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Characterizing Dependence of Pesticide Load in Surface Water on Precipitation and Pesticide Use for the Sacramento River Watershed

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Transport of pesticides by surface runoff during rainfall events is a major process contributing to pesticide contamination in rivers. This study presents an empirical regression model that relates pesticide loading over time in the Sacramento River with the precipitation and pesticide use in the Sacramento River watershed. The model closely simulated loading dynamics of diazinon, simazine, and diuron during 1991−1994 and 1997−2000 winter storm seasons. The coefficients of determination for regression ranged from 0.168 to 0.907, all were significant at <0.001. The results of this study provide strong evidence that precipitation and pesticide use are the two major environmental variables dictating the dynamics of pesticide transport into surface water in a watershed. The capability of the statistical model to provide time-series estimates on pesticide loading in rivers is unique and may be useful for total maximum daily load (TMDL) assessments.

Introduction

In recent years, surface water contamination has received increased attention because of total maximum daily load (TMDL) requirements. Section 303 (d) of the 1972 Clean Water Act was previously ignored, but it requires states to identify all of its water bodies that fail to meet applicable water quality standards and to establish TMDLs for these impaired, polluted water bodies so that they can be cleaned up and comply with applicable water quality objectives. The fundamental difference of the TMDL approach from previous water quality management concepts is its requirement to address nonpoint source pollution. Owing to their dispersed nature of distribution in the environment, transport of nonpoint source pollutants is difficult to predict, especially in large watershed scales.

The estimation of contaminant concentration or load in surface water from both point and nonpoint sources has been a prime focus in surface water hydrology. Among the analysis methods employed to interpret regional monitoring data of contaminant transport, statistical modeling has been recognized and proven useful in explaining transport patterns observed at watershed scales (*1*−*5*). Several previous studies using regression analysis were able to relate mean or total transport of contaminants in surface water to explanatory variables such as watershed properties, chemical use, and physicochemical characteristics of the contaminant (*3*, *5*, *6*). Mechanistic models, based on detailed descriptions of transport processes, have also been used to simulate fate and transport of contaminants in watersheds. Although these models can be calibrated quite well with their numerous parameters, they generally do not perform well for prediction purposes because of the high complexity of natural hydrological systems and the uncertainty in determining some of the model parameters.

Adequate prediction of contaminant transport to surface water is a necessary component of successful TMDL development and implementation. In this analysis, we adopt a hybrid approach of statistical and mechanistic modeling in analyzing pesticide monitoring data obtained from the Sacramento River, the largest river in northern California, during various winter storm seasons of 1991−2000. The method intended to seek system response of pesticide loading by extracting information from existing pesticide use and watershed data. The specific objectives of this analysis were to explore the dependence of pesticide load in the Sacramento River on precipitation and pesticide use, and to establish an empirical equation that describes the relationship. We believe that such a relationship operationally characterizes the vulnerability or resistance of a watershed to pesticide contamination, and therefore would be useful for evaluating the potential success of mitigation measures in reducing pesticide runoff into surface water at the watershed scale.

The Regression Model

Pesticides are transported from the field to the surface water mainly by the process of runoff. Although numerous factors affect runoff, and therefore pesticide concentrations in surface water, many of these factors such as soil type, stream channel network, land use, and landscape remain virtually unchanged over time and thus reduce essentially to constants for a given watershed. In such cases, the temporal and spatial changes of pesticide concentrations in surface water are primarily dependent on two major environmental variables, both of which are very well documented: precipitation and pesticide use. Precipitation determines the total amount of runoff water, and pesticide use represents the source of contamination.

The basic form of the regression equation we proposed, based on the above physical premise, is a power function containing the product of two factors: precipitation (P) and pesticide use (U). Therefore, an impact on surface water results when the two factors co-occur. The general form of the equation can be expressed as follows:

$$Y = a(P - b)^n U \tag{1}$$

where Y is the pesticide load in surface water (kg d^{-1}), a is a regression coefficient (cm^{-n}, where n will be defined in the following), P is the precipitation (cm d^{-1}), b is a parameter related to the minimum precipitation that results in runoff, U is the pesticide use (kg d^{-1}), and n is an exponential parameter that defines the nonlinear dependence of load on precipitation. When n is less than unity, the effect of P on Y reduces progressively as P increases.

The application of eq 1 to a watershed is more complicated when both temporal and spatial scales are considered. In this study, the data analysis was conducted at two spatial scales: the single basin scale and the multi-subbasin scale. For the single basin scale, eq 1 can be written as

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$$Y = a[(\sum_{j=1}^{M} P_j - b)^n]\sum_{k=3}^{N} U_k \quad (2)$$

where P_j is the daily precipitation (cm d^{-1}) for the watershed on day j, U_k is the daily use of the pesticide (kg d^{-1}) in the watershed on day k, and M and N denote, respectively, the time span for calculating cumulative P and U, counted backward in time with the current day being 1. In this analysis, the lower limit of N was set to be 3 to allow a 2-day travel time of pesticide from the application field to the rivers. The upper limits of M and N were optimized by changing their values from the lower limits up to 60 days systematically to determine the best relationship between load, and precipitation and use in eq 2.

For the multiple subbasin scale, the watershed can be further subdivided into several subbasins. Equation 1 therefore can be expanded as

$$Y = \sum_{i=1}^{L} a_i \{[(\sum_{j=1}^{M} P_{ij} - b)^n]\sum_{k=3}^{N} U_{ik}\} \quad (3)$$

where L denotes number of subbasins in the watershed, and a_i, P_i, and U_i are the partial regression coefficients, cumulative precipitation, and cumulative pesticide use, respectively, for the respective subbasins. The partial regression coefficient a_i is an aggregated variable that describes the relative impact of both pesticide use and rainfall in the subbasin on pesticide load. Mechanistically, the value of a_i is related to the geographic characteristics of the subbasin such as hydrology, soils, land use, and landscape, etc. that affect the runoff transport process.

In addition to surface runoff, atmospheric deposition may also contribute to pesticide load to the surface water, especially for pesticides with a high volatility. Loading of pesticides by this route, however, also happens during precipitation events, conforming to the power function of our model formulation.

Methods

Watershed Description. The Sacramento River is the largest river in northern California, draining an area of approximately 70 000 km^2. With its 515-km length, the river is almost confined in the Sacramento Valley, one of the seven physiographic regions in the Sacramento River Basin (*7*). Two major tributaries to the Sacramento River are the Feather River and American River, both located on the east side of the Sacramento River.

The major land use in the Sacramento Valley is agriculture with limited urban areas. Almost all farming activities impacting the Sacramento River happen in the Sacramento Valley. The Sacramento Valley has a semi-arid climate characterized by hot summers and mild winters, with average temperature ranging from the low 40s °F in the winter to the upper 90s °F in the summer. The soils of the valley are mostly fine-grained with low permeability (*7*, *8*). The mean annual precipitation in the valley ranges from 36 to 64 cm. Most of the precipitation, however, occurs during the months of November to April, which was termed "winter storm season" for this study. The water requirement of plant growth in other months is dependent on irrigation.

To characterize changes in pesticide loading in the Sacramento River, the Sacramento Valley was considered as a single basin for the Sacramento River, and only data of precipitation and pesticide use in the Sacramento Valley were considered in the analysis. At the single basin scale, precipitation data from the weather stations scattered in the valley were pooled for the calculation of daily means without considering locations. Although there were variations in rainfall amount among these locations, the mean value probably best represented the precipitation condition of the basin. Daily total pesticide use in the valley was also calculated regardless of application locations.

For the subbasin model, the valley was further divided into the following six subbasins according to McClure et al. (*9*): (1) the Sacramento River above Colusa; (2) Colusa Drain; (3) Butte/Sutter Basin; (4) Lower Feather River Basin; (5) Natomas-Cross Canal Area; and (6) Lower American River Basin (Figure 1). The precipitation and pesticide use in the Sacramento Valley were calculated individually for each subbasin. The a_i in the subbasin model eq 3 for the subbasins were numbered in the same order as listed above.

Source of Surface Water Monitoring Data. The source of the surface water monitoring data was the Surface Water Database compiled by the California Department of Pesticide Regulation (http://www.cdpr.ca.gov/docs/sw/surfdata.htm). The database documents the pesticide monitoring results of over 30 surface water monitoring studies conducted by federal, state, and local government agencies, and other private industrial and environmental groups, including the United States Geological Survey (USGS), California State Water Resources Control Board (SWRCB), California Department of Pesticide Regulation (DPR), California Central Valley Regional Water Quality Control Board, Sacramento River Watershed Program (SRWP), etc. Collectively these monitoring studies represented approximately 100 000 records of pesticide analyses in surface water samples as of August 2002. Water quality data are available from 151 monitoring sites. On the basis of representativeness of their hydrological locations and the completeness of data set, two monitoring sites covering different periods of time were selected to represent the surface water conditions for the Sacramento River: the I Street Bridge (1991−1994) and the Alamar Marina Dock (1997−2000). The locations of these monitoring sites are illustrated in Figure 1. The I St. Bridge site is located downstream of the entire Sacramento Valley, and captures all agricultural runoff from the watershed during nonflooding years. Data from this site, however, are available only for the period up to April 1994. The Alamar Marina site is located about 19 km upstream of the I St. Bridge, and receives surface water contributions from five of the six subbasins, excluding the American River subbasin. Pesticide use in the American River subbasin, however, was very limited, generally <0.25% of the total reported use in the Sacramento Valley. There were no monitoring data for the Sacramento River at either of these locations from 1995 to 1996.

Among 36 pesticides monitored, only diazinon, simazine, and diuron were analyzed for this study (Table 1). These pesticides were identified based on the detection frequency of historic sampling results. A ≥10% frequency of detection, defined as the number of detections above the method detection limit over the number of total analyses, was set arbitrarily as the screening criterion for selecting candidate pesticides for modeling. The pesticides with a detection frequency of ≥10% were considered as "significant surface water contaminants" and were retained for the regression analysis. This selection procedure was probably biased against pesticides with a higher detection limit (DL). However, a high DL combined with a large number of nondetects (NDs, i.e., concentrations below the DL) precludes estimation of actual pesticide loads. The DLs for the three pesticides analyzed in this study are given in Table 1. All NDs were treated as $^1/_2$ of the DL in the calculation.

Though monitoring data for some pesticides were available throughout the years, the bulk of the data in the Surface Water Database were collected during the winter storm seasons from November to April. We focused only on data collected during the winter storm seasons when the precipitation was the primary driving force for pesticide

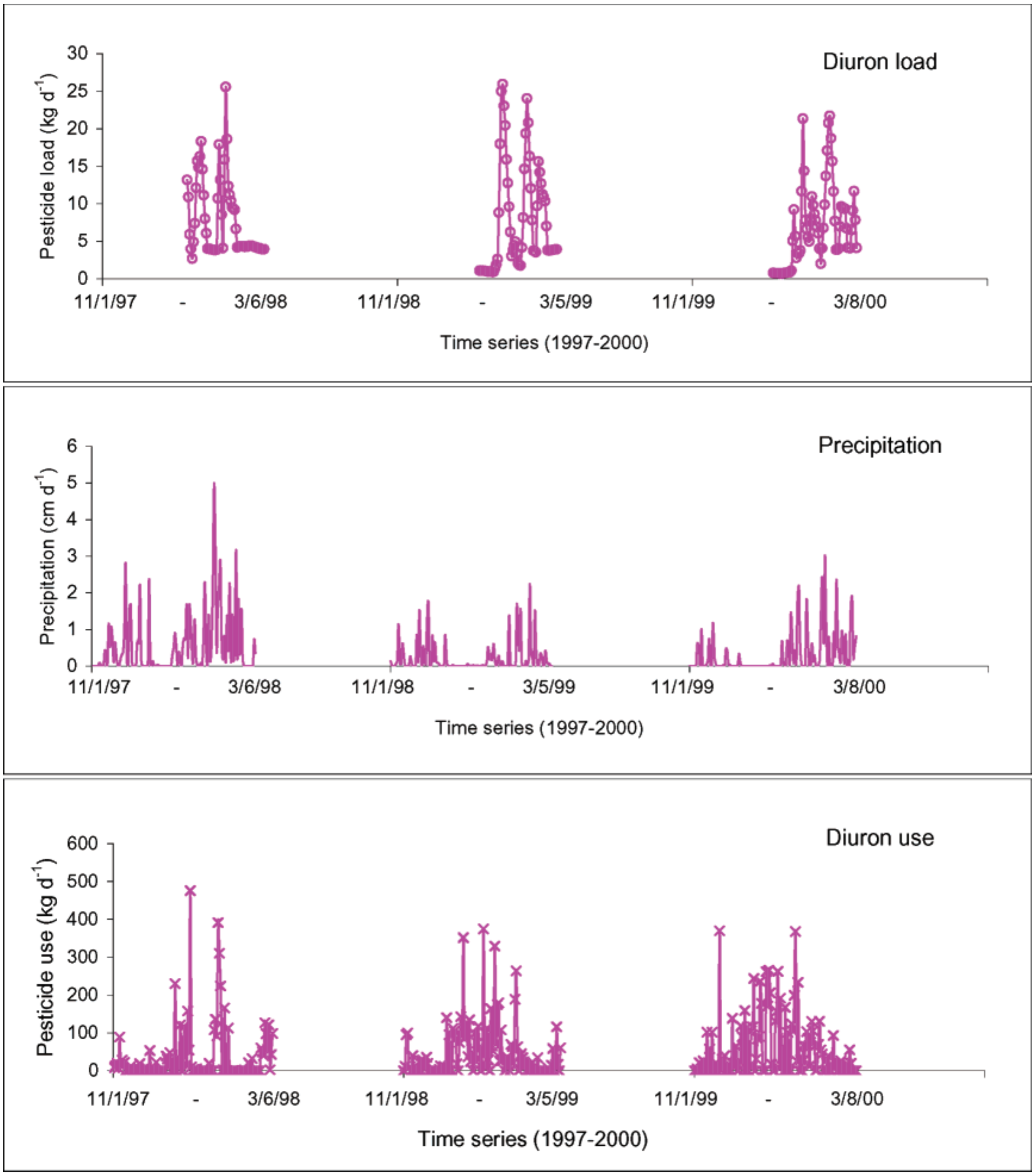

FIGURE 6. Time series of diuron load *Y*(*t*) in the Sacramento River, precipitation *P*(*t*), and diuron use *U*(*t*) in the Sacramento River basin during 1997 to 2000 winter storm seasons. The pesticide load was calculated from data collected at the Alamar Marina Dock.

high unaccounted diuron uses such as rights of way applications, landscape maintenance applications, and structure pest control, etc., which reached more than 40% of the total reported use for the counties located or partially located in the Sacramento Valley for the three years monitored (1998–2000). The highest daily load in the Sacramento River reached 25.9 kg d^{-1}, with an average daily load as high as 7.4 kg d^{-1}.

Model Performance: Alamar Marina Dock Site. The simulation of diazinon load with the regression model agreed very well with the observed data (Figure 7). The calculated load using the precipitation and diazinon use as the only explanatory variables showed a close match with those observed, which can be seen from the high r^2 (0.907 and 0.726 for single- and subbasin models, respectively) achieved (Table 4). The relative values of the fitted partial regression coefficients a_i for these subbasins also agreed generally with those obtained for the I St. Bridge data.

The regression model generally predicted diuron loading at both the basin and subbasin scales (Figure 7), but underestimated the loads most of the times for 1998 and 1999 winters, and overestimated loads for 2000 winter. Although the regression r^2 values of diuron (0.397 and 0.168, Table 4) were not as high as those obtained for diazinon, both model fits were highly significant ($p < 0.001$).

Comparisons of single basin and subbasin r^2 indicated that decreasing the spatial scale to the subbasin level did not improve the model prediction. In fact, in most cases, the value of r^2 decreased (Table 4). To retain the spatial resolution of the original pesticide use and precipitation data, monitoring data at the subbasin scale should be collected so that a full prediction model can be developed for each of the subbasins. The individual subbasin load models can then be combined to increase the prediction accuracy of the regression model for the main stem river of the whole watershed.

Results of the regression analyses presented in this study demonstrated that, for a given watershed, precipitation and pesticide use are the two major factors controlling the dynamics of pesticide transport into surface water. It should be noted, however, that as is true for any statistical modeling, the reliability of the model prediction is limited by the quality

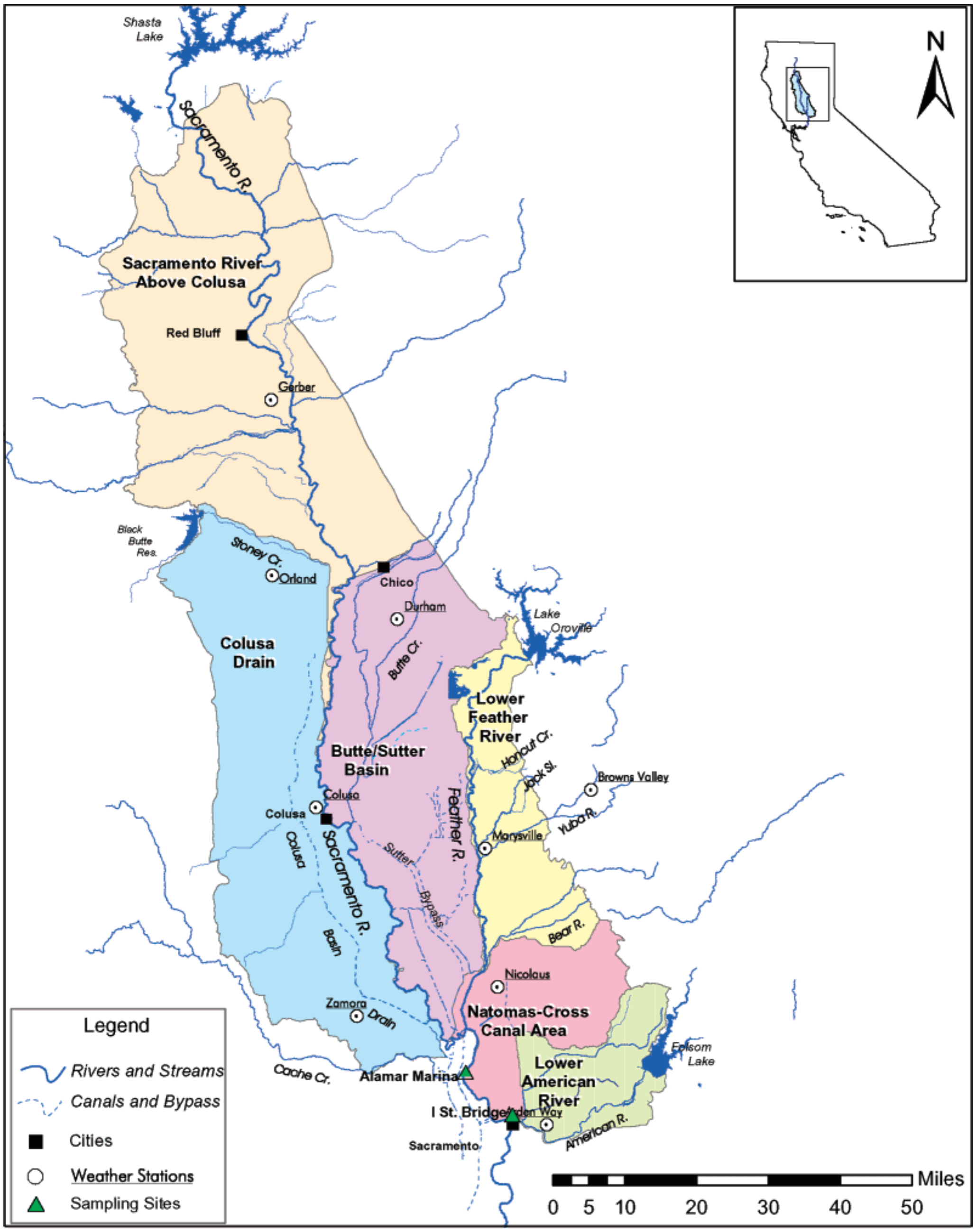

FIGURE 1. Delineation of the subbasins in the Sacramento River Watershed—Sacramento Valley.

TABLE 1. Summary of Historic Surface Water Sampling Data for Pesticides Analyzed in the Regression Model

pesticide	no. of analyses	no. of detections	detection frequency, %	detection limit, μg L^{-1}	concentration percentile[a], μg L^{-1} 95th	75th	50th
			Sacramento River at the I St. Bridge				
diazinon	562	78	13.88	0.019–0.038	0.223	0.096	0.052
simazine	562	152	27.05	0.047–0.06	0.33	0.156	0.101
			Sacramento River at the Alamar Marina Dock				
diazinon	101	17	16.83	0.02–0.04	0.14	0.088	0.072
diuron	132	73	55.3	0.05	0.4	0.19	0.102

[a] Percentile was based on detected concentrations only.

transport. Transport in the other months when the precipitation is rare and sparse is driven by irrigation drainage, which was not considered in this study because information on irrigation drainage is very difficult to obtain. The overall sampling frequency, that is the number of days sampled divided by the number of days analyzed over all sampling periods, ranged from 45.2 to 47.9% for the three pesticides analyzed.

Source of Precipitation Data. The precipitation data used in this analysis were obtained from the California Weather Database (http://www.ipm.ucdavis.edu/weather/abtgetwx.html) of the University of California Statewide

TABLE 2. Names and Locations of the Weather Stations Used for Calculating Daily Precipitation in the Sacramento River Watershed

basin/subbasin	name	network/operator[a]	county	coordinates	
				latitude	longitude
Sacramento River above Colusa	Gerba	CIMIS 8	Tehama	40.050	−122.167
Colusa drain	Orland	CIMIS 61	Glenn	39.700	−122.150
	Colusa	CIMIS 32	Colusa	39.233	−122.017
	Davis	CIMIS 6	Yolo	38.533	−121.783
Butte/Sutter basin	Durham	CIMIS 12	Butte	36.600	−121.833
	Nicolaus	CIMIS 30	Sutter	38.867	−121.550
Feather River	Marysville	NOAA 5385	Yuba	39.150	−121.583
Natomas-Cross canal area	Nicolaus	CIMIS 30	Sutter	38.867	−121.550
American River	Arden Way	Sacramento County	Sacramento	38.596	−121.413

[a] CIMIS stands for California Irrigation Management Information System; NOAA stands for National Oceanic and Atmospheric Administration.

Integrated Pest Management Program (UC IPM). The UC IPM database stores current and historical weather data for approximately 400 weather stations throughout California. Daily precipitation data are available from weather stations of three network sources: (1) the California Irrigation Meteorological Information System (CIMIS) stations by the California Department of Water Resources; (2) National Oceanic and Atmospheric Administration (NOAA) stations of the U.S. Department of Commerce; and (3) TouchTone (TT) Stations of the UC IPM's TouchTone Network. One station in the Sacramento River basin, Arden Way in Sacramento County, was not covered by the UC IPM database. Precipitation data for this station were obtained from the web site of the California Department of Water Resources, California Data Exchange Center: http://cdec.water.ca.gov/misc/dailyprecip.html.

The stations used for calculating the precipitation for each subbasin and the entire watersheds are listed in Table 2. Locations of these stations are also shown in Figure 1. Factors considered in selecting the weather stations include the representativeness of the location and the availability of precipitation data. When there was no suitable station within a subbasin, the closest available station was chosen. If the watershed or subbasin had more than one station, the mean precipitation was used.

Source of Pesticide Use Data. The Pesticide Use Report (PUR), also a database developed by the California Department of Pesticide Regulation (http://www.cdpr.ca.gov/docs/pur/purmain.htm), contains data on agricultural and other pesticide applications. Production agricultural records include information on pesticide application date, amount, and location accurate to the scale of a section in the Public Land Survey System (roughly one square mile or 2.6 km^2). Full use records started from 1989 and are added annually when they become available.

For the purpose of this analysis, daily PUR data were compiled for all sections within the watershed and were summed for each subbasin according to the sections they contained. If an application was reported without geological location, it was not used in the analysis. Because many pesticide uses, such as rights of way applications, landscape maintenance applications, and structure pest control, were not reported with specific sections, those uses were not included in the analysis. The inability of the regression analysis to include the nonsection-specific uses introduces errors into the prediction. Some of the error, however, would be overcome by the inverse approach of the model solution if such uses remained relatively low and steady. To increase the model accuracy, several probable reporting errors in the PUR were also excluded from the analysis.

Streamflow Data. Streamflow data were used to convert surface water concentrations into loading estimates. The United States Geological Survey web site, http://waterdata.usgs.gov/nwis/sw, provides access to water resources data, including the streamflow data for stations throughout the United States. For the Sacramento River, the streamflow data were not directly available at the two sites selected. The flow data for the I St. Bridge were estimated from a surrogate site at Freeport (USGS #11447650). The Freeport site is located about 20 km downstream from the I St. Bridge, but there are no major inlet or outlet flows between the two locations. The estimation of flow data for the Alamar Marina Dock was obtained by subtracting the inflow from the American River measured at Fair Oaks (USGS #11446500) from the Freeport data. The American River is the only major tributary joining the Sacramento River between Alamar Marina Dock and the I St. Bridge.

Processing of Surface Water Data. The regression analysis used weekly or biweekly moving average of daily loads as the dependent variable. To obtain daily pesticide load, the original concentration data in the Surface Water Database were used first to obtain the estimated concentrations for the unsampled days using linear interpolation (*10*):

$$\hat{C}(t) = C(s_j) + \left((t - s_j)\,\frac{C(s_{j+1}) - C(s_j)}{s_{j+1} - s_j}\right) \qquad (4)$$

where $\hat{C}(t)$ is the estimated concentration for any unsampled day t, and $C(s_j)$ and $C(s_{j+1})$ are, respectively, the measured concentrations for the two sampling days s_j and s_{j+1} bracketing time t. The time series of the concentration data were then converted to loads by making use of the flow rate and assuming a homogeneous distribution:

$$Y(t) = 0.00245\ C(t)\ F(t)\ \ or\ \ 0.00245\ \hat{C}(t)F(t) \qquad (5)$$

where $Y(t)$ is the estimated pesticide load (kg d^{-1}) for t, $C(t)$ or $\hat{C}(t)$ is the measured or estimated pesticide concentration (μg L^{-1}), and $F(t)$ is the stream flow rate (cfs, or cubic foot per second), and 0.00245 is a conversion factor. Finally, the weekly or biweekly moving average of daily load, denoted as $\bar{Y}_T(t)$, for any given day was calculated as the arithmetic average of the loads for the preceding 7(T = 7) or 14 (T =14) days. This moving average of pesticide load was used in the regression analysis. The biweekly $\bar{Y}_{14}$ (t) was used only when the weekly $\bar{Y}_7$ (t) failed to produce a satisfactory fitting.

Regression Analysis. The regression analysis employed a nonlinear least-squares procedure called the Lenvenberg–Marquardt procedure (*11*). This procedure is based on χ^2 merit function:

$$\chi^2 = \sum_{t=1}^{NDP}\left\{\frac{\bar{Y}_T(t) - Y[P(t)_i,U(t)_i;a_i,b,n]}{\delta_t}\right\}^2 \qquad (6)$$

where NDP is the total number of data points, i.e., the number of moving averages of pesticide daily load, $\bar{Y}(t)$ is the moving average of pesticide daily load based on surface water

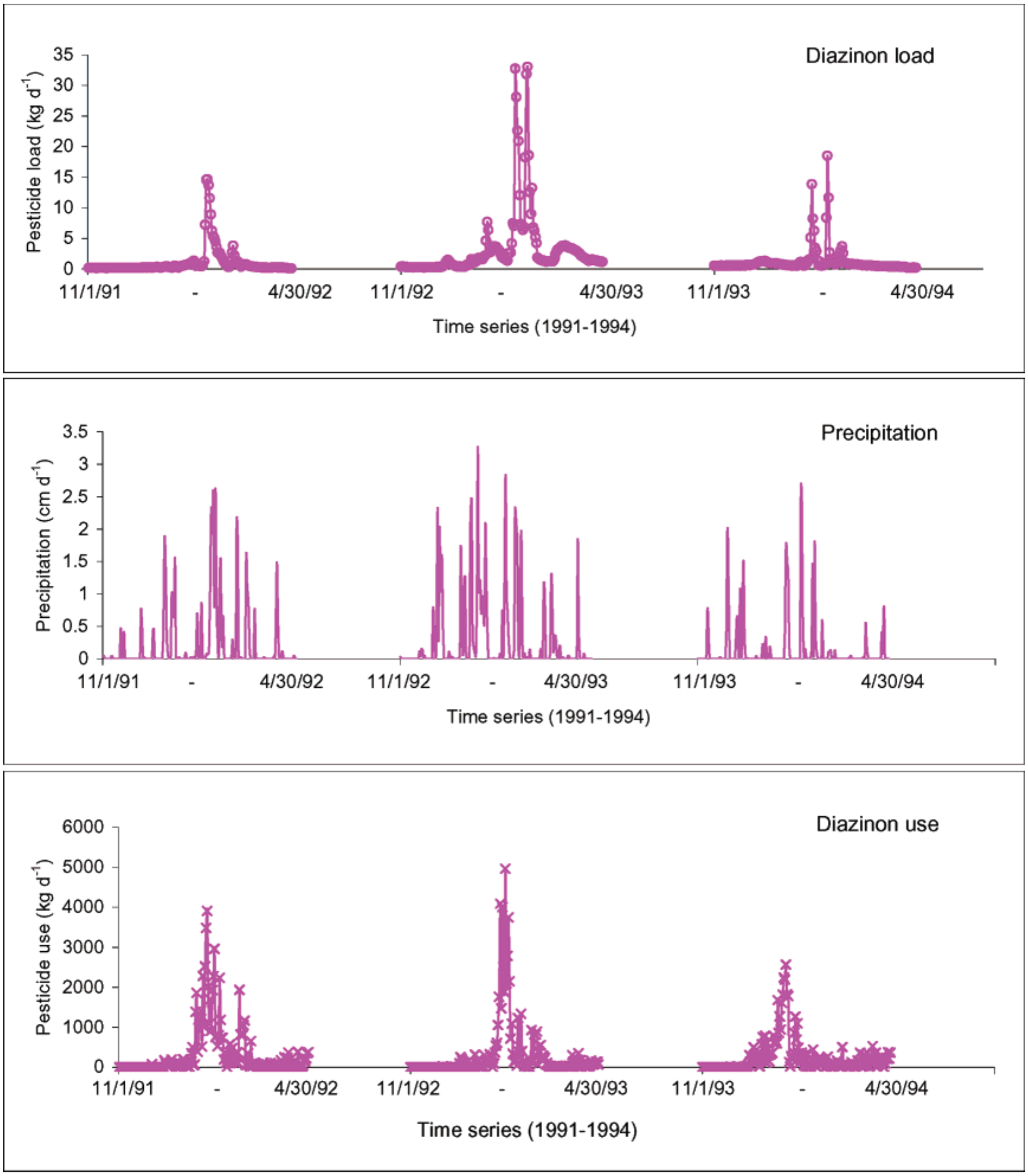

FIGURE 2. Time series of diazinon load *Y*(*t*) in the Sacramento River, precipitation *P*(*t*), and diazinon use *U*(*t*) in the Sacramento River basin during 1991 to 1994 winter storm seasons. The pesticide load was calculated from data collected at the I St. Bridge.

monitoring data, and $Y[P(t)_i,U(t)_i; a_i,b,n]$ is the load based on model (i.e., eq 2 or 3), and δ_t is the standard deviation for each data point. The Lenvenberg–Marquardt method is a robust inverse tool in solving nonlinear models. A FORTRAN program was written that accepted the data of pesticide load, precipitation, and use in the watersheds, and output the optimal values of a_i, b, and n in eq 2 or 3 that best describe the input data. To avoid singular matrix in the inverse procedure, the "0.0" values in P and U, or the negative values when cumulative P is less than b, were all replaced by a value of 0.0001.

Because the regression model contained multiple parameters that are more or less correlated, there are numerous local solutions that fit the load data. The final solution yielded from a fitting procedure is dependent to a large extent on the initial guesses of the parameter values. To identify the empirical solution that probably represents the real world situation, the regression analysis proceeded in the following steps: (a) estimate a rough range of parameter values for each parameter; (b) divide each range into 10 000 intervals; (c) conduct a Monte Carlo analysis of fitting by randomly choosing 60 000 combinations of the initial parameter values within those intervals; (d) filter all the solutions based on pesticide use data within each basin to eliminate unreasonable solutions; (e) identify the subgroup of reasonable solutions; and (f) choose the solution that has the minimum χ^2.

Results and Discussion

Pesticide Load: I St. Bridge. Four pesticides, diazinon, simazine, molinate, and 2,4-D, showed a detection frequency above 10% at the monitoring site of the I St. Bridge. But only diazinon and simazine were retained in the analysis (Table 1). The pesticide molinate, with a detection frequency of 11.1%, was excluded because all of its monitoring activities occurred during the summer months from May to August. The pesticide 2,4-D was eliminated because there were only 16 analyses. The detection frequency was 13.9% for diazinon and 27.1% for simazine.

The daily loads of diazinon and simazine in the Sacramento River during the winter storm seasons of 1991 to 1994

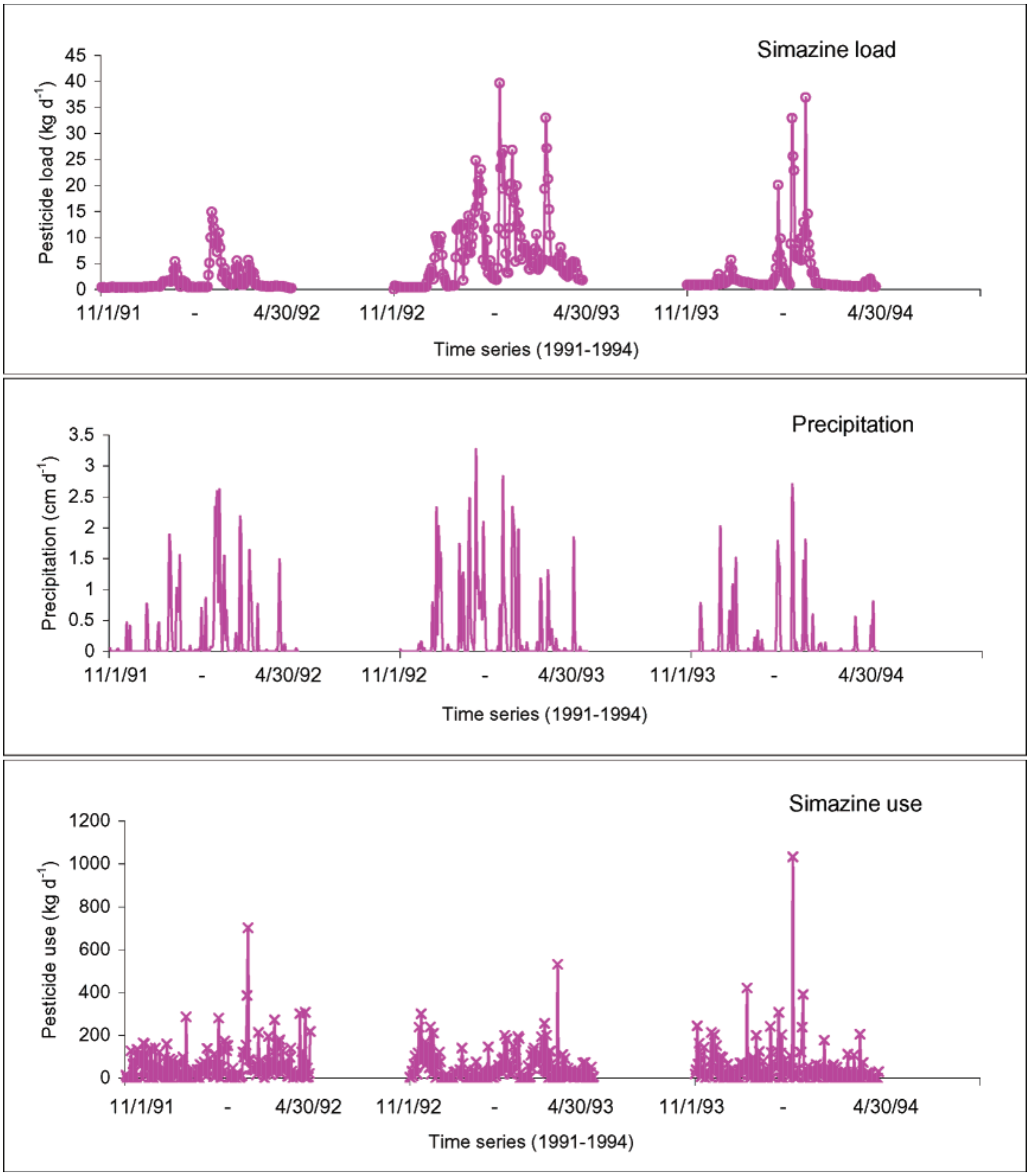

FIGURE 3. Time series of simazine load *Y*(*t*) in the Sacramento River, precipitation *P*(*t*), and simazine use *U*(*t*) in the Sacramento River basin during 1991 to 1994 winter storm seasons. The pesticide load was based on data collected at the I St. Bridge.

TABLE 3. Summary of Pesticide Loading Data for the Sacramento River at the I St. Bridge (1991−1994) and Alamar Marina Dock (1997−2000)[a]

	I St. Bridge		Alamar Marina Dock	
load statistics	**diazinon**	**simazine**	**diazinon**	**diuron**
total load[b], kg	951.0 (590.9)	2073.2 (1685.5)	782.5 (454.2)	1388.3 (1100.5)
maximum daily load, kg d^{-1}	33.2	39.7	29.6	25.9
mean daily load, kg d^{-1}	1.8	3.8	4.2	7.4
loading rate, % of use[c]	0.59 (0.37)	6.72 (5.46)	1.16 (0.67)	16.2 (12.85)

[a] Load and use data were for the monitoring periods from November to April. [b] Total loads were based on measured and interpolated data assuming 1/2 detection limit for nondetects. Data within parentheses were calculated assuming zero concentration for nondetects. [c] Only the reported agricultural use of pesticides was included.

are shown in Figures 2 and 3, respectively. For illustration purposes, the daily precipitation and pesticide use in the watershed over the same periods of time are also presented. The statistics of the pesticide loading data are summarized in Table 3. Visual inspection of Figure 2 showed that the curve of the diazinon load in the Sacramento River almost mirrored that of the diazinon use in the watershed, clearly indicating a correlation between these two variables. The diazinon use seemed to be a more dominant factor affecting loading than rainfall, which only acts as a medium between the two. Consistent with the physical premise of our model, precipitation alone did not correspond to increased load

TABLE 4. Estimated Regression Model Parameters for Pesticides Analyzed for the Sacramento River

	I St. Bridge		Alamar Marina Dock	
	diazinon	simazine	diazinon	diuron
		single basin model (eq 2)		
T	7	14	7	14
a, cm^{-n}	2.285×10^{-4}	5.405×10^{-4}	3.857×10^{-5}	1.507×10^{-3}
b, cm	5.204	1.547	1.752	2.186
n	0.124	0.763	0.815	0.166
M	12	23	28	32
N	33	38	35	57
r^2	0.674	0.379	0.907	0.397
P^a	<0.001	<0.001	<0.001	<0.001
		subbasin model (eq 3)		
T	7	14	7	14
a_1, cm^{-n}	1.362×10^{-4}	3.612×10^{-4}	2.275×10^{-4}	6.978×10^{-4}
a_2, cm^{-n}	3.408×10^{-5}	3.408×10^{-4}	1.321×10^{-4}	3.795×10^{-4}
a_3, cm^{-n}	3.305×10^{-5}	2.242×10^{-4}	1.101×10^{-4}	1.587×10^{-3}
a_4, cm^{-n}	3.479×10^{-5}	8.411×10^{-4}	1.461×10^{-4}	1.957×10^{-3}
a_5, cm^{-n}	1.000×10^{-7}	1.221×10^{-3}	1.000×10^{-7}	5.448×10^{-5}
a_6, cm^{-n}	5.095×10^{-4}	1.000×10^{-7}		
b, cm	2.665	2.747	1.397	1.000
n	0.583	0.992	0.421	0.600
M	23	27	19	43
N	29	33	31	37
r^2	0.595	0.394	0.726	0.168
P^a	<0.001	<0.001	<0.001	<0.001

[a] The significance level (P) was based on measured and interpolated data.

when there was a lack of use. For example, the early high precipitation seen in November and December of these years did not lead to much increase in loading because of the low use of diazinon in this period (Figure 2). Daily diazinon load was the highest on February 22, 1993, and reached a level of more than 33 kg d^{-1}. The average daily load of diazinon for the three winter storm seasons between November 1991 to April 1994 was 1.8 kg d^{-1}, and the total load was 951 kg, corresponding to 0.59% of that applied during the same periods of time (Table 3).

For simazine, the use pattern was more steady, being spread more evenly over the time of the winter storm seasons. In this case, the loading dynamics of simazine, unlike diazinon, seemed to be more responsive to the precipitation (Figure 3). These observations agree with our model formulation: the dynamics of pesticide loading would be more controlled by the limiting factor, whether pesticide use or precipitation.

The highest daily load of simazine was about 39.7 kg d^{-1}, with an average load of 3.8 kg d^{-1}, and the total load reached 2073 kg, representing 6.72% of the total reported agricultural use in the watershed (Table 3). On the basis of these statistics, simazine seems to be more susceptible to runoff than diazinon. However, comparison of runoff potential based on the measured loading and use data may not be meaningful because these pesticides were applied to different sites and under different conditions.

Model Performance: I St. Bridge. The regression results for diazinon and simazine detected at the I St. Bridge are presented in Table 4. Comparisons between the measured and calculated pesticide loads are shown in Figure 4. For both pesticides, the regression model largely described the variation of their loading over time, demonstrating the statistical validity of our model assumptions and formulation. As Figure 4 shows, the model described both the loading trend and magnitude of diazinon very well at both the single basin and subbasin scales for the 1991−1992 and 1993−1994 winter storm seasons, but underestimated the peaks for the 1992−1993 winter season. Overall, the coefficients of determination (r^2) were 0.674 and 0.595 for the single basin and subbasin models (eqs 2 and 3), respectively, and both were significant at $P < 0.001$ (Table 4).

For the subbasin model (eq 3), the estimated a_i for diazinon ranged from 1.0×10^{-7} to 5.095×10^{-4} for the six subbasins, and was in the numerical order of $a_6 > a_1 > a_4 > a_2 > a_3 > a_5$ (Table 4). Because a_i represent the weighting factor of loading, these fitted a_i values mean that, under the same precipitation conditions, the impact of pesticide use on the Sacramento River is in the order of Lower American River Watershed > Sacramento River above Colusa > Lower Feather River Watershed > Colusa Basin Drain > Sutter Basin/Butter Creek > Cross Canal Area. Although this order of impact conforms roughly to the limited observed data of relative loading from four of the subbasins reported in McClure et al. (*9*), without further monitoring data at all the subbasins, this relationship cannot be confirmed or invalidated at this stage. The estimated b, i.e., the minimum cumulative precipitation that must be reached to create a loading effect, was 5.204 cm during a period of 12 days, with a corresponding n of 0.124 for the single basin model. The estimated b was 2.665 cm for a period of 23 days, with a corresponding n of 0.583 for the subbasin model. Note that the lower b in the subbasin model is associated with a higher n than in the single basin model. It should be recognized that, in solving multi-parameter models, any solution obtained through the inverse approach as we used in this study is not unique, because the model parameters may be correlated. In other words, a change in the value of one parameter affects the values of others. The higher the correlation among the model parameters, the less certain the model solution is. As an example, Table 5 shows the correlation coefficients among the model parameters for diazinon detected at the I St. Bridge. As can be seen from this table, the model parameters are all somewhat correlated, with a maximum correlation of −0.722 found between b and n of the subbasin model. Therefore, as an empirical equation, the values of the model parameters should not be interpreted in rigorous mechanistic terms.

The regression model also described simazine loading in the Sacramento River well, especially for the 1991−1992 and 1993−1994 winter storm seasons (Figure 4). For the 1992−1993 season, both the single basin model and subbasin model generally simulated the shape of the loading curve well, but underestimated the peaks. Overall, the coefficients of de-

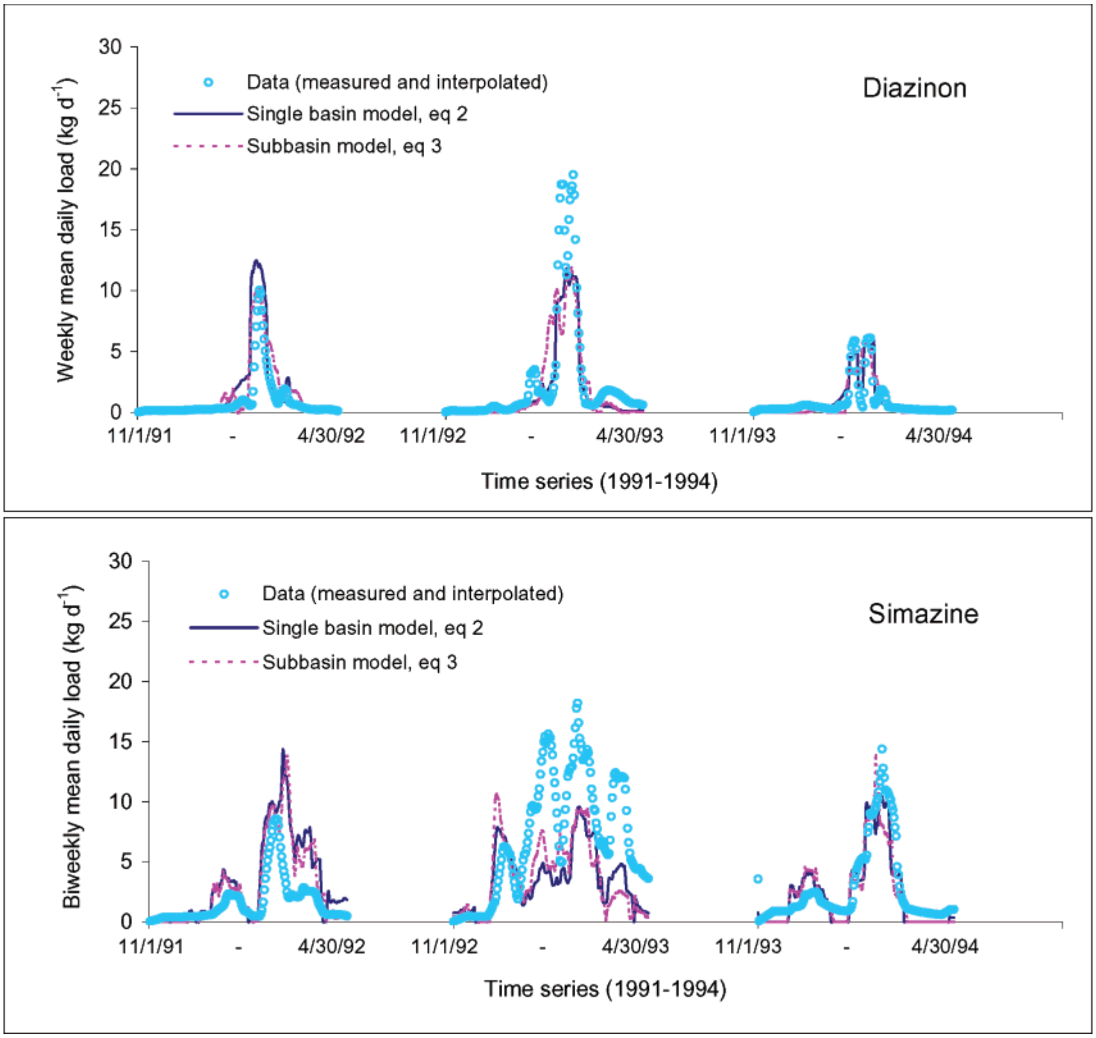

FIGURE 4. Comparison of observed and regression model fitted (eq 2 or 3) weekly or biweekly mean daily loads of diazinon and simazine for the Sacramento River at the I St. Bridge.

TABLE 5. Correlation Coefficients of Regression Model Parameters for Diazinon Detected for the Sacramento River at the I St. Bridge

Single Basin Model

	a	*b*	*n*
a	1		
b	0.315	1	
n	−0.214	−0.182	1

Subbasin Model

	a_1	a_2	a_3	a_4	a_5	a_6	*b*	*n*
a_1	1							
a_2	−0.291	1						
a_3	−0.216	0.094	1					
a_4	0.385	−0.508	−0.533	1				
a_5	0.045	0.126	−0.104	−0.091	1			
a_6	0.114	−0.276	0.25	−0.139	−0.149	1		
b	0.542	−0.048	0.412	0.072	0.015	0.212	1	
n	−0.58	−0.175	−0.524	0.04	−0.109	−0.133	−0.722	1

termination for the regression were 0.379 and 0.394 for the single basin model and subbasin model, respectively. These r^2 values were both significant at $P < 0.001$.

Pesticide Load: Alamar Marina Dock. Diazinon and diuron are the two pesticides identified at the Alamar Marina site with a detection frequency of above 10% during 1997 to 2000 winter seasons (Table 1). The detection frequency of simazine dropped to 5.30% during these monitoring periods and thus the pesticide was not analyzed. A query of PUR for simazine indicated that the use of this pesticide during the three winter seasons of 1997 to 2000 in the counties located or partially located in the Sacramento River watershed reduced almost 60% compared to that used during the three winter seasons of 1991 to 1994.

The daily load and use of diazinon and diuron in the Sacramento River watershed, along with the precipitation, for the three winter seasons monitored are shown in Figure 5. Although the use and precipitation data were shown from

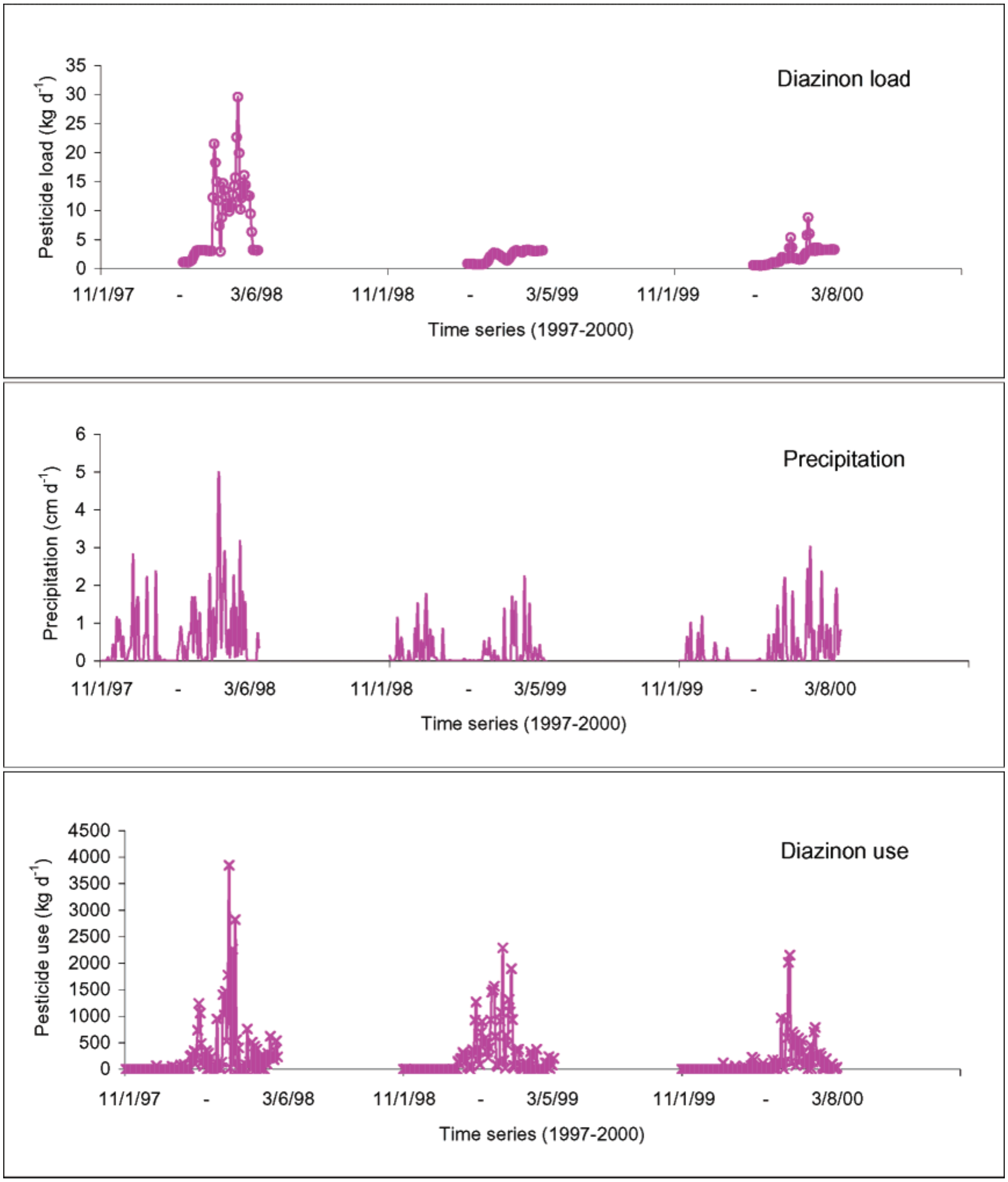

FIGURE 5. Time series of diazinon load *Y*(*t*) in the Sacramento River, precipitation *P*(*t*), and diazinon use *U*(*t*) in the Sacramento River basin during 1997 to 2000 winter storm seasons. The pesticide load was calculated from data collected at the Alamar Marina Dock.

November 1, the monitoring data were only collected during the later session of the seasons. As Figure 5 shows, the reduced loads of diazinon in the later two seasons were caused by both the reduced use and lower precipitation, compared to the first season of 1997−1998 winter. The peak daily load was 29.6 kg d^{-1}, which was lower, but comparable to that observed at the I St. Bridge (33.2 kg d^{-1}, Figure 2). The total diazinon load for the three monitoring periods was 782.5 kg, and most of it came from the 1997−1998 applications. Although there were no monitoring data for the early session of the three seasons, the sampling plan probably captured the bulk of the load because there was only limited use of diazinon during these early periods (Figure 5).

The observed load of diazinon for the three monitoring periods was about 1.16% of that used in agricultural fields in the watershed (excluding the Lower American River subbasin), substantially increased from the 1991−1994 result of 0.59% measured at the I St. Bridge (Table 3). The overall loading rate for all the monitoring periods between 1991 and 2000 averaged 0.76% of the total agricultural use for the Sacramento River watershed.

Diuron is the most frequently detected pesticide in the Sacramento River. This pesticide was not monitored prior to the 1997−1998 winter at the I St. Bridge. Its detection frequency reached 55.3% during the 1998−2000 monitoring periods at the Alamar site (Table 1). The measured load of diuron over the three monitoring periods (Figure 6) did not show large variation as was seen for diazinon (Figure 5). The reduced effect of the lowered precipitation on load in the later two seasons seemed to be compensated by the increased use of diuron (Figure 6).

The total load of diuron calculated from flow and monitoring data was 1388 kg for the three monitored storm seasons, corresponding to a loading rate of 16.2% of the amount used in agriculture in the watershed (Table 3). The surprisingly high loading rate was probably caused by the

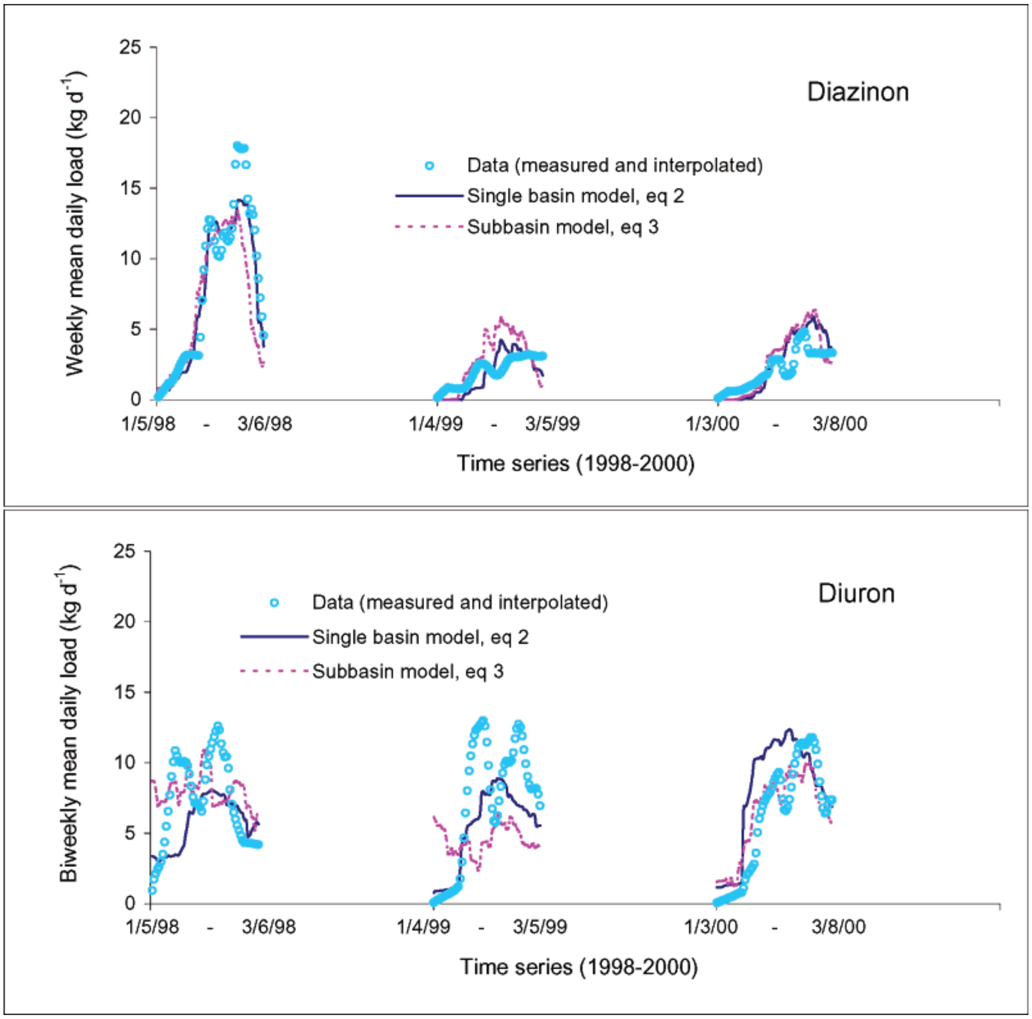

FIGURE 7. Comparison of observed and regression model fitted (eq 2 or 3) weekly or biweekly mean daily loads of diazinon and diuron for the Sacramento River at the Alamar Marina Dock.

of the original data that enter into the regression. The capability of the statistical modeling approach to provide time-series estimates on pesticide loading in the river is unique and may be useful for TMDL assessment. The empirical model established in this study will be used as a reference for the baseline use−loading relationship in the Sacramento River watershed to evaluate the effect of any future changes in agricultural management practices or land use on impact of pesticide use on the Sacramento River.

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Supporting Information Available

An independent prediction of diazinon load in the Sacramento River using the model developed in this study (eq 2 and Table 4 parameters) was performed for 2001. A comparison of this prediction with the observed data is presented. This material is available free of charge via the Internet at http://pubs.acs.org.

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