Semi-Empirical Prediction of Pesticide Loading in the Sacramento and San Joaquin Rivers during Winter Storm Seasons

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ABSTRACT

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 describes pesticide loading over time in the Sacramento and San Joaquin Rivers. The empirical model is physically based, but uses highly aggregated parameters, allowing the prediction of pesticide loading with the knowledge of precipitation and pesticide use only. The model was applied to analyze pesticide monitoring data obtained from the two California rivers during various 1991-2000 winter storm seasons, and closely simulated loading dynamics of the pesticides for six out of seven cases studied, which involved four pesticides identified based on historical sampling results with a detection frequency of ≥10%. The coefficients of determination for regression ranged from 0.167 to 0.907, all were significant at <0.001. The unresolved discrepancy between the model and data may be attributable to a number of sources including limitations related to sampling, laboratory analysis, pesticide use reporting as well as model formulation etc. The accuracy of the model predictions, however, are well within the limits of the expected model performance, given the time and spatial scales of the data analyzed. 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 these watersheds. 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.

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1. Introduction

The Sacramento River (SR) and the San Joaquin River (SJR) are the two major rivers draining Central and Northern California. These two rivers serve as an important source of water supply in California. Extensive monitoring activities were taken in the past decade to monitor the surface water qualities of these rivers and their tributaries. The Surface Water Database, developed by the California Department of Pesticide Regulation (DPR), 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. Collectively these monitoring studies represent approximately 100,000 records of pesticide analyses in surface water samples as of August 2002. Results of these studies revealed the presence of numerous pesticides not only in small streams, but also in major rivers.

In order to understand the underlying relationship of pesticide loads in surface water and governing environmental factors, we conducted a regression analysis of the historical data of surface water concentration, river flow, precipitation, and pesticide use in the watersheds. The objectives of this analysis were to explore the dependence of pesticide load in Sacramento and San Joaquin rivers 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 is useful for evaluating the success of mitigation measures in reducing pesticide runoff into surface water at the watershed scale. This report presents the procedures and results of the data analysis for pesticides detected in the Sacramento and San Joaquin rivers during selected winter storm seasons between 1991 and 2000. Implications and significance of the results of the analysis are also discussed.

2. Methods

2.1 The Regression Model

Pesticides are transported from the field to the surface water 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 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:

$$Y = a(P - b)^n U \qquad [1]$$

where *Y* is pesticide load in surface water (lb/d), *a* is a regression coefficient, *b* is a parameter related to the minimum precipitation that results in runoff, 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:

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

where P_j is daily precipitation (cm/d) for the watershed on day *j*, U_k is daily use of the pesticide (lb/d) in the watershed on day *k*, and M and N denote, respectively, the time span for calculating cumulative P and U, counted backwards 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 Sacramento River basin and San Joaquin River basin were further subdivided into several subbasins. In this case, Eq [1] can be expanded as

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

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 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 the calculated SR or SJR 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.

2.2 Delineation of the Watersheds

The delineation of the SR and SJR watersheds and their subbasins followed the methodologies and schemes used by Regional Water Quality Control Board, Central Valley Region (RWQCB) for pesticide TMDL (Total Maximum Daily Load) development (McClure et al., 2002; Azimi-Gaylon et al., 2002). At the single basin scale, the Sacramento Valley was treated as a single watershed for the SR (Figure 1), and both the precipitation and pesticide use data within the watershed were processed for the calculation of mean or total without consideration of geographic locations. For the SJR watershed, the Lower SJR (LSJR) watershed, containing the lower stem of the SJR, was considered as a single basin (Figure 2). The precipitation and pesticide use data were likewise treated the same way within the LSJR watershed regardless of geographic locations.

For the subbasin scale modeling, the SR watershed was further divided into six drainage subbasins based on hydrological and other geographic characteristics: 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). For the SJR watershed, seven subbasins were adopted: 1) San Joaquin River upstream of

Salt Slough; 2) Merced River; 3) Tuolumne River; 4) Stanislaus River; 5) East Valley Floor; 6) Northwest Side Drain; and 7) Grassland Watershed (Figure 2). The a_i in Eq. [3] for the subbasins were numbered in the same order as listed above for both the SR and SJR watersheds.

2.3 Source of Data

2.3.1 Surface Water Monitoring Data.

The source of the surface water monitoring data was the DPR's Surface Water Database as of August 2002. Water quality data from 151 monitoring sites are collected in the database. Based on 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 I Street 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, is only available until April 1994. The Alamar Marina site is located about 12 river miles upstream of the I Street 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 SR at either of these locations for 1995 and 1996. The monitoring data for the San Joaquin River were all from the sampling site near Vernalis. This site receives stream flow from the entire San Joaquin Valley and is considered an integrator site in USGS National Water Quality Assessment Program (Gilliom et al., 1995). As such, Vernalis reflects the overall characteristics of hydrology, land use, pesticide application, and other factors in the SJR watershed.

Three pesticides for the SR watershed and four for the SJR watershed were analyzed for this study (Table 1). These pesticides were identified based on the detection frequency of historic sampling results. A ≥10% of detection frequency, defined as the number of detections above the method detection limit over the number of total analyses, was set arbitrarily as the screen 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. In these calculations, all NDs were treated as ½ of the DL.

Table 1. Summary of historic surface water sampling data for pesticides analyzed in the regression analysis. The source of data was based on the Surface Water Database of DPR as of August 2002.

Pesticide	# of analyses	# of detections	Detection frequency, %	Concentration percentile[a], ug/L		
				95th	75th	50th
	Sacramento River at the I St. Bridge					
Diazinon	562	78	13.88	0.223	0.096	0.052
Simazine	562	152	27.05	0.33	0.156	0.101
	Sacramento River at the Alamar Marina Dock					
Diazinon	101	17	16.83	0.14	0.088	0.072
Diuron	132	73	55.30	0.4	0.19	0.102
	San Joaquin River near Vernalis					
Diazion	799	211	26.41	0.294	0.102	0.062
Simazine	750	327	43.60	0.713	0.273	0.14
Diuron	142	131	92.25	2.678	1.109	0.492
Cyanazine	292	58	19.86	0.602	0.267	0.208

a. Percentile was based on detected concentrations only.

Though monitoring data for some pesticides were available throughout the years, the bulk of the data in the Surface Water Database was collected during the precipitation seasons from November to April. For this study, we termed the period as "winter storm seasons". We focused only on data collected during the winter storm seasons when the precipitation was the primary driving force for pesticide 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 specific periods selected for analysis varied for each pesticide, depending on the sampling frequency (Table 2). In general, a minimum of weekly sampling frequency was set arbitrarily in order to ascertain the reliability of the estimated concentrations for the unsampled days. 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 53.9% for the four pesticides analyzed (Table 2).

2.3.2 Pesticide Use Data

The Pesticide Use Report (PUR) collected by DPR contains data on agricultural and urban pesticide applications. It includes 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). Records started from 1990 and are added annually when they become available.

For the purpose of this analysis, daily PUR data were compiled for all sections within the watersheds 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 nonagricultural uses (such as rights of way applications, landscape maintenance applications, 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 nonagricultural uses introduces errors into the prediction, especially when those uses are high. Figures 3 and 4 show agricultural and nonagricultural uses of the four pesticides during 1990 to 2000, based on data reported for the counties which are located or partially located within the SR or SJR watersheds. The nonagricultural uses of simazine and diuron in the counties of the SR watershed were high, reached >50% of the total use for some years. The prediction error for these pesticides due to the unaccounted nonagricultural uses is also relatively higher in those years. Some of the error, however, would be overcome by the inverse approach of the model solution if the nonagricultural uses remain relatively steady. The nonagricultural use of diazinon was much lower

Table 2. Dates of the surface water sampling periods included in the regression analysis and overall sampling frequencies.

	Sacramento River							
Winter year	I St. Bridge		Alama Marina Dock		San Joaquin River near Vernalis			
	Diazinon	Simazine	Diazinon	Diuron	Diazinon	Simazine	Diuron	Cyanazine
1990-1991					1/13/91-4/30/91	1/13/91-4/30/91		
1991-1992	11/1/91-4/29/92	11/1/91-4/29/92			11/2/91-4/30/92	11/2/91-4/30/92		
1992-1993	11/2/92-4/30/93	11/2/92-4/30/93			11/1/92-4/30/93	11/1/92-4/30/93		
1993-1994	11/1/93-4/29/94	11/1/93-4/29/94			11/2/93-4/29/94	11/2/93-4/29/94		11/2/93-4/29/94
1994-1995					2/2/95-3/21/95	2/2/95-3/21/95		2/2/95-3/21/95
1995-1996								
1996-1997					1/20/97-3/7/97			
1997-1998			1/5/98-3/6/98	1/5/98-3/6/98	1/5/98-3/6/98	1/5/98-3/6/98	1/5/98-3/6/98	
1998-1999			1/4/99-3/5/99	1/4/99-3/5/99	1/4/99-3/5/99	1/4/99-3/5/99	1/4/99-3/5/99	
1999-2000			1/3/00-3/8/00	1/3/00-3/8/00		1/3/00-3/3/00	1/3/00-3/3/00	
Overall sampling frequency[a],%	47.9	47.9	45.2	45.2	54.4	53.9	46.9	49.4

a. The overall sampling frequency was calculated as # of days sampled divided by # of days analyzed in the regression analysis over all sampling periods.

compared to simazine and diuron, and its prediction error due to use reporting should be much smaller. For the SJR watershed, the reported nonagricultural uses of all four pesticides in the counties were low and remained relatively steady during all the years, except for diazinon of 2000, during which it showed an atypical surge (Figure 4). Because of this irregularity, the diazinon 2000 data for the SJR was excluded from the analysis. To increase the model accuracy, several probable reporting errors in the PUR were also excluded from the analysis.

2.3.3 Stream Flow Data

Stream flow data were used to convert surface water concentrations into loading estimates. The United States Geological Survey (USGS) web site, http://waterdata.usgs.gov/nwis/sw, provides access to water-resources data, including the stream flow data for stations throughout the United States. For the SR, the stream flow 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 was located about 12.5 miles 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 SR between Alamar Marina Dock and I St. Bridge. The flow data for the SJR was available at the Vernalis site (USGS #11303500).

2.3.4. 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 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) CIMIS (The California Irrigation Meteorological Information System) stations by the California Department of Water Resources; 2) NOAA (National Oceanic and Atmospheric Administration) stations of the U.S.

Department of Commerce; and 3) TouchTone (TT) Stations of the UC IPM's TouchTone Network. One station in the SR basin, the Arden Way Station in the Sacramento County, was not covered by the UCIPM database. Precipitation data for this station was 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 3. Locations of these stations are also shown in Figures 1 and 2. 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. For watersheds or subbasins with more than one station, the mean precipitation was used.

2.4 Processing of Surface Water Data

The regression analysis used weekly or biweekly moving average of daily loads as the dependent variable. The original concentration data in SURF was used first to obtain the estimated concentrations for the unsampled days using linear interpolation (Reinelt and Grimvall, 1992):

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

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:

$$Y(t) = 0.00539\,C(t)F(t) \;\; or \;\; 0.00539\,\hat{C}(t)F(t) \qquad [5]$$

where $Y(t)$ is the estimated pesticide load (lb/day) for t, C(t) or $\hat{C}(t)$ is the measured or estimated pesticide concentration (µg/L), and $F(t)$ is the stream flow rate (cfs, or cubic foot per second), and 0.00539 is a conversion factor. Finally, the weekly or biweekly

Table 3. The name and location of the weather stations used for calculating daily precipitation in the basin/subbasins of the Sacramento River and San Joaquin River watersheds.

Basin/subbasin	Weather station name	Network/ operator	County	Coordinates latitude	Coordinates longitude
Sacramento River (SR) Basin					
SR above Colusa	Gerba	CIMIS 8	Tehama	40.045	-122.164
Colusa drain	Orland	CIMIS 61	Glenn	39.692	-122.152
	Colusa	CIMIS 32	Colusa	39.226	-122.024
	Zamora	CIMIS 27	Yolo	38.808	-121.908
Butte/Sutter basin	Durham	CIMIS 12	Butte	36.609	-121.823
	Nicolaus	CIMIS 30	Sutter	38.871	-121.545
Feather River	Marysville	NOAA 5385	Yuba	39.150	-121.583
Natomas-Cross canal area	Nicolaus	CIMIS 30	Sutter	38.871	-121.545
American River	Arden Way	Sacramento County	Sacramento	38.596	-121.413
San Joaquin River (SJR) Basin					
SJR upstream of Salt Slough	Madera	TT 32	Madera	36.933	-120.100
	Merced	NOAA 5523	Merced	37.283	-120.517
Merced River	Ballico	TT 51	Merced	37.467	-120.750
	Cressey	TT 41	Merced	37.400	-120.667
Tuolumne River	Modesto-NCDC	NOAA 5783	Stanislaus	37.650	-121.000
	Waterford	TT 11	Stanislaus	37.633	-120.750
Stanislaus River	Modesto-CIMIS	CIMIS 71	Stanislaus	37.633	-121.183
East Valley Floor	Modesto-CIMIS	CIMIS 71	Stanislaus	37.633	-121.183
Northwest Side	Modesto-CIMIS	CIMIS 71	Stanislaus	37.633	-121.183
	Newman	NOAA 6168	Stanislaus	37.300	-121.033
Grassland	Los Banos	NOAA 5118	Merced	37.050	-120.867

moving average of daily load, $\bar{Y}(t)$, for any given day was calculated as the arithmetic average of the loads for the preceding 7 or 14 days. This moving average of pesticide load was used in the regression analysis. The biweekly $\bar{Y}(t)$ was used only when the weekly $\bar{Y}(t)$ failed to produce a satisfactory fitting.

2.5 Regression Analysis

The regression analysis employed a nonlinear least square procedure called the Lenvenberg-Marquardt procedure (Press et al., 1986). This procedure is based on χ^2 merit function:

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

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 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]), 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 accepts the data of pesticide load, precipitation, and use in the watersheds, and outputs the optimal values of a_i, b, and n in Eq. [2] or [3] that best describe the input data. In order 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. In order to identify the empirical solution that probably represents the real world situation, the regression analysis proceeded in the following steps:

- Estimate a rough range of parameter values for each parameter
- Divide each range into 10,000 intervals
- Conduct a Monte Carlo analysis of fitting by randomly choosing 60,000 combinations of the initial parameter values within those intervals
- Filter all the solutions based on pesticide use data within each basin to eliminate unreasonable solutions
- Identify the subgroup of reasonable solutions
- Choose the solution that has the minimum χ^2.

3. Results and Discussion

3.1 The Sacramento River Watershed

3.1.1 I Street Bridge

Based on the I St. Bridge monitoring data, four pesticides showed a detection frequency of above 10%: diazinon, simazine, molinate, and 2,4-D. But only two pesticides (diazinon and simazine) were analyzed (Table 1). The pesticide molinate, with a detection frequency of 11.1%, was excluded from the analysis 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 for diazinon was 13.9% and for simazine was 27.1%.

The daily loads of diazinon and simazine in the SR during the winter storm seasons of 1991 to 1994 are shown in Figures 5 and 6, respectively. For illustration purpose, the daily precipitation and pesticide use in the watershed over the same periods of time are also shown. A correlation between the load and precipitation and use is evident from visual inspection, indicating that precipitation and use are two major factors dictating winter season pesticide transport into surface water. A summary of the statistics of the loading data for all pesticides analyzed for the SR is presented in Table 4. Daily diazinon load was the highest on February 22, 1993, and reached a level of more than 72 lb/d. The

Table 4. Summary of pesticide loading data for the Sacramento and San Joaquin Rivers[a].

Load statistics	Pesticides			
	Sacramento River			
	I St. Bridge		*Alamar Marina Dock*	
	Diazinon	*Simazine*	*Diazinon*	*Diuron*
Total load[b], lb	2096.6 (1302.7)	4570.6 (3715.8)	1725.2 (1001.4)	3060.7 (2426.2)
Maximum daily load, lb/d	72.8	87.5	65.2	57.2
Mean daily load, lb/d	3.9	8.4	9.2	16.3
Loading rate, % of use[c]	0.59 (0.37)	6.72 (5.46)	1.16 (0.67)	16.2 (12.85)
	San Joaquin River			
	Diazinon	*Simazine*	*Diuron*	*Cyanazine*
Total load[b], lb	882.1 (540.1)	2566.8 (2317.9)	5341 (5341)	166.9 (133.2)
Maximum daily load, lb/d	13.8	65.2	280.3	9.8
Mean daily load, lb/d	1.0	2.9	29.2	0.73
Loading rate, % of use[c]	0.16 (0.10)	0.60 (0.54)	4.03 (4.02)	0.47 (0.38)

a. Load and use data were for the monitoring periods as given in Table 2.
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.

average daily load of diazinon for the three winter storm seasons between November 1991 to April 1994 was 3.85 lb/d, and the total load was 2097 lb, corresponding to 0.59% of that applied during the same periods of time. For simazine, the highest daily load was about 87.5 lb/d, with an average load of 8.40 lb/d, and the total load reached 4571 lb, representing 6.72% of the total reported agricultural use in the watershed.

The regression results for diazinon and simazine detected at the I Street Bridge are presented in Table 5. Comparisons between the measured and calculated pesticide loads are shown in Figures 7 and 8. For both pesticides, the regression model described largely the variation of their loading overtime, demonstrating the statistical validity of our model assumptions and formulation. As Figure 7 shows, the model described 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 coefficient of determination (r^2) were 0.674 and 0.595 for the single basin and subbasin models (Eq. [2] and Eq. [3]), respectively, both were significant at $P<0.001$.

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 5). Since 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 SR is in the order of Lower American River Watershed > the SR above Colusa > Lower Feather River Subwatershed > 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 the RWQCB report (McClure et al., 2002), 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

Table 5. Estimated regression model parameters for pesticides analyzed for the Sacramento River.

Model		Model parameter			
		I St. Bridge		*Alama Marina Dock*	
		Diazinon	*Simazine*	*Diazinon*	*Diuron*
Single basin (Eq.[2])	a	2.285E-04	5.405E-04	3.857E-05	1.507E-03
	b	5.204	1.547	1.752	2.186
	n	0.124	0.763	0.815	0.166
	L	7	14	7	14
	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 (Eq.[3])	a_1	1.362E-04	3.612E-04	2.275E-04	6.978E-04
	a_2	3.408E-05	3.408E-04	1.321E-04	3.795E-04
	a_3	3.305E-05	2.242E-04	1.101E-04	1.587E-03
	a_4	3.479E-05	8.411E-04	1.461E-04	1.957E-03
	a_5	1.000E-07	1.221E-03	1.000E-07	5.448E-05
	a_6	5.095E-04	1.000E-07		
	b	2.665	2.747	1.397	1.000
	n	0.583	0.992	0.421	0.600
	L	7	14	7	14
	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 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 6 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

Table 6. The correlation coefficients of regression model parameters for diazinon detected for the Sacramento River at the I Street Bridge.

Parameter	Correlation coeffient							
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

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 SR well, especially for the 1991-1992 and 1993-1994 winter storm seasons (Figure 8). 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 determination 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 $P<0.001$. The reduced r^2 for simazine compared to diazinon may be related to its higher unaccounted nonagricultural uses as well (Figure 3).

3.1.2 Alamar Marina Dock

Diazinon and diuron are the two pesticides identified at the Alamar site with a detection frequency of above 10% (Table 1). The daily load and daily use of these two pesticides in the SR watershed, along with the precipitation, for the three winter seasons monitored during 1998 to 2000 are shown in Figures 9 and 10. Diazinon use was greatly reduced for the later two years, and so were its loads. The peak daily load was 65.2 lb/d, which was comparable to that observed at the I St. Bridge (72.8 lb/d, Table 4). The total diazinon load was 1725 lb over the three monitoring periods, and most of it came from the 1997-1998 applications. This load 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 4). The overall loading rate for all the monitoring periods between 1991 and 2000 averaged 0.76% of the total agricultural use for the SR watershed. The simulation of diazinon load with the regression model agreed very well with the observed data (Figure 11). 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 5). 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 exact agreement in a_5 was due to a boundary condition placed in the parameter.

Diuron is the most frequently detected pesticide in the SR. 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 total load of diuron calculated from flow and monitoring data was 3061 lb for the three monitored storm seasons, corresponding to a loading rate of 16.2% of the amount used in agriculture in the watershed (Table 4). The unreasonably high loading rate was probably caused by the unaccounted nonagricultural uses, which reached 25 to 40% for the three years simulated (1998-2000, Figure 3). The highest daily load in the SR reached 57.2 lb/d, with an average daily load as high as 16.28 lb/d. The regression model generally predicted diuron loading at both the basin and subbasin scales (Figure 12), but underestimated the loads most of the times for 1998 and 1999 winters, and overestimated loads for 2000 winter. Although the regression r^2 of diuron (0.397 and 0.168, Table 5) were not as high as those obtained for diazinon, both model fits were highly significant ($p<0.001$).

3.2 The San Joaquin River Watershed

Four pesticides were analyzed for the SJR watershed: diazinon, simazine, diuron and cyanazine (Table 1). The pesticide diuron had a highest detection frequency of 92.3%, followed by simazine (43.6%), diazinon (26.4%) and cyanazine (19.9%). One other pesticide, metolachlor, also showed a detection frequency of >10% (11.1%), but its detections all occurred outside the winter storm seasons and were thus not analyzed.

The calculated daily loads for the four pesticides in the SJR, together with their use and precipitation data, are shown in Figures 13 through 16. A summary of the load statistics is provided in Table 4 along with the SR data. The daily load fluctuated greatly for all pesticides, presumably in response to the joint effects of precipitation and use. The diazinon loads were substantially lower in the SJR as compared to the SR, with the highest daily load of only 14 lb/d (Figure 13), compared to 73 lb/d observed for the SR

(Figure 5). The total cumulative load was 882 lb for the nine monitoring years (1991-1999), which was less than half of that measured in the SR (2097 lb) during the four monitoring years of 1991-1994 (Table 4). This load represented about 0.16% of the total reported agricultural use in the SJR watershed, much less than that (0.76%) calculated for the SR watershed. Similar observations were also made for simazine. Despite much higher use of simazine in the SJR watershed (Figures 3 and 4), its highest daily load in the SJR (65.2 lb/d, Figure 14), was still lower than that measured for the SR (87.5 lb/d, Figure 6). The total load (2567 lb/) of simazine as a percentage of use in the SJR watershed was calculated as 0.60% compared to 6.72% (4571 lb) for the SR watershed (Table 4). These results suggest that a much larger proportion of winter applied pesticides in the SR basin moves off-site to surface water than in the SJR basin.

The time series of diuron data include three consecutive winter seasons from November 1997 to March 2000 (Figure 15). The daily load of diuron in the SJR ranged from below detection limit to >280 lb/d, with an average load of 29.2 lb/d. The total load reached 5341 lb during the three seasons, which was about 4.03% of the total use applied in the watershed during the same periods of time (Table 4). Again, this loading rate was substantially less than that measured for the SR watershed (16.20%).

The load, precipitation and use data of cyanazine are shown in Figure 16. In order to help to understand the load data, the cyanazine concentration data and the river flow data are also shown. As can be seen from this Figure, the high daily loads of cyanazine obtained during the sampling period of January to March 1998 were most likely false estimates due to the coincidence of abnormally high DL for the samples and concurrent high flow rates. An inspection of the historical concentration data showed that the surface water samples collected during this period and later (1998-2000) were all below the DL of 0.2 μg/L, which was at least four times that of the previous DL (0.004 or 0.05 μg/L). The calculation of pesticide load for these NDs using ½DL obviously led to false high estimates due to the concurrent high flow rates (Eq. [5]). Because of the difficulty to estimate cyanazine loads for the 1998-2000 sampling periods, only the 1993-1995 data were retained for analysis. The total load of cyanazine during these sampling periods was calculated as 167 lb, which was about 0.47% of that used in the watershed for the same periods (Table 4).

Comparison of the load statistics of the four pesticides analyzed for the SJR indicated that diuron probably has a higher potential for runoff than diazinon, simazine and cyanazine. The observed loading rate of diuron as a percentage of use was at least six times of that observed for others (Table 4). This trend was less certain for the SR due to the higher unaccounted nonagricultural use of diuron (Figure 3). Comparison of runoff potential based on the measured loading and use data, however, generally is not meaningful because these pesticides were applied to different sites and under different conditions.

Fitting of the pesticide loads in the SJR to the regression models showed variable results (Figures 17 to 20). Neither Eq.[2] nor Eq. [3] explained the observed daily loading of cyanazine (Figure 20). Extended fitting using unsmoothed daily load continuously to monthly moving average of daily load as the independent variable did not improve the regression either (results not shown). The reason why the regression model failed to simulate the cyanazine loading is unknown, but only two explanations are possible: 1) the existence of other controlling factor(s) which are not reflected by the model formulation, and/or 2) poor quality of the original regression data. The model, however, simulated reasonably the loading dynamics of diazinon, diuron, and simazine at both the spatial scales, with a significance level of <0.001 (Figures 17 to 19). The simulated loads for all the three pesticides matched well with the observed loads, except for two occasions: the 1997 winter season for diazinon and the 1991-1992 winter season for simazine. In the former case, the model substantially underestimated diazinon loads. The observed weekly moving average of daily load reached as high as 9.0 lb/d, but the model only produced a peak of 2.6 lb/d (Figure 17). In the latter case, the model overestimated the simazine load, predicting an abrupt increase in loading when the data showed only a flat trend. It is likely that the peaks of simazine during that winter were either not measured properly or missed by the sampling plan of the monitoring study.

The fitted model parameters, along with the regression r^2 and significance level P, are presented in Table 7. The r^2 for the single basin model ranged from 0.385 to 0.530 for

Table 7. Estimated regression model parameters for pesticides analyzed for the San Joaquin River.

Model	Model parameter				
		Diazinon	*Simazine*	*Diuron*	*Cyanazine*
Single basin (Eq.[2])	a	1.563E-04	8.105E-04	8.775E-05	2.895E-04
	b	12.903	6.906	1.038	1.929
	n	0.185	0.221	0.904	0.146
	L	7	7	14	7
	M	29	11	20	13
	N	32	40	58	9
	r^2	0.385	0.53	0.503	0.012
	P[a]	<0.001	<0.001	<0.001	>0.05
Subbasin (Eq.[3])	a_1	1.458E-05	4.357E-03	1.261E-03	2.979E-04
	a_2	3.467E-05	2.205E-03	4.439E-03	1.000E-02
	a_3	1.000E-07	3.532E-04	7.100E-03	9.553E-04
	a_4	4.760E-06	1.734E-03	1.000E-02	1.000E-03
	a_5	9.579E-05	1.207E-03	1.653E-03	7.767E-04
	a_6	6.787E-05	6.974E-03	1.439E-03	1.000E-07
	a_7	1.000E-06	1.000E-07	3.652E-04	3.533E-05
	b	1.830	6.258	6.773	0.150
	n	0.615	0.248	0.177	0.099
	L	7	7	14	7
	M	19	12	22	25
	N	19	12	30	13
	r^2	0.422	0.23	0.167	0.012
	P[a]	<0.001	<0.001	<0.001	>0.05

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

diazinon, simazine, and diuron, which are all significant at $P<0.001$. The r^2 for cyanazine was 0.012 which was not significant at $P=0.05$. At noted before, the solutions obtained for the pesticides should not be regarded as being rigorous, but only empirical. They were obtained through the approach of Monte Carlo analysis based on minimum χ^2, and were not unique. For the subbasin model, the partial regression coefficients a_i for the subbasin model varied by as much as 3 to 5 orders of magnitude, indicating substantial differences in the impact of pesticide use on the SJR in the respective subbasins. The fitted values of b were 1.830, 6.258, and 6.773 cm for diazinon, diuron, and simazine for a period of 19, 12, and 22 days, respectively, with the corresponding n of 0.615, 0.248, and 0.177 (Table 7). All regressions were significant at $P<0.001$. Again, without monitoring data at the subbasin scale, the values of these a_i in the subbasin model cannot be validated. The r^2 for cyanazine was 0.012 for the subbasin model, equal to that obtained for the single basin model, and the regression was not significant at $P=0.05$.

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 (Tables 5 and 7). In order not to lose 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 subbasin. 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.

4. Conclusions

This analysis evaluated geographic characteristics of the Sacramento River and San Joaquin River watersheds, river flow, precipitation, pesticide use, and pesticide monitoring data, and integrated this information into an empirical statistical model that can be used to predict pesticide loading in the Sacramento and San Joaquin Rivers. The prediction was based on the time series of two environmental variables: the precipitation and pesticide use. The proposed model explained most of the observed changes of pesticide loading over time in the rivers during 1991-2000 winter storm seasons for six out of seven cases analyzed, demonstrating that precipitation and pesticide use are the two major factors controlling the dynamics of pesticide transport into surface water in a watershed. To increase the prediction accuracy of the regression model, it is recommended that monitoring data be collected for the subbasins to further refine or calibrate the subbasin models. It should be noted, however, that as is true for any statistical modeling, the reliability of the model prediction is limited by the quality of the original data that enter into the regression. The empirical model established in this study can be used as a reference for the baseline use-loading relationship in the watersheds to evaluate the effect of any future changes in agricultural management practices on impact of pesticide use on the SR and SJR.

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