Revised Framework for Pesticide Aquatic Environmental Exposure Assessment that Accounts for Vegetative Filter Strips

GEORGE J. SABBAGH,* † GAREY A. FOX, † RAFAEL MUÑOZ-CARPENA,§ AND MARK F. LENZ† Bayer CropScience, 17745 South Metcalf, Stilwell, Kansas 66085, Department of Biosystems & Agri Engineering, Oklahoma State University, 120 Agricultural Hall, Stillwater, Oklahoma 74078, and Agricultural and Biological Engineering, University of Florida, 287 Frazier Rogers Hall, P.O. Box 110570, Gainesville, Florida 32611

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For pesticides that do not pass higher-level environmental exposure assessments, vegetated filter strips (VFS) are often mandated for use of the compound. However, VFS physiographic characteristics (i.e., width) are not currently specified based on predictive modeling of VFS performance. This has been due to the lack of predictive tools that can explain the wide range of field-reported efficacies. This research hypothesizes that mechanistic modeling of VFS runoff and sediment trapping, integrated with an empirical, regression-based pesticide trapping equation and the U.S. Environmental Protection Agency’s (EPA) exposure framework, is able to effectively derive these VFS characteristics. To test this hypothesis, a well-tested process-based model for VFS (VFSMOD) was coupled with the pesticide trapping equation and integrated with EPA’s PRZM/EXAMS exposure package. The revised framework was applied to a prescribed U.S. EPA exposure assessment for four hypothetical pesticides: more mobile (i.e., organic carbon (OC) sorption coefficients, KOC, of 100 L/kg OC) and less mobile (2000 L/kg OC) pesticides that are fast degrading or stable (i.e., 10 or 10,000 d aquatic dissipation half-lives). A nonlinear and complex relationship was observed between pesticide reduction, VFS length, and rainfall plus runon event size. The impact of VFS on environmental exposure concentrations (EECs) was found to be dependent on the pesticide sorption and dissipation half-life and whether calculating an acute or chronic EEC. While acute and chronic EECs were equivalent for fast degrading pesticides, the acute EEC depended on specific loading events. Therefore, while VFS may reduce the cumulative pesticide loading, a corresponding reduction in the acute EEC may not always be observed. Such results emphasize the need to incorporate physically based modeling of VFS reductions for pesticides that do not pass the current U.S. EPA exposure assessment framework.

Introduction

For aquatic organisms, such as plants, fish, aquatic-phase amphibians, and invertebrates, the U.S. EPA Environmental Exposure and Effect Division (EFED) uses computer simulation models to calculate estimated pesticide environmental exposure concentrations (EECs) in surface water. The EECs are compared to critical toxicological values to determine the level of potential risks to aquatic species. A tiered system of modeling is considered, with the Tier I GENEEC model representing a highly conservative screening tool (1). For compounds with uses resulting in unacceptable TIER I EECs, EFED implements a Tier II modeling system that reflects labeled uses for the compounds (2). The Tier II assessment procedure is based on simulation modeling with PRZM/EXAMS using the linking program PE5 (additional details are provided in the Supporting Information, see Supporting Information, S1). PRZM simulates pesticide fate and transport from an agricultural field to an adjacent water body (3, 4), while EXAMS models pesticide fate in the water body (5, 6). The U.S. EPA has created various benchmark scenarios by crop (7). These scenarios are static in terms of the field and pond geometry but include variations in soil, weather, and management practices. PRZM/EXAMS simulations are typically conducted for a 30-year period (1961–1990) using daily weather data and assuming the maximum use rates and patterns as specified on the pesticide label. Risks are determined based on the upper 90th-percentile annual peak, 4-d, 21-d, 60-d, or 90-d mean concentrations depending on the target critical toxicological end point. For acute risk assessments, peak and 4-d EECs are used, while the chronic risk assessments are based on the longer mean averages.

For pesticides with uses that do not pass the Tier II risk assessments, vegetation filter strips (VFS) are required on the label as a mitigation practice. For example, a typical label might read the following: “construct and maintain a minimum 3.0-m wide vegetative filter strip of grass or other permanent vegetation between field edge and down gradient aquatic habitat.” The VFS can reduce pesticide movement to streams by reducing runoff volumes through infiltration in the filter strip’s soil profile, through contact between dissolved phase pesticide with soil and vegetation in the filter strip, and/or by reducing flow velocities to the point where eroded sediment particles, with sorbed pesticide, can settle out of the water (8–13). Therefore, VFS can provide both retention and detention mechanisms through infiltration and hydraulic resistance. Other potential mechanisms of pesticide removal include sorption of pesticides to vegetation and enhanced or phytomediated degradation of pesticides within the VFS.

However, currently specification of the required VFS characteristics is largely subjective due to the lack of a predictive tool that can explain the wide range of field-reported VFS efficacies. Two VFS with equivalent lengths, slopes, and vegetation characteristics may yield drastically different pesticide reductions dependent on the hydrologic and sedimentological conditions experienced by the VFS at the time of the study. For example, some studies report little reductions in low to moderately sorbed pesticides by VFS (14); other researchers report significant reductions in similarly sorbed pesticides by VFS (15). Review papers have concluded that a significant effect of VFS length on pesticide trapping was not uniformly observed in all of the studies, primarily due to the fact that the removal depended largely on the pesticide properties, nature of the runoff event, and antecedent moisture content (12). The most common

* Corresponding author phone: (913)433-5371; e-mail: george.sabbagh@bayercrops.com.
† Bayer CropScience.
§ Oklahoma State University.
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approaches for attempting to predict VFS effectiveness are statistical analyses that attempt to relate physiographic characteristics of the VFS (i.e., slope, vegetation, area ratio, and VFS length) to sediment and/or contaminant removal (16–18). These statistical approaches showed poor predictive power with little confidence in being able to accurately predict VFS reduction given the wide range of conditions likely to be experienced by the VFS.

Recent research has proven that simple physiographic characteristics of the VFS are not explicitly driving contaminant reductions. Rather it is the VFS hydrologic conditions, only partially controlled by the physiographic characteristics, which control sediment and contaminant removal (18–20).

Consider, for example, that the presence of sheet versus concentrated flow will significantly impact the resulting contaminant removal efficiencies. Numerical process-based models have been available for some time for predicting runoff and sediment reduction by VFS, such as the Vegetative Filter Strip Modeling System, VFSMOD (9, 21). VFSMOD is a finite-element, field-scale, storm-based model developed to route the incoming surface flow hydrograph and sedimentograph from an adjacent source area (field, road, urban area, etc.) through a VFS and to calculate the resulting outflow, infiltration (based on the extended Green-Ampt equation for unsteady rainfall), and sediment trapping (based on GRASSF) (9, 21). Researchers have demonstrated the model’s ability to predict reductions in runoff volume and sediment concentration moving through VFS (10). Such numerical models can account for site-specific conditions not able to be captured by the empirical models. VFSMOD has been used by state regulators and city engineers for the design and evaluation of VFS to control surface runoff pollution.

Recent research has developed and evaluated an empirical model for pesticide trapping by VFS with a foundation of hydrological, sedimentological, and chemical specific parameters (19, 20):

\[ \Delta P = a + b(\Delta Q) + c(\Delta E) + d\ln(F_{ph} + 1) + e(C) \]  
(1)

where \( \Delta P \) is the pesticide removal efficiency (%), \( \Delta Q \) is the infiltration (%) defined as the difference between total water input to the VFS (i.e., rainfall plus inflow runoff) minus the runoff from the VFS, \( \Delta E \) is the sediment reduction (%), \( C \) is the clay content of the sediment entering the VFS, \( F_{ph} \) is a phase distribution factor (i.e., ratio between the mass of pesticide in the dissolved phase relative to the mass of the pesticide sorbed to sediment), and \( a, b, c, d, \) and \( e \) are regression parameters (i.e., 24.8, 0.54, 0.53, −2.42, and −0.89, respectively) with \( R^2 = 0.86 \). Mathematically, \( F_{ph} \) was written as the following

\[ F_{ph} = \frac{Q}{K_sE} \]  
(2)

where \( Q \) and \( E \) are the volume of water (L) and mass of sediment (kg) entering the VFS, and \( K_s \) is the distribution coefficient defined as the product of the organic carbon sorption coefficient (\( K_o \)), and the percent organic carbon in the soil, divided by 100 (19). Additional details of the derivation of this equation are provided in the Supporting Information (see Supporting Information, S1). Parameters within this equation were used to represent some of the processes within the filter strip, including infiltration (\( \Delta Q \)), sedimentation (\( \Delta E \)), and sorption (\( F_{ph} \)). Degradation processes were not simulated in the VFS due to the assumption of a small residence time during typical rainfall-runoff events. The focus was on immobilization of the pesticide by the VFS due to the assumption that the most significant surface water loading threat was due to surface runoff in the immediate runoff event.

The previous research also proposed a procedure linking VFSMOD with the proposed empirical trapping efficiency equation (19, 20). For a wide range of data sets with sufficient information, the linked numerical and empirical models significantly improved predictions of pesticide trapping over conventional equations based solely on physiographic characteristics of the vegetated filter strip (\( R^2 = 0.74 \) with a slope not significantly different than 1.0 and intercept not significantly different than 0.0). Others (20, 22, 23) further evaluated VFSMOD, which included the empirical pesticide trapping efficiency equation. The integrated numerical model was capable of predicting runoff volume, sediment, and chemical reductions by the VFS under both uniform and concentrated flow in good agreement with the measured reductions (20).

Because of these recent advancements, the objective of this research was to test the hypothesis that mechanistically incorporating the effect of VFS into the current evaluation framework for pesticide EECs can provide a tool for determining the required level (i.e., width) of VFS protection for surface water bodies. This tool was based on an integrated modeling system (PRZM/VFSMOD/EXAMS) that was able to predict the nonlinear relationships between rainfall plus runoff event size, VFS characteristics, and pesticide reduction. The integrated modeling package was used to highlight differences in calculating acute versus chronic EECs for mobile and immobile, stable (i.e., persistent), and fast degrading pesticides for one U.S. EPA aquatic exposure assessment scenario with prescribed field and receiving water body characteristics (7).

Materials and Methods

The integrated modeling system was demonstrated for a standard U.S. EPA, Illinois corn scenario (24) with various VFS lengths. The current U.S. EPA EFED PRZM/EXAMS assessment approach models pesticide transport from a 10 ha circular field flowing into a 1 ha, 2-m deep circular pond located in the center of the field. The volume of water and mass of sediment in the pond is assumed constant by EXAMS (7). The philosophy of the U.S. EPA is to be conservative in estimating exposure. It should be realized that results presented in this research are limited to the scenarios that the U.S. EPA developed for regulatory aquatic exposure assessments, specifically the static water body assumption in EXAMS. However, the tools are applicable to other more realistic field and VFS conditions (19–23).

To account for effect of VFS on exposure, VFSMOD was internally coupled with eq 1 and linked into the current PRZM/EXAMS modeling framework (additional details of the process provided in the Supporting Information, see Supporting Information, S1). In the proposed PRZM/VFSMOD/EXAMS modeling system, daily outputs from PRZM (runoff volume, sediment mass, and total pesticide mass) were processed by VFSMOD (see Supporting Information, S5) to calculate the reduction in runoff volume, sediment, and pesticide mass (\( \Delta Q, \Delta E, \) and \( \Delta P \), respectively), and the results were used to update the PRZM output files. The modified PRZM output files are then input into EXAMS to calculate daily EECs in the receiving surface water body (Figure 1). It should be noted that VFSMOD does not consider chemical degradation processes in the VFS due to the assumed small VFS residence times during typical rainfall-runoff events. The model also assumes that whatever pesticide is removed from runoff by the VFS will not eventually escape the VFS. Therefore, no chemical mass balance is being simulated in the VFS. Future versions of the model will simulate such processes in performing a VFS mass balance.
VFSMOD required inputting the characteristics of the VFS, geometry of the field and the VFS (Figure 1), and durations of storms. Field length was defined as the distance from the edge of the field to the edge of the VFS, and field and VFS width was the area of the field (10 ha) divided by the field length (Figure 1). Several VFS lengths were simulated: 1.5, 3.0, 4.6, 9.1, 15.2, and 30.5 m. For the circular layout, changes in the ratio of the field length to the VFS length in all scenarios resulted in only small differences in the amount of flow and chemical received by the VFS.

For the U.S. EPA, Illinois corn scenario, VFS soil characteristics were input into VFSMOD as the same soil (clay loam, hydrologic soil group C, 33% clay, and 2.3% organic carbon content) as the upslope field (Table 1). Soil hydraulic parameters were derived from the USDA SSURGO database (Table 1). Field and VFS slopes were assumed uniform at 6%, as prescribed in the U.S. EPA Illinois corn scenario (Table 1). Vegetation type in the VFS was assumed to be bluegrass and default parameters for VFS vegetation characteristics were used.

While the current EPA exposure assessment approach used daily weather data from 1961–1990 for the scenario location to predict infiltration, flow routing, and sediment transport, VFSMOD required storm-based subdaily rainfall data. In this research, hourly rainfall data were used for the Illinois corn scenario (1961–1990) with consideration for the storm duration for each event. Durations of storms were calculated from hourly rainfall data provided on the EPA Web site for each EPA scenario.

Four hypothetical pesticides were simulated to demonstrate the PRZM/VFSMOD/EXAMS linkage: more mobile (i.e., organic carbon sorption coefficients, $K_{oc}$, of 100 L/kg OC) and less mobile (i.e., $K_{oc}$ of 2000 L/kg OC) with short (10 d) and long (10,000 d) aquatic dissipation half-lives to simulate fast degrading and stable pesticides. For the scenarios, it was assumed that each year 0.11 kg of active ingredient per ha was applied four times with the first application on July 1st and a three day period between applications (Table 1). For these simulations, it was assumed that 100% of the applied granular material was deposited to the field (i.e., no input to pond via spray drift). Future research should be devoted to scenarios that consider both runoff and spray drift loading to receiving water bodies.

Output from EXAMS included the EEC for each day of the 30-year simulation. Chronic exposure concentrations were calculated as the annual average of daily EEC for each of the 30-year period. Acute concentrations were determined as

![FIGURE 1. Field and vegetative filter strip physical system simulated (figure not drawn to scale) as prescribed by U.S. EPA exposure assessment scenarios.](image)

**TABLE 1. Input Parameters for the PRZM/VFSMOD/EXAMS Modeling Package for the U.S. EPA Illinois Corn Scenario (24)**

<table>
<thead>
<tr>
<th>parameter</th>
<th>model input value</th>
<th>model</th>
<th>comment</th>
</tr>
</thead>
<tbody>
<tr>
<td>EPA modeling scenario</td>
<td>Illinois corn scenario</td>
<td>PRZM, VFSMOD, EXAMS</td>
<td>standard EPA scenario</td>
</tr>
<tr>
<td>soil type</td>
<td>Adair clay loam with 6% slope, 33% clay content, and 2.3% organic carbon</td>
<td>PRZM and VFSMOD</td>
<td></td>
</tr>
<tr>
<td>soil hydraulic conductivity</td>
<td>3.2 cm/h</td>
<td>VFSMOD</td>
<td>SSURGO - S5Map Unit: IA0133</td>
</tr>
<tr>
<td>soil bulk density</td>
<td>1.32 g/cm³</td>
<td>PRZM and VFSMOD</td>
<td></td>
</tr>
<tr>
<td>pesticide molecular weight</td>
<td>500 g/mol</td>
<td>PRZM and EXAMS</td>
<td></td>
</tr>
<tr>
<td>pesticide solubility at 20 °C</td>
<td>1 mg/L (0.002 mol/m³)</td>
<td>PRZM and EXAMS</td>
<td></td>
</tr>
<tr>
<td>Henry's law constant</td>
<td>1.3 $\times$ 10⁻¹⁰ atm</td>
<td>PRZM and EXAMS</td>
<td></td>
</tr>
<tr>
<td>hydrolysis and aqueous photolysis</td>
<td>stable</td>
<td>EXAMS</td>
<td>Biological degradation was assumed to be the only path for the product to dissipate in water. Aerobic and anaerobic degradations were assumed to occur at the same rate (both were set at 10 days or assumed stable)</td>
</tr>
<tr>
<td>aerobic and anaerobic aquatic metabolism half-life</td>
<td>10 d or 10,000 d</td>
<td>PRZM</td>
<td></td>
</tr>
<tr>
<td>aerobic soil metabolism</td>
<td>stable</td>
<td>PRZM and EXAMS</td>
<td></td>
</tr>
<tr>
<td>adsorption coefficient ($K_{oc}$)</td>
<td>100 or 2000 L/kg OC</td>
<td>PRZM</td>
<td></td>
</tr>
<tr>
<td>pesticide use pattern</td>
<td>4 applications of 0.11 kg/ha with 3 days between applications (first application - July 1st)</td>
<td>PRZM, VFSMOD, EXAMS</td>
<td></td>
</tr>
<tr>
<td>percent deposition</td>
<td>100%</td>
<td>PRZM</td>
<td>granular application – 100% of applied material deposited in the field; no loss due to drift</td>
</tr>
</tbody>
</table>
the peak annual concentration for each year. Therefore, 30 EEC values were calculated from which probability distribution functions could be generated, and the 90th percentile values, following exposure assessment approaches, were quantified.

Results included the percent pesticide reduction relative to VFS length, rainfall plus runon event size, and aquatic dissipation half-life for both acute and chronic EECs. Also, in order to demonstrate the importance of process-based modeling for predicting VFS response as opposed to empirical models only dependent on related physiographic characteristics of the VFS, output results from the linked PRZM/VFSMOD/EXAMS package were compared to PRZM/EXAMS results assuming a constant value of VFS pesticide reduction (i.e., independent of rainfall plus runon event size) for each VFS length.

Results and Discussion

The linked PRZM/VFSMOD/EXAMS modeling package simulated runoff, sediment, and pesticide loadings to adjacent surface water bodies. For the U.S. EPA, Illinois corn scenario with multiple pesticide applications, this process-based modeling package was capable of accounting for VFS response relative to specific hydrologic and sedimentological inputs. The commonly reported nonlinear relationship was observed between total water input (i.e., rainfall plus runon) during a storm event and percent pesticide reduction (Figure 2). Smaller VFS lengths possessed wider distributions in observed pesticide trapping as compared to larger VFS lengths. For example, percent pesticide trapping for the 1.5-m long VFS and a 5-cm rainfall and runon event ranged between approximately 30 and 90%, with some of this large distribution explained by differences in antecedent moisture content.
within the VFS (Figure 2). The lower percent reductions were events that occurred during higher moisture content in the soil profile leading to lower infiltration capacity within the VFS. Additional factors controlling the range of responses for each filter length are linked to the range of rainfall intensities and durations that resulted in differences in sediment characteristics (particle size distribution) in runon from the source area (22, 23). For the 9.1-m long VFS, pesticide trapping or reduction was generally greater than 60% unless the total water input (rainfall plus runon) during a storm event exceeded 10 cm (Figure 2).

The primary implication for environmental exposure assessment that arose from simulations with the integrated modeling package was that a percent mass reduction of pesticide entering the pond does not always correlate to an EEC percent reduction. The EEC percent reduction was in fact a function of the reduction in pesticide mass loading by the VFS, the pesticide’s mobility ($K_{oc}$) and persistence (aquatic dissipation half-life), and whether one was calculating an acute or chronic EEC. For stable pesticides with long aquatic dissipation half-lives (i.e., 10,000 d), percent reductions in acute and chronic EECs were approximately equivalent for a specific VFS length (Figure 3). More specifically, the acute EEC occurred at the end of the 30-year simulation. This is due to the fact that the EFED pond is static, and water and sediment are neither added to nor removed from the water body as prescribed in the U.S. EPA assessment approach. Therefore, the effect of the VFS for a stable compound was cumulative (Figure 4). If the mass loading was reduced by using VFS for a stable pesticide, a corresponding reduction in the EEC was observed. The approximately equivalent reductions in acute and chronic EECs were greater for larger VFS lengths (Figure 3) and less mobile (i.e., higher $K_{oc}$) pesticides (Figure 5).

For fast degrading pesticides (i.e., 10-d aquatic dissipation half-life), reductions in acute and chronic EECs were not equivalent (Figure 3). An acute EEC arose due to a pulse, as opposed to a cumulative, loading of pesticide from adjacent fields (Figure 4). Therefore, the reduction in the acute EEC was more directly related to the reduction in mass loading for specific storm events (i.e., rainfall plus runon), which has already been shown to be a complex and nonlinear function of total water input and VFS length (Figure 2). In the example, the VFS can significantly reduce the cumulative mass pesticide loading into the surface water body and therefore result in large percent reductions in chronic EECs for fast

![FIGURE 4. Daily environmental exposure concentrations (EECs) for the U.S. EPA Illinois corn scenario predicted by EXAMs for (a) a stable pesticide (10,000-d aquatic dissipation half-life) and (b) a fast degrading pesticide (10-d aquatic dissipation half-life) with and without a 5-m long vegetated filter strip (VFS).](image)

![FIGURE 5. Percent reduction in the acute environmental exposure concentrations (EECs) for the U.S. EPA Illinois corn scenario relative to vegetative filter strip (VFS) length (1.5, 3.0, 4.6, 9.1, 15.2, and 30.5 m) for pesticides with organic carbon sorption coefficient, $K_{oc}$, of 100 and 2000 L/kg and for both fast degrading (10-d aquatic dissipation half-life) and stable (10,000-d aquatic dissipation half-life) pesticides.](image)
deteriorating compounds. However, the acute EEC may not correspondingly be reduced because of its dependency on a specific storm event (Figure 3). Acute EEC reductions with VFS were lower than reductions in chronic EECs, especially for small VFS lengths (Figure 3).

As the VFS length increased beyond 15 m for these scenarios, equivalent reductions were observed in both the acute and chronic EECs (Figures 3 and 5). However, this 15-m length is scenario dependent, i.e. the length would change for other sites and products. The advantage of using VFSMOD is that the model can help to identify this particular distance for various exposure assessment scenarios under different hydrologic and sedimentological conditions.

Changing the Koc affected the mass of chemical loading from the field and VFS. A lower Koc resulted in a higher dissolved phase mass in runoff, higher trapping in the VFS with infiltration, and faster degradation in the dissolved phase (Figure 5). As expected, for the stable pesticide the percent reductions in acute EECs were greater for a higher Koc (Figure 5). However, percent reductions in acute EECs for the fast degrading pesticide were lower for the higher Koc, even though the actual acute EECs were lower.

For larger Koc pesticides, the majority of the pesticide mass loading was associated with erosion, while for low Koc pesticides, the majority of the pesticide mass loading was associated with the runoff water. Although flow and sediment transport are usually commonly correlated, field conditions (i.e., soil vegetative cover) can influence this relationship. Therefore, a large runoff event may occur without sediment transport. As such, the mass loading from high Koc pesticides was different than the mass loading from low Koc pesticides because the events that drive them might be different, irrespective of the dissipation half-life in water.

For slow degrading pesticides, acute exposure was driven by accumulation of mass loading; therefore, the effect of VFS exposure was directly related to the VFS effects on total mass loading reduction (Figure 5). For fast degrading pesticides, acute exposure was determined by mass loading from a particular event as well as the mass of pesticide in the water prior to the event. It was not possible to a priori predict the relationship between Koc and acute EEC reduction for a given scenario due to this event-specific response influenced by a variety of parameters (i.e., soil cover). Such results further stress the need for a process-based modeling framework for estimating EECs.

An alternative and commonly used approach for estimating VFS effectiveness is to use regression or empirical equations that are dependent solely on the physiographic characteristics of the VFS (i.e., slope and/or VFS length) (17, 18). While simple and easy to use, such formulations incorrectly predict equivalent VFS removal efficiencies for all rainfall plus runon events (18). For example, if in our testing scenarios one assumed a constant VFS reduction independent of rainfall plus runon event size (i.e., 50%), equivalent reductions were incorrectly predicted in both acute and chronic EECs independent of the pesticide’s persistence for all VFS lengths.

These results are critical for aquatic exposure assessments because they highlight the fact that consistent and unique reductions cannot be assumed for VFS. It should be noted that the EEC reduction curves will be different for the specific U.S. EPA scenario and the pesticide being considered. The standard EPA scenarios utilized in this research were simulated for the sole purpose of demonstrating the differences between reductions in acute and chronic EECs relative to the pesticide’s mobility and persistence. The integrated modeling system with VFSMOD was capable of predicting the commonly observed nonlinear relationship (i.e., greater reductions for smaller events as shown in Figure 2) between percent reduction and rainfall plus runon event size with consideration for the hydrologic and sedimentological conditions experienced by the VFS. Process-based modeling, such as with the integrated PRZM/VFSMOD/EXAMS modeling system, is critical for accurately predicting VFS reductions of pesticide transport to surface water systems.

Supporting Information Available
Flowcharts of the prior and revised modeling schemes used in the Tier II assessment process (Figure S1); a description of the empirical pesticide trapping equation shown in eq 1, including descriptions of the pesticide characteristics used in model development (Table S1) and evaluation (Table S2); and an example pesticide output file from VFSMOD. This material is available free of charge via the Internet at http://pubs.acs.org.

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