip are found in Table 1.

Coupling SWAT, PRZM, and VFSMOD. PRMT is used to simulate the hydrologic cycle occurring within an agriculturally managed watershed (Fig. 1). A large watershed may include nonagricultural land such as prairies,

urban areas, forests, and so on, all of which contribute to the hydrology within the watershed that is routed to the watershed outlet. We hypothesize the most vulnerable watersheds for pesticide runoff are predominately agricultural and that noncrop pesticide uses are unimportant. This constraint/assumption is most likely true for smaller watersheds within the heartland of the United States. PRMT currently does not consider hydrology inputs from other land use categories (only agricultural land).

Generation of a SWAT input file is the first task that must be performed in implementing PRMT. The flowchart for PRMT illustrates the interconnectivity of SWAT, PRZM, and VFSMOD models (Fig. 4). Upon SWAT execution, a SWAT project database file is generated and populated with both input parameters and output predictions. The SWAT database provides the necessary information for parameterizing PRZM field simulations using properties associated

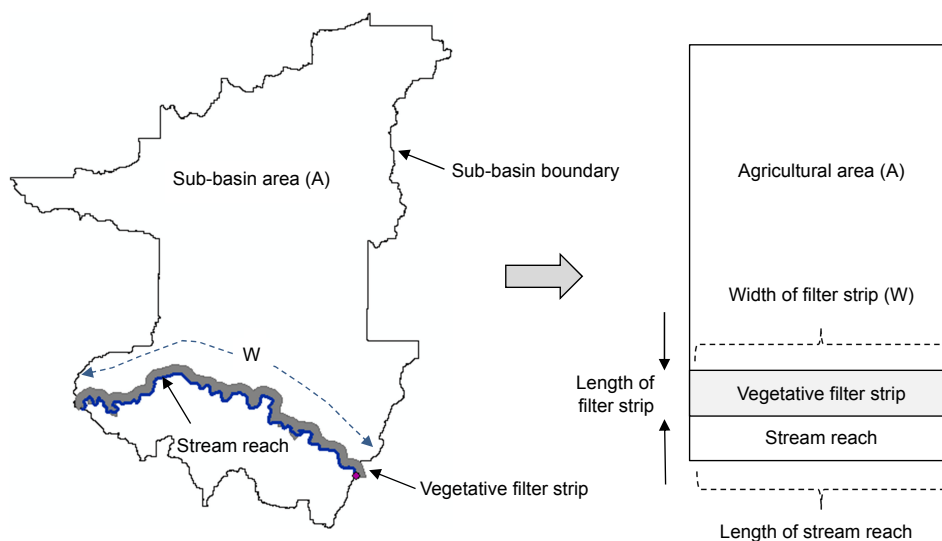


Figure 3. Calculating the width of the filter strip in an irregularly shaped sub-basin.

**Table 1.** VFS properties used in the assessment.

VFS PROPERTIES	VALUE	UNITS
Mannings roughness	0.4	–
Slope at each segment	0.03	%
Distance from the beginning of the filter	Varied	m
Saturated hydraulic conductivity	0.000035	m s ⁻¹
Green-Ampts average suction	0.268	m
Saturated soil water content	0.31	m ³ m ⁻³
Max surface storage	0.001	m
Spacing of filter media	4	cm
Filter media Manning's coefficient	0.20	–
Initial soil water content	0.53	m ³ m ⁻³
Height of grass	10	cm
Bare surface Manning's coefficient	0.02	–
% clay content in incoming sediment	50	%
Relative distance from upper filter edge check	0.5	–
Soil erodibility	0.04	–
Soil type	Silty clay	–
Courant number	0.8	–
Buffer length	8.65	m

with each specific HRU within the sub-basin and watershed boundary. Pesticide use rates and management practices are specified by the user as input via the PRMT GUI.

PRZM is executed to generate daily runoff, sediment yield, and pesticide in runoff and eroded sediment. When a pesticide producing runoff event is encountered, PRMT runs VFSMOD using the PRZM-predicted edge-of-field hydrology and pesticide runoff as input. Hourly values provide the necessary hydrology input for VFSMOD such that reduction of runoff, sediment, and pesticide mass can be simulated for each HRU in the watershed. PRZM runoff hydrographs are discretized into hourly events using results tabulated in Figure 5.3 of the PRZM runoff manual, which lists runoff event durations (hour) as a function of the time of the year and region of the US. Thus, runoff events are characterized each month by hourly runoff durations for the region of interest. A GUI, programmed in C#, was written to automate the process of connecting SWAT, PRZM, and VFSMOD and in acquiring all required input parameters for the various model executions. PRMT generates the PRZM input file by extracting data from the SWAT-generated watershed database and from user supplied PRZM inputs. Outputs include daily values for runoff and eroded sediment, pesticide loadings from each HRU simulated, and pesticide reductions as a result of VFS assumed at the sub-basin outlet (Fig. 3).

Case Study: MN Seven Mile Creek Watershed

The Middle Minnesota Basin (HUC 8 ID: 07020007) located in South central Minnesota covers an area of 3496 km² and is 1 of 12 basins draining to the Minnesota River. The Seven Mile Creek Watershed (SMCW), located in Nicollet

County, MN and lying east and south of the cities of Mankato and St. Peter, respectively, drains to Middle Minnesota Basin and is a tributary of the Minnesota River (Fig. 5). The Seven Mile Creek is a designated trout stream (8.34 km long) having a series of public drainage ditches in the upland agricultural drainage area that feed the creek. The SMCW was selected for investigation because in 2010, a single observation of CHP was found by the Minnesota Department of Agriculture in Seven Mile creek as part of their state monitoring program. This CHP residue detection occurred on September 2, 2010, with a magnitude of 0.24 µg L⁻¹. Data sets having multiple CHP runoff hits were not available at the time. However, the MN watershed offered a single CHP loading, which caused significant regulatory concern that prompted further investigation. And since this largely agricultural MN watershed could be easily discretized and modeled, simulation results were offered to the MN Department of Natural Resources (DNR) in support of CHP use within the state.

This watershed was selected by MN DNR since the majority of pesticide applications used CHP, CHP surface water concentrations were observed, and the large majority of the watershed was agricultural. As one deviates from these assumptions, then addition model refinement would be required as appropriate. Only if field runoff had occurred were the impacts of reduction due to filter strip BMP's used.

Filter strip estimates were assumed to follow the hourly hydrographs obtained in Figure 5.3 of the PRZM manual. In many cases for small runoff events, a vegetated filter strip (VFS) of standard geometry proved adequate to eliminate the entire chemical component. As the runoff magnitude is increased, then the VFS would lead to losses downstream of the buffer (ie, not all runoff producing events are eliminated from the simulation).

All model outputs summarized in this report are for the Seven Mile Creek basin in MN. This watershed was of concern to the MN DNR and thus selected since it offered the ability of comparing runoff predictions with modeling with little input required for runoff not containing pesticides. The MN DNR used monitoring data for this sampled watershed as a source for representative CHP usage throughout the state. Modeling an agricultural watershed simplifies the problem of determining CHP concentrations in surface water. Transient loadings for CHP within the watershed could be estimated. It would be difficult to obtain this type of information for watersheds that are made up of multiple different loads and load types (ie, ag and non-ag land), obtaining pesticide loadings for non-ag regions, and so on.

The SMCW is an agricultural dominated watershed with cultivated lands in over 79% of the watershed, while 10.3% has remained wetlands, mostly on the north side of the watershed. Deciduous forest land makes up 3.7% of the total watershed, mostly near the creek corridors. The SMCW is mostly flat with slopes between 0% and 3%, but steep slopes (>3%) are observed near creek corridors. The most recent glacial deposits

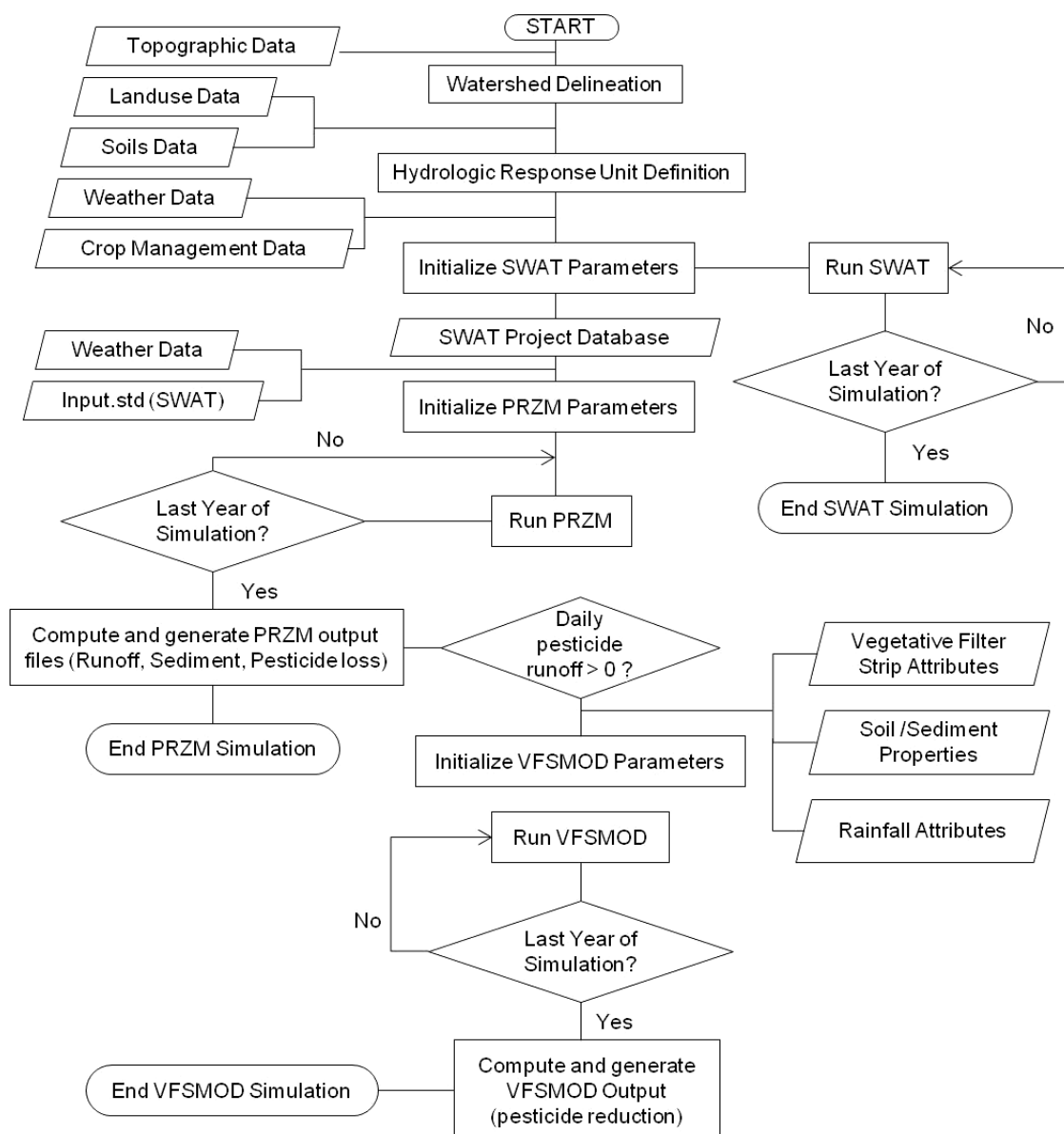


Figure 4. PRMT operation flow chart.

in this area produced deep nutrient rich but poorly drained soils. Therefore, much of the watershed contains subsurface tile drainage to remove excess water from subsurface soils to create healthy soil conditions for crops. Although not considered in this analysis (that only focuses on pesticides), the SMCW has about 20 feedlots, and the manure generated by these feedlots is used as fertilizer to supplement N and P to crops.

PRMT model inputs for study area. A 3-m resolution United States Geological Survey Digital Elevation Model¹² was used in this study to delineate streams, HRUs, sub-basins, and the watershed boundary using the built in algorithms of SWAT. The majority of the watershed (84%) is less than 3% slope. The area of SMCW is approximately 90.9 km². The USDA National Agricultural Statistic Service conducted an agricultural census in 2010 and developed a 1:100,000 land

use Crop Land Data layer for Minnesota. This land use layer was used to extract crop land data in the SMCW and major crops in the watershed [corn (46%) and soybean (32%)].

The USDA-NRCS Soil Survey Geographic database was used for soil input parameters for the SMCW. The soils in the watershed are mostly clay loam and silty clay loam. Daily precipitation estimates were obtained from the NWS NEXRAD database and were based upon centroid coordinates of the watershed (<http://www.roc.noaa.gov/WSR88D/NewRadarTechnology/NewTechDefault.aspx>).

CHP was applied to randomly selected fields in the SMCW using the CHP typical application rate of 1.3 kg ha⁻¹. Knowing the average CHP rate and the amount of material sold in the county from Dow AgroSciences sales records, the amount of treated acreage in the watershed could be estimated. A crop rotation of corn–soybean in all corn and soybean fields

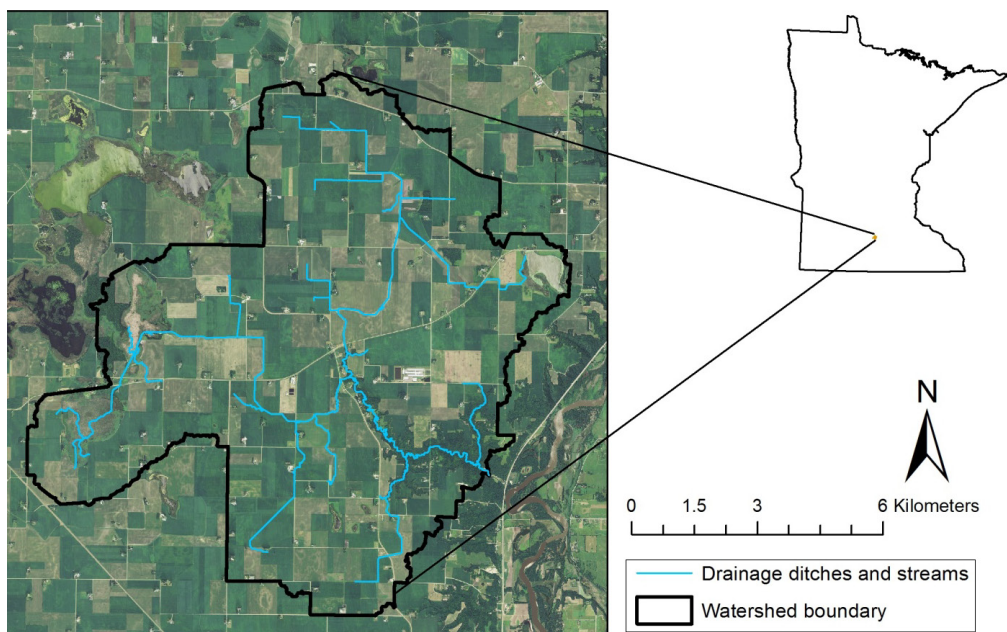


Figure 5. Location of SMCW in Minnesota, drainage ditches and streams in the watershed.

was used, and the total CHP applications in SMCW were 7795 kg in 2010 and 2012 and 3897 kg in 2011.

Sub-basin division. Five scenarios were created for the SMCW by varying the number of sub-basins (low, middle, and high) to assess the effects of watershed discretization on SWAT and PRMT output (Fig. 6). As the number of sub-basins that discretize the full watershed increases, the number of HRUs in the watershed also increases. This exercise was performed to understand if the number of HRUs in a watershed is a sensitive parameter for pesticide output calculations.

Watershed size surrounding the SMCW. An assumption of PRMT is that runoff from all fields is instantaneously combined to estimate runoff at the watershed or sub-basin

outlet. This assumption ignores the residence times associated with flow from the top of the watershed to the watershed outlet. To explore the ramifications of this assumption, three watersheds with different drainage areas were selected to compare the effects of stream routing on SWAT and PRMT output. The watersheds were centered on or near the SWCW (Fig. 7).

Results and Discussion

Hydrology. PRMT was used to simulate CHP runoff from the SMCW for three consecutive years (2010–2012) using historical daily weather records. Predicted runoff water yield was approximately 20% of the rainfall received by the watershed for each year simulated (Table 2). The cumulative

ID	# of sub-basins	# of HRUs
1	9	2272
3	27	2008
5	67	5643



Figure 6. Minnesota SMCW discretized into various sub-basins increments to explore impact of sub-basin scale/HRU density on simulated watershed behavior.

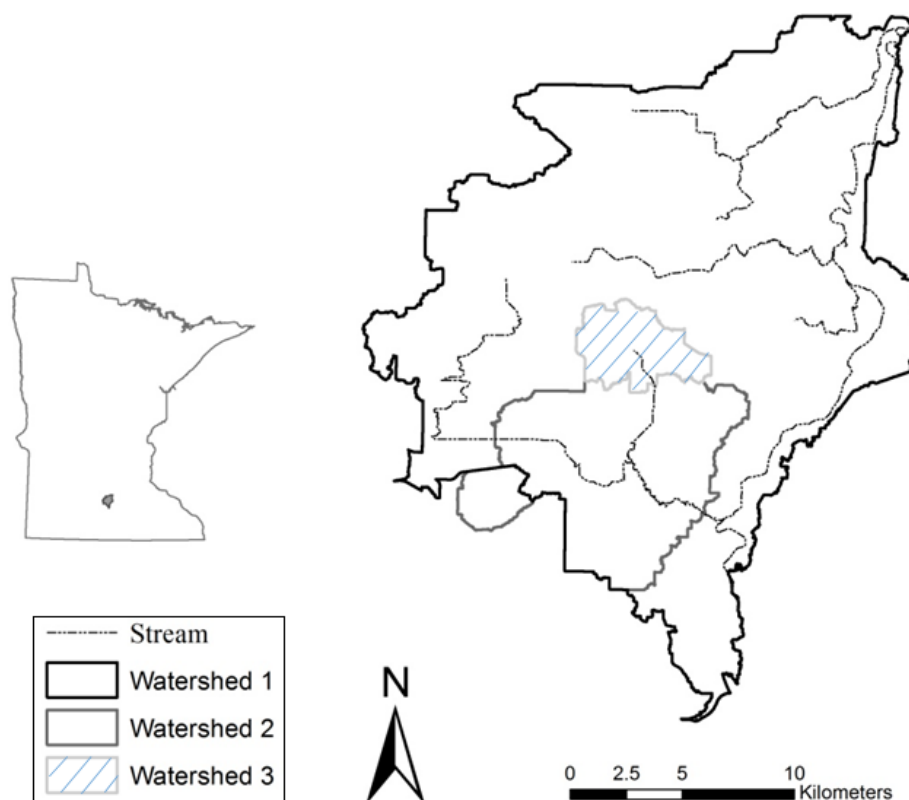


Figure 7. Increased drainage area surrounding the SMCW (Watershed 2 was the geometry used for the sub-basin discretization exploration for SMCW).

sum from all HRUs for CHP mass loss in runoff is also tabulated, illustrating relatively uniform percent CHP loss across the three years simulated. The lower amounts of CHP applied in year 2011 is due to the historical corn–soybean–corn rotation cycle that is common for this region, where more CHP is applied to corn than soybean.

PRMT daily output includes precipitation, runoff water and eroded sediment, and pesticide loadings in runoff (in water and sediment, Fig. 8). Pesticide interactions with water and sediment are often difficult to quantify. PRZM and VFSMOD does offer the user the ability to simplistically address different pesticides based upon easily measurable physical properties such as the pesticide equilibrium partition coefficient and degradation half-life. However, tabulated results for the highly sorbed insecticide CHP are assumed appropriate and acceptable for this molecule. Triangles on primary Y-axis represent PRMT-simulated CHP loads (kg). The CHP load in runoff, both dissolved and

bound to eroded sediment, varied from 0 to 0.8 kg, with CHP mass occurring in only a fraction of runoff events. Gray lines on secondary Y-axis represent daily rainfall, black lines on primary Y-axis represent PRMT-simulated daily runoff depth. The peak CHP load (0.8 kg d^{-1}) was observed on May 23, 2012, over the three years simulated. A simulated crop rotation of corn–soybean in all corn and soybean fields was used. CHP losses were 1.32 and 1.62 kg in 2010 and 2012, respectively, and 0.71 kg in 2011 (Table 2). Overall edge-of-field CHP losses in SMCW in 2010, 2011, and 2012 were approximately constant in terms of the percentage of CHP applied, typically less than 0.02% before any VFS management practices is assumed.

CHP is strongly sorbed to eroded sediment, and therefore, pesticide lost via erosion processes are dominant. For less strongly sorbed pesticides, such as many herbicides, then physical processes represented by PRZM should be addressed for correct order of magnitude predictions. PRZM was used

Table 2. Hydrology and chemical output from PRMT for the case study watershed.

YEAR	RAINFALL (mm)	RUNOFF (mm)	RAINFALL AS RUNOFF (%)	PESTICIDE APPLIED (kg)	PESTICIDE LOSS (kg)	PESTICIDE LOSS (%)
2010	695.2	138.8	19.9	7795	1.32	0.017
2011	487.2	100.2	20.5	3897	0.71	0.018
2012	504.8	96.7	19.1	7795	1.62	0.021

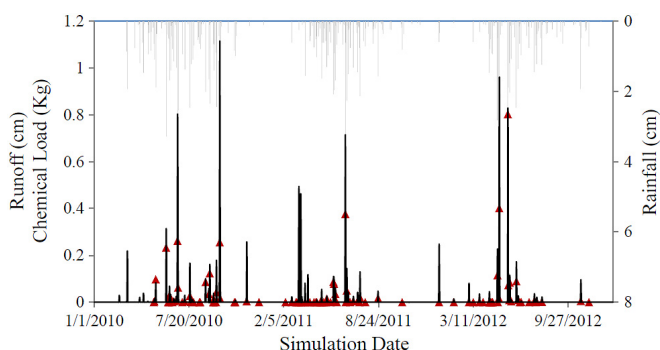


Figure 8. Daily runoff and chemical load in SMCW.

since this is the model of choice by the USEPA with regard to pesticide movement in and through soil.

Watershed size and sub-basin division. One advantage of PRMT is that a fully functional SWAT representation of the watershed is obtained and can be used for direct comparison against the PRMT representation of the watershed as a summation of individual HRU's runoff behavior within the watershed. The average annual runoff water (mm) and annual sediment load ($t\ ha^{-1}$) at SMCW outlet from SWAT and PRMT simulations is provided in Figure 9 for different sub-basin discretization for SMCW (Fig. 6). As the number of sub-basins increased, the SWAT model estimate for average annual runoff increased slightly, whereas the PRMT estimate in PRMT indicated little/no change in average annual runoff. The annual sediment load ($t\ ha^{-1}$) simulated by SWAT showed a small decrease in loads (% change ~10%), whereas output from PRMT remained constant, although the sensitivity of sub-watershed discretization is small. Similar order of magnitude trends, in both runoff and sediment output from PRMT, when contrasted with SWAT simulations was observed. Discrepancies between models may be attributed to lack of accounting for stream losses for the PRMT but are most likely created by the 21% of the SMCW that was nonagricultural and thus did not contribute hydrology and erosion to the watershed

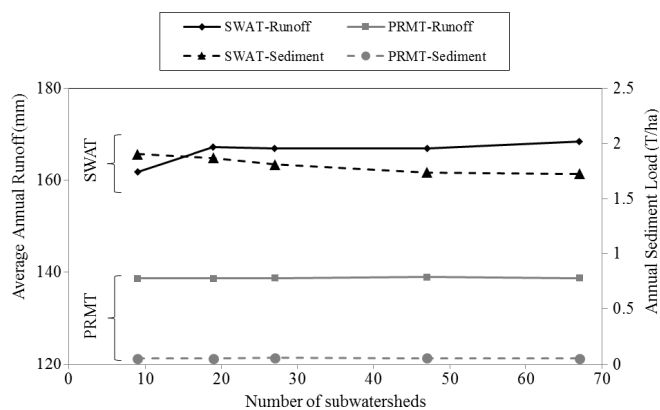


Figure 9. Annual runoff and sediment (no chemical) output from SWAT and PRMT.

outlet in the PRMT simulations. Differences between PRMT and SWAT results for runoff and eroded sediment are ~20%. Simulated pesticide concentrations at the watershed outlet are different between PRMT and SWAT since the hydrology and sediment transport differ by 20%–30%. However, the total pesticide mass leaving the watershed are similar since pesticides are not applied to the nonagricultural land in the SMCW that SWAT also would consider in its analysis.

PRMT output (runoff depth, sediment, and CHP load) from three watersheds, centered around the SMCW but with different drainage areas (Fig. 7) shows that runoff depth was lower for watersheds with higher drainage area and low agricultural land area percentage (Fig. 10). As anticipated, the pesticide load remains constant as the size of the watershed increases since the pesticide mass is governed by the percent of the watershed that received a pesticide application. For watersheds 2 and 3 (Fig. 7), the average annual runoff was 138 and 73.5 mm, respectively. As the proportion of agricultural land decreased, runoff from the watershed decreased. A similar trend of decreasing sediment (erosion) load with increased watershed area was observed. The simulated CHP load was approximately $0.00048\ kg\ ha^{-1}$ for all watersheds.

Daily concentrations of CHP at the watershed outlet predicted from PRMT are estimated by dividing the total CHP mass transported by the total volume of water for each runoff producing event. CHP concentrations in runoff water from this calculation ranged from 0 to $0.91\ \mu g\ L^{-1}$, which is of identical magnitude as the single measured value by MN DNR in their monitoring program of $0.24\ \mu g\ L^{-1}$ (occurring on September 2, 2010). This suggests the approach of discretizing a watershed into unique sub-basins and HRUs, and superpositioning results to represent watershed behavior is appropriate for small watersheds that are predominantly agricultural. Concentration predictions from PRMT will tend to overestimate due to the extent that dilution from pesticide-free water and sediment contributed by nonagricultural land is ignored. However, this tool is useful for managers and growers to address the effectiveness of VFS in reducing pesticide loadings to surface waters and in simulating watershed behavior at large.

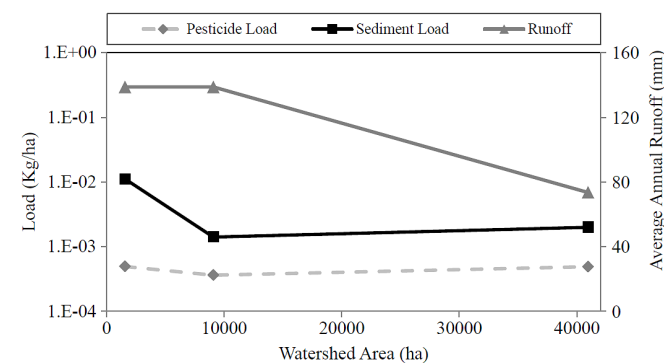


Figure 10. Simulated hydrology and chemical output for the three watersheds (summarized in Fig. 7).

CHP runoff management using VFSs. The efficiency of vegetative filter strips was simulated using VFSMOD to explore pesticide loss reductions in sub-basins when CHP applications were made. Filter strip load reductions for CHP are dependent on runoff water infiltration, sediment input and deposition, pesticide phase distribution factor, and percentage of clay content in sediment. The phase distribution factor and percentage of clay content in sediment (inputs for VFSMOD) and other parameters are assumed constant for the entire simulation period (Table 1), which is a source of uncertainty for PRMT output. When a pesticide producing runoff event was simulated by PRZM for a unique HRU, the hydrology and sediment predicted by PRZM were routed across a filter strip using VFSMOD.

Approximately 90% of the runoff producing CHP loads (dissolved in runoff water and entrained in eroded sediment) observed in all the sub-basins in SMCW were less than 2.24 g d^{-1} (maximum daily CHP runoff load simulated was 58.1 g d^{-1}). The runoff water, eroded sediment, and CHP mass reduction (%) for every simulated pesticide runoff event are given by Figure 11. Load reductions in Figure 11 represent the water, sediment, and pesticide reductions achieved through VFS for each sub-basin for all runoff producing storm events. Each symbol represents the mass reduction via a VFS for every pesticide runoff producing event that occurred over the three-year simulation period (Y-axis) as a function of either the runoff volume, eroded sediment yield, or the total CHP load, respectively. VFS becomes less effective as the runoff water volume increases (Fig. 11A). The larger runoff volumes swamp the VFS and thus reduce the overall effectiveness for chemical

removal in the aqueous phase. However, VFSs are extremely effective at removing eroded sediment (Fig. 11B) where all of the sediment entering the VFS is removed for most runoff events. Chlorpyrifos removal in VFS is dependent upon the runoff water, dissolved CHP in water, and CHP absorbed to eroded sediment. Simulation results suggest all CHP runoff-producing events are not created equal with respect to VFS reductions (Fig. 11C). CHP load reductions across the simulated filter strip varied with the amount of CHP entering and timing of the load. CHP reductions by VFS ranged between 0.41% and 100% for representative runoff events having a three-year return frequency. When summed across all runoff events and years of simulation, the overall CHP reduction was 92.6% when a VFS was used at field edge, heavily driven by sediment reduction through the VFS and CHP's affinity for the soil phase. Approximately 50.6% and 49.4% of the total simulated CHP mass lost in runoff water and sediment, respectively, was predicted by PRMT. This range for the MN SMCW is within the range of observations for a multiyear CHP runoff study for an Iowa watershed study, where the percentage of CHP transport in water and sediment was 1.3%–53% (average 21.3%) and 47.0%–98.7% (average 78.7%), respectively.¹³

Conclusion

The impact of field-scale BMPs on overall watershed behavior has historically been difficult to address. Pesticide manufacturers can control the inclusion of field-scale BMP through proper label language and farmer adherence to the product label. A numerical tool, known as the PRMT, was developed that focuses on field-scale BMPs and insight into the impact they can have on small watersheds. Watershed-scale (SWAT) and field-scale runoff (PRZM, VFSMOD) models were successfully coupled into PRMT to create an easy to use numerical system capable of simulating pesticide runoff and impacts from VFS management practices. Advantages of the PRMT include the watershed being approximated as linear combinations of unique fields (HRUs) within the watershed such that BMPs (and various levels of adoption) at the field scale can be considered. An added benefit is that comparisons between PRMT and SWAT are readily deduced. It was found that watershed subdivision has little effect on predicted hydrology for the small and largely agricultural SMCW in MN. Management practices such as a VFS at field edge can be imposed, and the impact for field-scale practices at the watershed scale can be addressed. The vegetative filter strip model (VFSMOD) suggests CHP reductions from 0.41% to 100% (average 92.6%) in runoff water, and eroded sediment is achievable for the SMCW for representative runoff events occurring between 2010 and 2012 (although different results could ensue depending upon the parameters chosen to parameterize VFSMOD).

PRMT performs well for agricultural dominated watersheds as validated against the monitoring data set of the Minnesota DNR for CHP [water residue level of 0 to $0.91 \mu\text{g L}^{-1}$ (simulated) vs. $0.24 \mu\text{g L}^{-1}$ (observed)], but

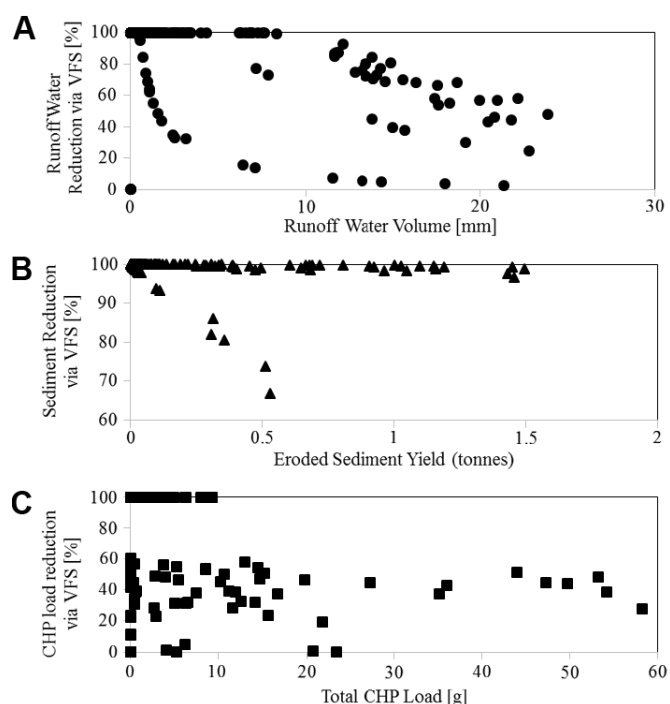


Figure 11. Pesticide management through vegetative filter strip management.



assumptions used in PRMT do break down as the percent of ag-capable land is reduced from near 100%. The PRMT can be used for any pesticide as long as the physicochemical properties of the pesticide are adequately selected and parameterized. Future work should investigate when the assumptions of PRMT are violated. Ideally, routines to estimate hydrology from non-ag land should be added if precise predictions of pesticide water concentrations in streams are sought.

Author Contributions

Conceived and designed the experiments: RKG, SAC, NNP, PKD. Analyzed the data: RKG, SAC, NNP, PKD. Wrote the first draft of the manuscript: RKG, SAC, NNP, PKD. Contributed to the writing of the manuscript: RKG, SAC, NNP, PKD. Agree with manuscript results and conclusions: RKG, SAC, NNP, PKD. Jointly developed the structure and arguments for the paper: RKG, SAC, NNP, PKD. Made critical revisions and approved final version: RKG, SAC, NNP, PKD. All authors reviewed and approved of the final manuscript.

REFERENCES

1. Arnold JG, Srinivasan R, Muttiah RS, Williams JR. Large area hydrologic modeling and assessment Part I: model development. *J Am Water Resour Assoc.* 1998; 34(1):73–89.
2. SWAT. *Soil and Water Assessment Tool.* 2014. Available at: <http://swat.tamu.edu/>. Accessed March 5, 2014.
3. Carsel RF, Mulkey LA, Lorber MN, Baskin LB. The pesticide root zone model (PRZM): a procedure for evaluating leaching threats to groundwater. *Ecol Modell.* 1985;30(1985):49–69.
4. PRZM. *Pesticide Root Zone Model.* 2006. Available at: <http://www2.epa.gov/exposure-assessment-models/przm-version-index>. Accessed March 5, 2014.
5. Muñoz-Carpena R, Parsons JE. A design procedure for vegetative filter strips using VFSSMOD-W. *Trans Am Soc Agric Biol Eng.* 2004;47(6):1933–1941.
6. VFSSMOD. *Vegetative Filter Strip Model.* 2011. Available at: <http://abe.ufl.edu/carpenna/vfssmod/>. Accessed March 5, 2014.
7. Suarez LA. *PRZM-3 A Model for Predicting Pesticide and Nitrogen Fate in the Crop Root and Unsaturated Oil Zones: User's Manual for Release 3.12.2.* Athens, GA: Ecosystems Research Division, National Exposure Research Laboratory; 2005.
8. Fennessey LAJ, Hawkins RH. The NRCS curve number, a new look at an old tool. *Proceedings of the 2001 Pennsylvania Stormwater Management Symposium. Rethinking Comprehensive Stormwater Management—Integrating Quality, Volume and Peak Controls October 17–18 2001.* Villanova, PA: Villanova University; 2001.
9. Williams JR. *Sediment Yield Prediction with Universal Equation Using Runoff Energy Factor. Present and Prospective Technology for Predicting Sediment Yields and Sources (ARS-S-40).* Oxford, MS: USDA Department of Agriculture Sedimentation Laboratory; 1975:244–252.
10. Muñoz-Carpena R, Fox G, Perez-Ovilla O, Ritter A. Does the incorporation of vegetative filter strip mass balance and degradation processes affect the long-term pesticide environmental exposure assessments? *250th American Chemical Society National Meeting and Exposition, Aug. 16–20, 2015.* Boston, MA: 2015.
11. Poletika NN, Coody PN, Fox GA, Sabbagh GJ, Dolder SC, White J. Chlorpyrifos and atrazine removal from surface runoff by vegetated filter strips: runoff experiments and predictive modeling. *J Environ Qual.* 2009;38:1042–1052.
12. USGS-National Elevation Data. Available at: http://nationalmap.gov/data_delivery/ned.html. 2013. Accessed March 2014.
13. Cryer SA. An integrated approach for quantifying pesticide dissipation under diverse conditions: III site specific model validation using GLEAMS and EPICWQ. In: Phelps W, Winton K, Effland WR, eds. *Pesticide Environmental Fate: Bridging the Gap Between Laboratory and Field Studies.* Washington, DC: American Chemical Society Books; 2002:813.