Environmental Pollution 158 (2010) 1629–1637

Contents lists available at ScienceDirect

Environmental Pollution

journal homepage: www.elsevier.com/locate/envpol

Spatially distributed pesticide exposure assessment in the Central Valley, California, USA

Yuzhou Luo, Minghua Zhang*

Department of Land, Air, and Water Resources, University of California, Davis, CA 95616, USA

Runoff generation and application timing are governing factors on spatiotemporal variability of pesticide sources.

ARTICLE INFO

Article history:
Received 24 September 2009
Received in revised form
25 November 2009
Accepted 2 December 2009

Keywords:
Chlorpyrifos
GIS
PRZM
Transport modeling
Basin level

ABSTRACT

Field runoff is an important transport mechanism by which pesticides move into the hydrologic environment of intensive agricultural regions such as California's Central Valley. This study presents a spatially explicit modeling approach to extend Pesticide Root Zone Model (PRZM), a field-scale pesticide transport model, into basin level. The approach was applied to simulate chlorpyrifos use in the Central Valley during 2003–2007. The average value of loading as percent of use (LAPU) is 0.031%. Results of this study provide strong evidence that surface runoff generation and pesticide application timing are the two influencing factors on the spatial and temporal variability of chlorpyrifos sources from agricultural fields. This is one of the first studies in coupling GIS and field-scale models and providing simulations for the dynamics of pesticides over an agriculturally dominated landscape. The demonstrated modeling approach may be useful for implementations of best management practice (BMP) and total maximum daily load (TMDL).

1. Introduction

According to the most recent U.S. National Water Quality Inventory, agricultural non-point source pollution (NPS) is the leading source of water quality impacts to surveyed rivers and lakes, and also a major contributor to groundwater contamination and wetlands degradation. Off-site movement of agricultural chemicals, such as pesticides, to hydrologic environment has been associated with adverse effects on human health and ecosystem, especially in California's Central Valley, the most dynamic agricultural region in the world. In 2007, about 60 million kg pesticide active ingredients were applied to the farmland of the Central Valley. Pesticide residues have been routinely detected in water quality monitoring projects in this area, and beneficial uses of waterways have been threatened by the evaluated concentration of pesticides. Partially because of pesticides, especially organophosphate (OP) insecticides of chlorpyrifos and diazinon, the Sacramento River and the San Joaquin River, and as well as the associated tributaries, delta, and estuary, have placed on the Clean Water Act 303(d) list of impaired waterways since 1998 (CEPA, 2009b). Specific restrictions on the quantities of pesticides towards surface waters are required by these listings.

Modeling approach is suggested for the development and implementation of watershed management plans (USEPA, 2008), e.g., those designed to reduce pesticide runoff to nearby water bodies. Identifying pesticide loadings from agricultural land and developing alternative practices are essential components in the watershed management planning. Environmental models have been developed to predict environmental impacts associated with surface water and groundwater contaminated by pesticides for either field or watershed scales. Field-scale models, such as EPIC (Erosion Productivity Impact Calculator), DRAINMOD (Model for Drainage-water Management), HYDRUS, LEACHP (Leaching Estimation and Chemistry Model – Pesticide), and PRZM (Pesticide Root Zone Model), are typically designed to simulate chemical leaching and horizontal movement with surface runoff and lateral flows with site-specific information as inputs. Watershed-scale water quality models, such as AGNPS (Agricultural Nonpoint Source), HSPF (Hydrologic Simulation Program – FORTRAN), SWAT (Soil and Water Assessment Tool), and WARMF (Watershed Analysis Risk Management Framework), are used to understand the relationship between farming activities and water quality processes occurring within a watershed. Compared to watershed-scale models, simulations at field scale better represent the spatial variability on field conditions and account for agricultural activities and hydrologic processes within each field.

Edge-of-field pesticide loadings from runoff and erosion are the major source of pesticide loadings to the surface water system.

---

* Corresponding author. Tel.: +1 5307524953; fax: +1 7525262.
E-mail address: mhzhang@ucdavis.edu (M. Zhang).

0269-7491/$ – see front matter
doi:10.1016/j.envpol.2009.12.008

Therefore, pesticide losses from agricultural fields and their spatial distribution are highly concerned. Researchers, and state and federal agencies, have developed BMPs to help control the movement of potential agricultural pollutants into water resources. While BMPs are usually designed for large regions of watersheds or basins, small-scale modeling and experiments are recommended to better understand transport and mitigation processes of pesticides. By lumping together all fields in a modeling unit, watershed-scale models describe BMP-related processes in a very simplified manner with ill-defined parameters (Gevaert et al., 2008). Pesticide applications and conservation practices could be different over fields in one watershed. Therefore, field-scale models for pesticide transport are increasingly being used to evaluate the effectiveness of BMPs in reducing pesticide fluxes towards rivers (Kalita et al., 1998; Moore et al., 2002; Cho and Mostaghimi, 2009).

Recent software techniques, especially geographic information system (GIS), enable mathematic simulations over a large landscape with heterogeneous spatial properties. Fernandez et al. (2005) applied the field-scale predictions by DRAINMOD to evaluate the cumulative impacts of land use and management practices in a poorly drained watershed. Priya et al. (1998) validated EPIC model in both national scale (50 km cell-size) and regional scale (10 km cell-size) for crop production in India. There are few but increasing number of studies modeling fate and transport of pesticides at area-varying regions based on field-scale modeling approaches. For example, Eason et al. (2004) coupled a leaching model with GIS to produce a state assessment of groundwater vulnerability to atrazine in Iowa. However, horizontal pesticide transport by surface- and subsurface runoffs were not considered. Parker et al. (2007) evaluated PRZM simulation for atrazine, metolachlor, and trifluralin in the Sugar Creek watershed, Indiana. Lumped analysis unit of similar crop and soil characteristics were used for model simulation, therefore spatial variability of actual agricultural fields were not taken into account. The exposure levels of chlorpyrifos and diazinon in the Orestimba Creek watershed, California, were demonstrated by Chu and Marino (2004) and Luo and Zhang (2009) with geo-referenced pesticide transport modeling approach. Potential sources of permethrin loadings to the Sacramento River and its tributaries, California, were identified by a probabilistic modeling assessment using PRZM (Dasgupta et al., 2008). Most of existing studies were based on a simplified spatial framework for land use and crop types, and not appropriate to predict the spatial variability of pesticide transport and mitigation for management purpose.

A spatially explicit approach was developed in this study to predict the spatiotemporal variations of pesticide outputs from agricultural landscape in California's Central Valley. According to the pesticide use, toxicity and detection frequency, chlorpyrifos was selected as test agent. At first, PRZM was configured for baseline simulation of historical uses and edge-of-field loadings of chlorpyrifos for a 5-year (2003–2007) period. Sensitivity analysis was performed to identify the key parameters and governing processes in the pesticide transport processes. Areas and seasons with high pesticide exposure were identified for future monitoring and mitigation efforts. Results of this study were anticipated to provide useful information for the development and implementation of BMPs in reducing pesticide exposures from agricultural watersheds.

2. Methods and materials

2.1. Site description

California's Central Valley is an agriculturally dominated region located in the central portion of the State of California. This valley is bounded by the Cascade Range to the north, the Sierra Nevada to the east, the Tehachapi Mountains to the south, and the Coast Ranges to the west. Northern half of the valley is drained by the Sacramento River and south by the San Joaquin River. The two halves meet at the shared delta of the two rivers. Three sub-regions of the valley are conventionally defined as, [1] Sacramento Valley and Sacramento Metro, [2] San Joaquin Valley, and [3] Tulare Basin. The study area was defined by the drainage divides of the streams that enter the Central Valley from the Sierra Nevada and Coast Ranges. This boundary coincides with the 8-digit hydrologic unit codes (HUCs) of 18020103–18020111 for Sacramento Valley, 18040001–18040005 for San Joaquin Valley, and 18030012 for Tulare Basin. The total area is 56 400 km2, with about 31 000 km2 (55%) as cultivated land.

The valley floor is arid to semiarid. Mean annual rainfall ranges from 5 inch in the south to 20 inch in the north, and almost all rainfall is in the winter. Rainfall season was conventionally defined as December through March, explaining more than 70% of annual precipitation. Early farming was concentrated close to the Sacrament-San Joaquin Delta with readily available water for irrigation. Subsequent irrigation projects, such as the Central Valley Project (CVP), have brought more parts of the valley into agricultural use by storing and redistributing water for summer irrigation. As one of the most productive agricultural regions in the world, the valley products over 250 different crops and leads the nation in production of 75 commodities (Fujimoto, 1998). Snow melt from Klamath Mountains, Cascade Mountains, and Sierra Nevada is the major source of fresh water in the Central Valley. Most westside tributaries that drain the Coast Ranges are intermittent or ephemeral and contributed an insignificant amount of water to the valley. Due to their stream flow rate, those streams showed high concentration of pesticides. For example, greater variety of pesticides were detected in the Orestimba Creek (on the southwest of Stanislaus County) compared with the other sites in the valley (Dubrovsky et al., 1998).

2.2. Model description

In this study, edge-of-field pesticide fluxes were simulated by the PRZM release 3.12.3, which is developed by the U.S. Environmental Protection Agency (USEPA, 2006b) for modeling pesticide fate and transport in the vadose zone. PRZM is a one-dimensional dynamic model, primarily designed to predict the influence of climate, land/soil properties, and agricultural management on physical and biochemical processes of pesticides, such as degradation, erosion, leaching, runoff, and volatilization. PRZM was selected for this study based on its modeling capability to simulate relevant governing processes of pesticide transport and the preference for its use by the USEPA for pesticide-associated risk assessment (USEPA, 2006a). PRZM simulates three-phase (dissolved, adsorbed, and vapor phase) pesticide portioning, and takes into account pesticide transport and transformation in the canopy-soil system. PRZM has undergone an extensive validation effort with numerous field-scale studies for pesticide runoff and leaching in the United States. Compared to other environmental models for unsaturated-zone solute transport, PRZM has advantages in modeling complex agricultural scenarios such as pesticide application techniques, plant development, and conservation practices (USGS, 2005).

PRZM is a "unit-area" model and each simulation unit, called a PRZM "zone", is considered as a uniform area in regard to environmental characteristics and management scenarios. Delineation of PRZM simulation zones in this study followed the Meridian-Township-Range-Section (MTRS) in the U.S. Public Land Survey System (USDI, 2009). An MTRS, referred as a section, is normally 1 by 1 mile squares (1 mile = 1.6 km). The section-based delineation was also consistent with the spatial resolution in the California Pesticide Use Reporting (PUR) system. PRZM was developed in FORTRAN in the early 1980s and uses formatted ASCII files for inputs. Consequently, preparing and formatting input parameters could be difficult and time consuming (USGS, 2005), especially when the model is applied at large scales with thousands of simulation zones. In this study, GIS technology was used to extent the PRZM capability for geo-referenced parameterization and application at a basin scale. Spatial analysis and geo-data management provided by the ESRI ArcGIS 9.3 platform were utilized to estimate spatially distributed model parameters and prepare input files for PRZM. For each section, PRZM requires input data of elevation, land use, soil, and climate. More details of the GIS integration and PRZM automation were presented in our previous study (Luo and Zhang, 2009), in which PRZM was applied to the Orestimba Creek watershed, a tributary watershed (563 km^2) at westside of San Joaquin River. Simulations were conducted for all crops in a section, and pesticide outputs at field edges, defined as "pesticide loading" in this study, were predicted for pesticide in dissolved and particulate forms with surface runoff and lateral flow. Pesticide loadings were summarized and reported at section level.

2.3. Input data

Weather data of rainfall, temperature, wind speed, and solar radiation are required by PRZM simulation. Daily data were retrieved from 42 weather stations operated by the California Irrigation Management Information System (CDWR, 2009a). One weather station was assigned to each simulation section based on nearest distance between the station locations and section centroid.

The GIS spatial layers required for PRZM parameterization include digital elevation model (DEM), land use map, and soil map. The National Elevation Dataset (NED) with 30-m resolution was used in this study for elevation-related parameters. Slope, flow direction, and flow accumulation were obtained from NED based on the

Table 1
Environmental properties used in the PRZM simulation for the Central Valley.

Parameter and description		Typical values	CV
ANETD	Minimum depth of which evaporation is extracted (cm)	18.0	0.20
BD	Bulk density of soil (cm)	1.23–1.98	0.06
CN2	SCS runoff curve number for moisture condition II	53–89	0.09
FEXTRC	Foliar extraction coefficient for pesticide washoff	0.5	0.20
MNGN	Manning's N for overland flow	0.023	2.00
OC	Organic carbon in the horizon (%)	0–29.0	2.00
PFAC	Pan factor	0.7	0.10
SLP	Land slope (%)	0–43.6	2.66
THEFC	Field capacity of soil	0.04–0.50	0.43
THEWP	Wilting point of soil	0.00–0.39	0.60
USLEC	USLE cover factor	0.123–0.396	0.39
USLEK	USLE soil erodibility factor	0.02–0.55	0.22
USLELS	USLE topographic factor	0–22.12	4.44
USLEP	USLE practice factor	1.0	0.60

Notes: CV = Coefficient of variance.
For soil properties of BD, OC, THEFC, and THEWP, only values for the first soil horizon are shown as example.

Spatial Analyst Extension in ArcGIS. The topographic length-slope factor in the universal soil loss equation (USLELS) was estimated from flow accumulation and slope (Haan and Barfield, 1978; USEPA, 2004). Soil properties, including bulk density (BD), organic carbon content (OC), and USLE soil erodibility factor (USLEK), were extracted from the Soil Survey Geographic (SSURGO) database (USDA, 2009). Soil water contents of field capacity and wilting point were estimated from ready variables of soil texture (Saxton and Rawls, 2006). Curve numbers (CN2) were estimated based on soil hydrologic group and land use type (USDA, 1986), and adjusted by slope in each section (Sharpley and Williams, 1990). Table 1 shows the typical values and coefficients of variance of major input factors for PRZM simulation. For parameters which were not derived from GIS database, recommended values were used based on PRZM documentation and USEPA guidance of model parameters for the study area (USEPA, 2004, 2006b).

Contemporary land use, crop type, and irrigation areas in the Central Valley were obtained from land use survey by California Department of Water Resource (CDWR, 2009b). Land use surveys were conducted during 1995–2005 for the enclosed 20 counties in the study area, and assumed to be representative during the entire simulation period in this study. The resultant land use map characterizes field size and location for 70 major crops. Cotton has largest cultivated area of 3000 km^2, followed by almond, vineyard, alfalfa, and corn. Above top five crops explained 45% of the total cropping land area in the Central Valley. PRZM parameters for cropping, including cropping dates (for emergence, maturation, and harvest), interception storage, maximum coverage/height, and maximum rooting depth, were derived from the USEPA Standard Tier 2 scenario for California (USEPA, 2004) (Table 2). Daily use amounts of irrigation water for each section are not available in the study area. Therefore, the built-in module for automatic irrigation in PRZM was enabled to simulate water application. Irrigation timing and amount were determined by the user-defined threshold value as fraction of available water capacity (PCDEPL). When average root-zone soil moisture falls below PCDEPL, irrigation would be activated with amount of soil moisture deficit to field capacity. For flood irrigation, USEPA suggested PCDEPL value of 0.55 for California was used in the simulation. For furrow irrigation, which is generally used for field crops and vegetables in Central Valley, the corresponding PCDEPL value was calibrated to be 0.15 as reported by Dasgupta et al. (2008). Evaluation of PRZM automatic irrigation results have been conducted in other studies for both Sacramento Valley (Dasgupta et al., 2008) and San Joaquin Valley (Luo and Zhang, 2009) by comparing the predicted and recorded annual irrigation water use and frequency.

Table 3
Physiochemical properties and mass transfer coefficients for chlorpyrifos.

Parameter and description		Unit	Mean	CV[a]
HENRYK	Henry's law constant	Pa-m^3/mol	0.001[b]	0.25
KOC	Organic carbon partition coefficient	L/kg	6025.6	1.20
DAIR	Molecular diffusivity in air	m^2/day	0.491	0.10
DGRATE	Vapor phase decay rate	day^{-1}	2.666	1.00
PLDKRT	Foliar decay rate	day^{-1}	0.210	1.00
DSRATE	Sorbed decay rate	day^{-1}	0.015	1.00
DWRATE	Solution decay rate	day^{-1}	0.013[c]	1.00

[a] CV = Coefficient of Variance.
[b] Measured at 25 °C.
[c] Indicating a overall decay rate. Hydrolysis and photolysis half lives of chlorpyrifos range from 30 to 70 days.

Selection of pesticide for case study was based on the list of 14 pesticides with "very high relative risk" identified by the Central Valley Regional Water Quality Board (CEPA, 2008). Chlorpyrifos, an organophosphate insecticide, was chosen as a test agent in this study, justified by its top ranks in the list for both use amount and use/toxicity quotient. Table 3 shows the physiochemical properties of chlorpyrifos and their coefficients of variance (CV), which were obtained from the supporting database of CalTOX model (McKone et al., 2003). Degradation of pesticides in soil involves processes as hydrolysis, photolysis, and microbial decay. PRZM3 simulates those processes based on a combined single decay rate and assumes first-order kinetics. Pesticide applications were retrieved from the PUR database maintained by California Department of Pesticide Regulation (CEPA, 2009a). The PUR database reports all daily agricultural uses of registered pesticides by active ingredient and crop in each MTRS geographic unit. Application efficiency was set as 95% for aerial spray and 90% for ground spray, according to the results of Spray Drift Task Force studies (USEPA, 2002). Spray drift was assumed to be distributed in the atmosphere and surface waters, hence did not contribute to the edge-of-field pesticide loadings. The portion of spray drift deposited back to the cropland was not considered in this study.

2.4. Simulation design

With chlorpyrifos as test agent, baseline PRZM simulation was conducted for the agricultural fields in the Central Valley at daily time interval during 2001 through 2007, the latest year with available PUR data at the time of study. The first two simulation years were applied as model initialization. Model results were aggregated at section level for monthly and annual averages of edge-of-field pesticide loadings. In this study, PRZM simulation was initialized by GIS-based landscape characterization and pre-calibrated cropping parameters recommended in the USEPA Standard Tier 2 scenarios. Simulation results were not calibrated at field level due to data limitations. The simulation results might associate with uncertainties due to the simplification in environmental description, limitations in input data, and the predictive capability of the PRZM3. Model practice in this study might not be expected to simulate accurate pesticide losses from individual fields. It's designed to identify the areas and seasons with high potentials in contributing pesticides loads to the nearby aquatic ecosystems. In order to evaluate model performance, predicted pesticide loadings were summarized at watershed scale and compared to the reported in-stream pesticide loads at the watershed outputs. The seasonality and spatial variability in pesticide outputs were evaluated by the value of "loading as percent of use (LAPU)" for each section during a given period. This variable was calculated as the cumulative pesticide outputs over the total pesticide use in the

Table 2
Crop-related input parameters for Central Valley, California.

Parameters [a]	Field crops	Citrus [b]	Non citrus	Grain	Grapes	Pasture	Tree nuts	Vegetable
AMXDR	65	60	30	23	100	60	120	90
CINTCP	0.2	0.25	0.25	0.1	0.25	0.25	0.25	0.1
COVMAX	100	80	90	100	70	100	90	90
HTMAX	100	250	250	100	200	45	250	30
EMM/EMD	05/05	01/02	01/21	09/01	09/01	01/10	01/18	03/01
MAM/MAD	10/03	01/03	06/21	03/10	03/10	12/28	08/02	07/01
HAM/HAD	11/11	12/31	08/01	07/01	07/01	12/31	09/31	09/01

[a] Parameters: AMXDR = Maximum rooting depth of the crop (cm), CINTCP = Maximum interception storage of the crop (cm), COVMAX = Maximum areal coverage of the canopy (%), HIMAX = Maximum canopy height at maturation date (cm), EMM/EMD = Month and day of crop emergency, MAM/MAD = Month and day of crop maturation, HAM/HAD = Month and day of crop harvest.
[b] Based on California citrus (southern), cropping scheduling values were set to a default evergreen cycle with no specific crop growth milestone such as flowering of fruit set.

corresponding simulation area and period. It's usually considered as an indicator for the potential of pesticide runoff and transport (Luo and Zhang, 2009).

Based on the Monte Carlo simulation module in PRZM, sensitivity analysis was conducted to identify the key parameters and governing processes in the pesticide yields from landscape. A set of 21 PRZM input parameters for landscape morphology and pesticide properties were selected in the sensitivity analysis (Tables 1 and 3). All input parameters were assumed to independent lognormal distributions, characterized by its mean and CV. For each PRZM simulation zone, 500 stochastic runs were executed and annual mean pesticide loading were reported as model output for each run. Model sensitivity was calculated based on Spearman rank correlation analysis, and the details have been documented in the previous study (Luo and Yang, 2007). With 500 Monte Carlo simulations, the critical values for Spearman rank correlation coefficient are 0.05 and 0.07 for significance levels of 5% and 1%, respectively.

3. Results

3.1. Chlorpyrifos use in the Central Valley

Fig. 1 shows the spatial pattern of chlorpyrifos use over the Central Valley, presenting annual average application rates during 2003–2007 at section level. For the study period, annual average use was 612.2 ton/year for the simulation period. About 2/3 chlorpyrifos were applied in the Tulare Basin, with median application intensity of 0.21 kg/ha during 2003–2007 compared to those of 0.07 and 0.13 kg/ha for Sacramento Valley and San Joaquin Valley, respectively. Spatial variability of chlorpyrifos use amounts was associated with the distribution of crop types. For the total pesticide use amount grouped by crop types, chlorpyrifos was mainly applied to tree nuts, field crops, and fruits. About 38% of chlorpyrifos was applied to almonds and walnuts, followed by cotton, and orange (Table 4). Higher application intensities (in kg/ha) were also observed for those crops compared to other crops. The high use of chlorpyrifos in the Tulare Basin was explained by the fact that about 85% citrus and 60% field crops (in planted area) of the Central Valley were grown in the Tulare Basin. Chlorpyrifos use during irrigation season accounted for 84% of annual use, especially in July (21%) and August (25%). Application during dormant season was mainly observed in the Tulare Basin, with an annual use of 74.5 ton or 74% of total chlorpyrifos applied in the Central Valley during dormant season.

3.2. Predicted chlorpyrifos loadings

Chlorpyrifos losses in surface and lateral runoffs predicted by PRZM were converted into total annual loadings for each Section. Fig. 2 shows 5-year annual average of chlorpyrifos loading and

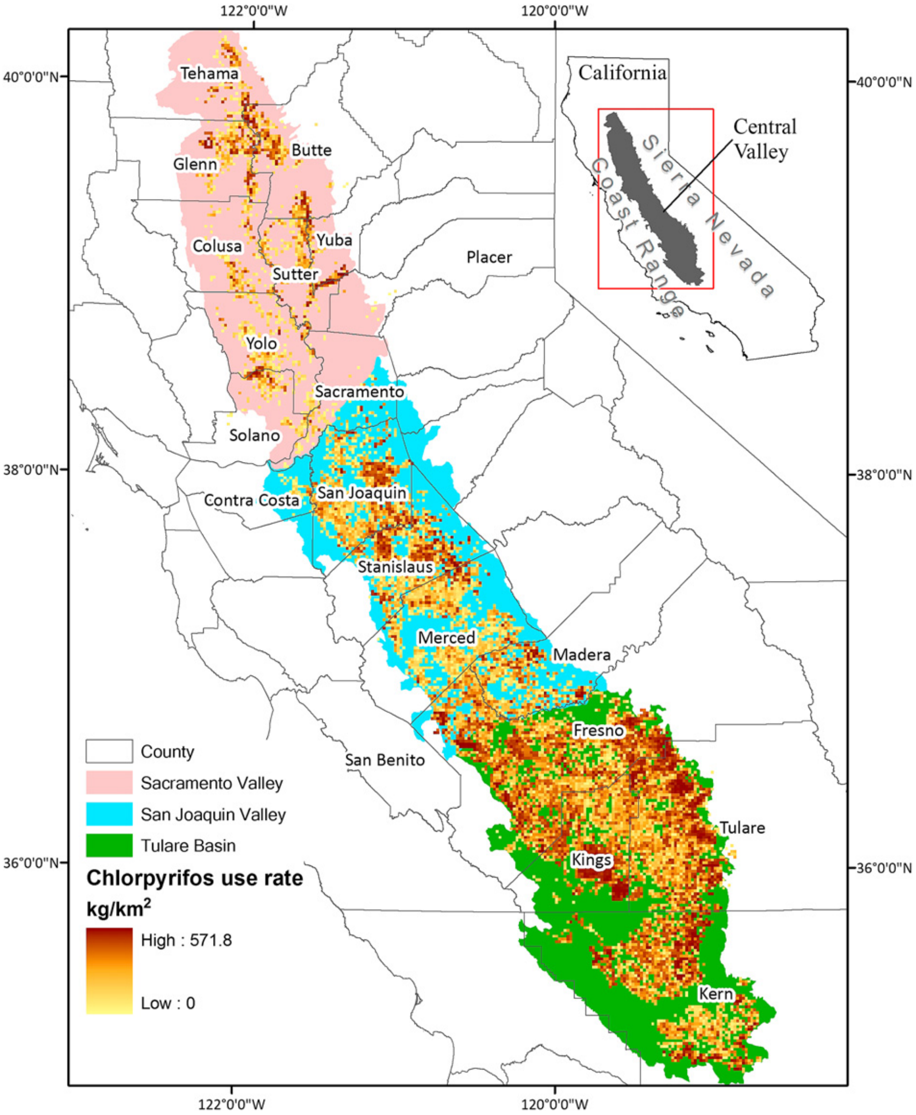

Fig. 1. Study area of California's Central Valley, showing annual chlorpyrifos application (kg/km^2) during 2003–2007.

Table 4
Annual chlorpyrifos applications and major commodities during 2003–2007.

Crop	All application		Ground application		Aerial application	
	ton	%	ton	%	ton	%
Almonds	154.9	24	133.4	31	21.4	10
Cotton	99.7	16	10.9	2	87.8	43
Orange	93.5	15	93.2	22	0.2	0
Walnuts	86.9	14	77.3	18	9.6	5
Alfalfa	83.2	13	13.9	3	69.2	34
Grapes	41.2	6	40.4	9	0.6	0
Total	632.5	100	428.3	100	203.7	100

LAPU values during the simulation period. Predicted annual loading in the Central Valley was 192.0 kg (CV $= 0.25$), indicating an overall LAPU of 0.031%. Generally, high chlorpyrifos loadings were predicted in the Tulare Basin and San Joaquin Valley, consistent with the spatial pattern of chlorpyrifos use as discussed previously. Although the overall spatial distribution of the PRZM-predicted loadings matched well with that of chlorpyrifos use (correlation coefficient $= 0.392$, $p < 0.001$), there are certain locations for which high application rates were not necessarily associated with high loading predictions. PRZM results indicated that areas with highest pesticide loadings were located along the major river streams and irrigation canals. Those areas are usually associated with high coverage of cultivated land and extensive agricultural activities. In Sacramento Valley, for example, high loadings occurred around the Tehama Colusa Canal, Feather River, and upper portion of Sacramento River. In San Joaquin Valley and Tulare Basin, “hot-spots” with high chlorpyrifos outputs were around the Delta-Mendota canal, California Aqueduct, Friant-Kern Canal, and rivers in the eastside of the Valley. Table 5 listed annual statistics of chlorpyrifos use and predicted loadings for each enclosed county in the Central Valley. Based on the annual loadings and LAPU values, 5 counties of Madera, Merced, Stanislaus, Sutter, and Tulare were identified as regions with highest potential risks to chlorpyrifos exposure. Covering 34.6% of total cropland in the Central Valley, those counties contributed 45.6% chlorpyrifos loadings as predicted by PRZM during 2003–2007.

Chlorpyrifos loading in the Sacramento Valley was predicted as 19.2 kg/year, mainly contributed by the croplands in Counties of Glenn, Sutter, and Yuba. LAPU values for the three Counties ranged

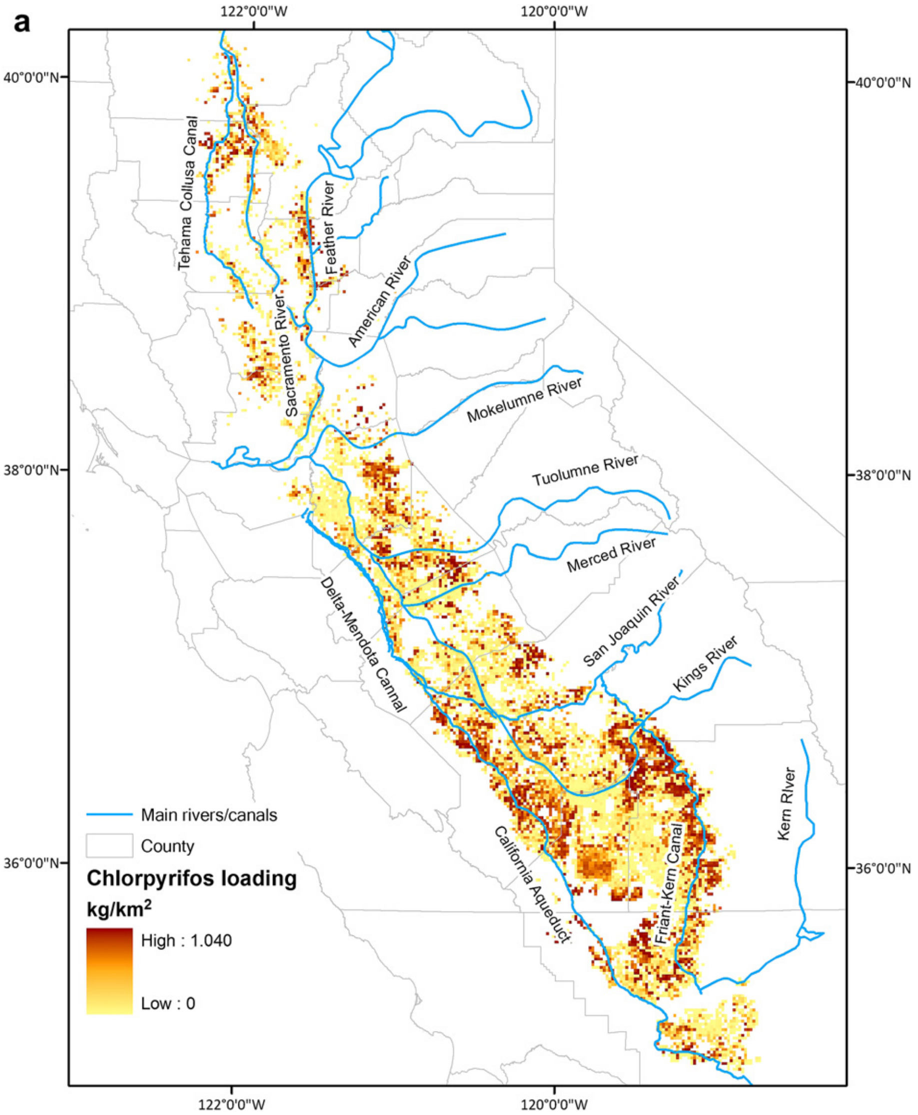

Fig. 2. PRZM-Predicted (a) loading (kg/km^2) and (b) LAPU of chlorpyrifos as annual average during 2003–2007.

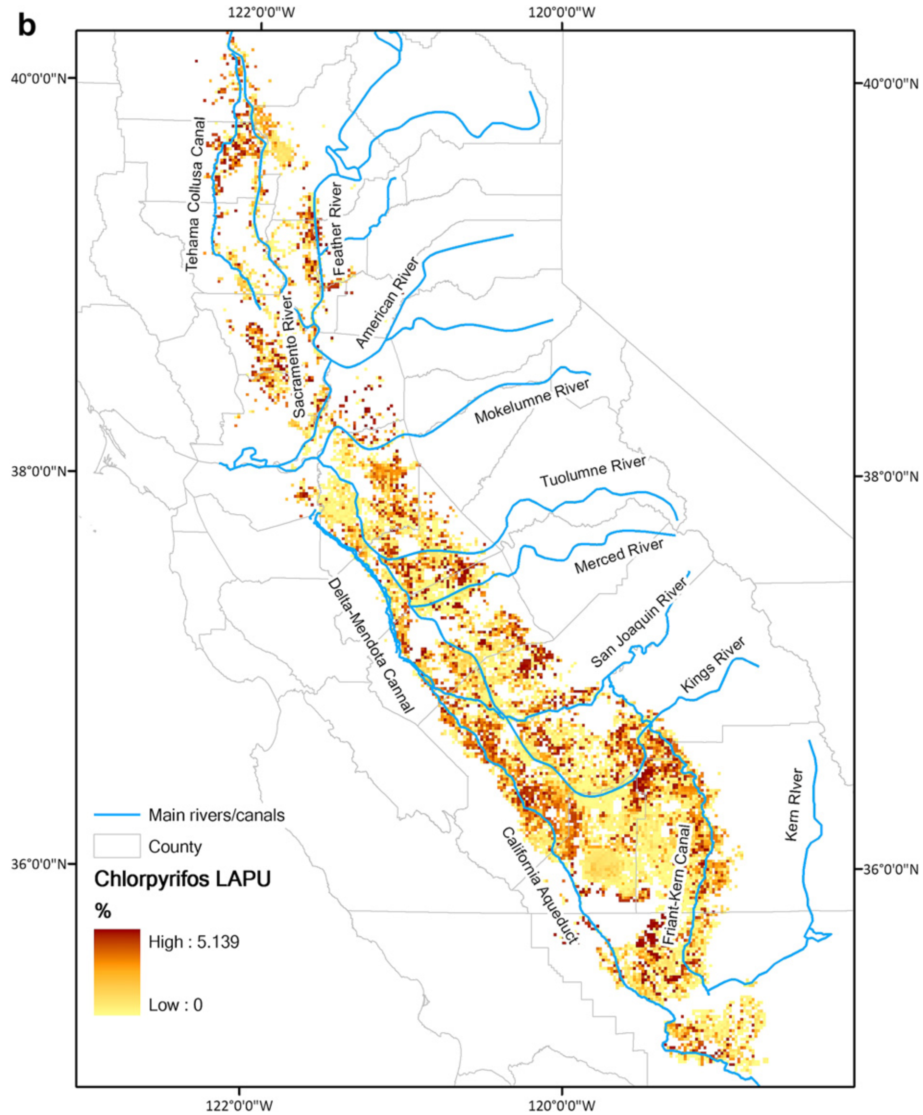

Fig. 2. (*continued*).

from 0.041% to 0.062%, significantly higher than the Central Valley-wide average. Pesticide loadings generated in Glenn County could be transported into upper Sacramento River and are diluted by the high stream flow volume. In-stream concentrations of chlorpyrifos were very low in the main stream of Sacramento River. Water quality measurements at USGS gauge #11447650 (Sacrament River at Freeport, CA, 38.46 N, 121.50 W), located downstream of the entire Sacrament Valley, is usually used to present the surface water condition with all agricultural runoff from the Valley. Based on USGS monitoring results (USGS, 2009), chlorpyrifos was detected (concentration > 0.005 µg/L) at this site in only 4 out of 71 sampling events during 2003–2007. However, chlorpyrifos sources from agricultural areas in the Sutter and Yuba Counties caused serious environmental problem in the lower Feather River. According to the 2006 California Regional Water Quality Control Board – Central Valley 303(d) list (CEPA, 2009b), 67.2 km of lower Feather River above the confluence with Sacramento River was impaired by chlorpyrifos pollution.

In the San Joaquin Valley, PRZM prediction suggested an annual chlorpyrifos loading of 59.2 kg, with Valley-wide LAPU value of 0.041%. About half of the chlorpyrifos loadings were predicted from the drainage area of the perennial San Joaquin River watershed as defined by USGS (Kratzer et al., 2002; Domagalski and Munday, 2003). This portion of chlorpyrifos loading would be transported into the San Joaquin River and its tributaries, resulting in high contamination level in the waterways. In the eastside of the San Joaquin Valley, the chlorpyrifos loading from agricultural fields was significantly diluted in streams by large amount of water from non-agricultural areas in the Sierra Nevada Mountains. However, streams in the western tributaries are dominated by agricultural drainage for much of the year and characterized by much higher concentrations of dissolved pesticides relative to their eastern companions (Luo et al., 2008). Most of westside reaches of San Joaquin River, such as Ingram Creek, Del Puerto Creek, Orestimba Creek, and Salt Slough, were placed on the 2006 Clean Water Act Section 303(d) list for aquatic toxicity due to chlorpyrifos (CEPA, 2009b). Predicted chlorpyrifos loadings were aggregated for watersheds in the San Joaquin Valley and compared to the in-stream loads measured at the watershed outlets (Table 6). Measurements were reported in our previous study based on monitoring data published by USGS during 1998–2005. Predicted loadings were significantly correlated with measured loads (Pearson coefficient $= 0.96$, $p = 0.002$), indicating that PRZM simulation reasonably captured the spatial variability of chlorpyrifos

Table 5
Statistics of chlorpyrifos uses and loadings at county level.

County	Valley	Farming area km^2	Use ton	Loading kg	LAPU %	Loading flux kg/km^2
Butte	SAV	546.6	17.4	2.2	0.013	0.004
Colusa	SAV	387.0	4.3	0.7	0.017	0.002
Glenn	SAV	541.0	11.5	4.7	0.041	0.009
Placer	SAV	32.3	1.4	0.1	0.009	0.004
Solano	SAV	327.2	4.7	1.0	0.022	0.003
Sutter	SAV	521.0	9.7	4.2	0.043	0.008
Tehama	SAV	290.4	5.3	1.2	0.022	0.004
Yolo	SAV	704.6	6.5	2.0	0.031	0.003
Yuba	SAV	157.8	4.6	2.8	0.062	0.018
Contra Costa	SJV	114.0	0.8	0.2	0.027	0.002
Madera	SJV	1117.7	22.8	9.9	0.043	0.009
Merced	SJV	1966.3	26.0	15.3	0.059	0.008
Sacramento	SJV	282.2	2.4	3.1	0.128	0.011
San Joaquin	SJV	1900.9	33.4	8.6	0.026	0.004
Stanislaus	SJV	1501.9	40.1	16.6	0.041	0.011
Fresno	TUB/SJV	4584.3	133.2	36.9	0.028	0.008
Kern	TUB	3099.3	99.2	27.8	0.028	0.009
Kings	TUB	2049.8	74.8	13.1	0.018	0.006
Tulare	TUB	3290.8	114.9	41.6	0.036	0.013
Sum		23415.1	613.1	192.1	0.700	0.008

Note: SAV = Sacrament Valley, SJV = San Joaquin Valley, and TUB = Tulare Basin.

distribution in the northern San Joaquin Valley. It's noteworthy that in-stream pesticides are contributed by both agricultural and urban sources, while only agricultural use of chlorpyrifos was simulated in this study. The comparison between predicted and measured in-stream pesticide loads was justified by the fact that use of chlorpyrifos in California urban areas has decreased significantly since 2000, and accounted for less than 1% of total use. Over San Joaquin River watershed, total chlorpyrifos loading was 1.2 times of in-stream loads measured, suggesting an average 20% loss of chlorpyrifos in the stream network. This finding was consistent with Luo and Zhang (2009) in which the corresponding loss rate for chlorpyrifos was reported as 27.8%. In addition to in-stream chemical loss, surface water quality was also determined by agricultural management practices, pesticide air drift and non-agricultural pesticide use, which were usually associated with great uncertainty. Pesticide routing in the stream network was not discussed in this study. Therefore, the comparison of predictions of chlorpyrifos loadings from field scale with the surface water quality measured at river outlet was performed only to demonstrate the model capability to capture the spatial variability on chlorpyrifos sources in the study area. Similar methods were used by other researches to characterize surface water quality based on pesticide uses or field loadings (Guo et al., 2004; Sparling and Fellers, 2007).

Table 6
Dissolved chlorpyrifos loadings predicted by PRZM at watershed scale and loads measured at watershed outlets.

Watersheds	Predicted loadings within the watershed (kg/year)	Measured loads at the watershed outlet (kg/year)[a]	Affected size (km)[b]
Tributaries			
Salt slough	5.04	5.45	27.2
Merced River	5.30	4.13	80.0
Orestimba Creek	0.49	0.50	19.2
Del Puerto Creek	0.18	0.31	10.4
Tuolumne River	3.05	3.36	–
Stanislaus River	5.20	4.26	–
Main Stream			
San Joaquin River at Vernalis	30.60	25.36	–

[a] Measured loads were taken from Luo et al. (2008), as annual average during 1998–2005.

[b] Affected size was taken from 2006 California 303(d) list for impaired waterways with chlorpyrifos pollution (CEPA, 2009b).

Table 7
Monthly averages of rainfall, chlorpyrifos use and loadings over the Central Valley during 2003–2007.

Month	Rainfall (mm)	Use (ton)	Loading (kg)	LAPU (%)
Jan.	66.1	31.2	27.5	0.088
Feb.	64.4	18.0	8.4	0.047
Mar.	41.1	43.4	12.7	0.029
Apr.	17.8	13.7	9.5	0.070
May	19.5	77.1	12.2	0.016
June	2.0	58.2	14.8	0.025
July	0.0	176.6	25.5	0.014
Aug.	0.1	141.3	30.6	0.022
Sept.	1.6	46.3	12.5	0.027
Oct.	21.8	14.2	16.2	0.114
Nov.	26.7	4.5	3.7	0.082
Dec.	55.8	8.1	18.3	0.225

For the Tulare Basin, annual chlorpyrifos loading was estimated at 113.5 kg or 56% of that for the entire Central Valley, with lower-than-average LAPU value of 0.025% over the basin. Since the Tulare Basin does not have an integrated surface-water-flow system, pesticide concentrations in surface water are not usually measured and reported (Domagalski, 1998). However, pesticide runoff may have negative impacts on the wetland ecosystem in this area. The unique native uplands and seasonal wetlands, interspersed by croplands, supported a diversity of native wildlife in the Tulare Basin. Ephemeral wetland habitats created by irrigation tail water are often used by shorebirds, such as killdeer and plover (USDI, 2004). Therefore, the results of this study suggested that assessment of organophosphate pesticides in the wetland habitats should be included in the future wildlife management planning.

3.3. *Factors controlling chlorpyrifos runoff from agricultural land*

Due to the fact that majority of chlorpyrifos was applied during irrigation season, PRZM-predicted loadings in those months were higher than in rainfall season. However, insufficient surface runoff during irrigation season lowered the capability and efficiency of pesticide yields from agricultural fields, indicating a relatively smaller pesticide runoff potential. The results of this study revealed higher LAPU during rainfall season (0.067%) relative to that in irrigation season (0.024%). This was consistent with the results in previous studies (Kratzer et al., 2002; Domagalski and Munday, 2003; Luo et al., 2008; Luo and Zhang, 2009) in which monitoring and modeling results showed higher chlorpyrifos loads normalized by use amounts in surface water during wet season compared to dry season in the Central Valley. These findings suggested that rainfall-induced runoff removed pesticide in the soils more efficiently relative to the agricultural drainage created by irrigation (Table 7). For the simulation period, 16% chlorpyrifos application in the Central Valley occurred during December to March, generating 35% of edge-of-field loadings over a year. Major commodity for dormant season spray of chlorpyrifos was tree nuts and grapes, with more than 70% of dormant spray during 2003–2007. And significantly higher LAPU values were predicted from those crops (0.043% and 0.054%, respectively) compared to other crops. Therefore, regulating dormant sprays to orchards could efficiently reduce the chlorpyrifos supply towards surface water in the study area.

Spatially, predicted chlorpyrifos loadings over sections were significantly correlated with the corresponding chemical use ($p < 0.001$). However, similar relationship was not observed

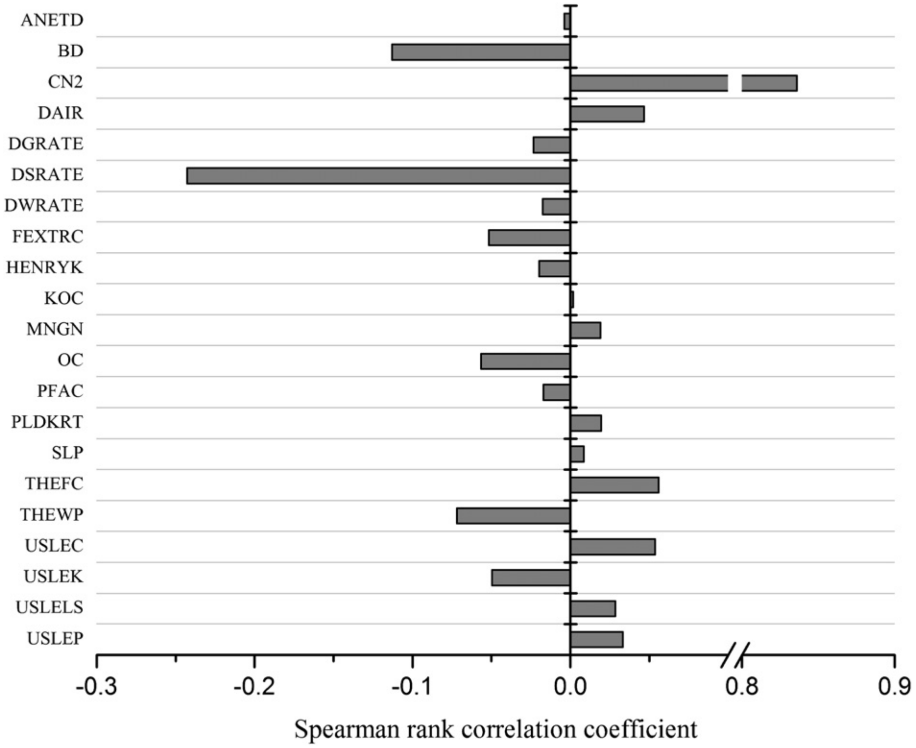

Fig. 3. Sensitivities (reported as Spearman's rank correlation coefficients) of chlorpyrifos loadings in the Central Valley, critical values of correlation coefficients are 0.05 and 0.07 at significance levels of 5% and 1%, respectively.

between chlorpyrifos use and predicted LAPU values. Results of variance analysis indicated that predicted LAPU values were significantly associated with crop type and soil properties. High LAPU values were predicted for orchards and grapes mainly relating to high rate of dormant sprays, as discussed before. Sections with high LAPU values were also associated with lower soil permeability. Mean LAPU value for sections with soil hydrologic group "D" was 0.044% during the simulation period, followed by that for group "C" (0.041%), group "B" (0.013%), and group "A" (0.007%). Hydrologic groups of C and D describe soils that have characteristically slow infiltration rates, commonly with a fine to moderately fine texture. Soils in Central Valley adjacent to the mountain areas, associated with alluvial fans, usually show high potential of surface runoff and soil erosion, indicated by relatively large slope and hydrologic group of "D". Significant negative correlation ($p = 0.001$) was also observed between LAPU values and saturated hydrologic conductivity of the first soil layer. This finding confirmed that surface runoff is the dominant factor in the generation of chlorpyrifos from non-point sources in agricultural watersheds. It's noteworthy that about 60–80% cropping areas of fruits, cotton, and irrigated pastures, which were associated with high chlorpyrifos application rates, were located in fields with low-than-average soil conductivities.

Governing input parameters to the PRZM predictions were identified based on sensitivity analysis (Fig. 3). Curve number (CN2) was the most important parameter ($r = 0.84$, $p < 0.001$) to the prediction of chlorpyrifos loadings. In PRZM, the hydrologic component for calculating surface runoff is based on modified curve number technique (USEPA, 2006b). CN2 is empirically determined as a function of land use, treatment/practice, hydrologic condition, and soil permeability (usually indicated by soil hydrologic group). With high CN2 values most of the rainfall appears as runoff, while lower values cause increased water retention in the soil. Parameters related to soil texture (bulk density, field capacity, wilting point, and organic carbon content in this study), KOC and half-life in soil were also identified as sensitive parameters to predicted edge-of-field loadings. All those parameters were involved in simulating hydrologic and transport processes in soil. Soil texture is associated with soil permeability, hence has substantial effects on runoff generation and soil erosion. Chemical partitioning between soil water and particulate phases is determined by OC, which had negative correlations to predicted loadings. With a KOC of 6025.6 L/kg, chlorpyrifos is moderately lipophilic and has a tendency to partition into organic materials in soil. The only chemical property that was in competition with the soil properties was degradation rate constant in soil (DSRATE), with correlation coefficient of -0.24. This parameter controls the total amount of chlorpyrifos in soils available to water runoff.

4. Conclusion

Evaluation of pesticide sources are required in the management planning for agriculturally dominated regions. In this paper a spatially distributed modeling system was presented by coupling GIS with field-scale transport model for basin-level assessment of pesticide source distribution. Spatial variability of the terrain and seasonality of agricultural practices were incorporated in the model parameterization for simulating pesticide fate and transport. The modeling capability of the system was demonstrated in California's Central Valley with chlorpyrifos as test agent. Total chlorpyrifos loading from agricultural fields in the study area was predicted as 192.0 kg as annual average during 2003 through 2007, indicating a valley-wide LAPU value of 0.031%. Due to the lack of field-scale measurements of chlorpyrifos loadings, model performance were evaluated by aggregating predicted loadings into watershed scale, and comparing with surface water quality measurements. The modeling system showed the capability in reasonably capturing the spatial distribution of chlorpyrifos sources in the Central Valley.

Watersheds with high chlorpyrifos loadings predicted in this study were in agreement with those shown in the Clean Water Act 303(d) list for impaired water with chlorpyrifos as major pollutant. Significant spatial correlation was also observed between the predicted loadings and measured chlorpyrifos mass in the main stream and tributaries in the San Joaquin River basin.

Results of model simulation suggested that predominant source of chlorpyrifos loading from cropland was predicted to occur from runoff events induced by precipitation and irrigation. About 65% of chlorpyrifos loadings were predicted during irrigation season of April–November, while higher chlorpyrifos runoff potential was observed during rainfall season with higher LAPU value of 0.067% compared to that for irrigation season of 0.024%. Regions generating the highest loadings were distributed around major rivers and canals. Further analysis indicated that those regions were associated with large land slope, high silt and clay contents (indicated by soils of hydrological groups C or D), and significant acreage of stone fruit and grapes which were major commodities of dormant spray of chlorpyrifos. The modeling system held promise as an analytical tool for pesticide source distribution and further non-target exposure assessment by providing evaluation of pesticide fate and transport in a spatial and temporal context.

References

CDWR, 2009a. California Irrigation Management Information System. California Department of Water Resources, the Office of Water Use Efficiency, Sacramento, CA. http://wwwcimis.water.ca.gov (verified 08/2009).

CDWR, 2009b. California Land and Water Use: Survey Data Access. California Department of Water Resources, Sacramento, CA. http://www.landwateruse.water.ca.gov/ (verified 08/2009).

CEPA, 2008. Relative Risk Evaluation for Pesticides Used in the Central Valley Pesticide Basin Plan Amendment Project Area. California Environmental Protection Agency, Regional Water Quality Control Board, Central Valley Region, Sacramento, CA.

CEPA, 2009a. Pesticide Use Reporting (PUR). California Environmental Protection Agency, Department of Pesticide Regulation, Sacramento, CA. http://www.cdpr.ca.gov/docs/pur/purmain.htm (verified 08/2009).

CEPA, 2009b. Total Maximum Daily Load Program. California Environmental Protection Agency, Water Resources Control Board, Sacramento, CA. http://www.swrcb.ca.gov/water_issues/programs/tmdl/ (verified 08/2009).

Cho, J., Mostaghimi, S., 2009. Evaluating cell-based components of DANSAT for predicting surface and subsurface transport of pesticides. Biosystems Engineering 102, 473–485.

Chu, X., Marino, M.A., 2004. Semidiscrete pesticide transport modeling and application. Journal of Hydrology 285, 19–40.

Dasgupta, S., Cheplick, J.M., Denton, D.L., Troyan, J.J., Wiliams, W.M., 2008. Predicted runoff loads of permethrin to the Sacramento River and its tributaries. In: Gan, J., Spurlock, F., Hendley, P. (Eds.), Synthetic Pyrethroids, Occurrence and Behavior in Aquatic Environments. Oxford University Press.

Domagalski, J.L., 1998. Pesticides in Surface and Ground Water of the San Joaquin-Tulare Basins, California: Analysis of Available Data, 1966 Through 1992. Water-Supply Paper 2468 U.S. Geological Survey. National Water-Quality Assessment Program, Denver, CO.

Domagalski, J.L., Munday, C., 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 Report 03–4088. United States Geologic Survey.

Dubrovsky, N.M., Kratzer, C.R., Brown, L.R., Gronberg, J.M., Burow, K.R., 1998. Water Quality in the San Joaquin-Tulare Basins, California, 1992–95. Circular 1159. United States Geological Survey.

Eason, A., Tim, U.S., Wang, X., 2004. Integrated modeling environment for statewide assessment of groundwater vulnerability from pesticide use in agriculture. Pesticide Management Science 60, 739–745.

Fernandez, G.P., Chescheir, G.M., Skaggs, R.W., Amatya, D.M., 2005. Development and tesing of watershed-scale models for poorly drained soils. Transaction of the American Society of Agricultural and Biological Engineers (ASABE) 48, 639–652.

Fujimoto, I., 1998. Building Civic Participation in California's Central Valley. California Institute for Rural Studies, Davis, CA.

Gevaert, V., Griensven, A.V., Holvoet, K., Seuntjens, P., Vanrolleghem, P.A., 2008. SWAT developments and recommendations for modelling agricultral pesticide mitigation measures in river basins. Hydrological Sciences 53, 1075–1089.

Guo, L., Nordmark, C.E., Spurlock, F.C., Johnson, B.R., Li, L., Lee, J.M., Goh, K.S., 2004. Characterizing dependence of pesticide load in surface water on precipitation and pesticide use for the Sacramento river watershed. Environmental Science and Technology 38, 3842–3852.

Haan, C.T., Barfield, B.J., 1978. Hydrology and Sedimentology of Surface Mined Lands. Office of Continuing Education and Extension, College of Engineering, University of Kentucky, Lexington, Kentucky.

Kalita, P.K., Ward, A.D., Kanwar, R.S., McCool, D.K., 1998. Simulation of pesticide concentrations in groundwater using Agricultural Drainage and Pesticide Transport (ADAPT) model. Agricultural Water Management 36, 23–44.

Kratzer, C.R., Zamora, C., Knifong, D.L., 2002. Diazinon and chlorpyrifos loads in the San Joaquin River Basin, California, January and February 2000. Water Resources Investigation Report 02-4103 United States Geological Survey.

Luo, Y., Yang, X., 2007. A multimedia environmental model of chemical distribution: fate, transport, and uncertainty analysis. Chemosphere 66, 1396–1407.

Luo, Y., Zhang, M., 2009. A geo-referenced modeling environment for ecosystem risk assessment: organophosphate pesticides in an agriculturally dominated watershed. Journal of Environmental Quality 38 (32), 664–674.

Luo, Y., Zhang, X., Liu, X., Ficklin, D., Zhang, M., 2008. Dynamic modeling of organophosphate pesticide load in surface water in the northern San Joaquin Valley watershed of California. Environmental Pollution 156, 1171–1181.

McKone, T.E., Maddalena, R.L., Bennett, D.H., 2003. CalTOX 4.0 a Multimedia Total Exposure Model. Lawrence Berkeley National Laboratory, Berkeley, CA.

Moore, M.T., Schulz, R., Cooper Jr., C.M., Smith Jr., S., Rodgers, J.H., 2002. Mitigation of chlorpyrifos runoff using constructed wetlands. Chemosphere 46, 827–835.

Parker, R., Arnold, J.G., Barrett, M., Burns, L., Carrubba, L., Neitsch, S.L., Snyder, N.J., Srinivasan, R., 2007. Evaluation of three watershed-scale pesticide environmental transport and fate models. Journal of the American Water Resources Association 43, 1424–1443.

Priya, S., Ryosuke, S., Ochi, S., 1998. Modeling Spatial Crop Production: A GIS approach, Proceedings of the 19th Asian Conference on Remote Sensing, 16–20 Nov, 1998 held at Manila. pp A-9-1 to A-9-6.

Saxton, K.E., Rawls, W.J., 2006. Soil water characteristic estimates by texture and organic matter for hydrologic solutions. Soil Science Society of America Journal 70, 1569–1578.

Sharpley, A.N., Williams, J.R., 1990. EPIC – Erosion/Productivity Impact Calculator: 1. Model Documentation. US Department of Agriculture, Technical Bulletin No. 1768. US Government Printing Office, Washington, DC.

Sparling, D.W., Fellers, G., 2007. Comparative toxicity of chlorpyrifos, diazinon, malathion and their oxon derivatives to larval Rana boylii. Environmental Pollution 147, 535–539.

USDA, 1986. Urban Hydrology for Small Watersheds. TR-55 (210-VI-TR-55), second ed. U.S. Department of Agriculture, Engineering Division, Soil Conservation Service, Washington, DC.

USDA, 2009. General Soil Survey Geographic (SSURGO) Database. U.S. Department of Agriculture, Natural Resources Conservation Service, Washington, DC. http://soils.usda.gov/survey/geography/ssurgo/ (verified 08/2009).

USDI, 2004. Proposed Tulare Basin Wildlife Management Area, Environmental Assessment, Land Protection Plan, and Conceptual Management Plan. U.S. Department of Interior, US Fish and Wildlife Service, Delano, CA.

USDI, 2009. The Public Land Survey System (PLSS). U.S. Department of the Interior, Bureau of Land Management, Washington, DC.

USEPA, 2002. Guidance for Selecting Input Parameters in Modeling the Environmental Fate and Transport of Pesticides, Version II. Office of Pesticide Programs. U.S. Environmental Protection Agency.

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. Environmental Protection Agency.

USEPA, 2006a. Organophosphate Pesticides: Revised Cumulative Risk Assessment. U.S. Environmental Protection Agency, Washington, DC.

USEPA, 2006b. 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. Environmental Protection Agency.

USEPA, 2008. Handbook for Developing Watershed Plans to Restore and Protect Our Waters. EPA 841-B-08-002. U.S. Environmental Protection Agency, Washington, DC.

USGS, 2005. Evaluation of Unsaturated-zone Solute-transport Models for Studies of Agricultural Chemicals. Open-File Report 2005-1196. U.S. Geological Survey, Reston, VA.

USGS, 2009. National Water Information System: Web Interface. United States Geographical Survey. http://waterdata.usgs.gov/nwis (verified 08/2009).