

Identification of hotspots for potential pyrethroid runoff: a GIS modeling study in San Joaquin River Watershed of California, USA

Xuyang Zhang · Minghua Zhang · Xingmei Liu

Received: 29 June 2007 / Accepted: 1 October 2007 / Published online: 23 October 2007
© Springer-Verlag 2007

Abstract This paper attempts to identify the high-risk areas for potential runoff of pyrethroid pesticides in the San Joaquin River Watershed. Pyrethroid pesticides have been detected in water and fluvial sediments in this watershed, creating concerns about potential negative impacts on water quality. However, little documentation exists regarding the distributions or the extent of the adverse effects caused by the use of pyrethroids. This study developed a geographic information systems (GIS) model to identify areas with high potential for pyrethroid runoff during the rainy season. The model was then validated using field-monitoring data. Nine factors were identified for the runoff risk assessment: amount of active ingredient used, soil erodibility factor, hydrologic group, surface layer depth, seasonal rainfall, seasonal number of rainy days, seasonal number of storm events, stream density, and land cover. The results indicated that high pyrethroid runoff risks were associated with basins such as the Stanislaus River Sub-basin, Newman Gustine Sub-basin and South Merced Sub-basin. This study demonstrated that the GIS model is capable of predicting high-risk areas of pyrethroid

runoff at sub-basin scale. The model can be used to prioritize sites for water quality monitoring and guide implementations of best management practices.

Keywords Pyrethroids · Dormant runoff · GIS modeling · Water quality

Introduction

Since the 1970s, there have been increasing concerns about the effects of agricultural pesticide use on water quality. Regulator laws such as the Clean Water Act and the Food Quality Protection Act (FQPA) have emerged in response to this issue. As a result, many growers have been affected through regulations restricting or eliminating popular organophosphate pesticides. New products have emerged in the form of synthetic pyrethroids, a group of insecticides derived from chrysanthemum flowers, which are high in efficacy and low in cost. As a result, the use of pyrethroid pesticide has been increased in California by about 80% from 1992 to 2004 (California's Pesticide Use Reporting database; <http://www.cdpr.ca.gov>). A wide variety of agricultural commodities including tree crops, horticultural crops, beans, grain corns, and cereals depend on pyrethroids to control insect pests throughout the season. As of 2005, there were 27 pyrethroid active ingredients registered for use in California (California's Pesticide Use Reporting database; <http://www.cdpr.ca.gov>). The most commonly used pyrethroid was permethrin [(3-phenoxyphenyl)methyl 3-(2,2-dichloroethenyl)-2,2-dimethyl-cyclopropane-1-carboxylate], followed by esfenvalerate [(1R)-cyano-(3-phenoxyphenyl)methyl 3-(2R)-2-(4-chlorophenyl)-3-methyl-butanoate], bifenthrin ((2-methyl-3-phenyl-phenyl)methyl 3-[(Z)-2-chloro-3,3,3-trifluoro-prop-1-enyl]-2,2-dimethyl-cyclopropane-1-carbox-

Electronic supplementary material The online version of this article (doi:10.1007/s00254-007-1065-3) contains supplementary material, which is available to authorized users.

X. Zhang · M. Zhang · X. Liu
Department of Land, Air and Water Resources,
University of California, Davis 95616, USA

X. Liu (✉)
Institute of Soil, Water and Environmental Sciences,
Zhejiang University, Hangzhou 310029, China
e-mail: xmlu@ucdavis.edu; xmlu@zju.edu.cn

ylate) and lambda-cyhalothrin [(RS)-alpha-cyano-3-phenoxymethyl 3-(2-chloro-3,3,3-trifluoropropenyl)-2,2-dimethylcyclopropanecarboxylate].

As a result of high use during the rainy season, pyrethroid chemicals have recently been detected in water and sediments sampled from Central Valley water bodies. The detected levels were high enough to be toxic to aquatic invertebrates and fish species, thus posing new water quality concerns for California (Weston et al. 2004; Zalom 2005). A review paper by Laskowski (2002) indicated that the partition coefficient between water and soil media (Koc) of pyrethroid chemicals range from 1×10^5 to about 7×10^5 . The physico-chemical properties of pyrethroids reflect a strong tendency to adsorb to organic carbons, and therefore, to potentially move off-site attached to sediment (Bacey et al. 2005).

Recently, the California Department of Pesticide Regulation plans to re-evaluate 608 pyrethroid insecticide products for environmental impacts (EPA Website, http://www.epa.gov/oppsrrd1/registration_review/explanation.htm). There is a strong need to understand their potential impacts on water quality. However, little has been documented regarding the distribution or extent of adverse effects caused by pyrethroids. In order to facilitate the re-evaluation of pyrethroid pesticides and gain a greater understanding of geographic “hotspots” for high-risk, the study developed a geographic information systems (GIS) model. The purpose of this model was to investigate the spatial variations of the off-site movement of pyrethroid pesticides from agricultural lands in the San Joaquin River Watershed. The model was designed to determine the factors influencing off-site movement of pyrethroid chemicals and the geographic locations where off-site movement was most likely to occur.

Pyrethroid runoff could be generated by either rainfall or irrigation. While winter rainfalls have been identified as a possible route of pyrethroid transport (Bacey et al. 2005), irrigation runoff is another possible reason accounting for the increasing detection of pyrethroids in water and sediments. The first step of the study focuses on the investigation on pyrethroid runoff generated by winter rainfalls. The second step, which is still ongoing, focuses on pyrethroid runoff generated by irrigation events. To assess the runoff potential generated by irrigation water, additional factors such as soil moisture and irrigation efficiency need to be taken into account. These factors are very important to water balance and thus will greatly affect the amount of pyrethroid runoff. Moreover, the spatial distributions of irrigation canals, which provide water inputs to fields in the watershed, are very different from those of the natural streams. Due to the above reasons, this study takes two steps to identify the hotspot areas. This paper reports the findings on the first part of the project,

which identified the hotspot areas of pyrethroid runoff due to rainfall events.

In general, there are three main approaches that have been employed to assess surface water vulnerability to agrochemical contamination (Zhang et al. 1996): (1) indexing and rating methods which provide relative scores or ranks according to specific characteristics that are considered as controlling vulnerability; (2) modeling approaches using physically based models to approximate contaminant transport; and (3) statistical methods that correlate contaminant occurrence with properties of the area. Examples of the index methods include the Phosphorus index (P-index) (Lemunyon and Gilbert 1993) and relative runoff potential index (Hornsby et al. 1993). P-index used transport and source factors to identify areas vulnerable to P export. A weighting factor was assigned to each of the selected factors such as soil erosion rates, runoff, and available P soil test levels to assess the degree of vulnerability of P movement from the site. The weights were given based on professional judgment. At the end, rating ranks of low, medium, high, or very high were given to each assessment unit. The relative runoff potential index used factors such as chemical properties (Koc), aquatic toxicity, soil hydrologic group, and slope to identify relative runoff potential of various pesticides. It also assigns ratings of high, medium and low to each pesticide being evaluated. The concept of indexing and ranking for vulnerability assessment usually relies on professional judgment and has been verified to be successful to identify vulnerable areas at both field and regional scale (Stevens et al. 1993; Sharpley et al. 1995; Birr and Mulla 2001). Examples of modeling approach include the VULPEST model (Villeneuve et al. 1990) and the GLEAMS model (Knisel 1993). These models have been used to predict the environmental fate and behavior of pesticides; however, their extensive data requirements often preclude spatial extrapolation to broad regional or watershed scales. Statistical models using regression analysis have been used to relate mean or total transport of contaminants in surface water to explanatory variables (Battaglin and Goolsby 1997; Chen et al. 2002; Gilroy et al. 1990). However, this approach heavily relies upon the amount of existing monitoring data. This paper was devoted to develop a GIS model to assess the site vulnerability specifically to pyrethroid pesticide contamination to surface water. The approach used here is a combination of the index approach and the modeling approach. First, different factors were chosen to capture the spatial variations of pyrethroid runoff potential. Secondly, the weightings of the variables were assigned based on professional judgment. Finally, the model was validated using monitoring data.

Materials and methods

Watershed

The San Joaquin River Watershed, which lies in the Central Valley of California, is comprised of San Joaquin, Stanislaus, Merced and Fresno counties. As illustrated in Fig. 1, there are four major rivers running through the watershed: the San Joaquin, Stanislaus, Tuolumne and Merced Rivers. There are over 200 crops grown on the, approximately, 19,023 km² of agricultural land in the watershed with dominant crops of almond, cotton and citrus. In fact, in 2003, approximately 60% of the total pyrethroid amount used in the state was applied to the crops in the San Joaquin Valley, half of which was applied during the winter months (California's Pesticide Use Reporting Database).

Data sources

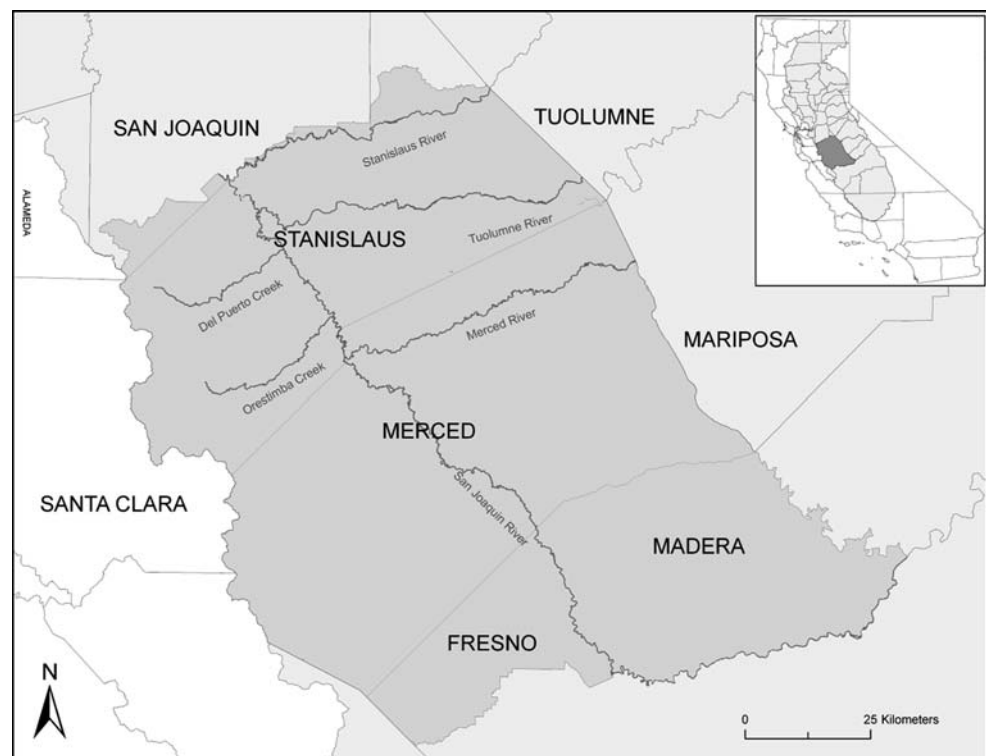
The study acquired data from various state and federal agencies. Precipitation data from year 1975 to 2005 was obtained for stations of the Western Regional Climate Center, and from 1990 to 2003 for stations of the California Irrigation Management Information System (CIMIS). Statewide pesticide use data from year 2001 to 2004 was

obtained from California's Pesticide Use Reporting Database. Soil data was obtained from the State Soil Geographic database from NRCS. Data about stream density was obtained from the 1:24000 National Hydrograph Dataset (NHD) developed by the US Geological Survey for all the hydrologic units within the watershed. Pyrethroid concentration data was obtained from the published study by Weston et al. (2004).

Factor identification and quantification

This study explored a set of potential factors influencing pyrethroid runoff through intensive review of literature and existing models such as the Modified Soil Loss Equation (MUSLE) (McCool et al. 2004), Groundwater Loading Effects of Agricultural Management Systems (GLEAMS) (Knisel 1993), Hydrologic Simulation Program Fortran (HSPF) (Barnwell 1980), SWAT (Neitsch et al. 2002) and Environmental Policy Integrated Climate (EPIC) (Sharply and Williams 1990). Most of the models use the MUSLE to assess soil erosion and the USDA curve number method to quantify surface runoff. However, the curve number method does not take into account the rainfall intensity, which is very important for estimating rain induced runoff (Oros and Werner 2005). Based on the review of the current models and parameters, the project simplified the

Fig. 1 Map of the San Joaquin River Watershed



modeling processes by incorporating the most important parameters from the MUSLE and USDA curve number methods into one model. As a result, the factors presented in Table 1 were included in this study.

Precipitation effects

The relationship between rainfall and surface runoff is one of the fundamental concepts in hydrology (Viessman and Lewis 1996). For calculating rainfall induced runoff, the importance of rainfall amount is self-explanatory. In addition, rainfall intensity affects the amount of energy arrive on land surface from precipitation. High rainfall intensity brings large amount of energy to land surface, forcing chemicals to move offsite. Rainfall intensity has been suggested to have linear correlation with runoff (Probst et al. 2005; Arnaez et al. 2007).

To quantify the effects of precipitation, the total long term monthly average rainfall (R), number of rainy days (RD) and number of severe storm events (SE) during the rainy season were calculated. The rainy season was defined as rainfall occurring from November 1 of the former year to March 31 the current year according to average monthly rainfall (Table 2). A severe storm was considered as an extreme rainfall event exceeding 25.4 mm in one day, which qualified approximate 0.2% of the days within a year as having storm events.

Table 2 Long-term average of monthly rainfall, number of rainy days and the number of storm events data include years from 1975 to 2005 for the stations from the Western Regional Climate Center and include years from 1990 to 2003 for stations from the CIMIS database

Month	Precipitation (mm)	Number of rainy days	Number of storm events
November	74.68	6.21	0.85
December	97.54	7.36	1.15
January	116.84	8.59	1.41
February	122.17	8.54	1.52
March	102.62	8.60	1.13

Use and land cover index (UV)

Use of pyrethroid chemicals is the source of runoff risk. The amount and the geographical distribution of the pesticide application affect runoff at the very beginning. In agricultural land, different types of crops will have different effects on runoff. Crop C-factors are generalized values for specific crops that determine the effectiveness of vegetation type and crop management systems in preventing soil loss (McCool et al. 2004). This study employed the C-factor values as defined in the MUSLE model (Electronic supplementary material Table S1). Different crops were assigned C-factor values to define the potential ease of pesticide runoff. High C-factor values indicate strong tendencies for pesticides to move offsite from agricultural fields.

Table 1 Factors used in the GIS model

Factor	Definition	Quantification
P	Pesticide use	Summation of pounds of pyrethroid active ingredient, 2001–2004
R	Rainfall	Summation of monthly rainfall: November 1–March 31
RD	Rainy days	Summation of number of rainy days: November 1–March 31
SE	Storm events	Summation of number of storm events: November 1–March 31
K_f	Soil K_f factor	Measure of erodibility and runoff potential of soil, taking into account organic matter and soil texture
H	Soil hydrologic group	Classification used by the US National Resource Conservation Service (NRCS) reflecting soil permeability; A, B, C and D reflect the ascending order of runoff potential (A = 0, B = 1, C = 2, D = 3)
D	Soil surface layer depth	Inverse of the thickness of the surface layer of the soil; Affects the permeability and infiltration process
C	Crop C-factor	Measurement of the effectiveness of the surface vegetation cover; This study employed the C-factor values as defined in the Universal Soil Loss Equation model (see Electronic Supplementary information Table S1)
SD	Stream density	Total stream length divided by area of each sub-watershed
UV	Use and land cover index	$P \times C$
SR	Soil runoff potential index	$D \times H \times K_f$

By combining pesticide use and land cover, UV values were calculated using the following equation:

$$UV = P * C \quad (1)$$

Pesticide use (P) factor was quantified by summing pounds of active ingredient for all the pyrethroids applied from 2001 to 2004. For each one square mile section, total pounds of active ingredients used on all crops were summed. A GIS layer of UV values was created at section scale, which is 1 square mile of land defined by the public land survey system (PLSS). If there was more than one type of crop grown within a section, the UV value was calculated as an area weighted average of UV values for all the crops within the section.

Soil runoff potential index (SR)

Soil runoff potential has been used by various equations and models, such as the P-index and the SWAT model, to calculate soil runoff potential (Renard et al. 1991; Lemunyon and Gilbert 1993; Hornsby et al. 1993; Manguerra and Engel 1998).

SR was defined as:

$$SR = D \times H \times K_f \quad (2)$$

Soil survey data was converted from map unit scale to sectional scale to conform to other model parameters. The depth of the surface layer (D) affects the permeability and infiltration process. Soils with a thin surface layer tend to have high runoff potential. Soil Hydrologic group (H) is a classification used by the US National Resource Conservation Service (NRCS) reflecting soil permeability. Groups A, B, C and D reflect the ascending order of runoff potential ($A = 0$, $B = 1$, $C = 2$, $D = 3$) (USDA NRCS 2002). Soil factor (K_f) is an adjusted K factor to include organic matter contents. K factor indicates the soil texture, erodibility, and potential for runoff from soil. Soils high in clay have low K values because they are resistant to detachment. Coarse textured soils, such as silt loam soils, are moderately susceptible to detachment, producing moderate runoff. Soils having high silt content are the most erodible among all soils. They detach easily, tend to crust, and produce high rates of runoff.

Stream density (SD)

Areas with high stream density tend to have quicker runoff response than those of low stream density (Domagalski et al. 1997; Bae and Ha 2005). Stream density was defined as total stream length divided by area of each sub-watershed, both of which were calculated using the NHD.

Stream density values were calculated for each sub-watershed and were then converted to sectional scale.

$$SD = \frac{\sum \text{Streamlength}}{\text{area}} \quad (3)$$

Standardization

Values of all the factors were standardized using the equation below to adjust the ranges of all the factors to values between 0 and 100.

$$x_{i(\text{new})} = \frac{x_i - x_{\min}}{x_{\max}} \times 100 \quad (4)$$

Cartographic modeling

A GIS database was constructed to store spatial and temporal information. Data from many different sources were analyzed using the SAS statistical packages and converted into a uniform format for the GIS system. GIS layers containing different factors were overlaid upon one another (Fig. 2). A model was developed to calculate risk scores by assigning weights to different factors as shown below:

$$Y = \beta_1 \times UV + \beta_2 \times R + \beta_3 \times RD + \beta_4 \times SE + \beta_5 \times SR + \beta_6 \times SD \quad (5)$$

Where regression coefficients $\beta_1 + \beta_2 + \beta_3 + \beta_4 + \beta_5 + \beta_6 = 1$. Y is the risk score.

High-risk areas were determined based on the integration of different factor values. Areas with high rainfall, high soil loss potential, high pesticide use value and high stream densities were considered to be the most prone to pyrethroid movement through soil erosion, and therefore the highest risk for water quality contamination. In

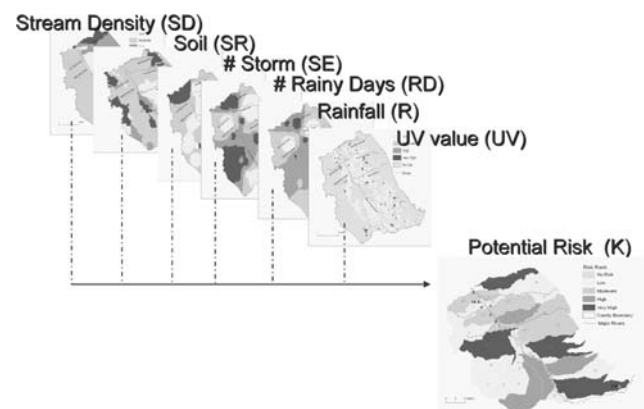


Fig. 2 GIS overlay of different factors to calculate potential risk index

contrast, areas with low values of the above factors were considered to be low risk areas.

The model assumes a linear correlation between runoff risk and each factor. Studies have shown that pesticide use and rainfall are major environmental variables for pesticide transport into surface water at a watershed scale (Guo et al. 2004; Schulz 2004). Therefore, rainfall and pesticide use were given heavier weights than the other factors. Areas with no rainfall or pesticide use were treated as having no runoff risk. In the study, it was found that a significant data gap exists in pyrethroid monitoring information. Little work has been done to monitor pyrethroid pesticides in the surface waters within the San Joaquin river watershed; therefore, the estimate of the model parameters relied on the mechanistic understandings of the runoff process as influenced by each factor.

Based on the assumption that the selected factors could explain the total variation of the potential risk, the coefficients of the variables add up to one. Each of the coefficients was assigned according to the relevant importance of the associated variable. The coefficient of determination (R^2) of a regression model developed by Guo et al. (2004) was 0.674, which indicated that precipitation and pesticide use alone explained 67.4% of the variation of diazinon load in surface water. Because pyrethroids are hydrophobic and more easily attached to soil than diazinon, the sum of $\beta_1 + \beta_2 + \beta_3 + \beta_4$ was less than 0.674. As a result, the values of 0.35 and 0.2 were given to β_1 (use and land cover index) and $\beta_2 + \beta_3 + \beta_4$ (precipitation effects) respectively. Due to the strong influence of soil runoff potential for pyrethroid runoff, a coefficient of 0.3 was designated for β_5 . The coefficient of stream density was determined to account for the remaining portion of the variance and given a value of 0.15 (β_6).

Risk classification

Risk scores calculated from the model were grouped into four classes according to the distribution of values and the standard deviation (STD): low, moderate, high and very high (Fig. 3). The values ranging from 0 to the mean – 0.5STD were assigned to low risk; values ranging from the mean – 0.5STD to the mean + 0.5STD were assigned to moderate risk; values ranging from mean + 0.5STD to the mean + 1.5STD were referred to as high-risk; and values ranging from mean + 1.5STD to 100 were referred to as very high-risk. Using this ranking method, hotspots of pyrethroid runoff were identified. The STD was defined calculated using the equation below:

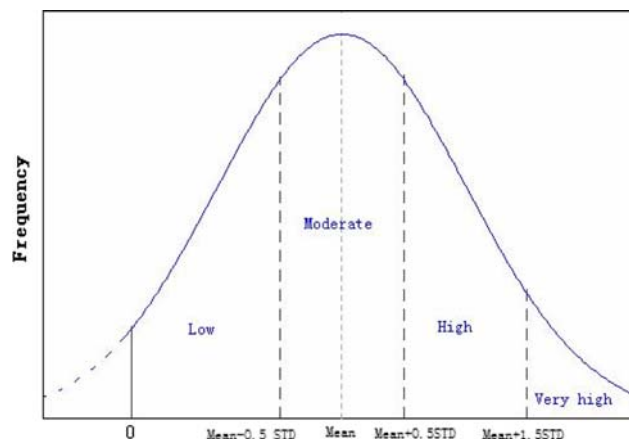


Fig. 3 Classification of overall risk

$$\text{STD} = \sqrt{\frac{1}{N} \sum_{i=1}^n Y_i^2} \quad (6)$$

where y_i is the standardized risk score calculated from Eq. 5.

Model validation

To validate the modeling results, the study used monitoring data from a published work by Weston et al. (2004). Sediment samples were taken from seven monitoring sites located in the San Joaquin River watershed. The watershed was delineated into sub-basins that contribute flows to the water quality monitoring sites. The watershed delineation was conducted through the BASINS (USEPA <http://www.epa.gov/waterscience/basins/>) auto delineation procedure using the Digital Elevation Model data and stream network. Runoff risk scores were predicted for each of the sub-watersheds using the developed model in the study. To evaluate the strength of the model's prediction capability, the study then compared the model's predicted risk score for each sub-basin to the detected pyrethroid concentration measured at each sub-basin outlet by Weston et al. (2004). For two reasons, the mean concentration of permethrin in sediment measured was used as a representation of the actual pyrethroid concentration in sediment. First, permethrin accounts for a majority of the uses among all the pyrethroid compounds. In 1993, among the six pyrethroid compounds that were used, permethrin comprised 60% of the total pyrethroid use. In 2002, permethrin accounted for 45% of the total use among 10 of the pyrethroid compounds (Amweg et al. 2005). Second, most of the other pyrethroid compounds were under detection level during their sampling study.

Results and discussion

Soil

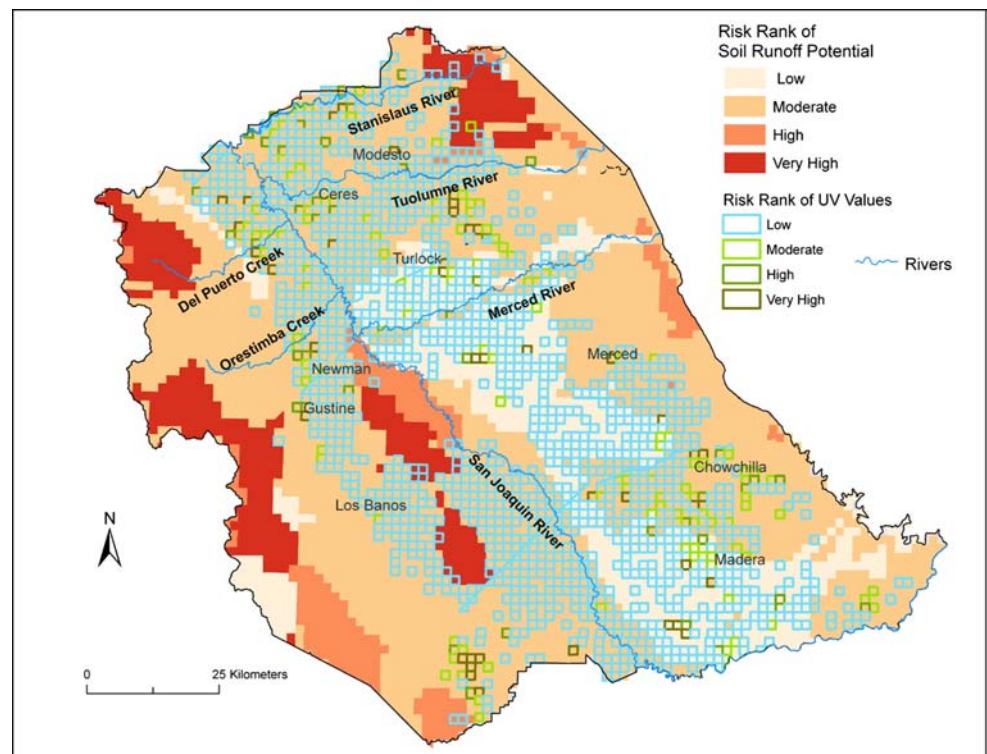
Within the watershed, approximately 50% of the soil was classified as hydrological group D, which has the lowest permeability among the four groups. About 25% percent of the soil was classified in hydrological group A or B, which have relatively low runoff, and high permeability. K_f factors of the soils ranged from 0 to 0.43, with over 75% of the soils having a K_f greater than 0.3. This indicated that most of the soils were generally high in erodibility. The depth of the first layers of the soils ranged from 0 to 76.2 cm with over 90% of the soils having a surface layer shallower than 25.4 cm. Overall, soils in the west side of the watershed were more prone to runoff compared to soils in the east side of the watershed. This pattern results in a quicker runoff response of sub-watersheds on the west bank than those on the east bank (Domagalski et al. 1997). Hotspots with high soil runoff potential were mainly located on the west side of the watershed, such as the areas to the southeast of Gustine, northeast of Los Banos and the area surrounding the South Dos Palos. The area between the upper stream of the Stanislaus River and the upper stream of the Tuolumne River was the only hotspot located on the east side of the watershed (Fig. 4).

Pesticide use and land cover

Sections with high UV values were not clustered. Most of the high use sections were far away from the river with the exception of the sections around the Stanislaus River (Fig. 4). Those sections with high UV values contained crops such as sunflowers, apples, strawberries, almonds, oranges and corn. The high UV values were either due to relatively high C-factors associated with the crops, such as strawberries and sunflowers, or because of the high amount of pyrethroid pesticides used for almond and apple crops. However, the crop C-factor did not take into account of the possibility that best management practices (BMPs), such as cover crop, were being employed by growers, which could greatly reduce the off-site movement of pyrethroid pesticides. If BMPs were used, the C-factor should be reduced to lower values for those fields.

When evaluating pesticide use and land cover in regards to soil runoff potential, the study found that most of the sections with high UV values were associated with soils of low to moderate runoff potential (Fig. 4). There was no significant pyrethroid use in the hotspot areas with high soil runoff potential. In these areas, most of the sections had low UV values, signifying little actual pesticide runoff from these areas. Hotspots that ranked high on both UV value and soil runoff potential were located near the Stanislaus River and the city of Newman Gustine (Fig. 4).

Fig. 4 Risk rank by pesticide use, land cover and soil runoff potential



Precipitation

The average monthly precipitation was highest in February, with an average of 122.17 mm of rain. February also had the most storm events among all the rainy season months. November had the lowest rainfall and the least amount of rainy days and storm events with an average of 74.68 mm of rain (Table 2). Spatially, the areas with the highest rainfall and the highest number of rainy days were the Modesto area and middle-eastern part of the valley (Fig. 5). However, the middle-eastern part of the valley had fewer storms than the Modesto or Los Banos areas during the rainy season (see Electronic supplementary material Figs. S1, S2). Since rain generates runoff, the spatial distribution of precipitation was considered as an important indicator for runoff potential. Areas with close to zero rainfall were considered as having no runoff potential.

Stream density

The watershed was divided into 13 sub-watersheds as defined by the California State Water Resource Control Board. Among these sub-watersheds, the Vernalis North sub-watershed had the highest stream density, followed by the Stanislaus River and Tuolumne sub-watersheds. All other sub-watersheds were relatively low in stream density measures (Fig. 6). The Stanislaus River sub-watershed also had high UV value sections, which were located close to

streams, indicating the high runoff potential for areas within this sub-watershed.

Overall runoff risk

According to the mechanisms of runoff generation and the specific properties of pyrethroid chemicals, the study developed a simple linear model to calculate risk index and then standardized the risk values for comparison among different areas. The risk model is shown as follows:

$$y_i = 0.35 \times UV + 0.1 \times R + 0.05 \times RD + 0.05 \times SE + 0.3 \times SR + 0.15 \times SD \quad (7)$$

Since the value of each variable was based on each section, the risk score Y was calculated first for each section within the watershed. The overall Y value of a delineated hydro-basin was then calculated using Eq. 7, where n is the number of sections within a hydro-basin and y_i is the Y value of the i th section in the basin. The values of n were from 11 to 1,569 for the 13 sub-watersheds. Risk score Y was later standardized so that all of the risk values ranged between 0 and 100.

$$Y = \sum_{i=1}^n y_i \quad (8)$$

The final risk map showed that the areas with high overall runoff potential were associated with the Stanislaus

Fig. 5 Risk rank by rainfall

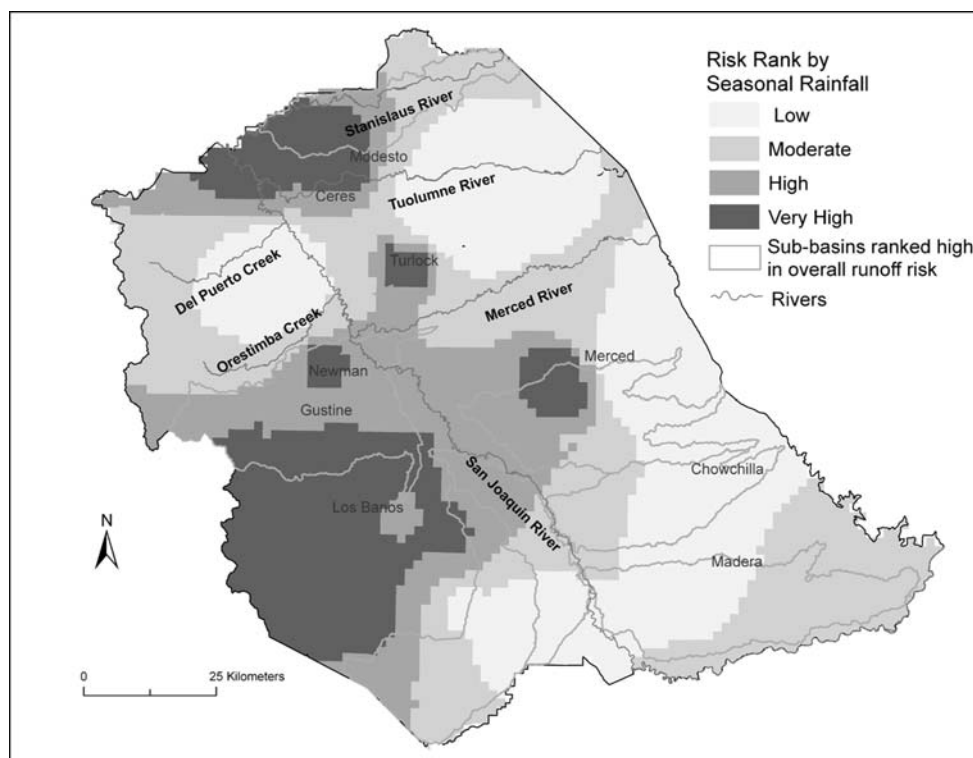
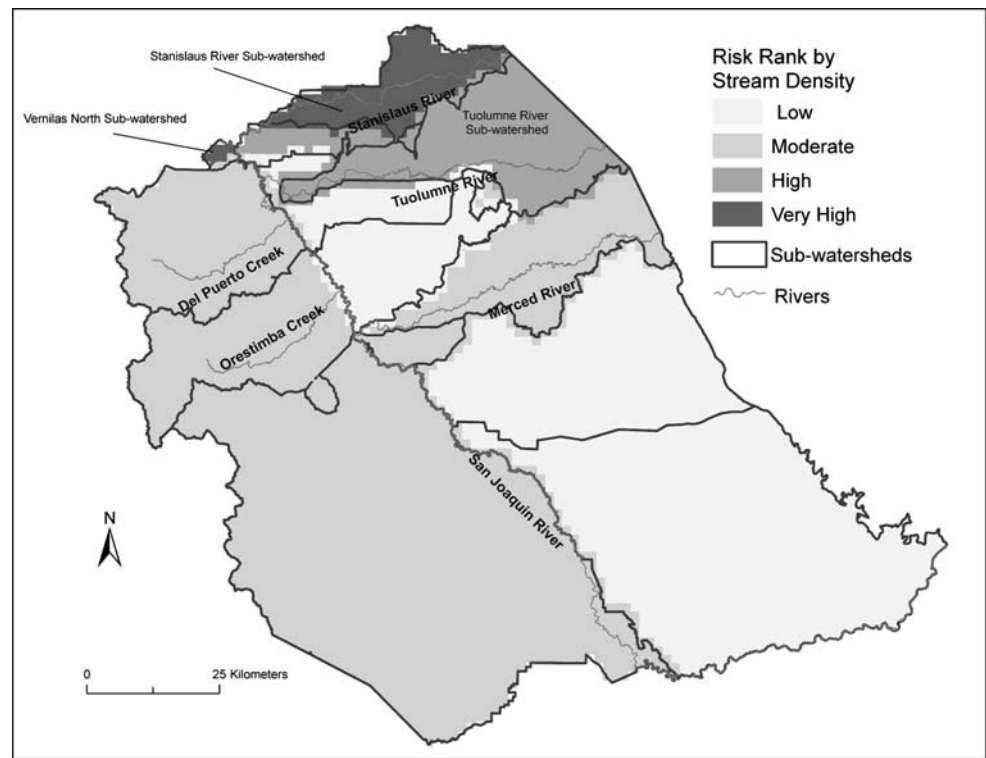


Fig. 6 Risk rank by stream density

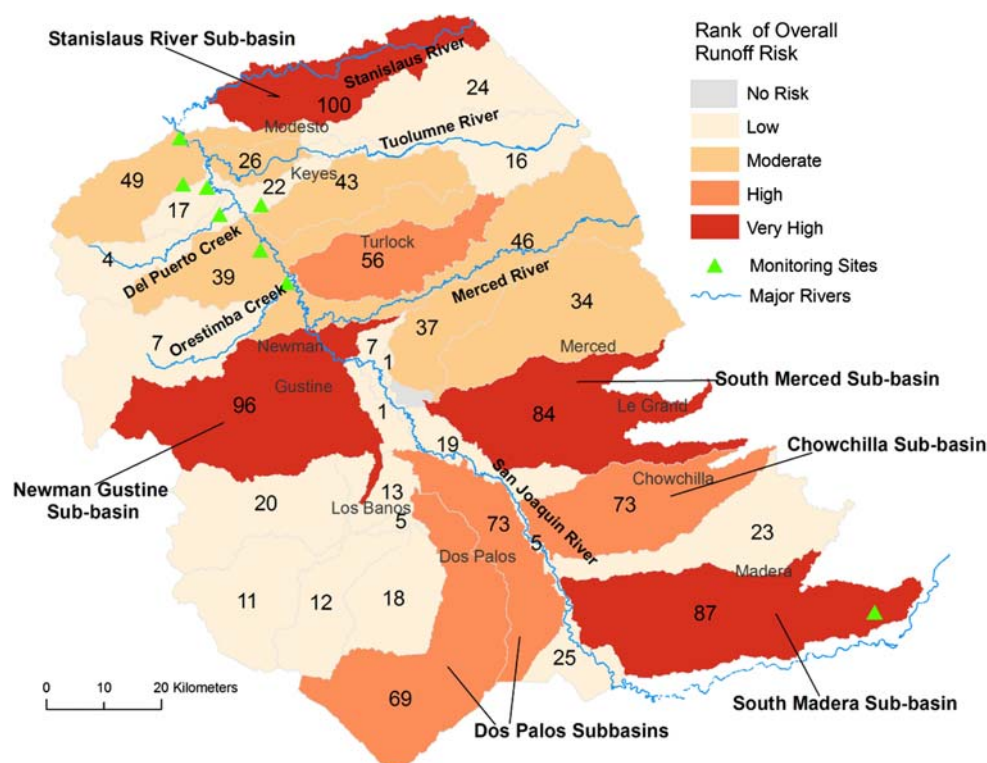
River Sub-basin, Newman Gustine Sub-basin, South Merced Sub-basin, South Madera Sub-basin, Dos Palos Sub-basins and the Chowchilla Sub-basin (Fig. 7). The Stanislaus river sub-basin had the highest overall runoff risk among all the sub-basins. This high-risk score can be attributed to the sub-basin ranking high to very high in all of the six variables. In addition, the high UV value sections were close to rivers. The second highest risk sub-basin was the Newman Gustine sub-basin. Factors that contributed to this high-risk rating were over seven high UV value sections, a number of high soil runoff potential areas and high to very high rainfall in the region. The Madera sub-basin was ranked high in overall runoff risk mainly because of high pesticide use and moderate rainfall. The South Merced sub-basin had high rainfall and many rainy days, which resulted in high overall runoff risk. Dos Palos sub-basins were ranked high in overall runoff risk due to high pesticide use and many storm events. Chowchilla sub-basin had relatively lower risk scores, although still high, because it was ranked high in UV values but moderate to low in other variables.

The hotspot areas identified in this study have high potential of pyrethroid pesticide off-site movement during the rainy season. Therefore, water quality monitoring sites should be located at the outlets of these sub-watersheds to quantify pyrethroid concentration in water and sediments. BMPs such as vegetated ditches, cover crops and constructed wetlands should be implemented in these areas to

reduce the off-site movement of pyrethroid pesticides. These strategies are necessary for preventing pyrethroid pesticides from impacting water quality in the San Joaquin River watershed.

Surprisingly, the Del Puerto Creek and Orestimba Creek areas on the western bank received relatively low ranks for overall runoff potential. Historical studies (Domagalski et al. 1997) indicated that these areas are more prone to runoff due to high pesticide use, heavy textured soils and steeper slopes than that of the east side of the San Joaquin River. Obviously, this was not found to be the case for pyrethroids. This study revealed that although there were a few high use sections located in the Del Puerto Creek and Orestimba Creek area, they were not located on soils with high runoff potential, which resulted in their relatively low scores in overall runoff potential. Given that the hotspot areas identified in this study had higher risk scores than the Del Puerto Creek and Orestimba Creek watershed area, the increase detection of pyrethroid pesticides in the Del Puerto Creek and Orestimba Creek indicated that there might be even higher detection rates for pyrethroid pesticides in the hotspot areas. Another possible explanation could be that the detected pyrethroid chemicals in these streams might not be transported mainly via rain generated runoff. Studies indicated that spray drift could be another important pathway for pesticides entering into surface water (Cryer et al. 2001). In addition, urban contribution

Fig. 7 Values of the risk score and monitoring sites with their corresponding sub-basins



could also be an important source of pyrethroid runoff (Oros and Werner 2005; Weston et al. 2005).

Model validation using monitoring data

The five monitoring sites were used as sub-basin outlets to delineate the watershed. The risk scores of each sub-basin predicted by the model and the mean detected concentration of permethrin from the monitoring sites are shown in the Table 3. The distributions of predicted risk scores and mean detected concentration numbers were well correlated with the exception of the OC site (Fig. 8). This was probably due to the difference between contributing areas defined during the watershed delineation and the actual contributing area to that site. The model under predicted the potential pyrethroid runoff at this sub-basin because the contributing area delineated by the GIS process was smaller than the actual contributing area. For the other sites, risk score were highly correlated with the monitoring site values as can be seen from the Pearson's correlation value of 0.862. The validation process was greatly limited by the amount of monitoring data available for the current condition. As more water and sediment monitoring data of pyrethroid pesticides become available, the model validation process could be improved in the future.

The prediction precision of the model could be further improved if in-season pyrethroid runoff generated by

irrigation and runoff from urban land were included. According to California's Pesticide Use Reporting database, urban uses of pyrethroids are increasing. Therefore, pyrethroid runoff from urban areas is another potential source of pyrethroid chemicals found in sediment and water. Pyrethroid runoff from urban areas could potentially account for detections of pyrethroid chemicals in many important waterways, especially those areas with high potential runoff. Irrigation induced runoff during the growing season could be another important contributor of pyrethroid runoff. A recent report by the San Francisco Estuary Institute suggested that the highest pyrethroid concentration in surface water and sediment appeared in late summer, when irrigation could be a significant

Table 3 Maximum detected concentration of pyrethroid chemicals in monitoring sites and predicted risk scores of their contributing basins

Site name ^a	Basin ID	Detected permethrin concentration (ng/g)	Risk score
DP	7	5.6	22
JN	5	3.8	17
IC	2	10.5	49
AD11	10	1.4	39
OC	13	5.7	7
RC	34	87.7	87

^a Site names were from Don Weston's paper. Please refer to Weston et al. 2004 for detailed descriptions of each site

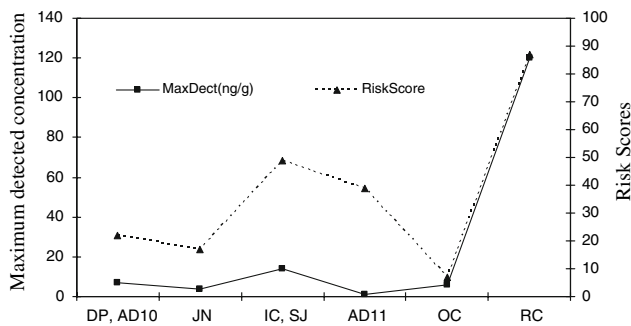


Fig. 8 Values of the risk score and maximum detected concentration for monitoring sites and their corresponding sub-basins

contributing factor (Oros and Werner 2005). The second step of the project; therefore, focus on quantifying irrigation and urban runoff.

A review paper by Hapeman et al. (2003) from the US Department of Agriculture evaluated recent studies on understanding agrochemical fate and transport. They pointed out that the new challenge for agricultural research is to identify the vulnerable areas and the temporal and spatial variations prior to use of chemical by predicting how it will behave in environmental matrices within a watershed. The finding of this study fill this data gap by spatially assessing the relative potential of pyrethroid runoff and identifying hotspots for future policy to target. This paper also fills the gap in literature on site vulnerability assessment for pesticide contamination in surface water. Once the second step is completed, the methods could be applied to assess the potential risk of other pesticides. The model will greatly assist in prioritizing sites for water quality monitoring and future implementation of management practices to reduce runoff. In addition, the model will be able to act as a template for use in other areas, serving as a tool to assist decision-making in watershed management over a wide geographic range.

Conclusion

Important factors affecting pyrethroid runoff include pesticide use amount, rainfall, number of rainy days, number of storm events, soil hydrological group, soil surface layer depth, soil erodibility, surface land cover, and stream density. The modeling results from this study further confirmed that these selected factors can explain a high proportion of pyrethroid runoff potential. Areas with high runoff potentials include the Stanislaus River Sub-basin, Newman Gustine Sub-basin, South Merced Sub-basin, South Madera Sub-basin, Dos Palos Sub-basins and the Chowchilla Sub-basin. These areas thus need more attention when pyrethroid pesticides are applied and

should be the priority locations for water quality monitoring and BMP implementation. The model developed during the study showed good prediction precision with statistically significant correlation to actual pyrethroid detection. The Pearson's correlation value of 0.867 indicates that GIS modeling was capable of predicting the relative risk of pyrethroid off-site movement at sub-basin scale.

Acknowledgments This work was partially funded by the Coalition for the Urban/Rural Environmental Stewardship (CURES). Authors thank Dr. Don Weston for providing the geographic coordinates for his monitoring sites from his published work. Authors thank the colleagues Kimberley Steinmann, Sarah Gatzke, Adam Hale, Darren Ficklin and Lisa Fernandez for providing precious review comments.

References

- Amweg EL, Weston DP, Ureda NM (2005) Use and toxicity of pyrethroid pesticides in the central valley, California, USA. *Environ Toxicol Chem* 24:966–972
- Arnaez J, Lasanta T, Ruiz-Flano P, Ortigosa L (2007) Factors affecting runoff and erosion under simulated rainfall in Mediterranean vineyards. *Soil and Tillage Research* (in press)
- Bacey J, Spurlock F, Starnes K, Feng H, Hsu J, White J, Tran DM (2005) Residues and toxicity of esfenvalerate and permethrin in water and sediment, in Tributaries of the Sacramento and San Joaquin Rivers, California, USA. *Bull Environ Contam Toxicol* 74:864–871
- Bae MS, Ha SR (2005) GIS-based influence analysis of geomorphological properties on pollutant washoff in agricultural area. *Water Sci Technol* 51:301–307
- Barnwell TO (1980) An overview of the hydrologic simulation program: FORTRAN, a simulation model for chemical transport and aquatic risk assessment. In: *The fifth annual symposium on aquatic toxicology*. ASTM Special Tech. Pub, Philadelphia, PA 19103
- Battaglin WA, Goolsby DA (1997) Statistical modeling of agricultural chemical occurrence in midwestern rivers. *J Hydrol* 196:1–25
- Birr AS, Mulla DJ (2001) Evaluation of the phosphorus index in watersheds at the regional scale
- Chen W, Hertl P, Chen S, Tierney D (2002) A pesticide surface water mobility index and its relationship with concentrations in agriculture drainage watersheds. *Environ Toxicol Chem* 21:298–308
- Cryer SA, Fouch MA, Peacock AL, Havens PL (2001) Characterizing agrochemical patterns and effective BMPs for surface waters using mechanistic modeling and GIS. *Environ Model Assess* 6:195–208
- Domagalski JL, Dubrovsky NM, Kratzer CR (1997) Pesticides in the San Joaquin River, California: inputs from Dormant Sprayed Orchards. *J Environ Qual* 26:454–465
- EPA Website. (http://www.epa.gov/oppsrrd1/registration_review/explanation.htm)
- Gilroy EJ, Hirsch RM, Cohn TA (1990) Mean square error of regression-based constituent transport estimates. *Water Resour Res* 26:2069–2077
- Guo L, Nordmark CE, Spurlock FC, Johnson BR, Li L, Lee JM, Goh KS (2004) Characterizing dependence of pesticide load in surface water on precipitation and pesticide use for the sacramento river watershed. *Environ Sci Technol* 38:3842–3852

- Hornsby AG, Buttler TM, Brown RB (1993) Managing pesticides for crop production and water quality protection: practical grower guides. *Agric Ecosyst Environ* 46:187–196
- Knisel WG (1993) GLEAMS: ground water loading effects of agricultural management systems, Ver. 2.10. VGA-CPESBAED Publ., Tifton
- Laskowski D (2002) Physical and chemical properties of pyrethroids. *Rev Environ Contam Toxicol* 174:49–170
- Lemunyon JL, Gilbert RG (1993) The concept and need for a phosphorus assessment tool. *J Prod Agric* 6:483–486
- Manguerra HB, Engel BA (1998) Hydrologic parameterization of watersheds for runoff prediction using SWAT. *J Am Water Resour Assoc* 34:1149–1162
- McCool DK, Foster GR, Yoder DC (2004) The revised universal soil loss equation, Version 2. In: The 13th international soil conservation organization conference, Brisbane, Australia
- Neitsch SL, Arnold JG, Kiniry JR, Srinivasan R, Williams JR (2002) Soil and water assessment tool users' manual version 2000. Texas Water Resources Institute TR-192, College Station
- Oros DR, Werner I (2005) Pyrethroid insecticides: an analysis of use patterns, distributions, potential toxicity and fate in the Sacramento-San Joaquin Delta and Central Valley. 415, San Francisco Estuary Institute, Oakland
- Probst M, Berenzen N, Lentzen-Godding A, Schulz R (2005) Scenario-based simulation of runoff-related pesticide entries into small streams on a landscape level. *Ecotoxicol Environ Saf* 62:145–159
- Renard KG, Foster GR, Weesies GA, Porter JP (1991) RUSLE: revised universal soil loss equation. *J Soil water Conserv* 46(1):30–33
- Schulz R (2004) Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution: a review. *J Environ Qual* 33:419–448
- Sharply AN, Williams JR (1990) In: Sharply AN, Williams JR (eds) EPIC—Erosion/Productivity Impact Calculator: 1. Model Documentation. USDA Technical Bulletin, Washington
- Sharpley A (1995) Identifying sites vulnerable to phosphorus loss in agricultural runoff. *J Environ Qual* 24:947–951
- Stevens RG, Sobecki TmM, Spofford TL (1993) Using the phosphorus assessment tool in the field. *J Prod Agric* 6:487–492
- Viessman W, Lewis GL Jr (1996) Introduction to hydrology, 4th ed. Harper Collins College Publ., p 760
- Villeneuve J-P, Banton O, Lafrance P (1990) A probabilistic approach for the groundwater vulnerability to contamination by pesticides: the vulpest model. *Ecol Modell* 51:47–58
- Weston DP, Holmes RW, You J, Lydy MJ (2005) Aquatic toxicity due to residential use of pyrethroid insecticides. *Environ Sci Technol* 39:9778–9784
- Weston DP, You J, Lydy MJ (2004) Distribution and toxicity of sediment-associated pesticides in agriculture-dominated water bodies of California's Central Valley. *Environ Sci Technol* 38:2752–2759
- Zalom FG (2005) Managing resistance is critical to future use of pyrethroids and neonicotinoids. *Calif Agric* 59:11–15
- Zhang R, Hamerlink JD, Gloss SP, Munn L (1996) Determination of non-point source pollution using GIS and numerical models. *J Environ Qual* 25:411–418