

EVALUATION OF SOURCES AND LOADING OF PESTICIDES TO THE SACRAMENTO RIVER, CALIFORNIA, USA, DURING A STORM EVENT OF WINTER 2005

LEI GUO,* KEVIN KELLEY, and KEAN S. GOH

Department of Pesticide Regulation, Environmental Monitoring Branch, Sacramento, California 95814, USA

(Received 29 November 2006; Accepted 22 May 2007)

Abstract—A monitoring study was conducted in the tributaries and main stem of the Sacramento River, California, USA, during the storm event of January 26 to February 1, 2005. The purpose of the study was to evaluate the sources and loading of pesticides in the Sacramento River watershed during the winter storm season. A total of 26 pesticides or pesticide degradates were analyzed, among which five pesticides and one triazine degradate were detected. Diuron, diazinon, and simazine were found in all streams with a total load of 110.4, 15.4, and 15.7 kg, respectively, in the Sacramento River over the single storm event. Bromacil, hexazinone, and the triazine degradate diaminochlorotriazine were only detected in two smaller drainage canals with a load ranged from 0.25 to 7 kg. The major source of pesticides detected in the main stem Sacramento River was from the most upstream subbasin, the Sacramento River above Colusa, where detected pesticides either exceeded or were close to those at the main outlet of the Sacramento River at Alamar Marina. The higher precipitation in this subbasin was partly responsible for the greater contribution of pesticides observed. Diazinon was the only pesticide with concentrations above water quality criteria, indicating that additional mitigation measures may be needed to reduce its movement to surface water.

Keywords—Pesticides Storm Runoff Stream Watershed

INTRODUCTION

The Sacramento Valley, California, USA, is a major agricultural production area and receives thousands of tons of pesticides every year ([1]; <http://www.cdpr.ca.gov/docs/pur/purmain.htm>). Movement of pesticides by surface water runoff during storm events is one of the key transport pathways that led to contamination of the Sacramento River (SR), its tributaries, and the Sacramento–San Joaquin Delta [2–6]. These water bodies not only provide physical habitat and migration routes for a variety of aquatic organisms, but also serve as a major water source for commercial, agricultural, and residential uses in California ([7]; <http://www.waterplan.water.gov/previous/cwpu2005/index.cfm>, [8]). Determining the spatial and temporal occurrence and magnitude of the pesticide sources is critical for developing mitigation strategies and measures to reduce pesticide movement to surface water, which has been a prime focus of water quality management in the Sacramento River watershed.

In the Central Valley of California, rainfall occurs primarily during the months of November to April, which coincides with the application of dormant spray insecticides, which are applied to deciduous trees during their dormancy, and the pre-emergent herbicides. These pesticides therefore are most prone to storm water runoff. For example, diazinon, simazine, and diuron, which commonly are used in winter or early spring, are among those pesticides that most frequently were detected in the streams of the Sacramento River watershed [2–6,9,10]. Diazinon is an organophosphate insecticide and has been used as a leading dormant spray pesticide in the Sacramento Valley. The presence of diazinon in surface water is of particular concern because of its high toxicity to fish and other aquatic organisms ([11]; <http://www.ipmcenters.org/ECotox/index.cfm>).

Due to repeated detection of diazinon above the concentrations of concern, diazinon has been placed on the U.S. Clean Water Act 303(d) list for the many streams in the Central Valley, such as the Sacramento River, the San Joaquin River, the Feather River, and the Delta waterways ([12]; <http://www.waterboards.ca.gov/tmdl/docs/2002reg5303dlist.pdf>). The Clean Water Act further requires the development of a total maximum daily load for each 303(d) listing to address sources and plans to control and restore water quality. In response to the total maximum daily load requirement, California Department of Pesticide Regulation recently imposed new regulations on dormant spray applications ([13]; <http://www.cdpr.ca.gov/docs/legbills/rulepkgs/05-004/final.pdf>).

The objective of the present study was to determine the sources and magnitude of pesticide loading to the Sacramento River during the storm season from its major subbasins in the Sacramento Valley where almost all pesticide applications occur, and to evaluate the environmental significance of pesticide detections, if any. The study also would provide important information and a check on the effectiveness of ongoing and future mitigation efforts on improving surface water quality in the Sacramento River watershed.

MATERIALS AND METHODS

Watershed description

The Sacramento River watershed is located in the northern part of the Central Valley, California. Its main stem, the Sacramento River, is 515 km long and drains an area of approximately 70,000 km². The Sacramento River mostly is confined in the Sacramento Valley, one of the seven physiographic regions in the Sacramento River Basin [14]. Two major tributaries to the Sacramento River are the Feather River and the American River, both located on the east side of the Sacramento River.

The major land use in the Sacramento Valley is agricultural

* To whom correspondence may be addressed (lguo@arb.ca.gov).
Published on the Web 7/12/2007.

with limited urban areas. Almost all farming activities impacting water quality of the Sacramento River and its tributaries occur in the Sacramento Valley. The Sacramento Valley has a semiarid climate characterized by hot summers and mild winters, with average temperature ranging from low 40°F in the winter to above 90°F in the summer. The soils of the valley are mostly fine-grained with low permeability [14,15]. 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. The water requirement of plant growth in other months is dependent on irrigation drawn from the Sacramento River or groundwater.

Selection of monitoring sites

Five monitoring sites were selected in the Sacramento Valley to monitor the output of pesticides from four subbasins and the main stem of the Sacramento River at Alamar Marina (Fig. 1). The four subbasins monitored included Sacramento River above Colusa, Colusa Basin Drain, Feather River, and Natomas Cross Canal. The two subbasins that were not monitored in the Sacramento Valley were the Lower American River and the Butte/Sutter subbasin. The lower American River basin is primarily urban and historically receives <0.05% of the total agricultural use of diazinon in the Sacramento Valley based on the Pesticide Use Report [1]. The Butte/Sutter subbasin, one of the five major subbasins upstream of the Alamar Marina site, was not monitored due to the difficulty in accurately characterizing the discharge. Stream discharge data at the monitored sites were either obtained from existing gage stations or measured in situ at the time of sampling if none was available. Table 1 lists the name, location, corresponding subbasin/watershed, and source of stream gage data for the selected monitoring sites.

Sample collection and analysis

The monitoring study was conducted from January 26 to February 1, 2005, after application of dormant spray pesticides started in the Sacramento River watershed. Surface water samples were collected at an interval of 12 h for the first 2 d following the initial storm of January 26 to catch the perceived rapid change of pesticide concentration. The sampling frequency then was reduced to once daily for the rest of the monitoring event. Except for the Feather River site, surface water samples were collected by taking a center channel grab from bridges or road crossings using a 4.2-L stainless steel Kemmerer sampler (Wildlife Supply Company, Buffalo, NY, USA) and then were split into two 1-L amber glass bottles for separate pesticide analyses. Due to the lack of accessibility to the river center, water samples at the Feather River site were collected directly with the amber glass bottles from a depth of at least 1 m using a telescoping rod from the shore. The ability of this sampling method to act representatively was checked against the center-channel sampling using a boat in a parallel study conducted in collaboration with the California Central Valley Regional Water Quality Control Board. The results obtained from both sampling methods were within a factor of 1.11, which are within the laboratory quality assurance/quality control limits of 1.25 for duplicates. All samples were sealed with Teflon®-lined lids and placed on wet ice during transportation. The samples then were stored at 4°C until delivered to the laboratory for chemical analysis. For each sampling event, general water quality parameters of pH,

temperature, dissolved oxygen, and specific conductance were measured in situ.

The chemical analyses of the water samples were performed by the California Department of Food and Agriculture Center for Analytical Chemistry (Sacramento, CA, USA). A total of 23 pesticides and three triazine degradation products were analyzed with three multiresidue analytical methods. Table 2 provides a list of the pesticides analyzed, laboratory reporting limits, and their respective physico-chemical properties. The organophosphorus insecticides were analyzed using a gas chromatograph equipped with a flame photometric detector and confirmed by mass selective detector. This gas chromatograph/mass selective detector procedure had a reporting limit of 0.03 to 0.05 µg/L. An analytical procedure using only mass selective detector was employed for diazinon and chlorpyrifos, which had a reporting limit of 10 ng/L. Herbicides were analyzed by liquid chromatography-atmospheric pressure chemical ionization mass spectrometry.

Calculation of pesticide load

Daily pesticide load was calculated based on the measured pesticide concentration and stream flow rate using the following equation:

$$Y(t) = 0.0000694 C(t)F(t)$$

where $Y(t)$ is the estimated pesticide load (kg/d) for day t , $C(t)$ is the pesticide concentration (µg/L), $F(t)$ is the stream flow rate (m³/s), and 0.0000694 is a conversion factor. The laboratory used two reporting notations for samples with concentrations lower than the method reporting limit: Trace and none detected. For samples with a reported concentration of trace, the pesticide load was calculated assuming one-half of the reporting limits. For samples with a reported concentration of none detected, pesticide load was assumed to be zero.

RESULTS AND DISCUSSION

Water quality parameters

The water quality parameters measured at the monitoring sites are presented in Figure 2. The parameter values were all within the historical range of observation, indicating no abnormality during the sampling periods. The pH for all sites was close to neutral, ranging from 7.2 to 8.0. The specific conductance varied between 100 to 600 µs/cm, with highest values found for the Colusa Basin Drain (≥387 µs/cm) and lowest for the Feather River (≤123 µs/cm). The total dissolved oxygen varied from 7.29 to 10.8 mg/L and was consistently higher for the main stem of the Sacramento River and the Feather River, and lower for the Colusa Basin Drain and Natomas Cross Canal. The mean values of dissolved oxygen were 10.26 and 10.10 mg/L for the Sacramento River and Feather River, respectively, and were 7.74 and 8.31 mg/L for the Colusa Basin Drain and Natomas Cross Canal, respectively. Water temperature was similar for all streams during the monitoring event, with an average of 10.6°C (Fig. 2).

Pesticide loading

A total of five pesticides and one breakdown product of triazine were detected in surface water samples collected from the Sacramento River or its tributaries. These include diazinon, simazine, diuron, hexazinone, bromacil, and diaminochlorotriazine. Table 3 presents the location, concentration, and loading of the pesticides detected, as well as the amount of their use in each subbasin upstream of the monitoring site prior to

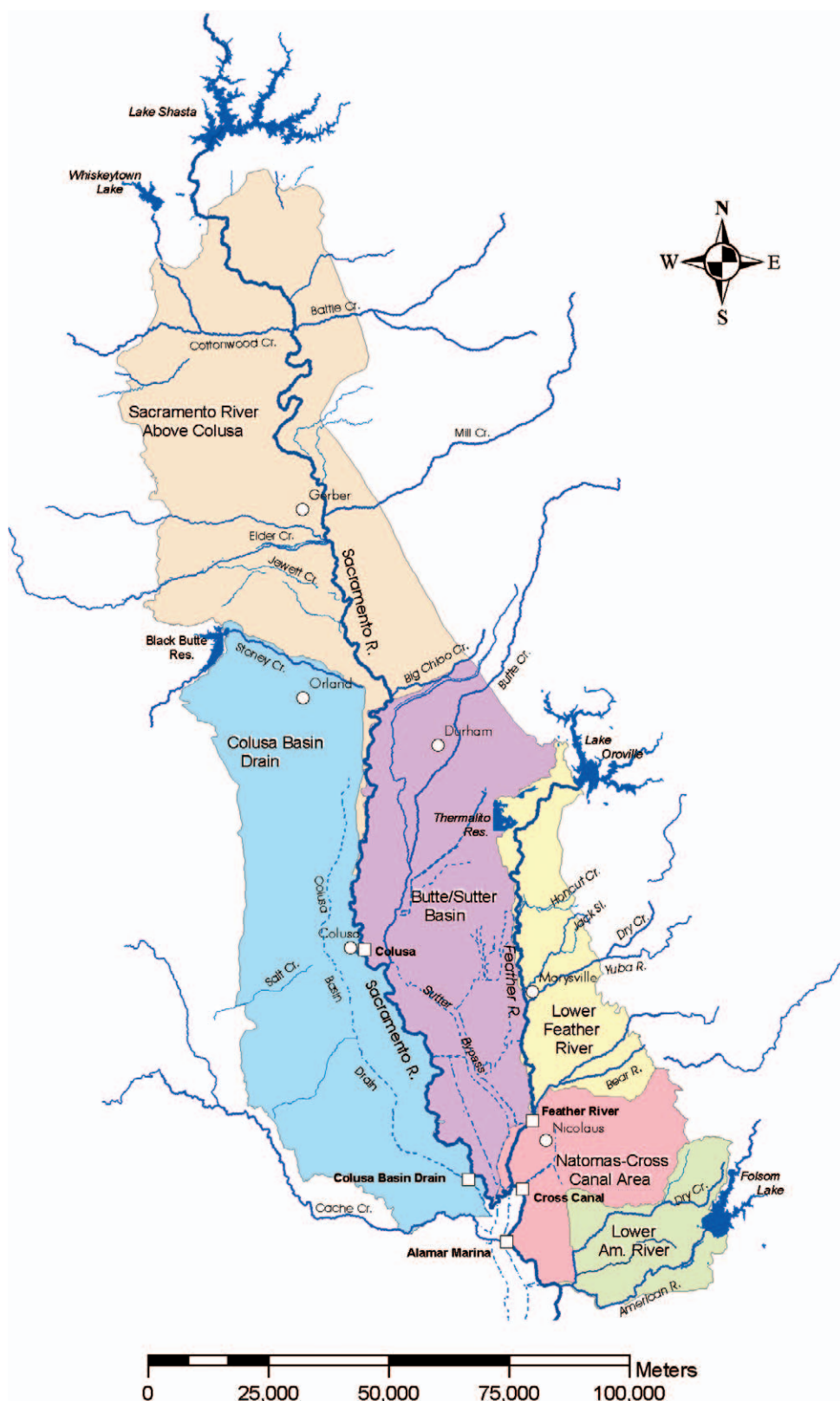


Fig. 1. Sampling and weather station locations for the Sacramento River (CA, USA) watershed. □, Sampling locations; ○, weather stations; —, rivers and streams; - - - -, canals and bypass.

the storm event from December 1, 2004. Figure 3 shows the temporal profile of the pesticide loading during the monitoring period.

Diuron was the most widely detected pesticide, and it was

found at all subbasins, with a maximum concentration ranging from 0.109 $\mu\text{g/L}$ in the Feather River to 0.972 $\mu\text{g/L}$ in the Colusa Basin Drain (Table 3). Most of diuron load in the Sacramento River, however, came from the subbasin of the

Table 1. Sampling sites and their corresponding subbasin/watershed (CA, USA) for storm event monitoring from January 26 to February 1, 2005

Site name	Latitude	Longitude	Subbasin/watershed	Gage station ^a
Colusa Basin Drain at County Road 99E	38.8122	-121.7732	Colusa Drain	CDR
Cross Canal at Garden Highway	38.7808	-121.6031	Natomas Cross Canal	Manually gauge
Feather River near Highway 99	38.8981	-121.5869	Feather River	GRL, MRY, BRW
Sacramento River at Colusa	39.2145	-121.9991	Sacramento River above Colusa	COL
Sacramento River at Alamar Marina	38.6748	-121.6265	Sacramento River watershed	VON

^a The three-letter designation of real-time discharge stations operated by California Department of Water Resources; discharge data available at <http://cdec.water.ca.gov/selectQuery.html>; discharge for the Feather River based on the sum of the three stations shown.

Sacramento River above Colusa. Both the peak and cumulative loads of diuron measured at this site exceeded those measured at the downstream Alamar Marina site (Fig. 3 and Table 3). The contributions of diuron from the Feather River and the Natomas Cross Canal to the Sacramento River were 4.9 kg and 1.4 kg, respectively. The Colusa Basin Drain had a cumulative load of 26.6 kg during the storm event. Most of the residue, however, was diverted to a constructed drainage ditch, the Knights Landing Ridge Cut, thus bypassing the Sacramento River. The water of the Colusa Basin Drains usually is diverted when the Sacramento River stage reaches the height of 7.62

m at Knights Landing. Historical hydrological data showed that the Sacramento River reached the 7.62-m threshold on January 28, 2005, and remained above this level throughout the remaining of the monitoring event. Despite the high diuron load and frequent detections, diuron concentrations were all below the known acute and chronic toxicological values and the lowest no-observed-effect concentration reported for protecting fresh water animals (26.4 µg/L) [11,16].

It is difficult to estimate the ratio of diuron loss to surface water as a percentage of that applied in the subbasins because a significant amount of diuron use in the Sacramento Valley was not for production agriculture, but was used in areas such as urban rights-of-way. Such uses were not included in Table 3 because they were only recorded in the Pesticide Use Report as a monthly sum for individual counties, whose boundaries differ from those of the subbasins. Pesticide use related to agricultural activities, however, was recorded daily at a resolution of a land section, which is approximately 2.6 km². Sources of pesticide loading from agricultural uses therefore can be characterized more accurately in both temporal and spatial terms. The loss ratios shown in Table 3 for diuron (0.25–16.9%) were overestimated because the Pesticide Use Report data indicated that the total urban uses of diuron in the nine counties of the Sacramento Valley amounted to 53.3% of that for agricultural uses in the months of December 2004 and January 2005 [1].

Diazinon also was detected in all monitoring sites at a maximum concentration of 0.021 µg/L in the Natomas Cross Canal and 0.257 µg/L in the Feather River (Table 3). The calculated load of diazinon in the Natomas Cross Canal was negligible (~0.1 kg) due to the low flow rate of the channel. Most of the contribution of diazinon in the Sacramento River also was from the subbasin of the Sacramento River above Colusa (Fig. 3 and Table 3), where diazinon load measured (13.9 kg) was only slightly below that detected at the main outlet of the Sacramento River at Alamar Marina (15.4 kg). Diazinon loads observed in the Feather River and Colusa Basin Drain were similar, at 4.7 and 4.0 kg, respectively. The cumulative export of diazinon from the Sacramento River watershed during this storm event was approximately 0.27% of that applied in the Sacramento Valley (Table 3), which was similar to that reported by Dileanis et al. [4] in their 2001 study. This loss ratio of diazinon is more accurate because almost all of the diazinon applications in the Sacramento River watershed during this period were agricultural uses, with more than 99% being dormant sprays applied on deciduous orchard trees such as peach, prune, and almond [1]. It should be noted that the higher contribution of diazinon from the subbasin of the Sacramento River above Colusa was not correlated to the amount of its use in this subbasin (624 kg), which was far less than that in the Colusa Basin Drain (1,836 kg) or the Feather River (1,541

Table 2. List of chemicals analyzed for the storm event sampling of January 26 to February 1, 2005, in the Sacramento River (CA, USA) watershed^a

Chemical	Reporting limit (µg/L)	K _{OC} (ml/g)	t _{1/2} (d)	Solubility (mg/L)
Ethoprop	0.05	161	34	843
Diazinon	0.01	1,520	32	60
Disulfoton	0.04	1,345	37	12
Chlorpyrifos	0.01	9,930	43	1.18
Malathion	0.04	1,200	9	130
Methidathion	0.05	400	7	240
Fenamiphos	0.05	100	50	700
Azinphos methyl	0.05	882	44	28
Dichlorvos	0.05	30	7	10,000
Phorate	0.05	1,057	37	50
Fonofos	0.04	1,920	37	13
Dimethoate	0.04	20	7	39,800
Methyl parathion	0.03	5,100	5	55
Profenofos	0.05	NA ^b	NA	NA
Atrazine	0.05	147	64	33
Simazine	0.05	140	89	6.2
Diuron	0.05	477	90	42
Prometon	0.05	95	1,300	720
Bromacil	0.05	13	120	700
Prometryn	0.05	383	76	33
Hexazinone	0.05	41	79	29,800
Metribuzin	0.05	52	47	1,000
Norflurazon	0.05	353	163	34
DEA ^c	0.05	NA	NA	NA
ACET ^d	0.05	NA	NA	NA
DACT ^e	0.05	NA	NA	NA

^a Sources for chemical property values are 1) U.S. Department of Agriculture, Agricultural Research Service; Pesticide Properties Database at <http://www.arsusda.gov/services/docs.htm?docID=14199>; 2) Pesticide Information Profile, the Extension Toxicology Network, University of California at Davis, Oregon University, Michigan State University, Cornell University, and the University of Idaho at <http://extoxnet.orst.edu/pips/ghindex.html>; and 3) Pesticide Action Network (PAN) North America, PAN Pesticides Database at <http://www.pesticideinfo.org/Index.html>.

^b NA = not available.

^c DEA = deethyl atrazine.

^d ACET = deisopropyl atrazine.

^e DACT = diamino chlorotriazine.

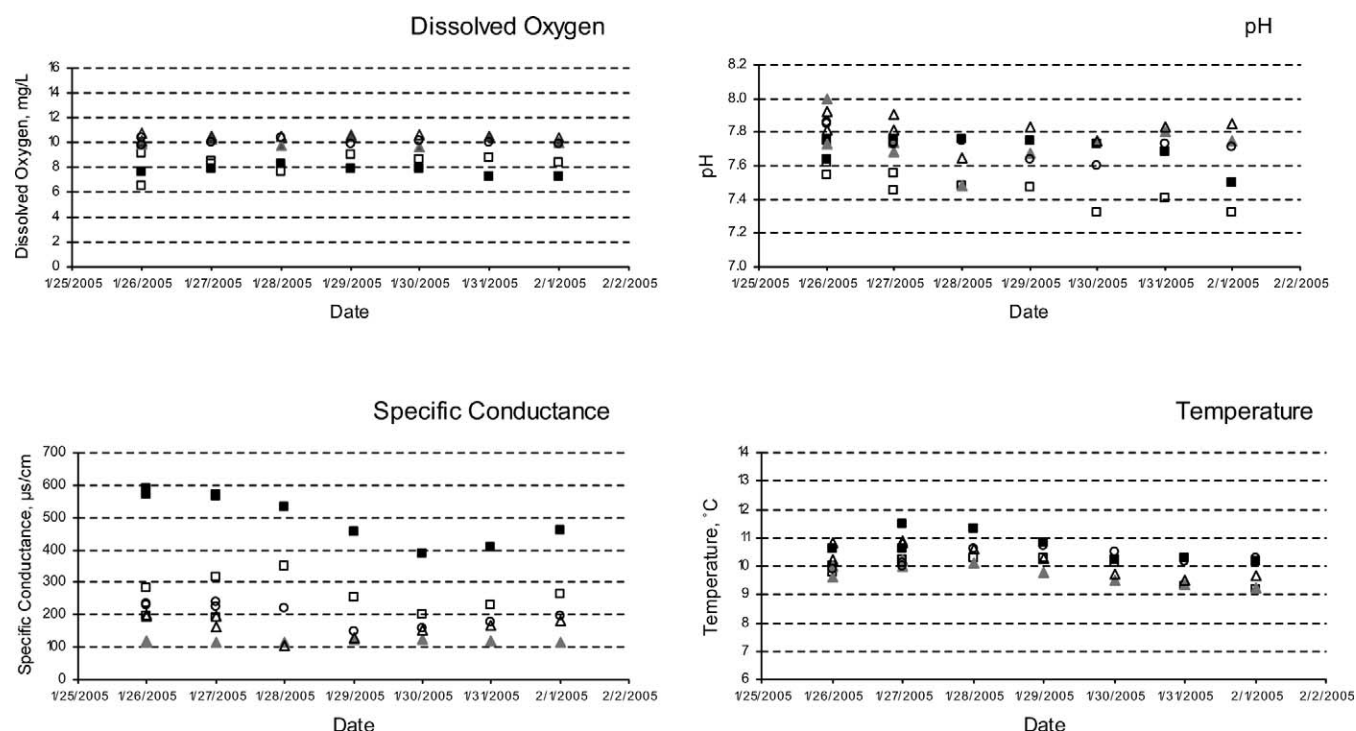


Fig. 2. The measured water quality parameters for the major subbasins and the main outlet of the Sacramento River (CA, USA) watershed during the storm event of January 26 to February 1, 2005. ■, Colusa Basin Drain; □, Cross Canal; ▲, Feather River; △, Sacramento River above Colusa; ○, Sacramento River at Alamar Marina.

Table 3. Summary of pesticide concentration detected, loading, and use in the major subbasins of the Sacramento Valley, Sacramento River watershed (CA, USA) during the storm event of January 26 to February 1, 2005

Site/subbasin	Pesticide	Concentration (µg/L)			Load (kg)	Use (kg) ^a	Load/use (%)
		Minimum	Maximum	Mean			
Colusa Basin Drain	Diuron	0.141	0.972	0.535	26.57	2,024	1.31
	Diazinon	0.012	0.234	0.081	4.1	1,836	0.22
	Simazine	0.051	0.644	0.298	13.37	573	2.33
	Bromacil	ND ^b	0.025	0.008	0.4	0	NA ^c
	Hexazinone	0.094	0.211	0.161	7.03	1,229	0.57
	DACT ^d	ND	ND	ND	0	NA	NA
Feather River	Diuron	ND	0.109	0.082	4.9	502	0.98
	Diazinon	0.020	0.257	0.070	4.72	1,541	0.31
	Aimazine	ND	0.025	0.003	0.2	416	0.05
	Bromacil	ND	ND	ND	0	0	NA
	Hexazinone	ND	ND	ND	0	39	0
	DACT	ND	ND	ND	0	NA	NA
Natomas Cross Canal	Diuron	ND	0.286	0.210	1.44	586	0.25
	Diazinon	0.014	0.021	0.017	0.11	90	0.12
	Simazine	ND	0.025	0.017	0.12	117	0.1
	Bromacil	0.025	0.219	0.095	0.640	0	NA
	Hexazinone	ND	0.187	0.028	0.25	164	0.15
	DACT	0.132	0.672	0.226	2.11	NA	NA
Sacramento River above Colusa	Diuron	ND	0.758	0.328	149.95	889	16.86
	Diazinon	ND	0.096	0.034	13.91	624	2.12
	Simazine	ND	0.129	0.042	18.95	1,105	1.72
	Bromacil	ND	ND	ND	0	0	NA
	Hexazinone	ND	ND	ND	0	253	0
	DACT	ND	ND	ND	0	NA	NA
Sacramento River at Alamar Marina	Diuron	ND	0.546	0.171	95.14	4,513	2.11
	Diazinon	0.021	0.057	0.033	13.8	5,658	0.24
	Simazine	ND	0.094	0.029	13.06	2,429	0.54
	Bromacil	ND	ND	ND	0	0	NA
	Hexazinone	ND	ND	ND	0	1,755	0
	DACT	ND	ND	ND	0	NA	NA

^a Use data were based on Pesticide Use Report [1] for agricultural uses during December 2004 and January 2005.

^b ND = none detected.

^c NA = not applicable.

^d DACT = diaminochlorotriazine.

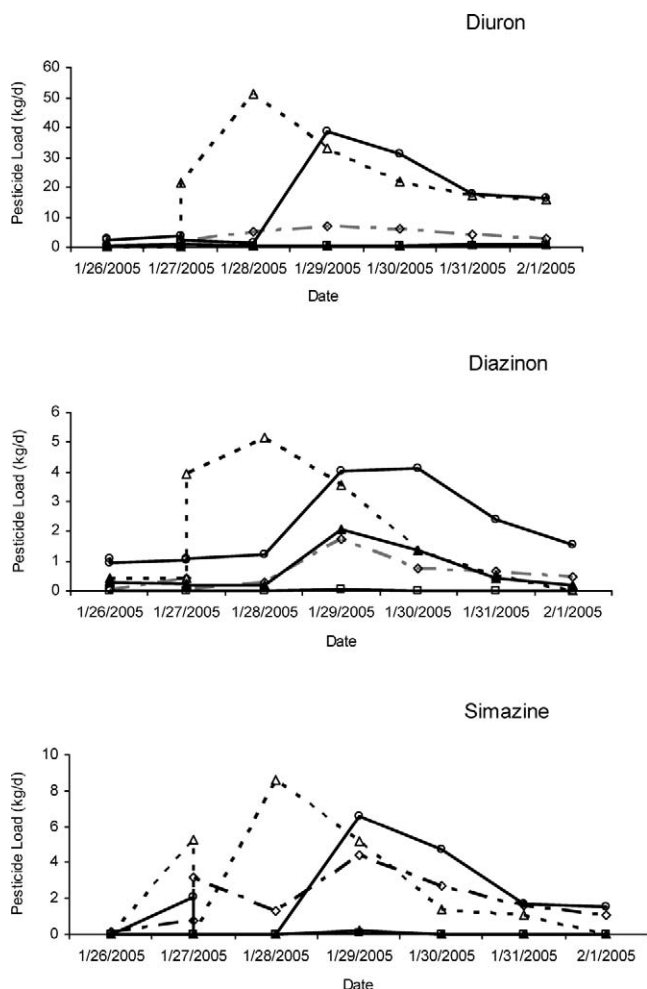


Fig. 3. Pesticide loading over time from the major subbasins and at the main outlet of the Sacramento River (CA, USA) watershed at Alamar Marina during the storm event of January 26 to February 1, 2005. ■, Colusa Basin Drain; □, Cross Canal; ▲, Feather River; △, Sacramento River above Colusa; ○, Sacramento River at Alamar Marina.

kg). As discussed later, the lack of simple correlation between the diazinon use and load in part was caused by differences in the amount of precipitation received in the subbasins.

The maximum concentrations of diazinon observed in the Feather River and Colusa Basin Drain (Table 3) exceeded the water quality criterion of $0.16 \mu\text{g/L}$ established by the California Department of Fish and Game for the protection of freshwater aquatic organisms based on chronic aquatic toxicity tests ([17]; <http://www.waterboards.ca.gov/centralvalley/programs/tmdl/sac.feather.diaz/sfr-bpa-staff-rpt.pdf>). These results, consistent with previous studies ([3,4,18]; <http://www.cdpr.ca.gov/docs/emppm/pubs/ehapreps/eh0101.pdf>), demonstrate that offsite movement of diazinon from dormant sprays has caused the impairment of streams in the Sacramento River watershed and continue to be a problem despite voluntary efforts in mitigation since its listing on the 303(d) list in 1994. Recently, the California Department of Pesticide Regulation adopted new dormant spray regulations to impose mitigate measures to reduce the movement of dormant spray pesticides [13]. The effectiveness of these regulations in improving water quality will be evaluated by future monitoring studies.

Simazine was the third most frequently detected pesticide with a maximum concentration that varied between 0.025 to

$0.644 \mu\text{g/L}$ at different sites (Table 3). The largest load of simazine was again from the subbasin of the Sacramento River above Colusa (Fig. 3). It reached approximately 19 kg over the sampling period and substantially exceeded that observed at Alamar Marina (15.7 kg). The Feather River and the Natomas Cross Canal both contributed less than 0.2 kg of simazine to the Sacramento River. The Colusa Basin Drain had a cumulative load of simazine approximately 13 kg. Most of the load, however, bypassed the Sacramento River through the Knights Landing Ridge Cut. The major simazine use during the two months preceding the storm was on grapes (56%), followed by walnuts (19.8%) and almonds (16.6%). All detected simazine concentrations were less than the no-observed-effect concentrations reported for freshwater organisms ($30 \mu\text{g/L}$) [11].

An accounting of pesticide mass balance revealed that the observed loads for diuron and simazine at the Colusa site both were greater than those measured at the downstream site of the Alamar Marina Dock (Table 3). This discrepancy might be attributable to the imperfect coincidence of sampling in time with the passing peaks of the pesticides through the two sites. It is also possible, however, that appreciable attenuation, such as degradation and adsorption, occurred during pesticide traveling between these two sites. Additional studies would be required to further validate and characterize any potential in-stream attenuation of pesticides in the Sacramento River.

The two other pesticides, bromacil and hexazinone, and the breakdown product of triazine diaminochlorotriazine, were only detected in the subbasins of Colusa Basin Drain and Natomas Cross Canal (Fig. 3). These contaminants may be diluted in the main stem of the Sacramento River so that their concentrations were below the detection limits. Approximately 1 kg of bromacil was exported to the Sacramento River from the Colusa Basin Drain and Natomas Cross Canal combined (Table 3). Because there were no production agriculture uses of bromacil in these two subbasins during the two months preceding the storm event, the residues would have originated from urban applications. A query of the Pesticide Use Report database [1] indicated that approximately 908 kg of bromacil urban uses were reported in the counties of Glenn, Colusa, and Sutter (CA, USA) in December 2004 and January 2005. The export of hexazinone was 7.0 kg from the Colusa Basin Drain and 0.25 kg from the Natomas Cross Canal. Diaminochlorotriazine was only detected in the Natomas Cross Canal at 2.1 kg. Bromacil and hexazinone concentrations were below reported aquatic no-observed-effect concentration values of 16,900 and 15,000 $\mu\text{g/L}$, respectively [11]. Diaminochlorotriazine detections could not be evaluated due to lack of aquatic toxicity data for diaminochlorotriazine.

It has been shown that rainfall-driven pesticide loads in the Sacramento River are directly related to pesticide use and precipitation [5]. A statistical model has been developed by Guo et al. [5] to predict pesticide loading in the Sacramento River based on historical use and precipitation records. However, a longer period of monitoring would be required to use this model, which predicts weekly or biweekly moving average of pesticide load in the Sacramento River. Examination of the precipitation data in the area indicated that precipitation at the Gerber station (CIMIS 8), located in the subbasin of the Sacramento River above Colusa (Fig. 1), was significantly higher than the other stations (Fig. 4). The cumulative precipitation from January 24 to 29 reached 5.41 cm for the Gerber station, which was more than twice those observed for the other sta-

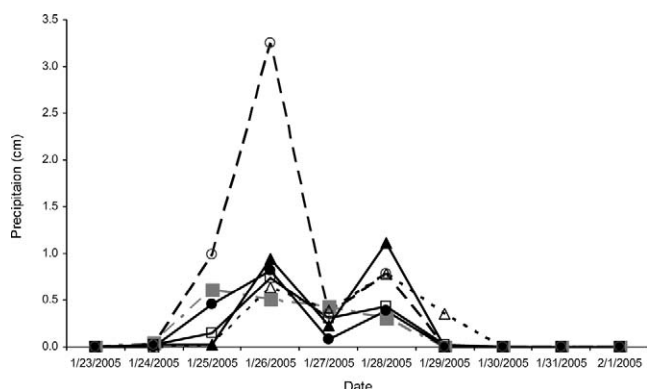


Fig. 4. Measured precipitation at representative weather stations of the subbasins in the Sacramento Valley (CA, USA) during the storm event of January 26 to February 1, 2005. Locations of the stations are shown on Figure 1. CIMIS = California Irrigation Management System; NOAA = National Oceanic and Atmospheric Administration. ■, Colusa Basin Drain (CIMIS 32); □, Colusa Basin Drain (CIMIS 6); ▲, Cross Canal (CIMIS 30); △, Feather River (NOAA 5385); ●, Butte/Sutter Basin (CIMIS 12); ○, Sacramento River above Colusa (CIMIS 8).

tions (<2.34 cm). The observed hydrographs at the outlet of the subbasins are consistent with the precipitation records, displaying a more pronounced and rapid rising limb for the subbasin of the Sacramento River above Colusa than those for the other subbasins (Fig. 5). The difference in precipitation explained at least partially the greater contribution of pesticides from the Sacramento River above Colusa observed during this storm event.

Pesticide travel time

Estimation of pesticide travel time from the field to the waterways can be achieved by examining the temporal relationship of pesticide peak in the streams to the occurrence of the storm event. Precipitation occurred from January 24 through 29, with the major storm falling on January 26 in most of the subbasins (Fig. 4). The earliest detection of pesticide peak in the streams, however, was only made on January 28 at the most upstream location of the Sacramento River at Colusa (Fig. 3). For the other sites, the peaks of pesticide loading were not detected until January 29th or 30th (Fig. 3). These

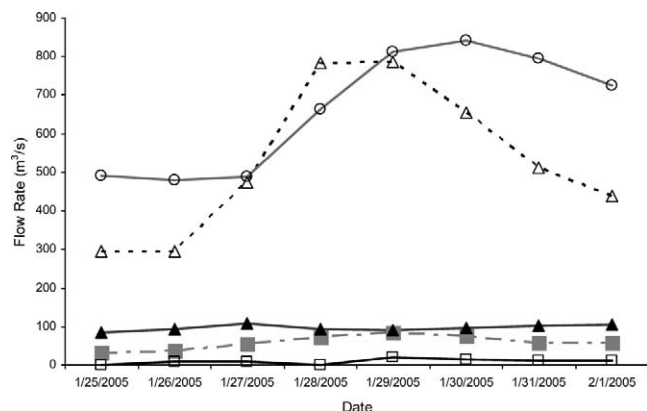


Fig. 5. The observed hydrographs of monitored streams at the outlet of major subbasins and the main outlet of the Sacramento River (CA, USA) watershed during the storm event of January 26 to February 1, 2005. ■, Colusa Basin Drain; □, Cross Canal; ▲, Feather River; △, Sacramento River above Colusa; ○, Sacramento River at Alamar Marina.

results indicated that it took at least 2 d for the pesticides to move from the field to the outlets for both the smaller subbasins and the main Sacramento River watershed. Although the travel times of pesticides observed in the present study are specific to the conditions of the precipitation event, the storm that we sampled was not untypical of the winter storms encountered in the Sacramento Valley in terms of its intensity and duration.

Likewise, comparison of peak detection time for the two main stem Sacramento River sites provided a way to estimate the travel time of pesticides within the Sacramento River. A 1-d delay occurred between the peaks of pesticide loading detected at the Colusa site and those at the downstream Alamar Marina site for all pesticides (Fig. 3). The estimated river distance from Colusa to Alamar Marina is 92 km. Thus the travel speed of the pesticides within the Sacramento River was approximately 3.8 km/h. In theory, pesticides are not ideal tracers of water flow, because their movement in the river would be retarded to some extent due to adsorption/desorption to sediment. Neglecting the retardation, the dissolved pesticides would be traveling at the same speed as the water movement in the Sacramento River. It is thus inferred that the flow rate of the Sacramento River in the segment between Colusa and Alamar Marina was approximately 4 km/h. Because our samples were taken close to the central channel of the river, the integrated flow rate for the entire cross-section of water column for the Sacramento River would be slower.

CONCLUSION

The present study provided a snapshot of pesticide transport in the Sacramento River watershed during one storm event. The results demonstrated that the subbasin of the Sacramento River above Colusa was the major source of pesticide loading in the main stem of Sacramento River. The higher precipitation in this subbasin was partly responsible for the greater contribution of pesticides observed. Diazinon was the only pesticide with measured concentrations above known water quality criteria. Based on the temporal relationship between the detection of pesticide peaks and the occurrence of precipitation, the estimated mean travel time for the pesticides to move from the field to the outlets of the subbasins was >24 h. Likewise, the estimated travel time from the field to the main outlet of the Sacramento River at Alamar Marina was >72 h, and the mean velocity of pesticides in the Sacramento River was estimated as 3.8 km/h.

Acknowledgement—The authors would like to express their thanks to S. Gill, N. Bacey, and R. Sava for their help in field sampling and to the chemists in California Department of Food and Agriculture, Center for Analytical Chemistry for their superior service in laboratory analyses of the water samples.

REFERENCES

1. California Department of Pesticide Regulation. 2006. Pesticide Use Report. Sacramento, CA, USA.
2. Domagalski JL. 1996. Pesticides and pesticide degradation products in storm water runoff: Sacramento River basin, California. *Water Res Bull* 32:953–964.
3. Dileanis PD, Bennett KP, Domagalski JL. 2002. Occurrence and transport of diazinon in the Sacramento River, California, and selected tributaries during three winter storms, January–February 2000. Water Resources Investigation Report 02-4101. U.S. Geological Survey, Sacramento, CA.
4. Dileanis PD, Brown DL, Knifong DL, Saleh D. 2003. Occurrence and transport of diazinon in the Sacramento River and selected tributaries, California, during two winter storms, January–February 2001. Water Resources Investigation Report 02-4111. U.S. Geological Survey, Sacramento, CA.

5. Guo L, Nordmark EC, 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.
6. Lydy MJ, Austin KR. 2005. Toxicity assessment of pesticide mixtures typical of the Sacramento-San Joaquin Delta using *Chironomus tentans*. *Arch Environ Contam Toxicol* 48:49–55.
7. California Department of Water Resources. 2005. California water plan update. Sacramento, CA, USA.
8. Petrusso PA, Hayes DB. 2001. Invertebrate drift and feeding habits of juvenile chinook salmon in the upper Sacramento River, California. *Fish and Game* 87:1–18.
9. Nordmark CE, Bennet K, Feng H, Hernandez J, Lee P. 1998. Occurrence of aquatic toxicity and dormant-spray pesticide detections in the Sacramento River watershed, Winter 1996–1997. Environmental Monitoring Report EH 98-01. California Department of Pesticide Regulation, Sacramento, CA, USA.
10. Domagalski JL, Dileanis PD, Knifong DL, Munday CM, May JT, Dawson BJ, Shelton JL, Alpers CN. 2000. Water-quality assessment of the Sacramento River Basin, California: Water-quality, sediment and tissue chemistry, and biological data, 1995–1998. Open File Report, OFR-00-391. U.S. Geological Survey, Sacramento, CA.
11. National Information System for the Regional Integrated Pest Management Centers. 2006. Pesticide Ecotoxicity Database. U.S. Environmental Protection Agency, Office of Pesticide Programs, Washington, DC.
12. California Central Valley Regional Water Quality Control Board. 2002. Clean Water Act: Section 303(d) list of water quality limited segment. Sacramento, CA, USA.
13. California Department of Pesticide Regulation. 2006. Dormant insecticide contamination prevention, Title 3, California Code of Regulations. Sacramento, CA, USA.
14. Domagalski JL, Knifong DL, MacCoy DE, Dileanis PD, Dawson BJ, Majewski MS. 1998. Water quality assessment of the Sacramento River basin, California—environmental setting and study design. Water Resources Investigations Report 97-4254. U.S. Geological Survey, Sacramento, CA.
15. Troiano J, Weaver D, Marade J, Spurlock F, Pepper M, Nordmark C, Bartkowiak D. 2001. Summary of well water sampling in California to detect pesticide residues resulting from nonpoint-source applications. *J Environ Qual* 30:448–459.
16. Mayer FL, Ellersieck MR. 1986. Manual of acute toxicity: Interpretation and database for 410 chemicals and 66 species of freshwater animals. Resource Publication 160. U.S. Department of the Interior, Fish and Wildlife Service, Washington, DC.
17. California Central Valley Regional Water Quality Control Board. 2007. Basin plan amendments to the water quality control plan for the Sacramento River and San Joaquin River basins for the control of diazinon and chlorpyrifos runoff into the Sacramento and Feather Rivers. Sacramento, CA, USA.
18. Spurlock F. 2002. Analysis of diazinon and chlorpyrifos surface water monitoring and acute toxicity bioassay data, 1991–2001. Environmental Monitoring Report EH01-01. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA, USA.