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Management-oriented sensitivity analysis for pesticide transport in watershed-scale water quality modeling using SWAT

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Selected structural BMPs are recommended for reducing loads of OP pesticides.

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ABSTRACT

The Soil and Water Assessment Tool (SWAT) was calibrated for hydrology conditions in an agricultural watershed of Orestimba Creek, California, and applied to simulate fate and transport of two organophosphate pesticides chlorpyrifos and diazinon. The model showed capability in evaluating pesticide fate and transport processes in agricultural fields and instream network. Management-oriented sensitivity analysis was conducted by applied stochastic SWAT simulations for pesticide distribution. Results of sensitivity analysis identified the governing processes in pesticide outputs as surface runoff, soil erosion, and sedimentation in the study area. By incorporating sensitive parameters in pesticide transport simulation, effects of structural best management practices (BMPs) in improving surface water quality were demonstrated by SWAT modeling. This study also recommends conservation practices designed to reduce field yield and in-stream transport capacity of sediment, such as filter strip, grassed waterway, crop residue management, and tailwater pond to be implemented in the Orestimba Creek watershed.

1. Introduction

In recent years, non-point source pollution from agriculture is increasingly responsible for the degradation of surface water quality. This, in turn, increases the need of integral water-quality management with enhanced hydrologic models. Off-site movement of agrochemicals, such as organophosphate (OP) pesticides, to streams and aquifers, in agricultural watersheds, may potentially cause adverse effects on human health and ecosystem. OP pesticides are widely used in orchards and other crops. According to the pesticide market estimates by U.S. Environmental Protection Agency (USEPA, 2004), OP use as a percent of total insecticide use has increased from 58% in 1980 to 70% in 2001. In the San Joaquin Valley of California, one of the most productive agricultural regions in the world, about 450 tons of active ingredients of OP pesticides were used per year from 1990 to 2007, and OP pesticide residues have been routinely detected in surface water bodies of the San Joaquin River watershed. According to the sampling results during 1992–1995, pesticide levels in 37% of the streams in the San Joaquin Valley exceeded the criteria for the protection of freshwater aquatic life (Dubrovsky et al., 1998).

GIS-based distributed or semi-distributed modeling is widely applied to simulate chemical transport and predict pollution reductions with management practices in agricultural watersheds. The in-field and in-stream transport processes of OP pesticides are determined to a great extent by the dominant hydrologic processes of a river watershed. Therefore, a reliable hydrologic simulation has to be established for the dynamic pesticide exposure assessment. Modeling of pesticide fate and transport might be more complex and associated with more sources of uncertainty than hydrologic simulation (Dubus et al., 2003; Holvoet et al., 2005). Even if the rates and timing of a particular pesticide application are fully recorded for some agriculturally dominated areas such as the San Joaquin Valley, there are other data inputs associated with greater uncertainties, such as soil properties (e.g., curve number and erosion factors) and chemical properties of pesticides (e.g., half-lives and partition coefficient). Therefore, it is very important to present clearly the propagation of input variances into model outputs for environmental persistence of OP pesticides.

In most studies of water-quality modeling at watershed scale, sensitivity analysis is usually performed for one catchment as a whole, without the consideration for spatial arrangement of sub-catchments in the stream network. Therefore, the spatial effects on the model performance and management implications are not fully evaluated. As indicated by Arabi et al. (2006), for example, in-stream transport processes and associated conservation practices must be discussed at watershed scale because their effects cannot be detected at fields. In order to provide useful information for agricultural management strategies, simulation of pesticide transport

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should consider hydrometeorology and water-quality processes at various spatial scales. The spatial dependence of environmental fate of pesticide species were traditionally evaluated based on measurement data. For example, Capel et al. (2001) examined monitoring data of 39 pesticides as a function of scale across 14 orders of magnitude. There are a few but increasing number of studies modeling fate and transport of pesticides at area-varying watersheds (Brown et al., 2002; USEPA, 2006; Luo et al., 2008).

The Soil and Water Assessment Tool (SWAT) was chosen in this study to predict pesticide loads of OP species in surface water. In addition to hydrologic simulation, SWAT also allows dynamic predictions of pesticide outputs at various spatial scale (Gassman et al., 2007). In our previous study, SWAT had been calibrated for the hydrologic conditions in the San Joaquin River basin (14 983 km^2), and applied to evaluate residue distribution of two OP pesticide diazinon and chlorpyrifos (Luo et al., 2008). Based on the calibrated model, effects of pesticide management practices on water quality were evaluated (Zhang et al., 2008). The modeling efforts were extended in this study by predicting pesticide transport and potential efficiency of structural best management practices (BMPs) at spatial scales of [1] small watershed (the Orestimba Creek watershed, a tributary watershed of the San Joaquin River, 563 km^2), and [2] agricultural fields (agricultural drainage area in the Orestimba Creek watershed, 146 km^2 in total). The objectives of this study were threefold: (1) to evaluate the modeling capability of SWAT in predicting the fate and transport of pesticides in agricultural watersheds with different spatial extents, by comparing with measured pesticide loads in surface water; (2) to identify the most influential model parameters for simulating pesticide distribution based on a management-oriented sensitivity analysis; and (3) to represent the functionality of selected management practices in SWAT, and to assess the water-quality impacts at both field and watershed scales. Results in this study were anticipated to provide useful information for agricultural BMP planning in reducing pesticide residues, and for future model development and evaluation in agrochemical transport and mitigation.

2. Methods and materials

2.1. Site description

The Orestimba Creek watershed was selected as a representative sub-region in the San Joaquin River basin for further investigation (Fig. 1). Large amounts of organophosphate insecticides are sprayed to almonds and other stone-fruit orchards in the watershed (Cryer et al., 2001). Compared to other regions in the San Joaquin Valley, a greater variety of pesticides were detected in this watershed (Dubrovsky et al., 1998). Chlorpyrifos and diazinon loadings per unit area from the Orestimba Creek watershed were significantly higher than those from other tributary watersheds of the San Joaquin River (Domagalski and Munday, 2003). In addition, the study area in the valley floor consists of confluent alluvial fans characterized by heavier textured soils and greater slopes compared to the eastern side (Cryer et al., 2001; Chu and Marino, 2004; Luo et al., 2008). Therefore, the Orestimba Creek watershed might be more vulnerable to runoff, and represents a worse-than-average condition for pesticide contamination and associated ecosystem risks.

As a western tributary of the San Joaquin River, the Orestimba Creek is originated in the Coast Range mountainous area and flows through agricultural lands in the San Joaquin Valley. The boundary of the watershed was defined by the California Environment Protection Agency (CEPA), with total area of 563 km^2 (CEPA, 2007). The main soil taxonomies of the watershed are Argixerolls in the mountainous area and Xerorthents in the valley floor, with saturated hydraulic conductivities ranging from 2.7 to 28.2 $\mu m\ s^{-1}$ for agricultural land. Annual average precipitation in this area is 290 mm, 71% of which is observed during rainfall season of December through March. During summer months, stream flow in the lower reaches of Orestimba Creek is dominated by agricultural drainages. Irrigation sources included San Joaquin River diversion, Central Valley Project diversion, and pumped groundwater. During summer months, irrigation tailwater are the main source of stream flow. The watershed was further delineated into 4 subbasins following the CalWater (California watershed delineation) version 2.2.1 (CDWR, 2004), as shown in Fig. 1. For the subbasins of north fork, south fork and middle Orestimba Creek, majority of the land was covered by forest and rangeland, with slopes of 20–40%. Croplands are mainly located in the flat valley floor in the lower Orestimba Creek subbasin at elevations of 66–20 m.

2.2. Pesticide simulation in SWAT

SWAT is a conceptual semi-distributed model for watershed hydrology and water-quality operating on daily time step (Neitsch et al., 2005). In the model, the watershed of interest is divided into explicitly parameterized smaller areas of subbasin and enclosed hydrological response units (HRUs). The HRUs are delineated by overlaying topography, soil, and land use maps, and assumed to be homogeneous with respect to their hydrologic properties. SWAT simulation can be separated into two major divisions of "land phase" and "routing phase". Model outputs from the two phases were defined as "yield" and "load" in this study, respectively. Yields were the amounts of water, sediment, nutrient and pesticide loadings delivered to the main channels, while loads were model outputs predicted at the output of a subbasin or watershed. Water and sediment yields were available in the SWAT HRU output file (output.hru) and pesticide yields could be obtained from the pesticide output file (output.pst). In-stream loads of all model outputs were stored in the SWAT reach output file (output.rch).

SWAT has the capability to predict pesticide yields from agricultural land to streams and in-stream transport processes for both dissolved and particulate forms. Simulated fate processes in agricultural lands include volatilization, wash-off, degradation, leaching and horizontal movement with surface runoff and lateral flow. SWAT simulates volatilization, photolysis, hydrolysis, biological degradation and chemical reactions in the soil based on a lumped parameter of pesticide half-life in soil. Similarly, half-life in foliage is used to estimate pesticide degradation and volatilization on the canopy. The governing factors of pesticide yield are surface and subsurface runoffs induced by rainfall and irrigation, especially the runoff events occurring soon after pesticide application (Luo and Zhang, 2009). Pesticide yield is also influenced by the terrestrial factors and chemical properties of pesticides. Phase distribution of pesticide in solution or attached to sediment is determined by organic carbon content of soil layer and organic carbon normalized partition coefficient (K_{OC}) of the pesticide. For in-stream pesticide processes, SWAT assumes a well-mixed layer of water and suspended sediment overlying a bed sediment layer. The main in-stream loss processes simulated for the water column include degradation, volatilization, and sedimentation. Pesticide degradation is estimated based on pseudo first-order kinetics with a rate constant reflecting the overall transformation effects. Volatilization of pesticide in the dissolved phase is formulated based on a user-defined volatilization mass-transfer coefficient. As suggested by the SWAT manual, the volatilization coefficient was estimated following Whitman's two-film theory by assuming an instantaneous equilibrium in the air–water interface (Chapral, 1997; Neitsch et al., 2005). Pesticide sedimentation is simulated as two-step process of sorption and settling/resuspension in SWAT. The fraction of pesticide in the dissolved phase (f_d) is calculated by solid–liquid partitioning,

$$f_d = \frac{1}{1 + \mathrm{CHPSPT\_KOC} \cdot \mathrm{SEDCONC}} \quad (1)$$

where CHPST_KOC ($m^3\ g^{-1}$) is the pesticide partition coefficient, calculated as the product of K_{OC} and organic carbon content of suspended sediment, and SEDCONC ($g\ m^{-3}$) is concentration of suspended solids in the water. Pesticide sorbed to suspended particle can be removed from the water column by sedimentation, characterized by a sedimentation velocity. Detailed information for the equations of hydrologic cycle and pollutant transport were documented in the SWAT manual (Neitsch et al., 2005).

SWAT provides options to simulate two types of edge-of-field BMPs, i.e., filter strips and tailwater ponds. The model assumes that a filter strip removes sediment, nutrients, and pesticides from surface runoff with the same trapping efficiency ($trap_{ef}$), calculated as a function of the width of the filter strip (FILTERW, m),

$$trap_{ef} = 0.367 \cdot \mathrm{FILTERW}^{0.2967} \quad (2)$$

In-pond transport processes are simulated by SWAT for water, sediment, and nutrients, but not for pesticides. However, SWAT includes a simulation module for pesticide losses in lakes and reservoirs, based on similar equations of in-stream pesticide transport and fate. In this study, SWAT was improved by incorporating the transformation and transport of pesticides in tailwater ponds, based on the equations used for the pesticide processes instreams and lakes. The modified SWAT model, therefore, had the capability to evaluate the removal of pesticides by tailwater ponds before entering the main channel. Representations of other BMPs, e.g., crop residue management, grassed waterway, are conducted in SWAT through alteration of its input parameters. Arabi et al. (2007) reviewed modeling studies in evaluating BMPs around the globe and developed a method for the representation of several agricultural BMPs with SWAT.

2.3. Data collection and simulation design

Daily data of precipitation, temperatures, wind speed, solar radiation, and relative humidity was taken from weather stations at Newman (37.28N, 121.02W) and Gilroy (37.00N, 121.57W), California, operated by the National Climate Data Center. The channel system was generated from the National Hydrography Dataset developed by U.S. Geological Survey (USGS). Contemporary land use was obtained from land surveys by California Department of Water Resources (CDWR, 2008), for

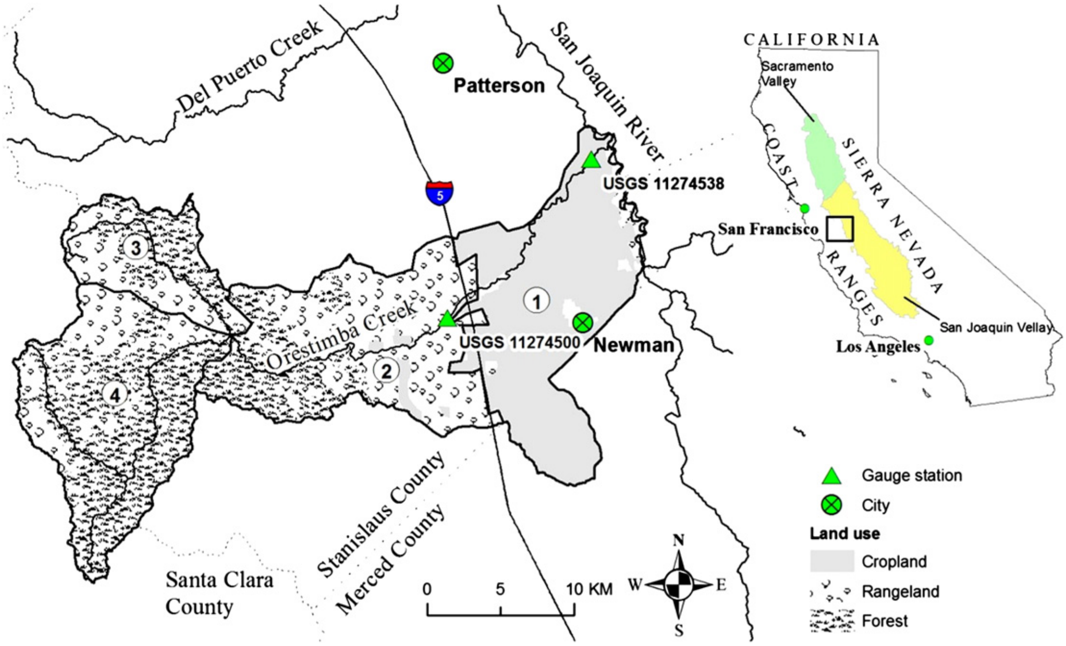

Fig. 1. Location of the Orestimba Creek watershed with subbasins of [1] lower Creek, [2] middle Creek, [3] north fork, and [4] south fork.

Stanislaus (in 2004) and Merced (in 2002) counties. Land use information from the surveys was considered to be representative of the study area during the entire simulation period. Total cropping area was 146 km^2 and mainly located in the lower Orestimba Creek subbasin. Planted crops were grouped as five major crop types of orchard (30.4%), beans (24.3%), irrigated pasture (22.0%), tomato (8.8%), and corn (7.7%). Other minor crops were aggregated and simulated as general crop. For each crop type, parameters for plant growth were taken from SWAT built-in crop database. Soil properties were extracted from the Soil Survey Geographic (SSURGO) database (USDA, 2008). ArcSWAT (Winchell et al., 2007), a graphic user interface of SWAT model, was used in this study for spatial analysis and data formatting for model inputs.

Daily data for pesticide use amounts of chlorpyrifos and diazinon in the study area during 1990–2007, the most recent year available at the time of study, was retrieved from the California Pesticide Use Reporting (PUR) database (CEPA, 2008a). The PUR data is organized for the Meridian-Township-Range-Section (MTRS) in the United States Land Survey System, and was summarized for each simulated crop type in this study. There were general decreasing trends for the uses of both pesticides in the Orestimba Creek watershed. An annual reduction rate averaged 5% was observed for application amounts of both chemicals during 1990–2007. In the investigated watershed, majority of chlorpyrifos (76%) and diazinon (53%) are applied during irrigation months of April to November. Chlorpyrifos and diazinon were sprayed to all major crops in the watershed, and their application efficiency was set as 0.75 for all crops as suggested by SWAT built-in pesticide property database. Chemical properties of chlorpyrifos and diazinon were based on the SWAT built-in data and USDA pesticide property database (Table 1).

The middle Orestimba Creek is gauged by USGS site #11274500 (“Orestimba Creek near Newman, California”), monitoring the water flows originating in non-agricultural areas of the Coastal Range during rainfall season (Fig. 1). Another USGS gauge, “#11274538, Orestimba Creek at River Road, Cross Landing, California”, is located at the watershed outlet. Measurements at this location reflect inputs of non-point source pollution from agricultural fields in the lower Orestimba Creek subbasin. Daily stream flow rate is available at both sites for the simulation years (USGS, 2008), with annual average stream flow rates of 0.58 and 1.26 cm at gauges #11274500 and #11274538, respectively. Concentrations of suspended sediment and dissolved pesticides are sampled by the USGS and CEPA at the watershed outlet of Orestimba Creek (#11274538) (CEPA, 2008b; USGS, 2008). No measurements were taken for chlorpyrifos and diazinon concentrations in particle-bound form. In-stream loads of dissolved pesticides were calculated from the concentration and stream flow at the same day, and organized as monthly averages for evaluating model performance.

The latest version of SWAT (SWAT2005) was used in this study to simulate hydrologic and transport processes in the Orestimba Creek watershed at daily time step for the period of 1990–2007. The first two simulation years were used for model initialization, while model calibration and validation for stream flow and sediment load were conducted for years 1992–1997 and 1998–2007, respectively. In this study, SWAT was calibrated and validated for monthly stream flow and sediment load based on measurements at the two gauging stations within the Orestimba Creek watershed. Automatic calibration was conducted and the Nash-Sutcliffe efficiency (NSE) was used as calibration criterion. Model performance was also evaluated by percent bias (PBIAS). As suggested by Moriasi et al. (2007), satisfactory simulation is indicated by NSE < 0.5 and PBIAS $\pm 25\%$ for stream flow, $\pm 55\%$ for sediment, and $\pm 70\%$ for other water-quality variables. Calibration with respect to stream flow was first performed based on input parameters of SCS curve number (CN2) and soil evaporation compensation factor (ESCO). Channel erosion factors (CH_COV and CH_EROD) and the linear parameter for channel sediment routing (SPCON) were calibrated sequentially for sediment loads. The calibrated model was assumed to provide reliable hydrologic framework for the study area, and applied for dynamic simulation of pesticide fate and transport.

2.4. Management-oriented sensitivity analysis

A management-oriented sensitivity analysis was performed to identify the SWAT input parameters that significantly affect model predictions of pesticide yields and loads. The sensitivity analysis was only conducted in the lower Orestimba Creek subbasin, where almost all pesticide applications occur. Currently, structural BMPs were not extensively implemented in the lower portion of the watershed. In addition, the sensitivity analysis in this study was conducted on calibrated parameters for the area of interest since the model sensitivity may vary with the magnitude of input values due to the nonlinearity in the model equations (Luo and Yang, 2007). Therefore, the results of this study reflected the “actual” sensitivity of model predictions in the study area, rather than the theoretical sensitivity of the model

Table 1
Physicochemical properties and mass-transfer coefficients for chlorpyrifos and diazinon.

Parameter	Description	Values	
		Chlorpyrifos	Diazinon
CHPST_REA[b]	Hydrolysis coefficient (d^{-1})	0.012	0.005
HENRY[b]	Henry's law constant (–)	3.0×10^{-4}	3.0×10^{-5}
HIFE_F[a]	Half-life on foliage (d)	3.3	4.0
HIFE_S[a]	Half-life in the soil (d)	30.0	40.0
MW[b]	Molecular weight (g mol^{-1})	350.6	304.4
SEDPST_REA[b]	Degradation coefficient in sediment (d^{-1})	0.005	0.043
K_{OC}[a]	Organic carbon normalized partition coefficient (L kg^{-1})	6070	1000
WOF[a]	Wash-off fraction (–)	0.65	0.9
WSOL[a]	Solubility (mg L^{-1})	0.4	60.0

[a] SWAT built-in pesticide property database.
[b] Agricultural Research Service (ARS) pesticide property database (USDA, 2001), data for 20 or 25 °C.

equations as provided in global sensitivity analysis or by aggregating contributing catchments into a single modeling unit. The results would be appropriate in evaluating agricultural BMPs in improving water quality in the watershed.

Selection of parameters for the sensitivity analysis was based on literature review and the pesticide simulation algorithm in SWAT as discussed above. A set of 24 SWAT input parameters for landscape morphology, channel characteristics, and chemical properties were selected in this study (Table 2). For soil properties, only parameters for the top soil layer were applied in the sensitivity analysis. For parameters of edge-of-field BMPs, typical values from literature review were taken as initial values, for example, the width of filter strip (FILTERW) was set as 5 m and the drainage fraction of tailwater pond (PND_FR) was 50%. Selected parameters fell into two categories according to their effects on the pesticide yield from agricultural fields, or in-stream pesticide loss. Only parameters related to agricultural conservation practices were considered. Therefore, some model inputs (e.g., groundwater parameters and wash-off coefficient), which might have significant effects on hydrology and pesticide transport, were not included here.

For each input parameter selected in the sensitivity analysis, 50 numerical values were sampled randomly in a relative way to its calibrated value within the corresponding range (Table 2), and then were applied in SWAT simulations. For each sampled value, the sensitivity was calculated as sensitivity index (S, also called condition number or relative sensitivity),

$$S_I = \frac{\partial P}{\partial I}\frac{I}{p(I)} \tag{3}$$

where I is the considered model parameter and P is the model prediction. Model sensitivity to a specific parameter was reported as the average of the corresponding sensitivity indices. Therefore, a total of 1200 ($=24 \times 50$) SWAT simulations was conducted for sensitivity analysis, and for each simulation only one input parameter was changed while keeping all others constant. Results of sensitivity analysis identified key processes and parameters for pesticide yield and transport, and provided guidance for selection of structural BMPs. In each BMP, multiple parameters are usually involved and inter-related based on the physical practices. Therefore, sensitivity of model prediction on each individual parameter in a BMP was not reported in this study. Instead, BMPs were evaluated by their effectiveness, defined as the relative changes of water, sediment, and pesticide outputs before and after BMP implementations.

3. Results and discussion

3.1. Baseline modeling

The results of statistical evaluation of the model performance for stream flow, sediment, and pesticides predicted at the two USGS gauges during 1992–2007 are summarized in Table 4, reported for rainfall season, irrigation season, and the entire simulation period. The model efficiencies (NSE) by comparing the SWAT-predicted monthly stream flow and USGS measurements were 0.82 and 0.78 at gauges #11274500 and #11274538, respectively, for the entire simulation period (Fig. 2). This indicated good simulations of hydrology for both non-agricultural and agricultural areas in the Orestimba Creek watershed. In our previous study an SWAT model was calibrated for the entire San Joaquin River watershed, and model prediction for the Orestimba Creek outlet showed NSE of 0.5 for 1992–2005 (Luo et al., 2008). Therefore, SWAT performance for hydrologic simulation was significantly improved by introducing multiple subbasins in the study area. Before entering agricultural areas, the annual average stream flow predicted at gauge #11274500 was 0.59 $m^3\ s^{-1}$, and usually dry during June through November. At the Orestimba Creek outlet, the annual average stream flow was predicted as 1.26 $m^3\ s^{-1}$, with about 50% of the flow contributed by agricultural return flows. Due to lack of data on daily actual irrigation water for the study area, the SWAT built-in module of automatic irrigation was used to estimate irrigation water application. Simulated irrigation water use was on average 622 mm yr^{-1} during 1990–2007, consistent with reported annual water application of 409–762 mm in the study area (CDWR, 2007). The irrigation algorithm in the SWAT model limited the irrigated water amount by the soil field capacity, implying an assumption of high efficiency in water use and water diversion. In addition, pesticide wash-off from canopy by irrigation is not simulated in SWAT, resulting in underestimation of pesticide residues in soil and runoff.

Predicted monthly average suspended sediment concentration and dissolved pesticides loads at the Orestimba Creek outlet were compared to monitoring data (Fig. 3). The NSE values of the model performance during the entire study period were 0.70, 0.55, and 0.58 for the predictions of suspended sediment concentration, dissolved chlorpyrifos load, and dissolved diazinon load, respectively. SWAT simulation presented satisfactory agreements with measured data for sediment and pesticides predictions at the Orestimba Creek watershed. The dependence of pesticide loads on the application timing and surface-runoff occurrence has been documented in our previous studies (Luo et al., 2008; Luo and Zhang, 2009). Another potential source of model uncertainty was the change in agricultural land cover (e.g., crop types and areas) of the studied watershed. SWAT parameterization in this study was based on the land use survey during 2002–2004, therefore, agricultural land cover changes before and after the survey years were not included in the model simulation. In addition, measured pesticide data, usually as instantaneous concentrations, are highly variable both spatially and temporally, and associated with field sampling uncertainty.

The average loads as percent use (LAPUs) and their annual variability were evaluated for total pesticide predictions (in both dissolved and particulate forms) at field and watershed scales (Table 3). There were general decreasing trends for both LAPUs and their coefficients of variance with the increase of simulated spatial scales (from field scale to small watershed to large watershed). This finding was consistent with the measured data compiled by Capel et al. (2001) for pesticide with moderate in-stream losses. LAPU values at field scale reflected the tendency toward runoff of the pesticides used in the agricultural land, while those predicted at the watershed outlets were also affected by the loss processes in riverine systems (e.g., degradation, volatilization and settling). At fieldscale, pesticide runoff was associated with high variability, and greatly influenced by individual storms, irrigation, and pesticide uses at each field. The variability would be less at larger spatial scales over which agricultural runoffs from multiple fields were integrated. The predicted LAPU values were in agreement with

Table 2
Parameters used in sensitivity analysis for pesticide yields at the edge of fields.

Name	Initial value	Range	Definition
Category I: parameters for pesticide yield and edge-of-field BMPs			
BIOMIX	0.2	0–1	Biological mixing efficiency
CN2	77	35–98	SCS runoff curve number for moisture condition II
FILTERW	5	0–10	Width of filter strip (m)
HRU_SLP	0.004	0–0.6	Average slope steepness
OV_N	0.14	0.1–0.3	Manning's "n" for overland flow
PND_FR	0.5	0–1	Fraction of the subbasin area draining into the pond
SOL_AWC	0.17	0–1	Available water capacity of the soil layer
SOL_K	8.5	0–100	Soil conductivity (mm h^{-2})
USLE_C	0.001–0.2	0–0.2	Minimal value of USLE equation cover and management factor
USLE_K	0.32	0–0.65	USLE equation soil erodibility factor
USLE_P	1	0.1–1	USLE equation support practice factor
Chemical properties: HLIFE_F, HLIFE_S, and K_{OC} (Table 1)			
Category II: parameters for in-stream pesticide loss			
CH_COV	0.5	0–0.6	Channel cover factor
CH_EROD	1	0–1	Channel erodibility factor
CH_N1	0.014	0.008–0.065	Manning's "n" value for the tributary channels
CH_N2	0.014	0.01–0.3	Manning's "n" value for the main channels
CH_S1	0.0051	0–1	Average slope for tributary channels
CH_S2	0.001	0–1	Average slope for the main channel
SPCON	5×10^{-4}	$1 \times 10^{-4} - 0.01$	A linear parameter used in channel sediment routing
Chemical properties: CHPST_REA, HENRY, and K_{OC} (Table 1)			

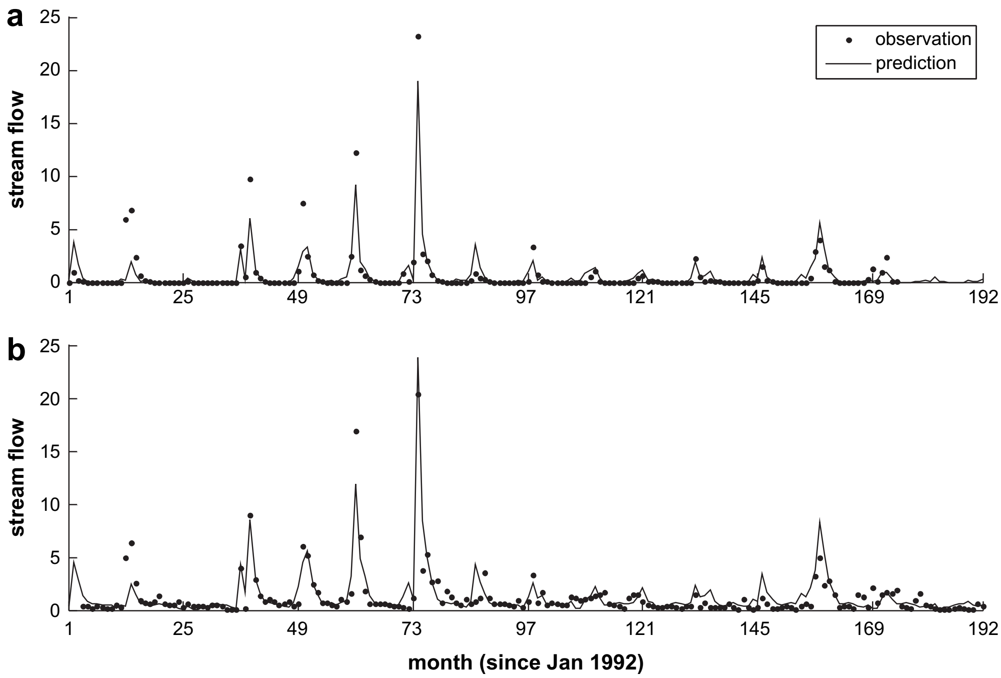

Fig. 2. Predicted and observed monthly stream flow ($m^3\ s^{-1}$) at USGS sites (a) #11274500 and (b) #11274538 (Fig. 1).

those reported in the literature. For example, Capel et al. (2001) reported the LAPU values of 0.220 ± 0.430% for diazinon, and 0.013 ± 0.030% for chlorpyrifos based on nation-wide sampling in large watersheds (>1000 km^2) of the United States. Simulation results also indicated that the LAPU values for a pesticide in wet years were significantly higher than those predicted in dry years. Similarly, precipitation also had effects on the monthly variations of pesticide LAPU values. The predicted monthly LAPU values during rainfall season (December–March) were up to 10 times of the annual averages, which was consistent with the results from field-scale studies in the Orestimba Creek watershed (Luo and Zhang, 2009). Similarly, rainfall-induced runoff generated higher pesticide yield relative to runoff caused by irrigation in the San Joaquin Valley (Luo et al., 2008). In California, many pesticides applied during winter cause problems when rain washes residues into rivers and stream; therefore, regulatory controls have been imposed to restrict pesticides used as dormant sprays (CEPA, 2006).

3.2. Factors controlling pesticide yields from agricultural land

Table 5 highlights the major influential parameters based on sensitivity analysis for pesticide yield from agricultural fields. A negative sensitivity index indicated that the model output was inversely correlated to the corresponding input parameter. Sensitivity analysis results indicated that the governing factors for pesticide supply to the Orestimba Creek were hydrological parameters involving the generation of water and sediment runoff (Table 5). The curve number for antecedent moisture condition (CN2) was identified to be the most important parameter. As a function of the soil permeability, land use, and hydrologic condition, CN2 is an empirical parameter used for predicting direct runoff from rainfall excess in SWAT. High CN2 values cause most of the rainfall to appear as runoff, while lower values correspond to increased water retention in the soil. As discussed before, the Orestimba Creek area was highly vulnerable to surface runoff. The sensitivity index of CN2 to total pesticide yield were 9.97 for chlorpyrifos and 8.05 for diazinon. The values were higher than those reported for various pesticides in the San Joaquin Valley (Luo et al., 2008), 7.53 for chlorpyrifos and 5.57 for diazinon, and in the Smith Fry watershed, Indiana (Arabi et al., 2007), 6.78 for atrazine. With sensitivity indices of 0.44 and 0.72 for chlorpyrifos and diazinon, respectively, dissolved pesticide yields were also sensitive to available water content of soil (SOL_AWC) which affects surface runoff and lateral flow as carrying media for pesticide transport. The yields of pesticides in particulate form were mainly determined by the sediment yields, sensitive to the USLE (Universal Soil Loss Equation) parameters (Table 2), such as soil USLE_C, USLE_K, USLE_P, and topographic factor (calculated based on slope, HRU_SLP). In this study area, both high pesticide use and high suspended sediment concentration were observed during irrigation season (Fig. 3). This condition suggested a very high pesticide runoff potential in the study area, especially for chemicals with large K_{OC} values. Therefore, field yield of pesticides in this area could be efficiently reduced by BMPs designed for sediment reductions.

K_{OC} had only a moderate impact on the total pesticide yield, although it affected pesticide partitioning between dissolved and particulate phases. The only chemical property that was in competition with the hydrologic parameters was degradation half-life in soil (HLIFE_S), which determined the amount of pesticides in the soils available to water and sediment runoff. Further data analysis indicated that the effects of the HLFE_S on the total pesticide yield were determined by the soil mobility and application timing of a pesticide. With lower mobility in the soils (higher K_{OC}), pesticides were more likely to remain in top soil layers and be extracted during surface-runoff events. Similarly, during irrigation seasons pesticides might accumulate in the soil columns due to the lack of mobile water. Therefore, large sensitivity on HLFE_S was associated with pesticides with higher K_{OC} and/or large fraction of irrigation-season use.

3.3. Factors of pesticide in-stream processes

Once released into streams, pesticides undergo physical and chemical processes such as volatilization, sedimentation, and

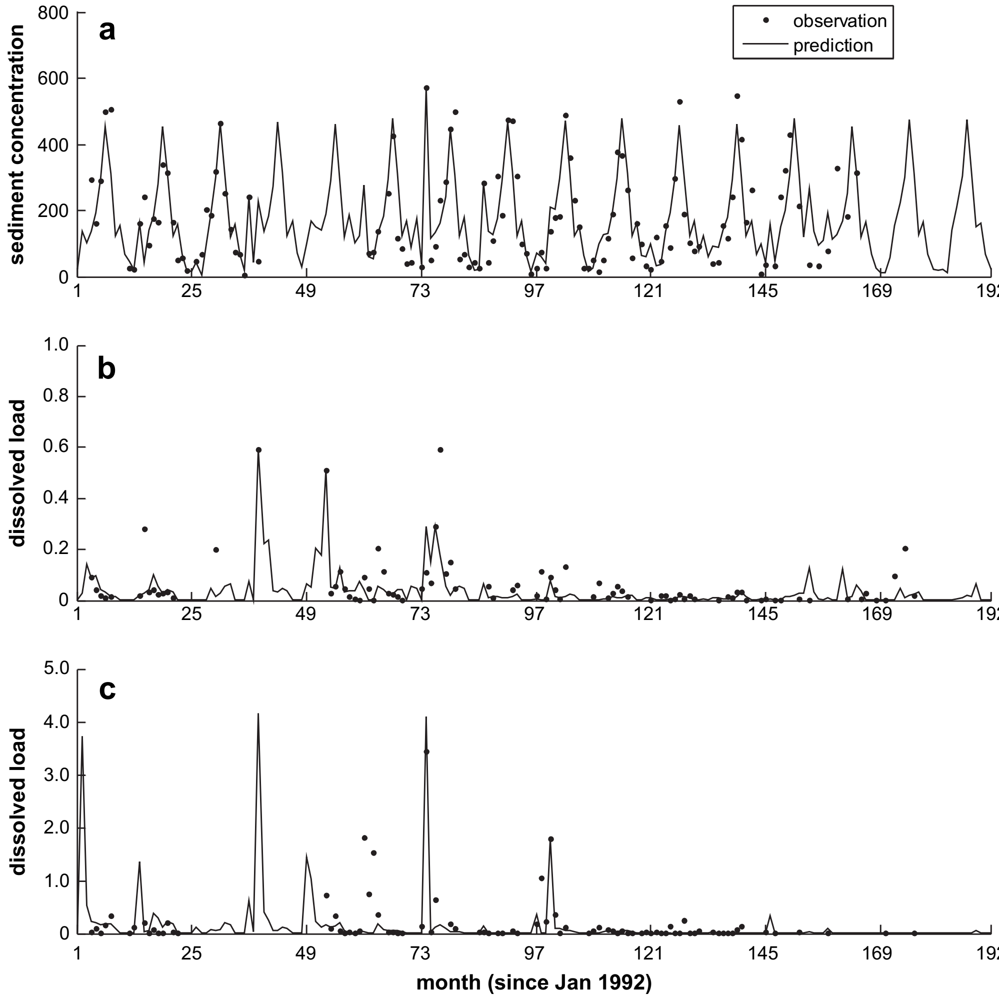

Fig. 3. Predicted and observed monthly average of (a) sediment concentration (mg L^{-1}), and in-stream loads (kg mon^{-1}) of (b) chlorpyrifos and (c) diazinon at Orestimba Creek outlet (USGS #11274538).

degradation. The relative importance of those processes were indicated by the results of sensitivity analysis, as reported by the sensitivity indices for selected SWAT input parameters for channel transport simulation (Table 6). Almost all parameters in Table 6 affected pesticide loads in both dissolved and particulate phases, since dynamic equilibrium was assumed to be established instantaneously between the two phases in the SWAT simulation. In the Orestimba Creek watershed, pesticide transport was mainly sensitive to the channel characteristics that influenced sediment transport capacity of the channel system, such as the sediment routing parameter (SPCON) and roughness coefficient (CH_N). Channel erosion, which was simulated based on the channel cover factor (CH_COV) and erodibility factor (CH_EROD), had negligible effects on the predictions of total pesticide loads. These results suggested that adsorption and consequent sedimentation were the governing processes in determining in-stream fate and transport of pesticides in the study areas. With increased sediment concentration in the stream, two competitive processes could occur simultaneously: [1] more pesticide partitioning to particulate phase as shown in Eq. (1), and [2] more pesticide being deposited into bed sediment due to elevated pesticide concentration in suspended sediment. The results of the sensitivity analysis indicated that the dominant process of a pesticide transport was mainly determined by its K_{OC} value. Predictions of total in-stream loads of chlorpyrifos were more sensitive to the sediment concentration, while elevated sediment concentration only had moderate influences on the total diazinon load. These results indicated that sedimentation was the primary in-stream process for the pesticides with high K_{OC} values.

Key processes for pesticide in-stream loss were also identified by comparing the sensitivities of chemical properties. Generally,

Table 3
Predicted LAPU (load as percent use) for pesticide at various spatial scales during 1992–2006 (coefficients of variance in parentheses).

Predictions	Drainage area (km^2)	LAPU	
		Chlorpyrifos	Diazinon
Pesticide yield from agricultural lands in the Orestimba Creek watershed	146	0.047 (0.839)	0.199 (1.151)
Pesticide in-stream load at the outlet of Orestimba Creek	563	0.034 (0.734)	0.185 (1.121)
Pesticide in-stream load at the outlet of San Joaquin River	14 983	0.033 (0.649)	0.137 (0.578)

Note: the results for pesticide in-stream load at the outlet of San Joaquin River were based on the modeling results from our previous study (Luo et al., 2008).

Table 4
Results of statistical evaluation comparing observations and model predictions of stream flow, sediment, and pesticides in the Orestimba Creek watershed during 1992–2007.

USGS gauge ID and variables	11274500	11274538			
	Stream flow	Stream flow	Sediment	Chlorpyrifos	Diazinon
Rainfall season (December–March)					
NSE	0.79	0.77	0.63	0.64	0.52
PBIAS	0.02	−0.16	−0.22	0.20	0.50
Irrigation season (April–October)					
NSE	–	0.59	0.62	0.50	0.70
PBIAS	–	0.02	−0.01	0.28	0.14
Overall					
NSE	0.82	0.78	0.70	0.55	0.58
PBIAS	−0.04	−0.09	−0.04	0.25	0.35

Notes: Measurements are not available at gauge #11274500 during summer months when the Orestimba creek is usually dry out at this site. NSE = Nash-Sutcliff efficiency; PBIAS = Percent bias.

K_{OC} had negative effects on the total in-stream load predicted for both pesticides, although the loads in particulate phase were significantly increased with high K_{OC} values. It was in consistence with the results of pesticide in-stream losses by Capel et al. (2001), in which pesticides with higher partition coefficient need shorter travel times to have a given in-stream losses. By comparing the corresponding sensitivity results of chlorpyrifos and diazinon, volatilization was shown to be an important process for pesticides with higher Henry's law constant (HENRY of 3.0×10^{-4} for chlorpyrifos and 3.0×10^{-5} for diazinon, Table 1). Model results also revealed that the model predictions were not sensitive to the transformation half-lives of both chemicals instreams. Therefore, degradation was not a governing process for in-stream transport of chlorpyrifos and diazinon in the study area.

3.4. Demonstration of BMPs in the Orestimba Creek watershed

Based on the results of sensitivity analysis, conservation practices were evaluated for their water-quality impacts at field and watershed scales in the Orestimba Creek watershed. Four types of BMPs were evaluated in this study: [1] crop residue management, [2] filter strip, [3] tailwater pond, and [4] grassed waterway. Crop residue management is implemented within agricultural fields. This practice decreases pesticide yields by increasing land cover and surface roughness and hence reducing surface runoff and soil erosion. Field strips and tailwater ponds are installed at the edge of agricultural fields to reduce sediment and pesticide in surface runoff. Grassed waterways are implemented within the channel network in order to trap sediment by reducing flow velocity and decreasing channel erosion. SWAT parameter adjustment for BMP representation was taken from literature review and USDA technical guidance (Table 7). All conservation practices were applied in agricultural lands in the lower portion of Orestimba Creek watershed. Effectiveness was defined as the relative reduction of monthly average predictions of sediment and pesticides before and after BMP implementation, and reported at both field and watershed scales.

The in-field practice of crop residue management is designed to decrease both soil erosion and water runoff. Under this practice, similar reduction effectivenesses were predicted for the yields of both pesticides. This was also in agreement with the sensitivity analysis results in Table 5, where similar sensitivity indices for CN2, USLE_P, and OV_N were reported for total pesticide yields of chlorpyrifos and diazinon. For filter strips, SWAT incorporates its effect through a single value of trapping efficiency used for sediment, nutrients and pesticides in surface runoff. As shown in Eq. (2), the trapping efficiency was calculated as 59% with FILTERW = 5 m. Lateral flows also contribute to pesticide yields, but are not treated in filter strips. Therefore, the reduction effectiveness of pesticides was lower relative to the theoretical value of 59% (Table 7). By applying a fixed value for pesticide reduction through filter strip, SWAT prediction might overestimate the reduction of pesticides in dissolved phase, especially for chemicals with lower K_{OC}. Other BMPs of tailwater pond and grassed waterway are mainly designed to reduce soil erosion and sediment amount. Therefore, in general higher effectivenesses were observed for chlorpyrifos with higher soil adsorption compared to diazinon as shown in Table 7.

Table 5
Sensitivities (reported as sensitivity indices) of water, sediment, and pesticide yields from agricultural fields of the Orestimba Creek watershed.

Parameters	Surface runoff	Sediment yield	Chlorpyrifos			Diazinon		
			Dissolved	Sorbed	Total	Dissolved	Sorbed	Total
BIOMIX	−0.01	0.03	−0.01	0.00	−0.01	−0.02	−0.02	−0.02
CN2	*9.90*	*8.93*	*4.72*	*12.21*	*9.97*	*5.70*	*10.73*	*8.05*
FILTERW	0.00	−0.41	−0.27	−0.42	−0.36	−0.26	−0.42	−0.32
HLIFE_F	–	–	0.01	0.01	0.01	0.02	0.00	0.01
HLIFE_S	–	–	*0.96*	*1.08*	*1.05*	0.69	0.50	*0.60*
HRU_SLP	−0.01	*1.27*	0.17	*1.08*	*0.81*	0.21	*1.15*	*0.65*
K_{OC}	–	–	*−0.94*	0.07	−0.23	*−0.71*	0.46	−0.16
OV_N	0.00	−0.08	0.00	−0.06	−0.04	0.00	−0.06	−0.03
PND_FR	−0.01	−0.61	−0.10	−0.68	−0.45	0.14	*−0.92*	−0.16
SOL_AWC	*0.16*	−0.04	0.44	−0.12	0.05	*0.72*	−0.29	0.25
SOL_K	*−0.06*	0.00	0.19	−0.01	0.05	0.20	−0.01	0.10
USLE_C	0.00	0.74	−0.01	0.65	0.45	0.00	0.69	0.32
USLE_K	0.00	0.58	0.00	0.49	0.35	0.00	0.53	0.25
USLE_P	0.00	*0.79*	−0.01	0.69	0.48	0.00	0.74	0.34

Notes: 1. Condition numbers with abstract values less than 0.005 were reported as 0.00. 2. Top three parameters in each category are italicised.

Table 6
Sensitivities (reported as sensitivity indices) of water, sediment, and pesticide loads at the outlet of Orestimba Creek.

Parameters	Stream flow	Sediment load	Chlorpyrifos			Diazinon		
			Dissolved	Sorbed	Total	Dissolved	Sorbed	Total
CH_COV	0.00	0.07	*−0.04*	0.02	0.00	0.00	0.01	0.00
CH_EROD	0.00	0.07	−0.04	0.03	0.00	0.00	0.01	0.00
CH_N1	0.00	0.01	0.01	−0.01	0.00	*−0.02*	−0.03	−0.02
CH_N2	0.00	*−0.43*	0.04	*−0.42*	*−0.24*	0.00	*−0.53*	*−0.04*
CH_S1	0.00	0.00	0.00	0.01	0.00	0.01	0.02	0.01
CH_S2	0.00	*0.26*	−0.02	0.19	*0.11*	0.00	0.31	*0.02*
CHPST_REA	–	–	0.00	0.00	0.00	0.00	0.00	0.00
K_{OC}	–	–	*−0.51*	*0.27*	−0.04	*−0.12*	*0.83*	*−0.05*
HENRY	–	–	−0.02	−0.01	−0.01	0.00	0.00	0.00
SPCON	–	*0.70*	*−0.13*	*0.44*	*0.21*	*−0.05*	*0.78*	0.01

Notes: 1. Condition numbers with abstract values less than 0.005 were reported as 0.00. 2. Top three parameters in each category are italicised.

Table 7
Predicted reduction effectiveness for water, sediment and pesticide with BMPs implemented in the agricultural land of Orestimba Creek watershed.

BMPs	Surface runoff	Sediment		Chlorpyrifos		Diazinon	
		Yield	Load	Yield	Load	Yield	Load
Crop residue management	20%	47%	8%	32%	22%	29%	27%
Filter strip	–	59%	14%	56%	48%	53%	51%
Tailwater pond	–	38%	4%	31%	19%	14%	11%
Grassed waterway	–	–	88%	–	54%	–	7%

Notes: Pond dimensions were calculated following the USDA NRCS Electronic Field Office Technical Guide (USDA, 2007), with PND_FR = 0.5 and an operating depth of 2.44 m (8 ft). Representations for other BMPs were taken from the SWAT modeling by Arabi et al. (2006; 2007) and Bracmort et al. (2004, 2006):
Crop residue management: reduce CN2 by 2 units; set USLE_*P* = 0.55 (for 500 kg ha^{-1} residue); OV_*N* = 0.2.
Filter strip: set FILTERW = 5.0 m.
Grassed waterway: set CH_*N*2 = 0.24, CH_COV = 0, CH_EROD = 0.

According to local surveys, BMPs being used or proposed in the study area include cover crops, filter strips, tailwater ponds, and grassed waterways (CURES, 2006). In addition to landscape characteristics, hydroclimatology conditions, and environmental concerns considered in model simulations, the choice of BMPs is also dependent on local agricultural pattern and economic consideration. Simulations of selected BMPs in this study evaluated influential factors and key processes in pesticide fate and transport. The simulation results could be extended to investigate other BMPs with similar mitigation mechanisms. For example, the sensitivity and effectiveness of pesticide reduction to CN2 and USLE factors demonstrated by crop residue management could also be applied to other BMPs such as contour farming, cover crop, parallel terraces, and strip-cropping.

4. Conclusion

In this paper, pesticide fate and transport in an agriculturally dominated watershed were evaluated by SWAT modeling. The model simulation was applied in the field conditions of the Orestimba Creek watershed, California, with two widely used organophosphate pesticides chlorpyrifos and diazinon during 1990–2007. The calibrated SWAT generated reliable simulation results for the stream flow, sediment, and pesticides in the studied watershed. By comparing with the results of SWAT model previously calibrated for the San Joaquin River basin, this study demonstrated model capability in evaluating pesticide transport and transformation at spatial scales of field, small watershed, and large watershed. Model results indicated that there were general decreasing trends for the amounts and variations of pesticide runoff with the increase of simulated spatial scales. This result suggested further investigations for spatial scaling effects on the model performance and predicted effectiveness of conservation practices.

By reviewing theoretical considerations of SWAT in simulating pesticide processes, management-oriented sensitivity analysis was conducted to identify governing parameters and processes to protect water quality. Sensitivity was calculated based on the calibrated model parameters and the actual subbasin connectivity in the study area. The results of sensitivity analysis in this study, compared to a global sensitivity analysis in "single-catchment" scenario, therefore, provided more meaningful information for the evaluation of local water quality and management practices. The curve number was identified as the most important factor in the field yield of pesticides, by affecting both runoff generation and soil erosion. The USLE parameters had substantial effects on the pesticide yields in particulate form, suggesting efficient removals of pesticides with large K_{OC} values by conservation practices designed for sediment reductions. For in-stream processes, channel erosion had negligible effects on the sediment and pesticide transport in the study area. In-stream pesticide loss was mainly sensitive to the parameters of channel roughness and sediment transport capacity.

Based on the sensitivity analysis, selected BMPs were evaluated in the agricultural portion of the study area. With recommended parameter settings for BMP representation, results of SWAT simulation indicated potential decreases of sediment and pesticide outputs at field and watershed scales. BMP representation by SWAT modeling provided useful information for regulatory agencies and local farmers in determining appropriate conservation practices. The methods exhibited in this study can be also used to investigate parameter sensitivity and conservation practices when applying a complex watershed model in management decision support to protect surface water quality.

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