A Geo-Referenced Modeling Environment for Ecosystem Risk Assessment: Organophosphate Pesticides in an Agriculturally Dominated Watershed

Yuzhou Luo and Minghua Zhang* Wenzhou Medical College, University of California–Davis

A geo-referenced modeling system was developed in this study to investigate the spatiotemporal variability of pesticide distributions and associated ecosystem risks. In the modeling system, pesticide fate and transport processes in soil-canopy system were simulated at field scale by the pesticide root zone model (PRZM). Edge-of-field mass fluxes were up-scaled with a spatially distributed flow-routing model to predict pesticide contaminations in surface water. The developed model was applied to the field conditions of the Orestimba Creek watershed, an agriculturally-dominated area in California's Central Valley during 1990 through 2006, with the organophosphate insecticides diazinon and chlorpyrifos as test agents. High concentrations of dissolved pesticides were predicted at the watershed outlet during the irrigation season of April through November, due to the intensive pesticide use and low stream flow. Concentration violations, according to the California aquatic life criteria, were observed for diazinon before 2001, and for chlorpyrifos during the entire simulation period. Predicted pesticide exposure levels showed potential adverse effects on certain genera of sensitive aquatic invertebrates in the ecosystem of the Orestimba Creek. Modeling assessments were conducted to identify the factors governing spatial patterns and seasonal trends on pesticide distribution and contamination potentials to the studied aquatic ecosystem. Areas with high pesticide yields to surface water were indicated for future research and additional studies focused on monitoring and mitigation efforts within the watershed. Improved irrigation techniques and management practices were also suggested to reduce the violations of pesticide concentrations during irrigation seasons.

Certain negative consequences of agricultural pesticides on ecosystem and human health have been recognized since the 1960s. Seeking to contain those threats, numerous models have been developed for pesticide transport in agricultural environments, especially in canopy-soil system. Widely-used leaching models describe pesticide attenuation in soils, as well as transport via outflows from soils at field scale. The representative field-scale models for pesticide transport and fate simulation include HYDRUS (2005), groundwater loading effects of agricultural management system (GLEAMS) (Knisel, 1980), leaching estimation and chemistry model for pesticides (LEACHP) (Hutson and Wagenet, 1993), pesticide emission assessment at regional and local scales (PEARL) (Boesten and van der Linden, 2001), and pesticide root zone model (PRZM) (USEPA, 2006). Within a regulatory framework, those field-scale models are typically used to simulate edge-of-field pesticide loads associated with surface runoff and lateral flow (USGS, 2005; Schulz and Matthies, 2007). Compared to watershed-scale models, such as hydrological simulation program- fortran (HSPF) and soil and water assessment tool (SWAT), the field-scale models better account for hydrologic processes within fields and have the capability to simulate most agricultural management practices. In an agriculturally-dominated watershed, a field-scale simulation of pesticide behaviors is required to reflect the cropping fields with distinct agricultural activities. Therefore, the field-scale models are used quite extensively in pesticide regulation decisions, especially for assessments of groundwater vulnerability and ecological risk to pesticide use.

The edge-of-field approach in the field-scale models usually disregards any retention of pesticides occurring between application areas and the receiving surface waters. Therefore, the impacts of landscape characteristics and of management practices on pesticide distribution and associated environmental risks over a watershed are not well represented. The capability of a field-scale model in predicting pesticide fate and transport can be improved by combining with a hydrologic routing algorithm which describes attenuation processes during horizontal transport from field edges to a downstream location (Gowda et al., 1999; Schulz and Matthies, 2007). By applying the field-scale models in watershed scale, spatiotem-

Published in J. Environ. Qual. 38:664–674 (2009).
doi:10.2134/jeq2008.0216
Received 5 May 2008.
*Corresponding author (mhzhang@ucdavis.edu).

677 S. Segoe Rd., Madison, WI 53711 USA

Y. Luo and M. Zhang, Wenzhou Medical College, Wenzhou 325035, China; Y. Luo and M. Zhang, Dep. of Land, Air and Water Resources, Univ. of California, Davis, CA 95616.

Abbreviations: CCID, Central California Irrigation District; GIS, geographic information systems; GLEAMS, groundwater loading effects of agricultural management system; HSPF, hydrological simulation program-Fortran; LAPU, load as percent of use; PEARL, pesticide emission assessment at regional and local scales; PRZM, pesticide root zone model; PUR, pesticide use report; SWAT, soil and water and assessment tool; USLE, universal soil loss equation.

poral variations on pesticide distribution could be correlated to pesticide species, soil properties, weather conditions, pesticide applications, and other agricultural management practices.

In recent years new software techniques, such as geographic information systems (GIS), have provided the capability to a growing number of studies in incorporating field-scale models in watershed modeling strategies. For example, Gowda et al. (1999) developed a watershed routing model to predict peak flows in agricultural watersheds based on field-scale simulation results from the GLEAMS model for each cluster of hydrological response units. Double triangle unit hydrographs were used to estimate storm flows in their study, but an agrochemical transport simulation was not performed. Eason et al. (2004) coupled the PRZM model with ESRI ArcView GIS to produce a statewide assessment of groundwater vulnerability to agricultural pesticide use. However, pesticide transport by surface and subsurface runoffs was not considered. Gustafson et al. (2004) used the convective dispersion equation to up-scale PRZM-generated concentrations to watershed scale. Chu and Marino (2004) used lumped regression models to describe the contributions of pesticide residues from several fields to a watershed outlet. These approaches included simplified algorithms for routing water and pesticide flows from field edges to a downstream river site, so they are not appropriate to predict the spatial variability of pesticide transport and mitigation in a watershed. Therefore, there is a need for spatially distributed routing procedures to apply field-scale water quality simulation models to watershed scale.

This paper describes a spatially explicit approach in simulating the spatiotemporal variations of pesticide transport at watershed scale, with the aim of better evaluating the potential risks associated with pesticide exposure in aquatic ecosystems. Variability in edge-of-field pesticide loads was predicted using the PRZM model. A linear routing model was used to generate hydro- and polluto-graphs and route the spatially distributed water and pesticide runoffs predicted by the PRZM throughout the landscape to a predefined watershed outlet. The developed modeling system was applied to make predictions for contamination levels of the organophosphate pesticides diazinon (*O*,*O*-diethyl-*O*-(2-isopropyl-6-methyl-4-pyrimidinyl) phosphorothioate, CAS 333–41–5) and chlorpyrifos (*O*,*O*-diethyl-*O*-(3,5,6-trichloro-2-pyridinyl) phosphorothioate, CAS 2921–88–2) in the Orestimba Creek watershed, California. Finally, potential ecosystem risks from pesticide exposure were evaluated by comparing the predicted contamination levels to water quality criteria and toxicity values of sensitive aquatic organisms at the watershed outlet.

Modeling Approach

Coupling Pesticide Root Zone Model with ArcGIS

In the modeling environment developed in this study, the edge-of-field water, sediment, and pesticide fluxes were simulated by the PRZM release 3.12.3 (PRZM3), which is currently considered by the U.S. Environmental Protection Agency (USEPA) for pesticide transport and associated risk assessment (USEPA, 2006). The PRZM3 is a one-dimensional dynamic model for simulating water and pesticide movements in canopy and unsaturated soil layers. It can also model complex agricultural scenarios such as pesticide application techniques, plant development, and other agricultural management practices. The PRZM3 predicts pesticide fate and transport at an appropriate scale and time interval for chemical dissipation with wide ranges of physiochemical properties, which supports the transferability of the modeling system in various landscape and pesticide types.

The PRZM3 is a "unit-area" model and the functional unit, called a PRZM "zone" in the model documentation, is represented as a uniform area in regard to landscape characteristics, climate conditions, and management practices. In this study, GIS technology was used to extend the capability of the PRZM3 for georeferenced parameterization and application at watershed scale. Spatial analysis and geodata management provided by the ESRI ArcGIS 9.2 platform were used to estimate spatially distributed parameters of the PRZM3. The GIS map layers required in this study included digital elevation model (DEM) data, land use map, soil map, and stream network for each simulation zone. These maps were first rasterized into a uniform grid system. Spatially distributed parameters were calculated over the grid system and then aggregated for each simulation zone as averages (for quantitative parameters, e.g., slope) or as coverage fractions for multiple components (for qualitative parameters, e.g., crop type).

Elevation-related parameters such as slope, flow direction, and flow accumulation were directly obtained from the Spatial Analyst Extension in ArcGIS. The topographic length-slope (LS) factor in the universal soil loss equation (USLE) was estimated from flow accumulation and slope (Haan and Barfield, 1978; USEPA, 2004). Spatially distributed soil properties required by the PRZM3 simulation include bulk density, water contents (initial water content, field capacity, and wilting point), organic C content, soil erodibility for the USLE, and soil hydrologic group. Those soil properties were extracted from soil maps and associated databases. The regression equations developed by Saxton and Rawls (2006) were used to estimate soil water characteristics from the ready variables of soil texture and organic matter content. Indices of land use classification were used for organizing crop management and pesticide application data. Curve numbers were estimated by considering the soil hydrologic group and land use type (USDA, 1986).

Spatially Distributed Flow and Transport Routing

The PRZM3 produces "edge-of-field" estimates of pesticide losses in surface runoff and lateral flow for each simulation zone. To link the zone-based prediction results at watershed scale, watershed hydrographs and pollutographs were generated based on the theory of linear routing systems. The routing model presented here generalized the unit hydrograph method for runoff and pollutant responses on a spatially distributed watershed. Therefore, hydrological responses from PRZM3 simulation zones of the watershed were simulated separately rather than being spatially averaged.

For flow simulation, surface and subsurface runoff flows predicted by the PRZM3 for each simulation zone were taken as inputs for the flow routing model. Two processes were involved in the routing calculation, that is, routing from the edge of field to the stream channel and routing along the channel system to a down-

stream location as routing destination. Before reaching the channel streams, edge-of-field surface and subsurface runoffs were assumed to travel over a distance, which was empirically determined based on the enclosed landscape management units and channel stream density. The stream flow at the routing destination was calculated as the sum of convolutions between runoff and watershed unit hydrograph yield in each simulation zone (Maidment et al., 1996),

$$Q(t)=\sum_i Q_i(t)$$

$$Q_i(t)=A_i\int_0^\infty [I_{Qi}(\tau)U_{Qi}(t-\tau)+I_{Si}(\tau)U_{Si}(t-\tau)]d\tau \quad [1]$$

where Q_i (m^3/s) is stream flow at the routing destination contributed by zone i, A_i (m^2) is the area of i, I_{Qi} and I_{Si} (m/s) are surface and subsurface runoff flows from i predicted by the PRZM3, respectively, and U_{Qi} and U_{Si} (s^{-1}) are the corresponding flow-path redistribution functions presenting the response at the routing destination by a unit instantaneous input in i. In this study, the flow-path redistribution functions (U's) were estimated according to the first passage time distribution by accounting flow velocity, flow diffusivity, and water loss (evaporation) rate (Olivera et al., 1996; Olivera and Maidment, 1999),

$$U_i(t)=\frac{1}{2t\sqrt{\pi(t/T_i)\Delta_i}}\exp\{-\frac{[1-(t/T_i)]^2}{4(t/T_i)\Delta_i}\}K_i \quad [2]$$

where T_i (s) is the lag time in the flow-path, Δ_i (-) represents the shear and storage effects on the flow, and K_i (-) is the flow-path loss factor. Those parameters can be derived by statistical analysis of the first passage time distribution as follows,

$$T_i=\sum_j (l_j/v_j) \quad [3]$$

$$\Delta_i=\frac{\sum_j (l_j/v_j^3)D_j}{[\sum_j (l_j/v_j)]^2} \quad [4]$$

$$K_i=\exp[-\sum_j (l_j/v_j)\lambda_i] \quad [5]$$

where j refers to the simulation zone along the flow-path, l_j (m) is the flow length, v_j (m s^{-1}) is the flow velocity, D_j (m^2 s^{-1}) is the flow diffusivity, and λ_j (s^{-1}) is the water loss rate.

The routing algorithm and parameter estimation for water flow routing could also be applied to pesticide transport routing, with I values denoting the zone-based pesticide yields in overland flow and lateral flow predicted by the PRZM3 for each simulation zone. Pesticide transport routing was based on the same parameters of flow lengths and flow velocities used in the water flow routing. Chemical dispersion coefficient was determined as the sum of molecular diffusivity and flow diffusivity for the corresponding flow paths. Pesticide decay rate was calculated from its half-life. Pesticide distribution between dissolved and sorbed phases was estimated based on the water/sediment partitioning coefficient, which is the product of the pesticide organic C partition coefficient (K_{OC}) and the organic C content of a typical soil in the study area.

Aquatic Risk Assessment for Pesticide Exposure

As organophosphate pesticides, diazinon and chlorpyrifos are considered as neurotoxins which inhibit the break down of the neurotransmitter acetylcholine at neural junctions. With the interference of those pesticides, the enzyme acethylcholinesterase accumulates and consequently the peripheral nervous system was overstimulated. The USEPA issues water quality criteria for the protection of aquatic organisms and their uses for approximately 150 pollutants (USEPA, 2007). For widely used pesticides such as diazinon and chlorpyrifos, the California Department of Fish and Game (CDFG) provides water quality objectives based on LC50 values (lethal concentration) for aquatic organisms. Summarized in Table 1a are water quality standards for diazinon and chlorpyrifos. Aquatic risk assessment in this study was first conducted by comparing the 96-h (4-d) moving averages of predicted in-stream dissolved concentration of a pesticide to the corresponding water quality criteria. The concentration violations were identified as exposure events for further risk characterizations.

Effects of predicted pesticide residues on an aquatic ecosystem were evaluated by comparing the exposure levels to the toxicity values for sensitive aquatic organisms (Table 1b). Typical and typical-worst conditions of pesticide exposure were calculated as concentrations at the 50th and 90th percentiles of all events with concentrations exceeding the water quality criteria, respectively. Toxicity data of EC50 (effect concentration) or LC50 for 48-h exposure duration were obtained from published laboratory toxicity studies. To be consistent with the exposure durations used in the USEPA and CDFG water quality criteria, the 96-h toxicity values in this study were estimated as 65% of the corresponding 48-h values (Bailey et al., 1997). All statistical analyses were done with SAS package version 9.2 (SAS, 2008).

Case Study in the Orestimba Creek Watershed, California

Site Description

The modeling framework developed in this study was applied to the field conditions of the Orestimba Creek watershed, California, with two widely used organophosphate insecticides chlorpyrifos and diazinon as test agents. Originating in mountains of the Coast Range in western Stanislaus County, the Orestimba Creek flows through farmlands in the San Joaquin Valley and discharges into the San Joaquin River at river mile 109 (Fig. 1). The forest and rangeland regions of the watershed have slopes of 0.2 to 0.4, while croplands are located in the flat valley floor at elevations of 66 to 20 m. The main soil types are loam and clay loam, with a representative porosity of 0.37 and saturated hydraulic conductivities ranging from 2.7 to 28.2 μm/s. Annual average precipitation is 290 mm, and annual crop evapotransportation rate is more than 700 mm (CDWR, 2007a). In the late 1940s, farmers in the San Joaquin Valley began installing subsurface drains in fields with drainage problems of an outgrowth of imported water from manmade infrastructures. Ac-

cording to the San Joaquin Valley Drainage Program, subsurface drains are installed by the Newman Drainage District in about 12 km^2 cropping land in the study area. Shallow groundwater table in this area is larger than 6.1 m (or 20 ft) below the ground surface, and not categorized as a "potential drainage problem area" (CDWR, 2007b). Large amounts of organophosphate insecticides are applied to almonds [*Prunus dulcis* (Mill.) D.A. Webb] and other stone-fruit orchards in the Orestimba Creek watershed (Cryer et al., 2001). Many previous studies have discussed the residual levels of organophosphate insecticides, especially chlorpyrifos and diazinon, in this area (Dubrovsky et al., 1998; Ross et al., 1999; Kratzer et al., 2002; Domagalski and Munday, 2003; Luo et al., 2008).

The boundary of the Orestimba Creek watershed was defined by the California Central Valley Region Water Quality Control Board (CEPA, 2007b). Delineation of PRZM3 simulation zones followed the Meridian-Township-Range-Section (MTRS) in the U.S. Land Survey System. An MTRS, referred as a section, is a fixed-boundary parcel of land approximately 2.6 km^2 or 1.0 mi^2 in area. The same geographic reporting unit is also used by the California Pesticide Use Reporting (PUR) system. The total area of the Orestimba Creek watershed is 536.2 km^2, enclosing by 200 sections in the counties of Stanislaus and Merced, while cropland area is 103.4 km^2, represented by 40 sections (Fig. 1). According to the farm activity and irrigation water diversion, the watershed could be divided into three regions of [1] nonagricultural area of the Coast Range (CR), [2] the Orestimba Creek Basin (ORE) irrigated by the Del Puerto Irrigation District, and [3] the Central California Irrigation District (CCID) (Cryer et al., 2001; Chu and Marino, 2004).

Input Data

The PRZM3 simulation requires climatic data of precipitation, temperature, wind speed, and solar radiation. Daily climate data was based on the measurements in Newman (37°16′48′′ N, 121°1′12′′ W), California, operated by the National Climate Data Center (NCDC). A preliminary analysis of rainfall data indicated that rainfall events occur mainly during winter, associated with the Mediterranean climate of the region. During summer, stream flow in Orestimba Creek is dominated by agricultural runoff. To interpret the seasonal variations on modeling results, the rainfall season was conveniently defined as December through March, averaging around 71% of annual rainfall. The remaining months were classified as the irrigation season.

Flow direction and flow accumulation in the study area were generated from the National Elevation Dataset (NED) with resolution of 30 m. The drainage system was defined based on the Na-

Table 1a. Water quality criteria (μg/L) by the U.S. Environmental Protection Agency (USEPA) and the California Department of Fish and Game (CDFG).

Exposure duration	Agency	Diazinon	Chlorpyrifos
1-h maximum concentration	USEPA	0.170	0.083
	CDFG	0.160	0.025
96-h average concentration	USEPA	0.170	0.041
	CDFG	0.100	0.015

Table 1b. Toxicity values (μg/L) for 48- and 96-h exposure for sensitive species (Poletika et al., 2002; USEPA, 2005).

		Diazinon		Chlorpyrifos	
Toxonomic name	Organism	48 h	96 h	48 h	96 h
Aedes aegypti	Mosquito	–	–	0.005	0.003
Ceriodaphnia dubia	Cladoceran	0.377	0.245	0.113	0.178
Culex pipiens	Mosquito	–	–	0.028	0.018
Daphnia magna	Cladoceran	1.048	0.681	1.700	1.105
Daphnia pulex	Cladoceran	0.776	0.504	0.210	0.136
Gammarus fasciatus	Amphipod	2.040	1.326	0.453	0.294
Gammarus pulex	Amphipod	–	–	0.099	0.064

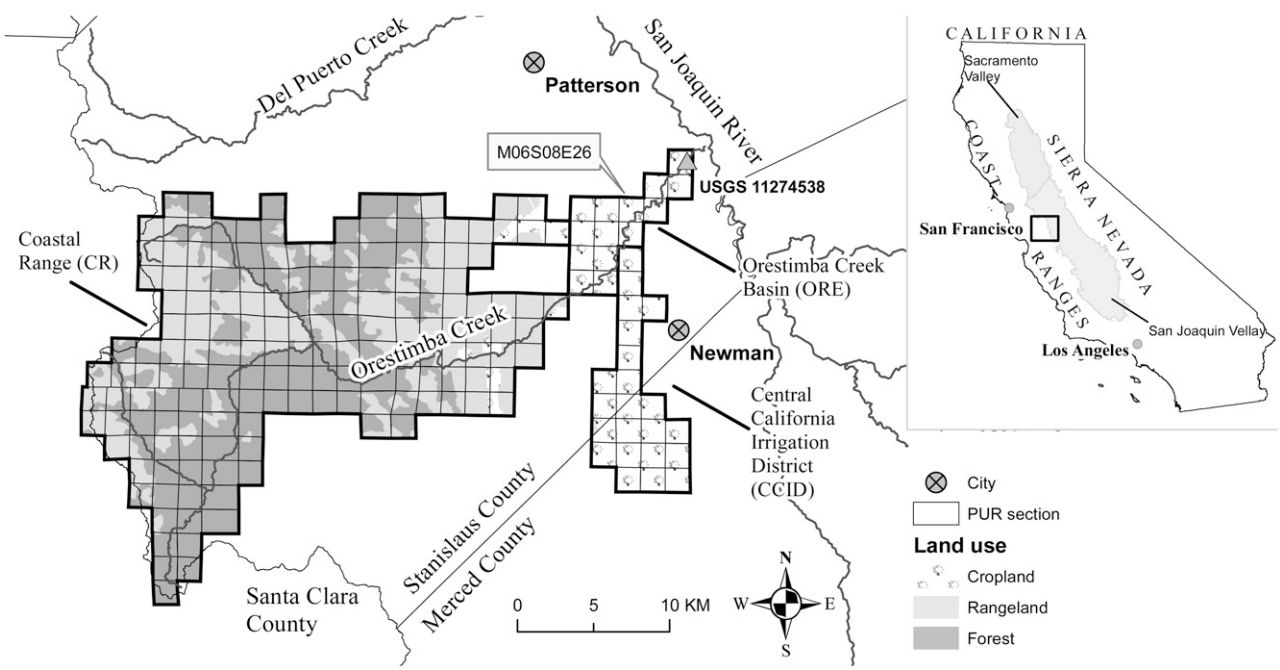

Fig. 1. Simulation zones defined following pesticide use reporting (PUR) sections for Orestimba Creek watershed (Small tributaries and canals are not shown in the map; USGS gauge #11274538 is set as the watershed outlet in this study).

tional Hydrography Dataset (NHD). The distance between field edges and open ditch drains was determined as 3.0 m based on local surveys and recommendations from farm advisors. For the PRZM3 simulation, the slope of each simulation zone was calculated from elevation data. For the flow and transport routing, the slope from field edges to open ditch drains was set as 0.06 for all cropping fields. Velocities of surface runoff were estimated based on Manning's equations, while Darcy's law was applied to calculate the velocities in subsurface-flow regions by assuming the hydraulic gradient was equal to the slope of the over land surface (Lee and Chang, 2005).With a slope of 0.06 between the field edges and the open ditch drains, the average corresponding pore-water velocity was calculated as 1.3 μm/s, ranging from 0.4 to 4.4 μm/s. Flow diffusivities for surface and subsurface flows were determined from hydrologic calibrations as 64.56 and 0.014 m^2/s, respectively, and assumed to be uniform over the watershed to simplify the flow routing processes. Soil properties were extracted from the Soil Survey Geographic (SSURGO) database (USDA, 2007). Restricted drainage was applied for the lower boundary condition in the PRZM3 simulation. Contemporary land use and cropping information were obtained from a spatial database developed by California Dep. of Water Resources (CDWR, 2007a). The latest maps for Stanislaus and Merced counties (2004 and 2002, respectively) were used in this study. The land cover derived from these maps was assumed to be representative of the study area during the entire simulation period. Coniferous forests and rangelands dominate the Coastal Range area of the watershed, while almond, alfalfa (*Medicago sativa* L.), bean, tomato (*Lycopersicon esculentum* Mill.), and walnut (*Juglans* spp.) are major crops in the farmlands of the ORE and CCID. For each section, dominant plant/crop types were determined in PRZM3 parameterization.

Cropping parameters, including cropping dates, interception storage, maximum coverage, active root depth, and irrigation-related parameters, were derived from the USEPA Standard Tier 2 scenarios (USEPA, 2004). For example, flood irrigation was assumed for crops of almonds and walnuts during cropping period. Due to the lack of data for daily irrigation water in the study area, the PRZM3 built-in module for automatic irrigation was used to simulate the irrigation water application. Irrigation is activated when the average root zone soil moisture falls below a threshold value defined by the user as a fraction of the available water capacity (PCDEPL). The amount of soil moisture deficit is then added per unit area to the system as irrigated water by the model. Based on the USEPA suggested PCDEPL value of 0.55 for almond/walnut fields in California, simulated irrigation water use in this study was averaged 659 mm/yr during 1990 to 2006. The results were consistent with reported annual water applications of 409 to 762 mm for 1998 to 2001 for the study area (CDWR, 2007a).

Table 2 lists the chemical-specific properties of diazinon and chlorpyrifos used in the simulation of the PRZM3 and flow routing. For pesticide application amount, daily data during 1990 through 2006, the most recent year available at the time of this study, was retrieved from the PUR database maintained by the California Dep. of Pesticide Regulation (CEPA, 2007a). As discussed before, the PUR data is organized following MTRS geographic units, and can be directly linked with the corresponding zones defined for the PRZM3 simulation. During the study period, annual average uses of pesticides were 742 and 2781 kg for diazinon and chlorpyrifos, respectively. There are general decreasing trends for the uses of both pesticides. Since 2001, an average of only 138 kg/yr of diazinon has been applied in the watershed, while annual chlorpyrifos use was averaged 1720 kg. Majority of both pesticides (75.7% of diazinon and 83.9% of chlorpyrifos) in the watershed are applied during the irrigation season.

Simulation Design

The PRZM3 and routing simulations were performed for the Orestimba Creek watershed at daily time interval for the period of 1990 through 2006. The first two simulation years were applied as model initialization and hydrologic calibration periods. Dynamic PRZM3 outputs were reported for profiles of water content and pesticide concentration in the soil column, and water and pesticide fluxes at the edges of sections. Section M06S08E26, where high use rates were observed of both diazinon and chlorpyrifos was chosen as a typical section for illustrating PRZM3 simulation results (Fig. 1). This section was representative to the cropland of the study area in regards to the major crop (walnuts) and dominated soil texture (clay loam). A monitoring gauge at the Orestimba Creek near the confluence with the San Joaquin River is operated by the U.S. Geological Survey (USGS), designated as "#11274538, Orestimba Creek at River Road, Cross Landing, California." This gauge location was set as the outlet of the creek watershed, that is, the destination of water flow and pesticide transport routing. Predicted stream flow rates and pesticide concentrations in surface water were reported at this location for model evaluation and risk assessment.

The spatiotemporal variability in pesticide transport was characterized by the "load as percent of use (LAPU)" (Capel and Larson, 2001; Capel et al., 2001; Konstantinou et al., 2006) for each section during a given period. The LAPU value of a section was calculated as the dissolved pesticide load contributed by the section to the watershed outlet, over the total pesticide use during the corresponding simulation period. By applying Eq. [1] for dissolved pesticide transport, the LAPU value for section i ($\mathrm{LAPU}_{i,t}$) to the watershed outlet during a period t could be expressed as,

$$\mathrm{LAPU}_{i,t} = \sum_t Q_i / \sum_t P_i \qquad [6]$$

where Q_i (kg/d) is dissolved pesticide load contributed by section i, P_i (kg/d) is the pesticide amount applied in i, and t is a prescribed timeframe, for example, the entire simulation period or selected seasons. The LAPU is a comprehensive indicator for pesticide yield and transport in the study area, which accounts for both edge-of-field loads and transport dispersion of pesticides. For example, a LAPU of 1% indicates that 1 kg of pesticide active ingredient applied in a section would finally contribute 0.01 kg pesticide as dissolved load at the watershed outlet during the simulation period t.

Model Evaluation

The PRZM3 simulation and the routing module in this study were evaluated by comparing the predicted stream flow and dissolved pesticide concentration observed at the watershed outlet. In addition to the average stream flow and pesticide concentrations, predicted pesticide yields and exposure events were also compared with those derived from measured data. Observation data at the watershed outlet were retrieved from the National Water Information System (USGS, 2007). Measured daily stream flow rates are available for the entire simulation period (1990–2006), while for dissolved pesticide concentrations 241 samples were taken to analyze for both compounds of diazinon and chlorpyrifos. Results of preliminary data analysis indicated that pesticide sampling was conducted weekly for 1992 and 1993, and biweekly or monthly since 1997. Only two samples were available for the period of 1994 to 1996. About 66% samples during rainfall season were taken within 3 d after rainfall events. In-stream pesticide concentrations are highly variable both spatially and temporally, and associated with field sampling uncertainty. Therefore, the statistics based on the measured data in this study was considered only as representative indications of the actual contamination levels.

Sources of uncertainties associated with hydrological and pesticide transport simulation in this study included simplifications required in presenting the system as a prototype, limitations in model input data, and the predictive capabilities of the PRZM3 model itself. The fields in each section were considered to be uniform in terms of landscape characteristics, pesticide application, and crop management. Therefore, the PRZM3 simulation generated results presenting the average levels of edge-of-field water and pesticide outputs from multiple landuse management units within each section. Due to the nonlinearity in the model equations and spatial variability in the landscape characterizations, it is worthy to note that modeling results with averaged parameters may not reflect some threshold processes (e.g., erosion) which may occur in a limited part of an area under specific conditions. Section-based PRZM3 simulations have been conducted in other studies of pesticide transport in the Sacramento River Watershed of California (Snyder and Williams, 2001, 2004; Dasgupta et al., 2006), and model results were comparable to measured pesticide concentrations.

Some physical processes were not simulated by the PRZM3, such as interception and transport via subsurface drains, preferential flow, nonequilibrium adsorption of pesticide, temperature-dependent pesticide decay, and direct loss of pesticide. Ignorance of those processes may introduce errors into the hydrology and transport simulations (Qing et al., 2000; Holvoet et al., 2005). Under flood irrigation, for example, water and pesticide yields might be enhanced at the edges of fields with subsurface drains installed. The drainage tiles could also significantly reduce the travel time for the edge-of-field fluxes transporting to the stream channels. In addition, results of field experiments indicated that with preferential flow pesticides move deeper than predicted by transport models (Flury, 1996). In this study, the PRZM3 simulation was based on precalibrated parameters recommended in the USEPA Standard Tier 2 scenarios, and the simulation results were not calibrated at field level due to data limitations. Simulation of edge-of-field loads did not represent reductions cased by natural configurations or constructed management practices. Deterministic simulations were performed for both the PRZM3 and routing simulations, and uncertainties in the pesticide properties and other input parameters were not evaluated. Therefore, this study might not be expected to simulate accurate pesticide losses from individual fields. Instead, it is designed to identify the areas and seasons with high potentials in contributing pesticide loads to the nearby aquatic ecosystem at watershed scale.

Table 2. Environmental fate properties for diazinon and chlorpyrifos (USDA, 2001; McKone et al., 2003).

Parameter	Unit	Diazinon	Chlorpyrifos
Henry's law constant	Pa-m^3/mol	0.011	0.001
Organic carbon partition coefficient (K_{OC})	L/kg	1431.0	6025.6
Molecular diffusivity in air	m^2/d	0.599	0.491
Molecular diffusivity in water	m^2/d	6.63×10^{-5}	4.41×10^{-5}
Half-life in air	day	4.59	0.26
Half-life in canopy	day	4.0	3.3
Half-life in soil	day	21.0	45.0
Half-life in water	day	84.0	53.0
Half-life in sediment	day	17.0	52.5

Results and Discussion

Pesticide Distribution in Canopy-Soil System

Demonstrated in Fig. 2 are application events and predicted concentrations of chlorpyrifos and diazinon in the shallow soil layers of M06S08E26, the representative section chosen in this study to demonstrate the field-scale simulation results of the PRZM3. During the simulation period, total diazinon use in the section was 817.6 kg. A total of 17 individual daily application events were observed, the last falling 12 Aug. 2000, with an average application rate of 2.52 kg/ha over treated fields in this section. Up to 90% of pesticide applied was intercepted by the crop canopy. During the growing season, due to the lack of precipitation and the absence of over canopy irrigation, the pesticide intercepted by crop was degraded or volatized before reaching the soil surface. For both diazinon and chlorpyrifos, <1% of intercepted pesticide was retained by crop canopy in 10 d of application. Total diazinon loss by decay and volatilization from crop canopy was predicted to be 681.3 kg during the simulation years in this section, accounting for about 83% of total diazinon use. Diazinon accumulated in the soil through direct application, as well as crop canopy washoff during rainfall. The concentration of dissolved diazinon was 1.02 µg/L in the shallow soil (0.01 m) of M06S08E26, averaged for the application years of 1992 to 2000 (Fig. 2). Generally, diazinon concentrations in the soil decreased rapidly with soil depth. During periods of rainfall, however, diazinon at top soil layer might be significantly diluted by intensive surface runoff. PRZM3 simulation results indicated that diazinon presence would be negligible in soil layers deeper than 1 m. Therefore, groundwater vulnerability to diazinon did not appear to be a serious environment concern in the study area. With organic C partition coefficient (K_{OC}) of 1431.0 L/kg, diazinon has moderate-to-low mobility in the soils and is not usually detected in groundwater samples (Burow et al.,

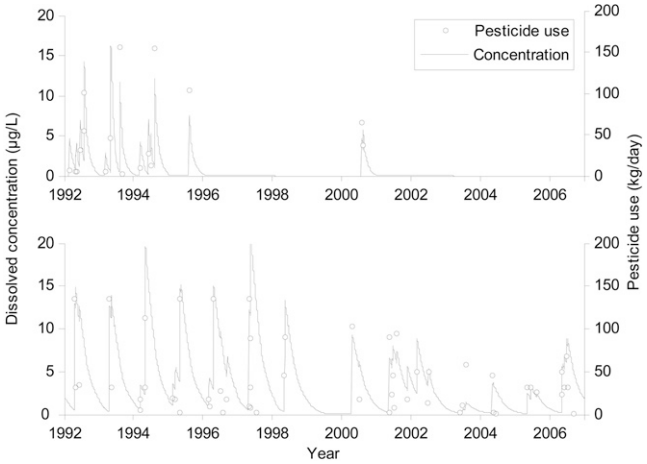

Fig. 2. Dissolved concentrations of diazinon (top) and chlorpyrifos (bottom) at 0.01 m below soil surface in section M06S08E26.

1998; Worrall and Besien, 2005). However, Flury (1996) indicated that even strongly adsorbing chemicals can move via preferential flows with a comparable travel time as conservative solutes, especially in loamy soils. Therefore, it's noteworthy that the risk of pesticide exposure in groundwater might be enhanced by vertical preferential flows which were not simulated in the PRZM3. About 0.35 kg diazinon (0.27 kg in the dissolved phase and 0.08 kg in the particle-bound phase) was predicted to exit the section horizontally as edge-of-field fluxes during the simulation period. Therefore, one might conclude that the majority of diazinon residues in the canopy-soil-water system are stored in soils, especially in the soil top layers.

Similar patterns of fate and transport were found in the simulation results of chlorpyrifos in canopy and soils. During 1992 to 2006, 2246.6 kg of chlorpyrifos were applied into section M06S08E26 in 54 daily application events, with an average application rate of 1.95 kg/ha over treated fields in this section. With a larger K_{OC} (6025.6 L/kg) than that of diazinon, chlorpyrifos is moderately lipophilic and has a tendency to partition into organic materials in soil and sediment. Therefore, a smaller fraction of applied chlorpyrifos (0.027%) was predicted as edge-of-filed loads, compared to 0.043% for diazinon. On application days, predicted concentrations were significantly correlated to pesticide application amount ($P = 0.007$ for diazinon, and $P < 0.001$ for chlorpyrifos, respectively). It's important to note the effects of rainfall on pesticide concentrations in the soil. The runoff and infiltration flows remove pesticide from soil layers, while rainfall-induced washoff might be expected to transport significant amount of pesticides into the soil from the interception storage on the crop canopy. As mentioned above, however, pesticides caught on canopy degrade or volatilize rapidly. Therefore, in sum rainfall is generally considered as a mechanism of pesticide dilution in soils. Only those rainfall events immediately following pesticide applications could have positive effects on pesticide accumulation in soils. For example, the rainfall event on 6 May 1994, 3 d after a chlorpyrifos application, increased the chlorpyrifos concentration in the shallow soil by about 40% in the section M06S08E26.

Pesticide Residues to Surface Water

During the simulation period, pesticide use and dissolved load over the sections were spatially correlated ($P < 0.001$ for chlorpyrifos, and $P = 0.002$ for diazinon, respectively). However, the spatial variability on pesticide transport could be demonstrated using LAPU values, calculated as the dissolved pesticide load contributed by a section to the watershed outlet divided by the total use in that section. Shown in Fig. 3 are LAPU values, categorized roughly by quartiles, over the watershed for diazinon and chlorpyrifos during 1992 through 2006. The diazinon LAPU values ranged from 0.010 to 1.008%, with a watershed-wide average of 0.189%. Based on water quality measurements during 2000 and 2001, the LAPU was estimated as 0.170% for the San Joaquin River basin (Kratzer et al., 2002; Domagalski and Munday, 2003). The slightly higher LAPU value predicted for the Orestimba Creek watershed indicated that the watershed might be more vulnerable to runoff, and represent a worse-than-average condition for aquatic ecosystem risk to pesticide exposures compared to other watersheds in the San Joaquin River basin. For chlorpyrifos, watershed-wide average LAPU value was predicted as 0.019%, in the range of the San Joaquin River basin-wide averages of 0.007 to 0.16% measured for different seasons (Kratzer et al., 2002; Domagalski and Munday, 2003). High LAPU values of both chemicals were identified in the Central California Irrigation District and along the main stem of Orestimba Creek. Simulation results indicated that pesticide LAPU values were related to soil properties, application timing, and flow paths.

With similar input parameters of climate, topography, and agricultural management for the sections with pesticide application, the tendency of pesticide yield was primarily determined by soil properties, for example, curve number, soil texture, and soil conductivity as input parameters in the PRZM3 simulation. For example, significantly negative correlations were observed between the LAPU values and the clay content in the top soil layer. For the CCID sections, soils are generally associated with the hydrologic group of C. Their grouping describes soils that have characteristically slow infiltration rates, commonly with a fine to moderately fine texture. Therefore, soils in the CCID had lower soil permeability relative to other cropping areas in the study region with the hydrologic group of B. The high pesticide LAPU values in the CCID were consistent with the results of our previous study, in which the cropland near Newman, CA, was identified as a "hotspot" for its high potential of pesticide runoff (Zhang et al., 2007).

Application timing of pesticides was also important in determining the spatial pattern of LAPU values. High LAPU values were observed for sections with high fractions of pesticide application during dormant seasons ($P < 0.001$ for diazinon and 0.015 for chlorpyrifos). For example, extremely high LAPU values for both pesticides were observed in section M07S08E09 (1.008% for diazinon and 0.040% for chlorpyrifos, respectively). In this section, 100% diazinon and 80% chlorpyrifos were applied between January and March. On the contrary, the lowest LAPU values for both pesticides were predicted at section M06S07E36 (0.010% for diazinon and 0.001% for chlorpyrifos) where all applications of the

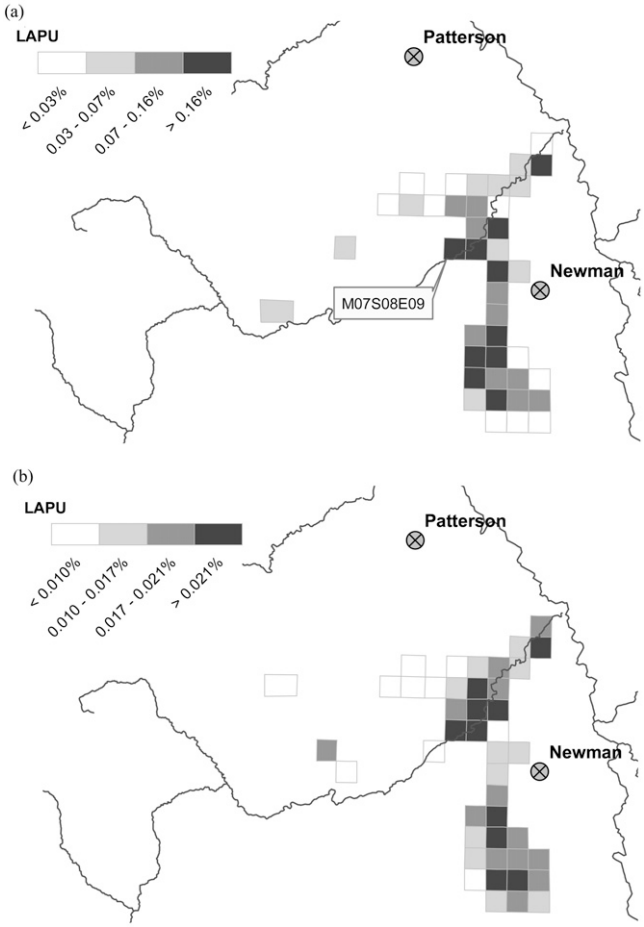

Fig. 3. The load as percent of use (LAPU) values for (a) diazinon and (b) chlorpyrifos over the Orestimba Creek watershed.

two compounds were observed in irrigation months. Illustrated in Table 3 are monthly pesticide yields reported as watershed-wide averages. Compared to the irrigation season, significantly higher LAPU values were observed during December to March, associated with heavy rainfall. For diazinon, the overall LAPU values for rainfall and irrigation seasons were 0.538 and 0.100%, respectively. For chlorpyrifos, the corresponding values were 0.028% for rainfall season, 0.017% for irrigation season, respectively. Diazinon uses during the rainfall season accounted for 24.3% of yearly total use, but generated 63.2% of total dissolved diazinon load over a year. For chlorpyrifos, 16.1% of total use and 24.0% of total dissolved load over a year were observed during rainfall season. These findings suggested that rainfall-induced surface runoff and soil erosion removed pesticide in the soils more efficiently relative to the agricultural drainage caused by irrigation.

The spatial variability of LAPU values were affected by the pesticide decay during transport to the watershed outlet. For the sections with pesticide applications, the average traveling time between the edge of fields and the watershed outlet was in the range of 0.1 to 3.0 d for pesticides associated with surface runoff predicted at the field edges, and 3.6 to 76.4 d for those with subsurface runoff. The losses of diazinon in the open water system were predicted as 7.1 to 66.2% of the edge-of-field loads with average loss rate of 17.6%, while the average loss rate for chlorpyrifos was 27.8%. Pesticide residues originated from sections along the Orestimba Creek main stem have shorter traveling time to the watershed outlet; therefore, the loss of pesticide through degradation during transport was significantly lower.

Table 3. Monthly averages of rainfall, pesticide use, and pesticide load to the watershed outlet of Orestimba Creek during 1992 to 2006.

Month	Rainfall	Diazinon			Chlorpyrifos		
		Use	Load	LAPU†	Use	Load	LAPU
	mm	kg	g	%	kg	g	%
Jan.	66.1	100.2	94.5	0.094	36.9	10.2	0.028
Feb.	64.4	31.6	658.7	2.087	20.1	18.8	0.094
Mar.	41.1	34.4	205.2	0.596	339.1	79.2	0.023
Apr.	17.8	49.3	96.1	0.195	324.7	44.8	0.014
May	19.5	88.2	104.5	0.118	481.8	121.9	0.025
June	2.0	112.6	119.0	0.106	309.0	72.4	0.023
July	0.0	91.9	117.2	0.128	508.5	62.5	0.012
Aug.	0.1	183.7	86.2	0.047	343.4	42.8	0.012
Sept.	1.6	29.3	37.0	0.126	117.2	14.4	0.012
Oct.	21.8	4.8	1.2	0.024	8.8	2.8	0.031
Nov.	26.7	0.0	2.8	–	2.4	2.2	0.092
Dec.	55.8	13.1	4.2	0.032	2.9	3.9	0.139

† LAPU = load as percent use.

Pesticide Contamination in Orestimba Creek

Shown in Fig. 4 and 5 are predicted daily stream-flow rates and dissolved pesticide concentrations, respectively, in comparison with USGS measurements at the outlet of the Orestimba Creek watershed (Fig. 1). Measured stream flows were generally matched by the simulation results. A comparison of monthly averages of predicted and observed stream flow rates showed a correlation coefficient of 0.83 ($P < 0.001$), indicating a satisfactory simulation of the watershed's hydrology. Some extremely high flow events were underestimated by the model since the model only predicted daily average flow rates and could not capture the instantaneous peak flow events.

Significant correlations were observed between observed and predicted monthly flow-weighted concentrations ($r = 0.691$ for diazinon and 0.723 for chlorpyrifos, and $P < 0.001$ for both chemicals), indicating that the temporal variations of in-stream concentrations of both compounds were successfully captured by the model (Fig. 5). During 1992 to 2006, average flow-weighted concentration of dissolved diazinon at the watershed outlet was predicted as 0.036 μg/L, consistent with that of 0.032 μg/L based on USGS measurements. High concentrations were observed before 2001. This could be explained by the relatively higher application rates averaged as 1140 kg/year during 1992 to 2000, relative to 139 kg/yr from 2001 to 2006. For chlorpyrifos, predicted flow-weighted concentration was averaged as 0.011 μg/L at the watershed outlet during 1992 to 2006, comparable to that of 0.012 μg/L based on USGS measurements. Comparison of dissolved pesticide loads with available measurements also indicated a satisfactory model performance. For example, the dissolved loads were measured as 192 and 125 g for diazinon and chlorpyrifos, respectively, during April through August of 2001 (Domagalski and Munday, 2003). The corresponding loads estimated from daily simulations in this study were 199 and 122 g. Some high-concentration events were not captured by the prediction, such as the two

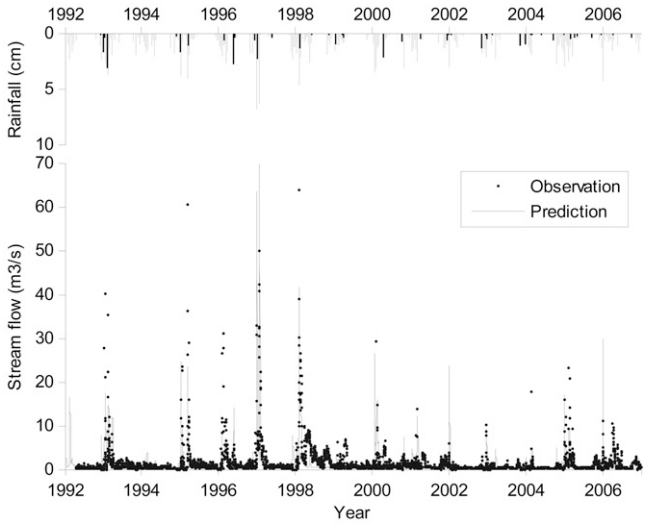

Fig. 4. Observed and predicted daily stream flow at the outlet of Orestimba Creek watershed and average daily precipitation over the watershed.

spikes of diazinon concentration measured in 2002 (0.533 μg/L on 6 May 2002 and 0.527 μg/L on 7 Aug. 2002). The model's deficiencies might be related to its lack of actual irrigation data, and to the exclusion of some important transport mechanism, such as direct pesticide loss and subsurface drainage.

Simulation results showed that temporal variations on in-stream concentrations of pesticides were dominated by the availability of carrying water supplied by rainfall and irrigation. During the simulation period, flow-weighted concentrations in irrigation and rainfall seasons were 0.051 and 0.030 μg/L for diazinon, and 0.033 and 0.004 μg/L for chlorpyrifos, respectively. During the irrigation season, irrigation tailwater and spillwater are the main sources of stream flow and carrying media of pesticide residues in the lower reaches of the creek. Relatively low stream-flow rate was observed in the Orestimba Creek during the summer months, resulting in quite high in-stream pesticide concentrations (Fig. 5). During rainfall season, however, the in-stream dissolved concentrations of pesticides were significantly diluted by the large water flows originating in nonagricultural areas of the Coastal Range. Simulation results showed that 67.4% of stream flow predicted at the watershed outlet was generated by those nonagricultural and pesticide-free areas. They play an important role in improving the water quality in the Orestimba Creek especially during rainfall season. Despite low pesticide concentrations, significant amount of pesticide loads were predicted during rainfall season with large LAPU values (Table 3). Therefore, regulating dormant spray pesticides could efficiently reduce the total pesticide residues to surface waters in the study area.

Risk Assessment and Management Strategies

Totally 27 exposure events of diazinon (indicating a 4-d average diazinon concentration above 0.1 μg/L) were predicted at the watershed outlet, with a median duration of 5 d. All exposure events were observed during 1992 to 2000 due to the high diazinon use amounts. Those exposure events accounted for 19.5% of the simulation days of 1992 to 2000, which was comparable to the probability (17.1%) of USGS-measured exposure events during the same period. Compared to the exposure scenario accepted by the USEPA (4-d average concentration does not exceed the criterion more than once every 3 yr on the average), serious violations of diazinon concentration were observed during 1992 to 2000. From the predicted diazinon exposure events, the typical (median) and typical worst-case (the 90th percentile) concentrations were determined as 0.191 and 0.388 μg/L, respectively. The typical worst-case concentration was above the 4-d toxicity values of some sensitive cladoceran species, such as *Ceriodaphnia dubia* (0.245 μg/L, Table 1b). Since 2001, however, diazinon concentrations in the Orestimba Creek have been significantly decreased to meet both the federal and state water quality criteria.

According to the modeling results, violations of chlorpyrifos concentration (4-d average above 0.015 μg/L) at the watershed outlet were predicted for all simulation years. Compared to di-

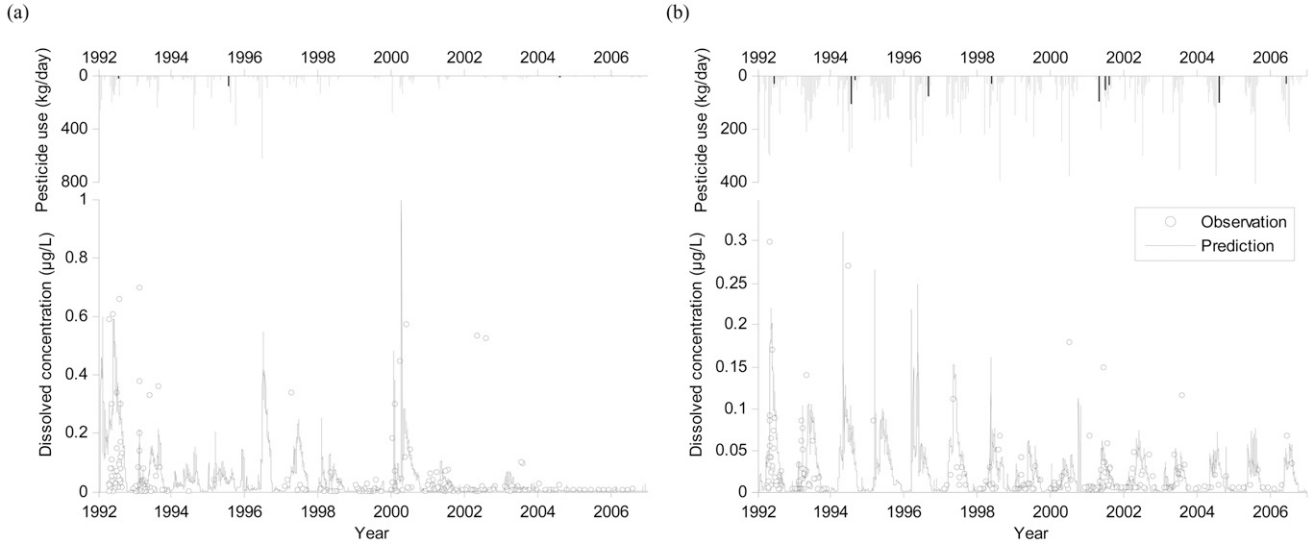

Fig. 5. Observed and predicted dissolved concentrations of (a) diazinon and (b) chlorpyrifos for the watershed outlet of Orestimba Creek (USGS site #11274538).

azinon, the exposure events of chlorpyrifos had longer duration (a median of 15 d, and >100 d for 12 out of 40 events), and mainly occurred during April to September. Chronic toxicity to aquatic organisms may occur at lower pesticide concentrations if exposure persists for several weeks or longer (Giddings et al., 2000). During rainfall seasons, rainfall-induced runoff events transported large pesticide amounts into streams and resulted in toxicological concerns for the aquatic ecosystem, even relatively lower in-stream concentrations were predicted. The percentage of time above water quality threshold was 42.2% during the entire simulation period, comparable to that of 35.3% based on USGS measurements. For the exposure events, the 50th and 90th percentiles of 4-d average chlorpyrifos concentrations were 0.036 and 0.085 μg/L, respectively. Comparison of those exposure concentrations to the toxicity values in Table 1b suggested that some species of mosquito (*Aedes aegypti* and *Culex pipiens*) could be impacted by the typical events, while an amphipod species of *Gammarus pulex* might be affected by the typical worst-case events.

Management implications could be derived based on modeling results for water quality control of pesticide contamination in the Orestimba Creek. Based on the LAPU values shown in Fig. 3, this study quantified the spatial effects of watershed morphology (soil properties and transport flow path) and pesticide applications on pesticide residues contributed to surface waters. Over the studied watershed, cropping areas which were close to aquatic sites or with high pesticide runoff potentials transported more pesticide residues, per unit of pesticide application, into surface waters. Those areas could be candidates for further management evaluation seeking to minimize the pesticide contamination in surface water. In the Orestimba Creek watershed, preventative and mitigative management practices for pesticides should be focused on the sections in the Central California Irrigation Districts and along the main stem of the creek. Temporally, high in-stream concentrations and frequent exposure events were observed during the irrigation season, when agricultural runoff induced by irrigation was the primary driving force for pesticide transport. Therefore, pesticide loads during the irrigation season could be significantly reduced by applying appropriate irrigation methods and scheduling to improve water use efficiency. To mitigate the chlorpyrifos exposure during April to September, facilities for pesticide control, such as constructed wetlands and vegetative buffers, should be developed for those areas with high LAPU values. With lower flow rate and hence higher hydraulic retention time, the operation of those facilities during the irrigation season might be more efficient than during rainfall season. Judging from this case study of Orestimba Creek water, the above agricultural management practices for water quality control might also be applicable to the entire San Joaquin Valley due to the similar climate and landscape.

Conclusion

In this paper a geo-referenced modeling system was presented by coupling the field-scale PRZM model with a linear routing model in GIS. The methodology presented in this study improves on the lumped and linear unit hydrograph models by including spatial variability of the terrain. The modeling system accounted for both spatial and temporal variability on the parameterization of landscape characteristics, cropping managements, and pesticide applications, transport and transformation. In the case study, the model's capability was demonstrated in the Orestimba Creek watershed in California with a spatially distributed simulation of pesticide fate and transport and consequent assessment of aquatic ecosystem risks. Residues of diazinon and chlorpyrifos were mainly predicted in top soil layers. Their concentration levels in surface water sometimes exceeded the water quality standards for aquatic organisms especially during the irrigation season. The simulation results indicated that at field level (defined as sections in this study), the spatial pattern of pesticide contribution to receiving surface waters was primarily determined by the soil properties, that is, high pesticide LAPU values were expected for soils with low permeability. At watershed scale, transport pathway for pesticides after being released from field edges also largely determined the pollutant responses at the watershed outlet. Therefore, pesticide applied along the main stem of the Orestimba Creek showed high LAPU values over the watershed. Temporally, the application timing of pesticides plays an important role in determining pesticide fate and distribution. Pesticides applied during the rainfall season can be efficiently removed and diluted by precipitation into the surface waters. Based on the simulation results, agricultural management techniques were suggested to minimize the pesticide exposure levels in surface waters. Future work was suggested to numerically evaluate the efficiencies of the suggested management strategies by implementing the relevant physical and chemical processes in the model simulation.

Acknowledgments

The authors would like to acknowledge funding support from the Coalition for Urban/Rural Environmental Stewardship and California State Water Quality Control Board. This research received partial financial support from the Wenzhou Medical College (award number XNK07035) and Wenzhou Science and Technology Bureau (award number S20070033). We are also grateful to the four anonymous referees who have helped improve the present article with their most appropriate suggestions.

References

Bailey, H.C., J.L. Miller, M.J. Miller, L.C. Wiborg, L. Deanovic, and T. Shed. 1997. Joint acute toxicity of diazinon and chlorpyrifos to *Ceriodaphnia dubia*. Environ. Toxicol. Chem. 16(11):2304–2308.

Boesten, J.J.T.I., and A.M.A. van der Linden. 2001. Effect of long-term sorption kinetics on leaching as calculated with the PEARL model for FOCUS scenarios. p. 27–32. *In* Pesticide Behaviour in Soils and Water, Proc. of a Symp. organized by the British Crop Protection Council, Hilton Brighton Metropole, Alton, UK. 13–15 Nov. 2001. British Crop Protection Council, Hilton Brighton, Metropole, Alton, UK.

Burow, K.R., J.L. Shelton, and N.M. Dubrovsky. 1998. Occurrence of nitrate and pesticides in ground water beneath three agricultural land-use settings in the eastern San Joaquin Valley, California, 1993–1995. Water-Resources Investigations Rep. 97-4284. U.S. Geological Survey, National Water-Quality Assessment Program, Sacramento, CA.

Capel, P.D., and S.J. Larson. 2001. Effect of scale on the behavior of atrazine in surface waters. Environ. Sci. Technol. 35(4):648–657.

Capel, P.D., S.J. Larson, and T.A. Winterstein. 2001. The behaviour of 39 pesticides in surface waters as a function of scale. Hydrol. Processes 15:1251–1269.

CDWR. 2007a. California land and water use: Survey data access. California Dep. of Water Resources, Sacramento.

CDWR. 2007b. San Joaquin Valley drainage monitoring program report. California Dep. of Water Resources, San Joaquin District, Sacramento.

CEPA. 2007a. Pesticide Use Reporting (PUR). California Environmental Protection Agency, Dep. of Pesticide Regulation, Sacramento.

CEPA. 2007b. San Joaquin river watershed surface water ambient monitoring program (SWAMP). California Environmental Protection Agency, Sacramento.

Chu, X., and M.A. Marino. 2004. Semidiscrete pesticide transport modeling and application. J. Hydrol. 285(1–4):19–40.

Cryer, S.A., M.A. Fouch, A.L. Peacock, and P.L. Havens. 2001. Characterizing agrochemical patterns and effective BMPs for surface waters using mechanistic modeling and GIS. Environ. Model. Assess. 6(3):195–208.

Dasgupta, S., J.M. Cheplick, and W.M. Williams. 2006. Pesticide loading analysis in the Sacramento River Watershed. U.S. Environmental Protection Agency, Region 9, San Francisco, CA.

Domagalski, J.L., and C. Munday. 2003. Evaluation of diazinon and chlorpyrifos concentrations and loads, and other pesticide concentrations, at selected sites in the San Joaquin Valley, California, April to August, 2001. Water-Resources Investigations Rep. 03-4088. U.S. Geol. Surv., Washington, DC.

Dubrovsky, N.M., C.R. Kratzer, L.R. Brown, J.M. Gronberg, and K.R. Burow. 1998. Water quality in the San Joaquin-Tulare Basins, California, 1992–95. Circ. 1159. U.S. Geol. Surv., Washington, DC.

Eason, A., U.S. Tim, and X. Wang. 2004. Integrated modeling environment for statewide assessment of groundwater vulnerability from pesticide use in agriculture. Pestic. Manage. Sci. 60(8):739–745.

Flury, M. 1996. Experimental evidence of transport of pesticides through field soils—A review. J. Environ. Qual. 25(1):25–45.

Giddings, J.M., L.W. Hall, and K.R. Solomon. 2000. Ecological risks of diazinon from agricultural use in the Sacramento—San Joaquin river basins, California. Risk Anal. 20(5):545–572.

Gowda, P.H., A.D. Ward, D.A. White, D.B. Baker, and J.G. Lyon. 1999. Using field scale models to predict peak flows on agricultural watersheds. J. Am. Water Resour. Assoc. 35(5):1223–1232.

Gustafson, D.I., K.H. Carr, T.R. Green, C. Gustin, R.L. Jones, and R.P. Richards. 2004. Fractal-based scaling and scale-invariant dispersion of peak concentrations of crop protection chemicals in rivers. 38:2995–3003.

Haan, C.T., and B.J. Barfield. 1978. Hydrology and sedimentology of surface mined lands. Office of Continuing Education and Extension, College of Engineering, Univ. of Kentucky, Lexington.

Holvoet, K., A. van Griensven, P. Seuntjens, and P.A. Vanrolleghem. 2005. Sensitivity analysis for hydrology and pesticide supply towards the river in SWAT. Phys. Chem. Earth 30:518–526.

Hutson, J.L., and R.J. Wagenet. 1993. A pragmatic field-scale approach for modeling pesticides. J. Environ. Qual. 22:494–499.

Knisel, W.G. 1980. CREAMS: A field-scale model for chemicals, runoff, and erosion from agricultural management systems, U.S. Dep. of Agric., Science and Education Administration, Conserv. Res. Rep. 26. USDA, Washington, DC.

Konstantinou, I.K., D.G. Hela, and T.A. Albanis. 2006. The status of pesticide pollution in surface waters (rivers and lakes) of Greece. Part I. Review on occurrence and levels. Environ. Pollut. 141(3):555–570.

Kratzer, C.R., C. Zamora, and D.L. Knifong. 2002. Diazinon and chlorpyrifos loads in the San Joaquin River Basin, California, January and February 2000. Water Resources Investigation Rep. 02-4103. U.S. Geol. Surv., Washington, DC.

Lee, K.T., and C.-H. Chang. 2005. Incorporating subsurface-flow mechanism into geomorphology-based IUH modeling. J. Hydrol. 311(1–4):91–105.

Luo, Y., X. Zhang, X. Liu, D. Ficklin, and M. Zhang. 2008. Dynamic modeling of organophosphate pesticide load in surface water in the northern San Joaquin Valley watershed of California. Environ. Pollut. 156(3):1171–1181.

Maidment, D.R., J.F. Olivera, A. Calver, A. Eatherral, and W. Fraczek. 1996. A unit hydrograph derived from a spatially distributed velocity field. Hydrol. Processes 10(6):831–844.

McKone, T.E., R.L. Maddalena, and D.H. Bennett. 2003. CalTOX 4.0 a multimedia total exposure model. Lawrence Berkeley Natl. Lab., Berkeley, CA.

Olivera, F., and D. Maidment. 1999. Geographic information systems (GIS)-based spatially distributed model for runoff routing. Water Resour. Res. 35(4):1155–1164.

Olivera, F., D.R. Maidment, and R.J. Charbeneau. 1996. Spatially distributed modeling of storm runoff and non-point source pollution using Geographic Information Systems (GIS). CRWR Rep. 96-4. Available at http://ceprofs.tamu.edu/folivera/UTexas/disstn/header.htm (verified 18 Dec. 2008). Ctr. for Res. in Water Resources, the Univ. of Texas, Austin.

Poletika, N.N., K.B. Woodburn, and K.S. Henry. 2002. An ecological risk assessment for chlorpyrifos in an agriculturally dominated tributary of the San Joaquin River. Risk Anal. 22(2):291–308.

Qing, L.M., P.T. Holland, T.K. James, D.E. McNaughton, and A. Rahman. 2000. Persistence and leaching of the herbicides acetochlor and terbuthylazine in an allophanic soil: Comparisons of field results with PRZM-3 predictions. Pest Manage. Sci. 56(2):159–167.

Ross, L.J., R. Stein, J. Hsu, J. White, and K. Hefner. 1999. Distribution and mass loading of insecticides in the San Joaquin River, California. EH 99-01. Environmental Hazards Assessment Program, Environmental Monitoring and Pest Management Branch, California Dep. of Pesticide Regulation, Sacramento.

SAS. 2008. SAS 9.2 documentation. Knowledge base. Available at http://support.sas.com/documentation/ (verified 18 Dec. 2008). SAS Inst., Cary, NC.

Saxton, K.E., and W.J. Rawls. 2006. Soil water characteristic estimates by texture and organic matter for hydrologic solutions. Soil Sci. Soc. Am. J. 70:1569–1578.

Schulz, M., and M. Matthies. 2007. Runoff of pesticides: Achievements and limitations of modelling agrochemical dislocation from non-point sources at various landscape related scales. Living Rev. Landscape Res. 1(2007):1. Available at http://www.livingreviews.org/lrlr-2007-1 (verified 23 Dec. 2008).

Snyder, N.J., and W.M. Williams. 2001. Exposure assessment model for diazinon sources in the Sacramento and Feather rivers. Sacramento River Watershed Program, Sacramento, CA.

Snyder, N.J., and W.M. Williams. 2004. Exposure assessment model for diazinon sources in the Sacramento River Basin's main drainage canal. Sacramento River Watershed Program, Sacramento, CA

USDA. 1986. Urban hydrology for small watersheds. TR-55 (210-VI-TR-55), 2nd ed. U.S. Dep. of Agric., Engineering Div., Soil Conserv. Serv., Washington, DC.

USDA. 2001. Agricultural Research Service (ARS) pesticide properties database. U.S. Dep. of Agric., Washington, DC.

USDA. 2007. Soil Survey Geographic (SSURGO) Database. U.S. Dep. of Agric., Washington, DC.

USEPA. 2004. Pesticide Root Zone Model (PRZM) field and orchard crop scenarios: Guidance for selecting field crop and orchard scenario input parameters. Office of Pesticide Programs, U.S. Environ. Protection Agency, Washington, DC.

USEPA. 2005. Aquatic life ambient water quality criteria for diazinon. EPA-822-R-05-006. Office of Science and Technology, U.S. Environ. Protection Agency, Washington, DC.

USEPA. 2006. PRZM-3, a model for predicting pesticide and nitrogen fate in the crop root and unsaturated soil zones: Users manual for release 3.12.2. EPA/600/R-05/111. Center for Exposure Assessment Modeling, U.S. Environ. Protection Agency, Washington, DC.

USEPA. 2007. Current national recommended water quality criteria. Office of Science and Technology, U.S. Environ. Protection Agency, Washington, DC.

USGS. 2005. Evaluation of unsaturated-zone solute-transport models for studies of agricultural chemicals. Open-File Rep. 2005-1196. U.S. Geol. Surv., Washington, DC.

USGS. 2007. National water information system: Web Interface. U.S. Geographical Surv., Washington, DC.

Worrall, F., and T. Besien. 2005. The vulnerability of groundwater to pesticide contamination estimated directly from observations of presence or absence in wells. J. Hydrol. 303(1–4):92–107.

Zhang, X., M. Zhang, and X. Liu. 2007. Identification of hotspots for potential pyrethroid runoff: A GIS modeling study in San Joaquin River Watershed of California, USA. Environ. Geol. 55(6):1195–1206. doi: 10.1007/s00254-00007-01065-00253.