Diazinon and Chlorpyrifos Loads in Precipitation and Urban and Agricultural Storm Runoff during January and February 2001 in the San Joaquin River Basin, California

By Celia Zamora, Charles R. Kratzer, Michael S. Majewski, and Donna L. Knifong

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CONVERSION FACTORS

Multiply	By	To obtain
inch (in.)	2.54	centimeter
cubic foot per second (ft^3/s)	0.02832	cubic meter per second
square mile (mi^2)	2.590	square kilometer

Temperature in degrees Celsius (°C) may be converted to degrees Fahrenheit (°F) as follows:

°F=1.8 °C+32.

VERTICAL DATUM

Vertical coordinate information is referenced to the North American Vertical Datum of 1988 (NAVD 88): horizontal coordinate information is referenced to the North American Datum of 1983 (NAD 83).

ABBREVIATIONS

lb a.i., pound active ingredient

lb a.i., pound active ingredient per day

mg/L, milligram per liter

μg/L, microgram per liter

$\mu g/m^2$, microgram per square meter

CDPR, California Department of Pesticide Regulation

CMC, criterion maximum concentration

CCC, criterion continuous concentration

GC/FPD, gas chromatograph with flame photometric detection

GC/MS, gas chromatograph/mass spectrometer

LRL, laboratory reporting level

MDL, method detection limit

NWQL, National Water Quality Laboratory

PCO, pest control operator

QC, quality control

RPD, relative percent difference

RWQCB, Regional Water Quality Control Board

SPE, solid-phase extraction

TMDL, Total Maximum Daily Load

Toxics, Toxic Substances Hydrology (Program)

USEPA, U.S. Environmental Protection Agency

USGS, U.S. Geological Survey

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ABSTRACT

The application of diazinon and chlorpyrifos on dormant orchards in 2001 in the San Joaquin River Basin was 24 percent less and 3.2 times more than applications in 2000, respectively. A total of 16 sites were sampled during January and February 2001 storm events: 7 river sites, 8 precipitation sites, and 1 urban storm drain. The seven river sites were sampled weekly during nonstorm periods and more frequently during storm runoff from a total of four storms. The monitoring of storm runoff at a city storm drain in Modesto, California, occurred simultaneously with the collection of precipitation samples from eight sites during a January 2001 storm event. The highest concentrations of diazinon occurred during the storm periods for all 16 sites, and the highest concentrations of chlorpyrifos occurred during weekly nonstorm sampling for the river sites and during the January storm period for the urban storm drain and precipitation sites. A total of 60 samples (41 from river sites, 10 from precipitation sites, and 9 from the storm drain site) had diazinon concentrations greater than 0.08 µg/L, the concentration being considered by the California Department of Fish and Game as its criterion maximum concentration for the protection of aquatic habitats. A total of 18 samples (2 from river sites, 9 from precipitation sites, and 7 from the storm drain site) exceeded the equivalent California Department of Fish and Game guideline of 0.02 µg/L for chlorpyrifos. The total diazinon load in the San Joaquin River near Vernalis during January and February 2001 was 23.8 pounds active ingredient; of this amount, 16.9 pounds active ingredient were transported by four storms, 1.06 pounds active ingredient were transported by nonstorm events, and 5.82 pounds active ingredient were considered to be baseline loads. The total chlorpyrifos load in the San Joaquin River near Vernalis during January and February 2001 was 2.17 pounds active ingredient; of this amount, 0.702 pound active ingredient was transported during the four storms, and 1.47 pounds active ingredient were considered as baseline load. The total January and February diazinon load in the San Joaquin River near Vernalis was 0.27 percent of dormant application; the total January and February chlorpyrifos load was 0.02 percent of dormant application. The precipitation samples collected during the January 2001 storm event were analyzed for pesticides to evaluate their potential contribution to pesticide loads in the study area. When the average concentrations of diazinon and chlorpyrifos in the precipitation samples were compared with concentrations in urban storm runoff samples, 68 percent of the diazinon concentration in the runoff could be accounted for in the precipitation. Chlorpyrifos, however, had average precipitation concentrations that were 2.5 times higher than what was detected in the runoff. Although no firm conclusions can be made from one storm event, preliminary results indicate that pesticides in precipitation can significantly contribute to pesticide loads in storm runoff.

INTRODUCTION

The organophosphate pesticides, diazinon and chlorpyrifos, are applied to control wood-boring insects in almond orchards and other dormant stone fruit orchards in December through February. The agricultural application of diazinon and chlorpyrifos includes aerial spraying or near-ground spraying from a tractor. Diazinon and chlorpyrifos have also been used in many urban applications, although this use is being phased out. The U.S. Environmental Protection Agency (USEPA) has taken steps to phase out and eliminate both diazinon and chlorpyrifos from household and nonagricultural use. Diazinon is one of the most commonly found pesticides in air, rain, and fog, and it is also commonly found in surface water in urban areas as a result of runoff from residential use (U.S. Environmental Protection Agency, 2000). The production and formulation of diazinon is scheduled to phase out and end completely during 2003. Effective December 31, 2003, diazinon will no longer be available for use by homeowners for lawn and garden pest control or for indoor pest control (U.S. Environmental Protection Agency, 2001). As of December 31, 2001 the USEPA has stopped the retail sale of chlorpyrifos to homeowners, limiting the use to certified, professional, or agricultural applicators (U.S. Environmental Protection Agency, 2001).

Diazinon persists for 10 to 12 weeks in most soils when applied at recommended rates (Howard, 1991). In water, it has a solubility of 68.8 mg/L (at 20°C) and may sorb moderately to sediments, but it should not bioconcentrate in aquatic organisms (Howard, 1991). Hydrolysis and biodegradation may be significant fate processes in natural waters. Hydrolysis half-life (at 20°C) is 185 days at pH 7.4 (Howard, 1991). Volatilization of diazinon from water can also be a very important transport process. If diazinon is released to the atmosphere, it will be expected to exist in both the vapor phase and particulate phase based upon its vapor pressure. The half-life for the vapor phase reaction of diazinon with photochemically produced hydroxl radicals is estimated to be 4.1 hours in an atmosphere under nonsmog conditions (Howard, 1991).

Chlorpyrifos has usually been found to persist for about 9 to 17 weeks in soils, although this persistence can vary greatly depending on soil type, climate, and other factors (Howard, 1991). Chlorpyrifos has a lower solubility than diazinon (1.12 mg/L at 24°C) and a much greater tendency to partition from the water column to the sediments. Unlike diazinon, chlorpyrifos has significant potential to bioconcentrate in aquatic organisms. Hydrolysis and adsorption to aquatic sediments are probably the most significant fate processes for chlorpyrifos in natural waters. The hydrolysis half-life of chlorpyrifos (at 20°C) is about 44 to 117 days near pH 7 (Howard, 1991). Biodegradation and volatilization are probably less significant fate processes, especially in the presence of significant levels of suspended sediment (Howard, 1991). When released into the atmosphere, the half-life of the vapor phase of chlorpyrifos is 6.34 hours when reacting with photochemically produced hydroxyls (Howard, 1991).

Water is one of the primary transport mechanisms by which pesticides are carried from their target areas to other parts of the environment resulting in movement into and through all components of the hydrological cycle (Majewski and Capel, 1995). The primary transport mechanism of diazinon and chlorpyrifos in the San Joaquin River Basin during January and February is winter storm runoff following dormant spray application by growers. Previous studies have examined this transport of diazinon and chlorpyrifos from dormant spray application in the San Joaquin River Basin (Domagalski and others, 1997; Kratzer, 1998). Studies that have monitored the basin outlet at Vernalis during winter storm runoff include Kuivila and Foe (1995) and MacCoy and others (1995). Some studies have monitored only one subbasin upstream of Vernalis (Ganapathy and others, 1997; Poletika and Robb, 1998), whereas others included the basin outlet at Vernalis and one to three subbasins upstream of Vernalis (Domagalski and others, 1997; Kratzer, 1998; Bennett and others, 1998; Panshin and others, 1998). Studies monitoring Vernalis and more than three subbasins upstream of Vernalis include Ross and others (1996), Kratzer (1999), and Kratzer and others (2002).

Urban use of pesticides includes homeowner application and application by licensed pest control operators (PCO). It is an important component to consider when monitoring the movement of pesticides in agricultural areas that are in proximity to urban areas. These pesticides become mobilized during storm events and move from the sites of application along impervious surfaces (such as driveways, sidewalks, and street gutters) to city storm drains, ending up in the nearest body of water. A study by Kratzer (1998) examined the transport of pesticides in storm runoff from urban and agricultural areas in the Tuolumne River Basin in the vicinity of Modesto, California.

The atmosphere is also an important component of the hydrological cycle to consider in assessing the effect of pesticides in the environment (Majewski and Capel, 1995). Pesticides have been recognized as potential air pollutants since 1946 (Daines, 1952). Three recent studies have specifically examined pesticide loading from the atmosphere in the Central Valley. One study included the collection of wet and dry deposition samples using an automatic wet–dry sensing collector to assess atmospheric contributions of insecticides to the San Joaquin River Basin as part of an overall examination of distribution and mass loading of insecticides in the San Joaquin River (Ross and others, 1996). A second study found high concentrations of diazinon and chlorpyrifos in rain and fog samples collected in the Central Valley as part of an overall study that examined the toxicity of diazinon and chlorpyrifos in samples collected from urban streams during the precipitation season (Howard and others, 2000). A third study examined atmospheric transport of pesticides from agricultural application areas to the Sacramento, California, metropolitan area (Majewski and Baston, 2002).

Studies have also been done on the toxicity of diazinon and chlorpyrifos in the San Joaquin River Basin (Bennett and others, 1998; Kuivila and Foe, 1995). The most commonly used guidelines in California for short-term exposure (the criterion maximum concentration or CMC) in terms of concentrations are 0.08 µg/L for diazinon and 0.02 µg/L for chlorpyrifos (Siepmann and Finlayson, 2000). The corresponding guidelines for long-term exposure (the criterion continuous concentration or CCC) are 0.05 µg /L for diazinon and 0.014 µg /L for chlorypyrifos.

The purpose of this report is determine the loads of diazinon and chlorpyrifos in the San Joaquin River Basin following application of dormant spray in the surrounding basins during January and February 2001. The study design was to sample two storms with the greatest potential for transporting diazinon and chlorpyrifos. Concentrations of diazinon and chlorpyrifos in the San Joaquin River are of special concern to the Regional Water Quality Control Board (RWQCB) during storm events following dormant spray application. The analysis in this report will be used by the RWQCB to assist in the development of a Total Maximum Daily Load (TMDL) for the San Joaquin River Basin. A TMDL is a process used to address water pollution problems caused by both point source and nonpoint source pollution. The data presented includes the calculation of diazinon and chlorpyrifos loads and the relation of these loads to application, runoff, atmospheric sources, and land use in each subbasin. The format and analysis used in this report is similar to a 2000 U.S. Geological Survey (USGS) study in the same area (Kratzer and others, 2002). Several comparisons will be made in this report to the diazinon and chlorpyrifos loads reported in 2000.

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STUDY AREA

The perennial San Joaquin River Basin drains 7,345 mi^2, of which 4,299 mi^2 are in the Sierra Nevada, 2,244 mi^2 in the San Joaquin Valley, and 802 mi^2 in the Coast Ranges (fig. 1). On the basis of USGS streamflow data for 1951–1990, 67 percent of the average streamflow in the San Joaquin River originates from the three main basins that drain from the east: the Merced (15 percent), Tuolumne (30 percent), and Stanislaus (22 percent) Basins. The remaining streamflow comes from the following sources: (1) Bear Creek Basin; (2) Mud and Salt Sloughs, and ephemeral creeks that drain from the west; (3) drainage canals that flow directly to the San Joaquin River; and (4) occasionally, the upper San Joaquin River above Bear Creek during high flow events.

The water quality, streamflow, and precipitation sites mentioned in this report are identified in figures 1A and 2 and in table 1. A total of seven river sites were sampled 19–64 times each in January and February 2001 for this study. The river sites include three sites on the main stem of the San Joaquin River (fig. 1A: sites 1, 6, and 13), three major east-side tributaries (fig 1A: sites 4, 9, and 12), and one west-side creek (fig. 1A: site 5). The water quality sampling sites on the Merced, Tuolumne, and Stanislaus Rivers were sampled downstream of USGS gaging stations (sites 3, 9, and 11 respectively). Streamflow at the water quality sampling sites was estimated using traveltimes in the tributaries from the gaging stations (Kratzer and Biagtan, 1997).

Additionally, urban storm-water runoff samples were collected at the McHenry storm drain (fig. 1: site 8) during the January 23–26, 2001, storm period. McHenry storm drain is located in Modesto, and land use in its associated basin is 100 percent urban: approximately 70 percent residential and 30 percent commercial (Kratzer, 1998). The Modesto urban area accounts for about 62 percent of the population in Stanislaus County (Gronberg and others, 1998). Land use in the valley part of the Tuolumne River at Modesto drainage basin is about 53 percent agricultural, 13 percent urban, and 34 percent other (Kratzer, 1998). The precipitation during the 2001 water year (October 1, 2000, through September 30, 2001) in Modesto was 13.10 in., with 6.54 in. falling between December 2000 and March 2001. In the urban area, approximately 40 percent of storm-water discharges to surface water, and 60 percent discharges to ground water by way of dry wells (Lisa Burns, City of Modesto, written commun., July 2002).

Four of the eight precipitation collection sites were placed in urban land use areas (fig. 2: sites B, C, E, and G) and four in agricultural land use areas (fig. 2: sites A, D, F, and H) outside of Modesto. The urban sites were placed throughout Modesto to give good spatial representation of the urban area. The location of the urban sites included the downtown area (site E), an industrial area (site G), an established residential area (site B), and a new residential development (site C). Agricultural site locations were chosen to give good spatial representation of almond and stone-bearing fruit orchards surrounding Modesto. The locations of the agricultural sites were north, south, east, and west of Modesto (sites H, A, F, D, respectively). These sites were positioned near predominant orchard land use areas rather than directly within an orchard to minimize any direct influence of spraying operations.

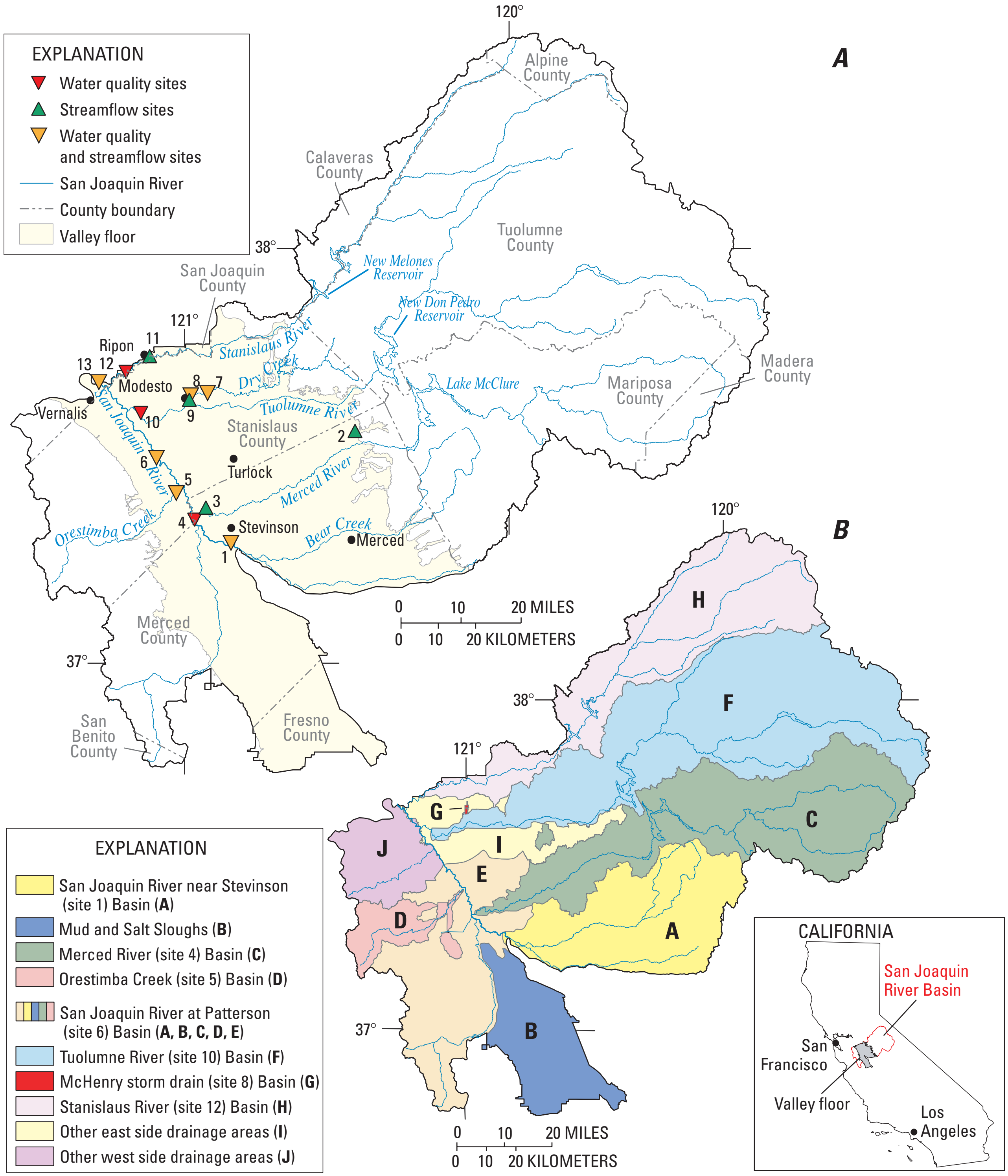


Figure 1. Locations of data sites and drainage basins in the San Joaquin River Basin, California. ***A***. Data sites. ***B***. Drainage basins. Basin names are slightly abbreviated; full versions are listed in table 2. Adapted from Kratzer and others, 2002.

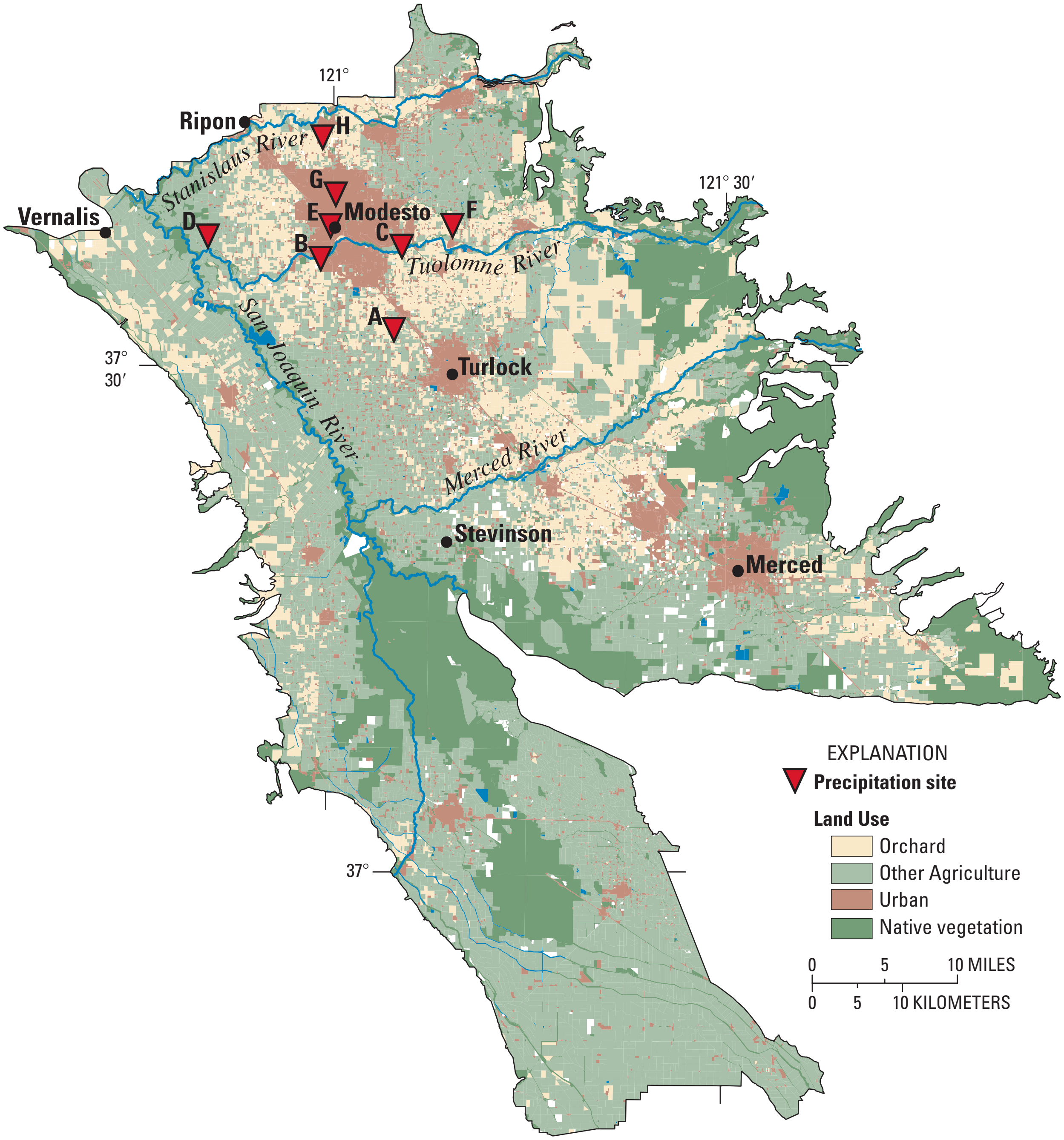


Figure 2. Locations of precipitation sites and land use in the San Joaquin Valley, California.

Table 1. Names, locations, and types of data available for sites in the San Joaquin River Basin, California, January and February, 2001

[See figures 1*A* and 2 for site locations. Site location: unless otherwise noted, double entries for distances are in river miles from the San Joaquin River and Vernalis, resepectively. NA, not applicable. x, data available; —, no data available]

Site number/ letter	Site name	Site identification number	Site location	Data at Sites		
				Precipitation	Streamflow	Water Quality
1	San Joaquin River near Stevinson	11260815	[1]60.5	—	x	x
2	Dry Creek near Snelling	11271320	[2]17.8; 49.5; 95.2	—	x	—
3	Merced River near Stevinson	11272500	4.8; 50.5	—	x	—
4	Merced River at River Road Bridge near Newman	11273500	1.1; 46.8	—	—	x
5	Orestimba Creek at River Road near Crows Landing	11274538	1.0; 37.7	—	x	x
6	San Joaquin River at Patterson Bridge near Patterson	11274570	[1]26.5	—	x	x
7	Dry Creek near Modesto	[3]BO-4130	[4]5.5; 21.9; 33.1	—	x	—
8	McHenry storm drain at Bodem Street at Modesto	373847120590801	NA	—	x	x
9	Tuolumne River at Modesto	11290000	16.2; 27.4	—	x	—
10	Tuolumne River at Shiloh Road Bridge near Grayson	11290200	3.6; 14.8	—	—	x
11	Stanislaus River at Ripon	11303000	15.7; 18.2	—	x	—
12	Stanislaus River at Caswell State Park near Ripon	374209121103800	8.5; 11.0	—	—	x
13	San Joaquin River near Vernalis	11303500	2 0.0	—	x	x
A	Precipitation Gage 4, TID lateral 3 Barnhardt Road near Turlock	373228120551201	NA	x	—	—
B	Precipitation Gage 6, Wastewater Treatment Plant Rooftop at Modesto	373637121004601	NA	x	—	—
C	Precipitation Gage 7, Cadoni Road Lift Station at Modesto	373725120543701	NA	x	—	—
D	Precipitation Gage 3, MID Lateral 4 near Modesto	373750121092601	NA	x	—	—
E	Wet/Dry Sampler 1 at MID Rooftop at Modesto	373834121000601	NA	x	—	—
F	Wet/Dry Sampler 2 at MID Gage, Albers Road near Turlock	373841120504801	NA	x	—	—
G	Precipitation Gage 8, Bowen and Aloha Street at Modesto	374028120594301	NA	x	—	—
H	Precipitation Gage 5, Tully Road near Modesto	374351121004701	NA	x	—	—

[1]River miles from Vernalis.
[2]River miles from Merced River, San Joaquin River, and Vernalis, respectively.
[3]Department of Water Resources site number.
[4]River miles from Tuolumne, San Joaquin River, and Vernalis, respectively.

APPLICATION OF DIAZINON AND CHLORPYRIFOS

The application of diazinon and chlorpyrifos during December through February to dormant almond and other stone-bearing fruit trees in the San Joaquin River Basin coincides with the rainy season for the region. To control the wood-boring insects, pesticides are most effective when applied during dry periods. Both diazinon and chlorpyrifos are intensely used during this time period (table 2). The distribution of chlorpyrifos and diazinon application in the study area for the December 2000 through February 2001 dormant spray season is shown in figures 3 and 4, respectively. This period generally has the most intensive agricultural application of diazinon in the San Joaquin River Basin (Kratzer and others, 2002). In contrast, the agricultural application of chlorpyrifos in the San Joaquin River Basin is somewhat dispersed, with intensive application on alfalfa in March and intensive in-season application on almonds and walnuts during May through July (Panshin and others, 1998). Diazinon and chlorpyrifos are also applied in urban settings for household lawn and garden pest control as well as for structural pest control.

The application data presented in this report were acquired from records maintained by the California Department of Pesticide Regulation (CDPR). The agricultural application data are reported by day of use, the crop on which used, and for area of use to the square mile. The agricultural application of diazinon and chlorpyrifos is presented (figs. 3 and 4, respectively) for the two dry periods (December 1, 2000, to January 26, 2001; and January 27 to February 24, 2001) that preceded the two storm periods sampled in this study. The agricultural data are plotted at the geographic level of a section (1 mi^2 within a township and range). The data are presented as three application categories of active ingredient (a.i.) per square mile (mi^2) representing relatively low (less than 33 lb a.i./mi^2 for diazinon and less than 31 lb a.i./mi^2 for chlorpyrifos), medium (33–70 lb a.i./mi^2 for diazinon and 31–102 lb a.i./mi^2 for chlorpyrifos), and relatively high (greater than 70 lb a.i./mi^2 for diazinon and greater than 102 lb a.i./mi^2 for chlorpyrifos) application areas. The only urban applications reported by CDPR are those by licensed PCO's by county. Household use, daily use, and place of use (except for county) are not reported. Most of the urban areas within the study area are in Stanislaus and Merced Counties (figs. 1 and 2). Urban applications reported in this report are only for those two counties and are only reported by month. The December 2000 and January 2001 urban application data are included in dry period 1, and the February 2001 application data are included in dry period 2 (table 2). The overall urban application of diazinon for Stanislaus and Merced Counties during the 2001 dormant spray period was three times greater than the reported agricultural application, whereas the overall urban application of chlorpyrifos was three times less than the reported agricultural application for the same counties (table 2).

The agricultural applications of diazinon and chlorpyrifos during dry periods 1 and 2 generally were dispersed unevenly across the study area. Diazinon application for dry period 1 occurred mostly in the northern half of the study area, with approximately 39 percent of that application occurring in the San Joaquin River at Patterson Basins (fig. 3: basins A–E). The diazinon application for dry period 2 was less than that of dry period 1, with approximately 74 percent of the application occurring in the San Joaquin River at Patterson Basins. The application of chlorpyrifos for dry period 1 was also dispersed unevenly, with approximately 69 percent of the application occurring in the Merced River Basin (fig. 4: basin C) and 58 percent occurring in the San Joaquin River near Stevinson Basin (fig. 4: basin A) during dry period 2. The amount of diazinon for agricultural application during December 2000 through February 2001 (table 2) was 24 percent less than the application during the same period in the previous year, while the chlorpyrifos application was 3.2 times greater (Kratzer and others, 2002; California Department of Pesticide Regulation, 2001, 2002). During December 2000 through February 2001, about 8,900 lb a.i. diazinon was applied to agricultural areas in the San Joaquin River Basin. This total compares with approximately 11,700 lb a.i. during the same period in the previous year, and about 83,000 lb a.i. in 1992–1993 and 56,100 lb a.i. in 1993–1994 (Panshin and others, 1998; Kratzer, 1999; Kratzer and others, 2002). During December 2000 through February 2001, about 11,200 lb a.i. chlorpyrifos was applied to agricultural areas in the San Joaquin River Basin compared with approximately 3,500 lb a.i. during the same period in 1999–2000 and 27,000 lb a.i. during the same period in 1992–1993 (Panshin and others, 1998; Kratzer and others, 2002).

Table 2. Basin areas, almond orchard areas, and diazinon and chlorpyrifos appplication amounts for drainage basins in the San Joaquin River Basin, California

[See figure 1*B* for basin areas and locations. Dry period 1: December 1, 2000 to January 26, 2001; Dry period 2: January 24, 2001 to February 24, 2001; mi^2, square mile]

Basin area	Site name	Total basin area (mi^2)	Valley basin area (mi^2)	Almond orchard area (mi^2)	Application (pounds active ingredient)			
					Diazinon, dry period 1	Diazinon, dry period 2	Chlorpyrifos, dry period 1	Chlorpyrifos, dry period 2
A	San Joaquin River near Stevinson	866	218	46	781	578	751	2,539
E	San Joaquin River at Patterson Bridge near Patterson	3,770	1,614	157	2,584	1,708	5,538	2,709
G	McHenry storm drain at Bodem Street at Modesto	1.3	1.3	0.0	0.0	0.0	0.0	0.0
C	Merced River at River Road Bridge near Newman	1,383	245	72.9	1,193	701	4,712	61.5
F	Tuolumne River at Shiloh Road Bridge near Grayson	1,862	149	20.8	237	39	74	378
H	Stanislaus River at Caswell State Park near Ripon	1,144	116	17.9	1,106	24	122	324
D	Orestimba Creek at River Road near Crows Landing	195	33	5.5	0.0	0.0	0.0	0.0
I	San Joaquin River (other east side areas)	298	282	74.3	2,591	506	1,074	961
J	San Joaquin River (other west side areas)	323	112	8.8	49	22.5	0.0	0.0
B	Precipitation Gage 6, Wastewater Treatment Plant Rooftop at Modesto	492	484	1.9	49	0.0	0.0	30
K	San Joaquin River near Vernalis	7,395	2,273	279	6,566	2,300	6,808	4,372
	Urban Application							
	Merced County	1,971	1,381	114	[1]4,089	[2]2,018	[1]1,544	[2]426
	Stanislaus County	1,514	851	127	[1]14,903	[2]7,305	[1]1,438	[2]676

[1]County application by licensed pest control operators is reported by month only (December 2000 and January 2001 is shown for dry period 1).

[2]County application by licensed pest control operators is reported by month only (February 2001 data is shown for dry period 2).

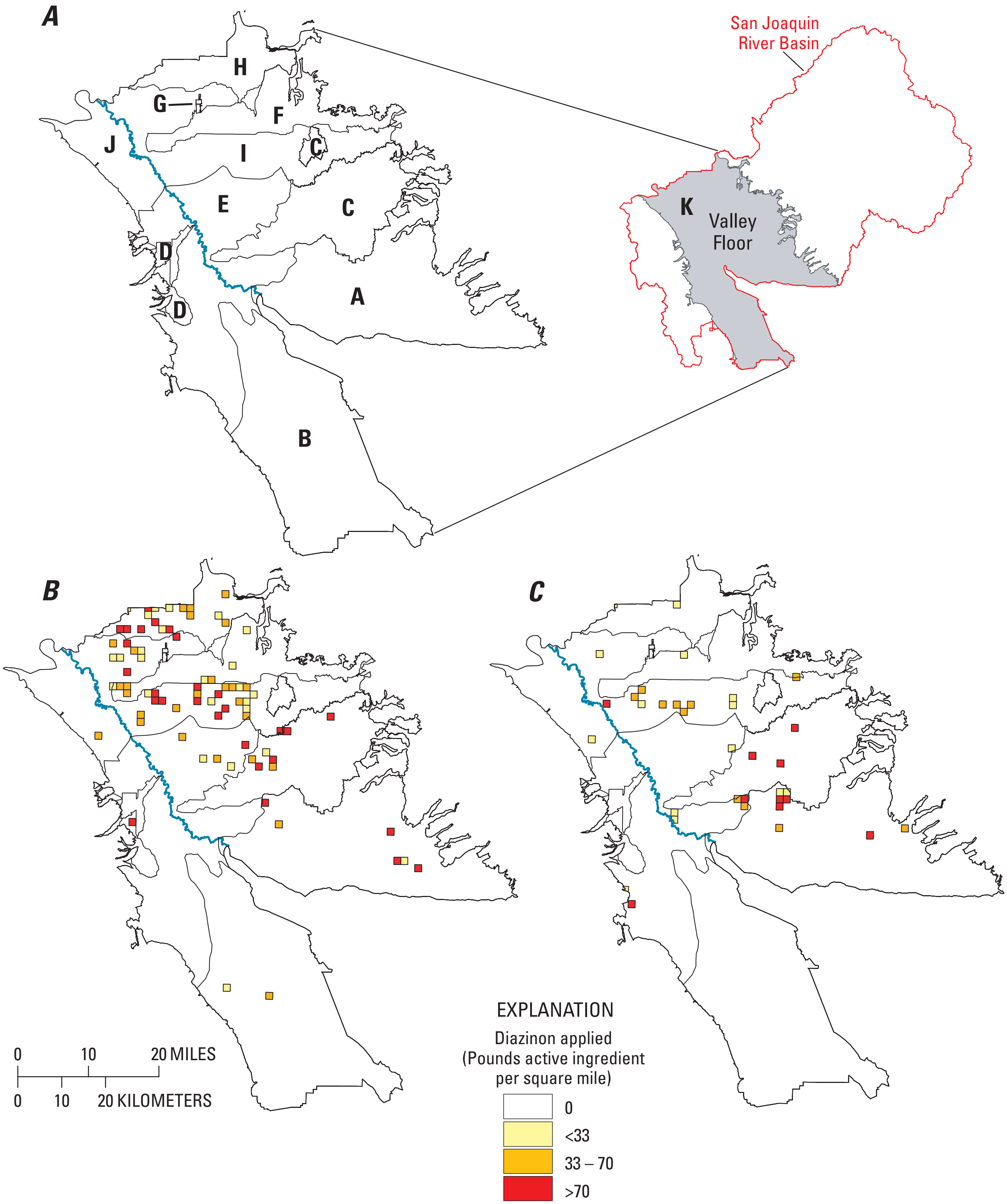


Figure 3. Diazinon application in the San Joaquin Valley part of the San Joaquin River Basin, California. ***A***. In major drainage basins. ***B***. During dry period 1 (December 1, 2000, to January 26, 2001). C. During dry period 2 (January 27, 2001, to February 24, 2001).

Adapted from Kratzer and others, 2002. "K" represents the valley floor and includes all hydrologic basins contained within.

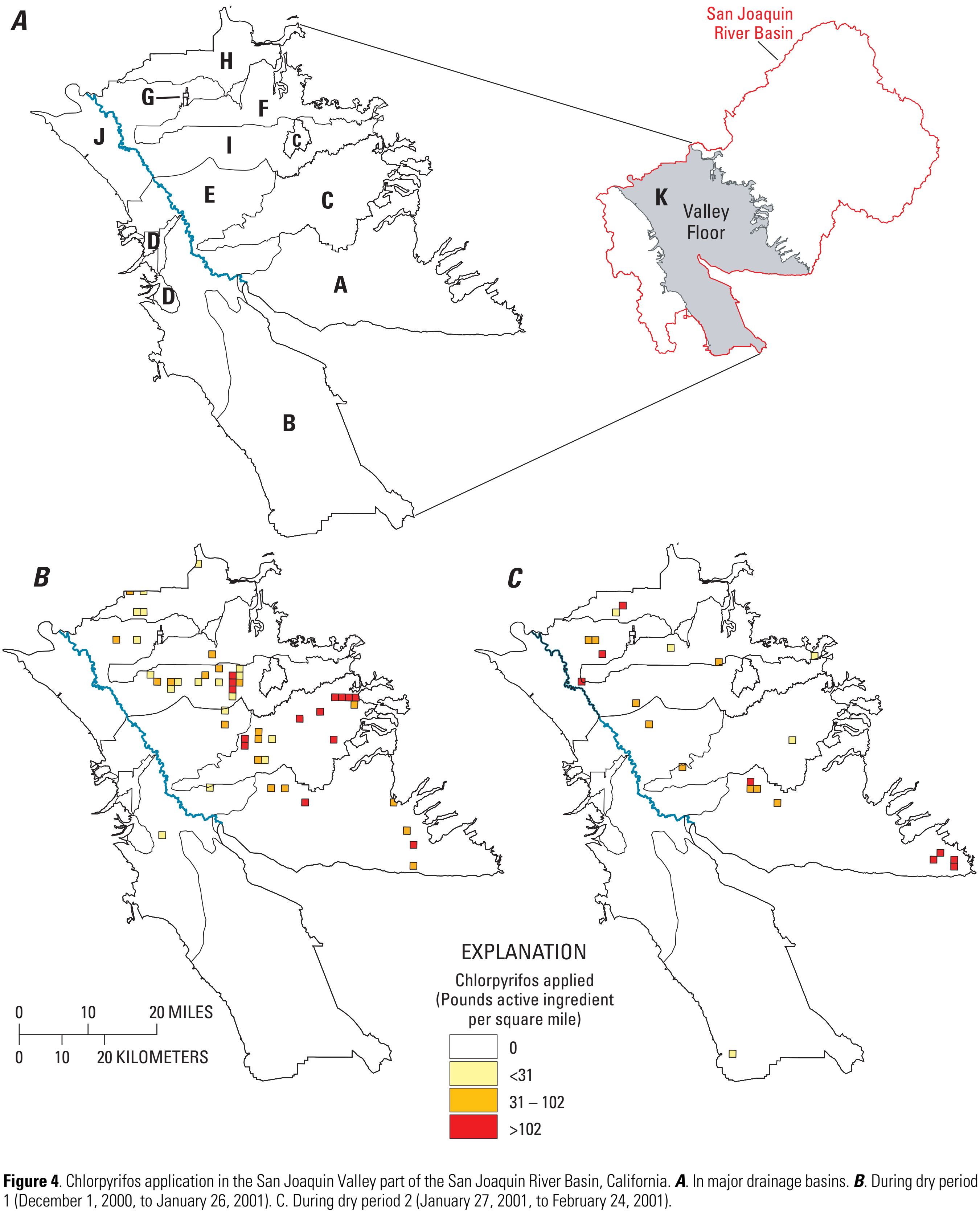


Figure 4. Chlorpyrifos application in the San Joaquin Valley part of the San Joaquin River Basin, California. ***A***. In major drainage basins. ***B***. During dry period 1 (December 1, 2000, to January 26, 2001). C. During dry period 2 (January 27, 2001, to February 24, 2001).

Adapted from Kratzer and others, 2002.

SAMPLING DESIGN AND METHODOLOGY

The primary transport mechanism for diazinon and chlorpyrifos to streams in the San Joaquin River Basin during January and February is runoff from winter storms (Kratzer and others, 2002). Figure 5 illustrates the daily precipitation totals as well as the diazinon and chlorpyrifos application amounts for the December 2000–February 2001 dormant spray-application period. The pesticides are applied to crops during dry periods to reduce the risk of "washing off" by precipitation. The sampling plan for this study was designed around two of these dry periods, identified as dry period 1 and dry period 2 (fig. 5). The definition of "dry period" includes application periods that occur preceding a storm period and the storm period itself (Kratzer and others, 2002). The storm period is included in the dry period because it is the runoff from the application that occurred preceding the storm that is sampled. The California Department of Pesticide Regulation (CDPR) records the amount of pesticide application during the dormant spray season. However, these totals are not available until the following year; therefore, any sampling design relies on information from county agriculture advisors with respect to applications in real-time.

The sampling design for this study was based on sampling the two storms during the January and February dormant season because this period had the greatest potential to transport diazinon and chlorpyrifos. These two storm periods are defined as "target" storm periods and occurred on January 23–26, 2001, and February 18–24, 2001, which had precipitation totals of 0.87 in. and 1.81 in., respectively. The defined dry periods preceding the storms were December 1, 2000, to January 26, 2001 (dry period 1), and January 27, 2001, to February 24, 2001 (dry period 2). Seven river sites throughout the San Joaquin River Basin (table 1) were sampled during the two target storm periods. Weekly samples also were collected from these river sites to assess the nonstorm transport of diazinon and chlorpyrifos during the dormant spray season. Additionally, storm runoff in an urban storm drain, McHenry storm drain (fig. 1: site 8), was sampled during the January 23–26, 2001 storm. Precipitation also was sampled for the following three storm events: January 8–12, 2001, January 23–26, 2001, and February 9–11, 2001, in both agricultural and urban land-use areas (fig. 2: sites A–H).

The sampling strategy for the river sites during the target storm periods was to begin sample collection and to collect several samples at each site throughout the storm runoff hydrograph. The river sites that were sampled in this study have either real-time streamflow data at the sampling locations or upstream from the sampling locations; therefore, it was relatively easy to discern the runoff as the storm progressed. Figure 6 illustrates the storm runoff hydrographs and sample collection times for the river sites and the McHenry storm drain. The timing of sample collection relative to storm runoff hydrographs at the river sites generally provided good coverage of the hydrographs, especially during the rising limb when higher concentrations are expected (fig. 6).

Although only two target storms were extensively sampled during the January and February dormant spray season, a total of four storm events occurred. These additional two storms, defined as "nontarget" storm periods, occurred on January 8–12, 2001, and February 9–11, 2001, and preceded each of the target storms. The weekly sampling date of January 11 coincided with the first nontarget storm, but the weekly sampling date of February 15 did not coincide with the second nontarget storm. For each of these defined nontarget storms, samples were collected once at all river sites during the weekly sampling dates of January 11 and February 15 with the exception of the most downstream site, San Joaquin River at Vernalis, (fig. 1: site 13) where samples were collected more frequently during both nontarget storm events (table 3) to ensure that enough samples were collected to allow for adequate load calculations. In addition to the river samples collected during storm and nonstorm periods at the San Joaquin River near Vernalis site for this study, the USGS's Toxic Substances Hydrology (Toxics) Program collected samples at this site from January through April 2001. The Toxics Program collected daily samples throughout the storm hydrographs for both target and nontarget storms, with more frequent sampling during critical periods, such as high application and runoff. The diazinon and chlorpyrifos concentrations of samples collected by the Toxics Program were included in this study for the San Joaquin River near Vernalis site (table 3). The addition of this sampling data ensures better coverage of the storm hydrographs throughout the dormant spray season at this farthest downstream sampling point.

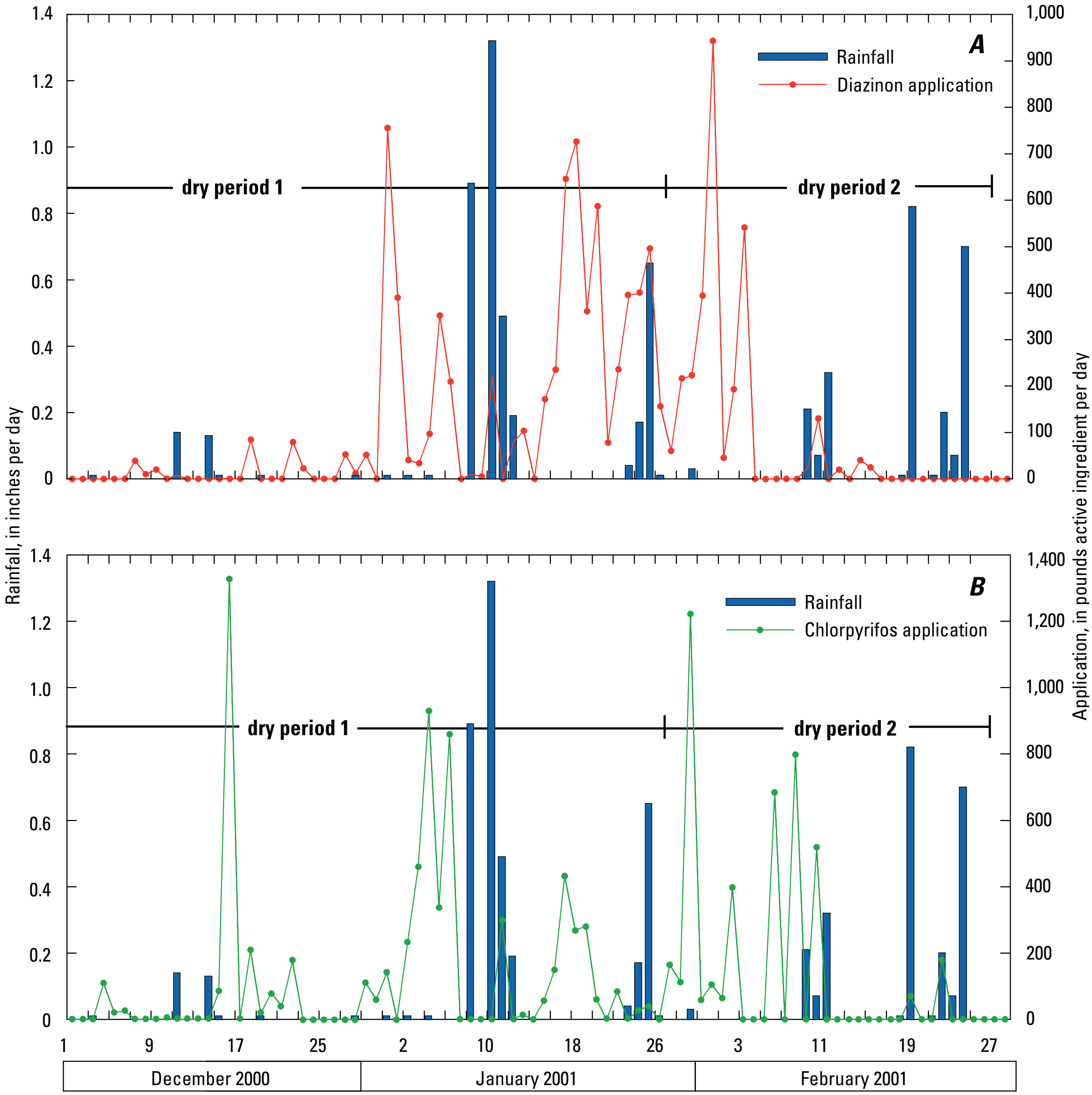


Figure 5. Daily precipitation at Modesto, California, and pesticide applications in the San Joaquin River Basin, California, December 2000 through February 2001. ***A***. Diazinon. ***B***. Chlorpyrifos.

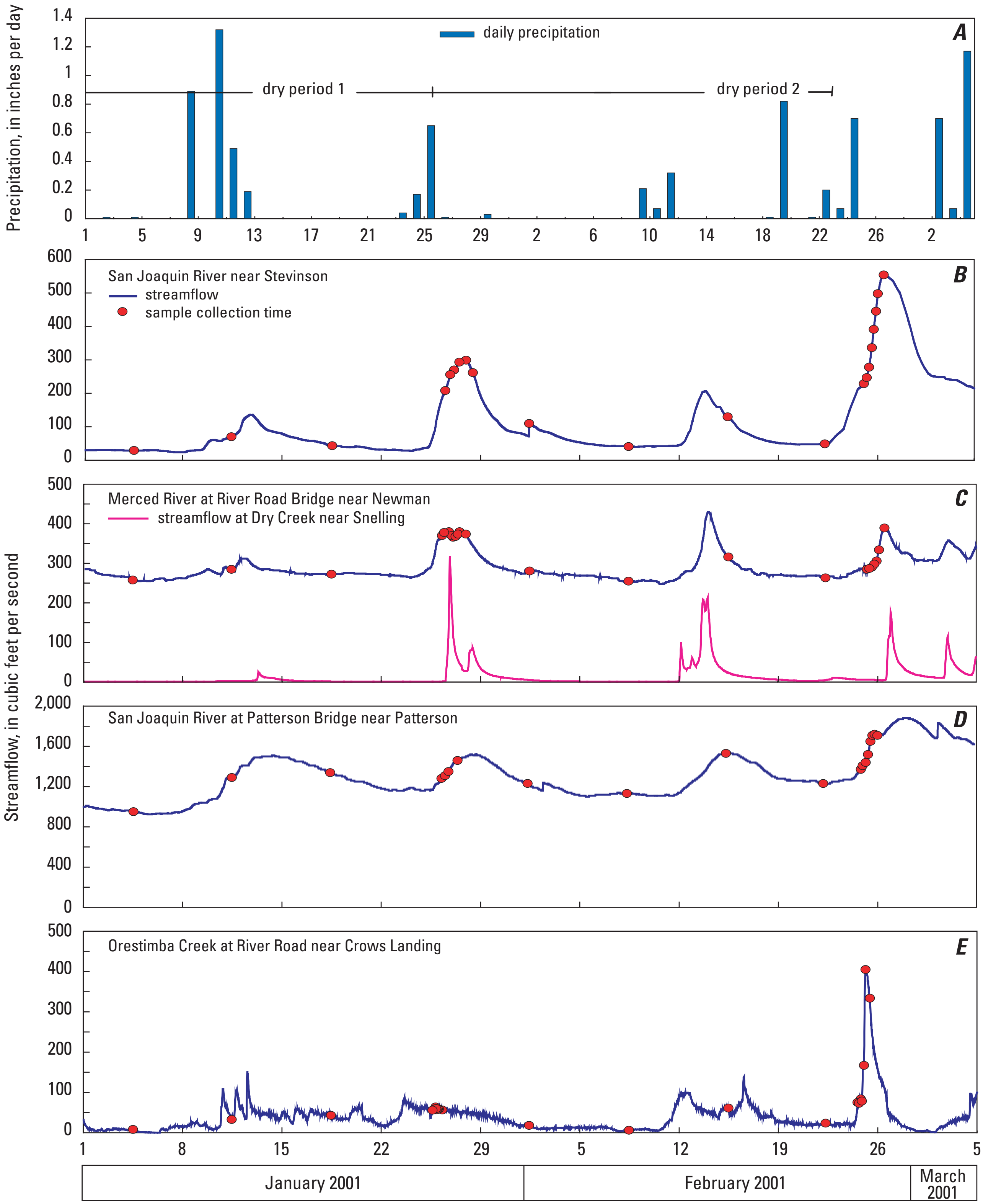


Figure 6. Daily precipitation, and streamflow and sample collection times, at river sites in the San Joaquin River Basin, California. ***A***. Daily precipitation at Modesto, California. B–H. Streamflow and sample collection times. I. Streamflow and sample collection times, and hourly precipitation at the McHenry storm drain site in Modesto, California.

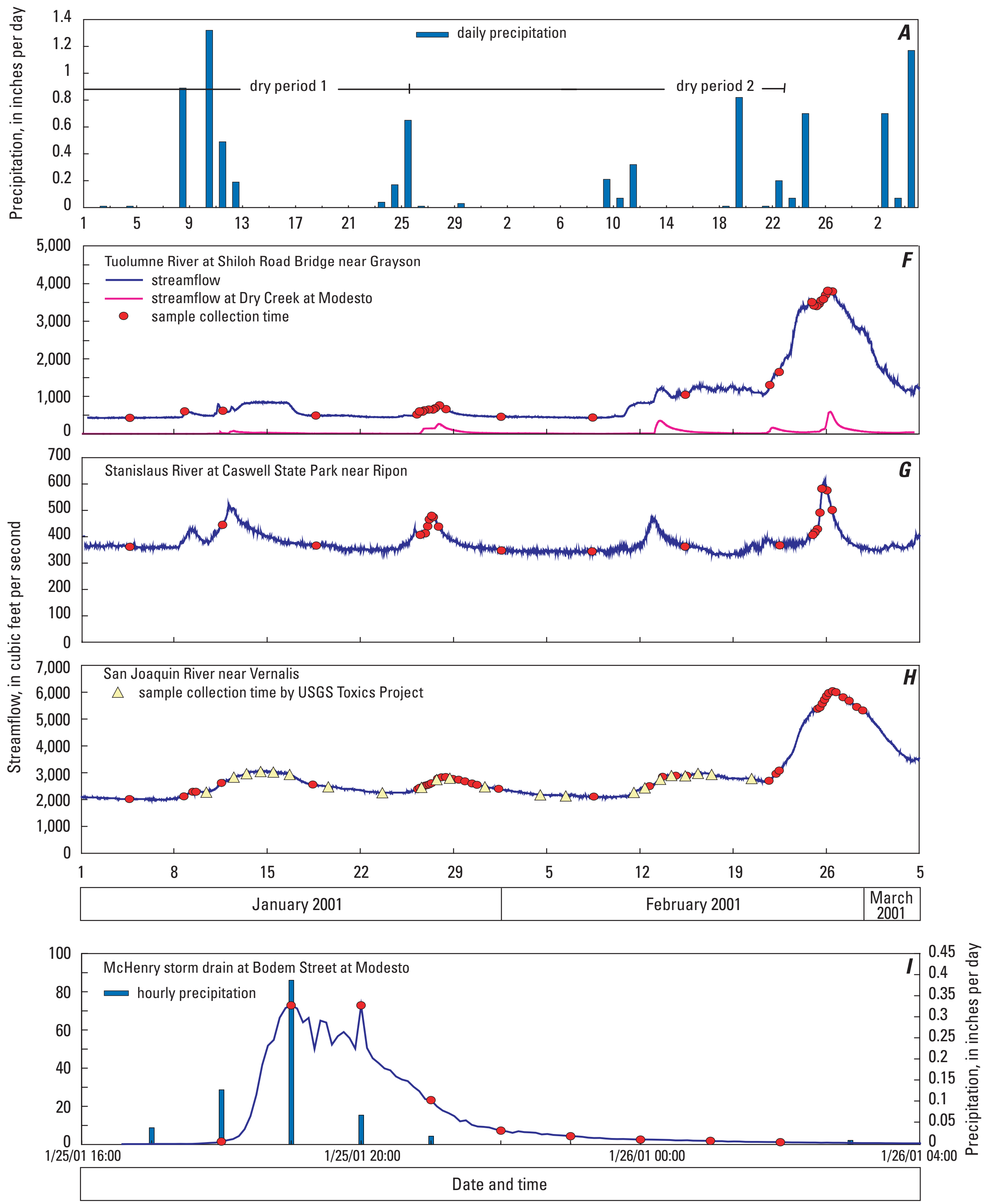


Figure 6.—Continued.

Table 3. Environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for water quality sampling sites in the San Joaquin River Basin, California

[See figure 1A for site locations. Collection method: a "t" following the collection method indicates that the sample was collected by the Toxics Substances Hydrology Program and analyzed at the California District laboratory. Streamflow is in cubic feet per second. IG, integrated grab; MG, midpoint grab; BG, bank grab; P, pumped; EWI, equal-width increment (width- and depth-integrated); AS, autosampler; E, estimate; lb a.i./day, pound active ingredient per day; µg/L, microgram per liter; <, less than]

Site number	Site name	Site identification number	Date and time	Collection method	Streamflow (ft^3/s)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rates (lb a.i/day)	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i/day)
1	San Joaquin River near Stevinson	11260815	1/4/01 1100	IG	29	<0.005	<0.001	E0.003	<0.001
			1/11/01 0950	IG	71	0.009	0.003	E0.004	E0.002
			1/18/01 1240	IG	43	0.131	0.030	E0.003	<0.001
			1/26/01 1230	IG	208	0.289	0.324	0.005	0.006
			1/26/01 2130	IG	256	0.205	0.283	0.007	0.010
			1/27/01 0340	IG	270	0.128	0.186	0.007	0.010
			1/27/01 1210	IG	293	0.156	0.246	E0.005	E0.008
			1/28/01 0000	IG	299	0.150	0.242	0.007	0.011
			1/28/01 1120	IG	262	0.140	0.198	0.006	0.008
			2/1/01 1140	IG	110	0.056	0.033	<0.005	<0.001
			2/8/01 1200	IG	41	0.024	0.005	<0.005	<0.001
			2/15/01 1210	IG	130	0.083	0.058	E0.004	E0.003
			2/22/01 0940	IG	49	0.014	0.004	<0.005	<0.001
			2/25/01 0420	IG	228	0.020	0.025	<0.005	<0.002
			2/25/01 0900	IG	247	0.018	0.024	<0.005	<0.002
			2/25/01 1300	IG	278	0.022	0.033	<0.005	<0.002
			2/25/01 1740	IG	336	0.039	0.071	<0.005	<0.003
			2/25/01 2120	IG	391	0.094	0.198	<0.005	<0.003
			2/26/01 0040	IG	446	0.130	0.312	<0.005	<0.004
			2/26/01 0440	IG	498	0.115	0.309	<0.005	<0.004
			2/26/01 1400	IG	554	0.070	0.209	<0.005	<0.004

Table 3. Environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for water quality sampling sites in the San Joaquin River Basin, California—Continued

Site number	Site name	Site identification number	Date and time	Collection method	Streamflow (ft^3/s)	Diazinon concentration ($\mu g/L$)	Diazinon instantaneous loading rates (lb a.i/day)	Chlorpyrifos concentration ($\mu g/L$)	Chlorpyrifos instantaneous loading rate (lb a.i/day)
4	Merced River at River Road Bridge near Newman	11273500	1/4/01 1150	IG	E258	<0.005	<0.002	E0.002	E0.003
			1/11/01 1020	IG	E285	0.021	0.032	E0.003	E0.005
			1/18/01 1200	IG	E273	0.016	0.024	0.006	0.009
			1/26/01 0710	IG	E370	0.013	0.026	<0.005	<0.003
			1/26/01 1050	IG	E378	0.014	0.029	<0.005	<0.003
			1/26/01 1850	IG	E380	0.050	0.102	0.006	0.012
			1/26/01 2340	IG	E370	0.095	0.189	0.006	0.012
			1/27/01 0200	IG	E366	0.044	0.087	0.008	0.016
			1/27/01 0610	IG	E368	0.047	0.093	0.008	0.016
			1/27/01 1000	IG	E374	0.276	0.556	0.009	0.018
			1/27/01 1250	IG	E380	0.413	0.846	0.010	0.020
			1/27/01 2300	IG	E374	0.435	0.876	0.016	0.032
			2/1/01 1100	IG	E280	0.042	0.063	<0.005	<0.002
			2/8/01 1120	IG	E254	E0.004	E0.005	<0.005	<0.002
			2/15/01 1140	IG	E316	0.068	0.116	0.012	0.020
			2/22/01 0850	IG	E263	E0.004	E0.006	<0.005	<0.002
			2/25/01 0700	IG	E285	E0.004	E0.006	E0.002	E0.003
			2/25/01 1100	IG	E287	E0.004	E0.006	E0.002	E0.003
			2/25/01 1510	IG	E292	0.006	0.009	E0.003	E0.005
			2/25/01 1910	IG	E298	0.016	0.026	E0.002	E0.003
			2/25/01 2310	IG	E306	0.044	0.073	<0.005	<0.002
			2/26/01 0300	IG	E334	0.037	0.067	<0.005	<0.003
			2/26/01 1300	IG	E389	0.025	0.052	<0.005	<0.003

Table 3. Environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for water quality sampling sites in the San Joaquin River Basin, California—Continued

Site number	Site name	Site identification number	Date and time	Collection method	Streamflow (ft^3/s)	Diazinon concentration ($\mu g/L$)	Diazinon instantaneous loading rates (lb a.i/day)	Chlorpyrifos concentration ($\mu g/L$)	Chlorpyrifos instantaneous loading rate (lb a.i/day)
5	Orestimba Creek at River Road near Crows Landing	11274538	1/4/01 1220	MG	7.9	0.023	0.001	<0.005	<0.001
			1/11/01 1050	IG	33	0.038	0.007	0.007	0.001
			1/18/01 1120	MG	43	0.009	0.002	E0.002	E0.001
			1/25/01 1450	IG	56	E0.004	E0.001	<0.005	<0.001
			1/25/01 1800	MG	59	E0.005	E0.002	<0.005	<0.001
			1/25/01 2000	MG	64	0.015	0.005	E0.002	E0.001
			1/25/01 2100	MG	60	0.019	0.006	E0.003	E0.001
			1/25/01 2200	MG	57	0.020	0.006	E0.002	E0.001
			1/26/01 0000	MG	59	0.012	0.004	<0.005	<0.001
			1/26/01 0200	MG	59	0.010	0.003	<0.005	<0.001
			1/26/01 0700	MG	56	0.008	0.002	<0.005	<0.001
			2/1/01 1030	IG	18	0.062	0.006	0.068	0.006
			2/8/01 1100	MG	6.6	0.022	<0.001	<0.005	<0.001
			2/15/01 1110	IG	61	0.041	0.013	<0.005	<0.001
			2/22/01 0830	IG	23	0.024	0.003	<0.005	<0.001
			2/24/01 1430	MG	75	0.020	0.008	<0.005	<0.001
			2/24/01 1630	MG	73	0.018	0.007	<0.005	<0.001
			2/24/01 1930	MG	84	0.017	0.008	<0.005	<0.001
			2/24/01 2120	MG	78	0.022	0.009	<0.005	<0.001
			2/25/01 0030	IG	167	0.032	0.029	<0.005	<0.001
			2/25/01 0330	IG	405	0.015	0.033	0.006	0.013
			2/25/01 1030	IG	334	0.015	0.030	0.007	0.013

Table 3. Environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for water quality sampling sites in the San Joaquin River Basin, California—Continued

Site number	Site name	Site identification number	Date and time	Collection method	Streamflow (ft^3/s)	Diazinon concentration ($\mu g/L$)	Diazinon instantaneous loading rates (lb a.i/day)	Chlorpyrifos concentration ($\mu g/L$)	Chlorpyrifos instantaneous loading rate (lb a.i/day)
6	San Joaquin River at Patterson Bridge near Patterson	11274570	1/4/01 1300	IG	950	0.005	0.026	<0.005	<0.013
			1/11/01 1140	IG	1290	0.023	0.160	E0.004	E0.028
			1/18/01 1050	IG	1340	0.020	0.144	E0.003	E0.022
			1/26/01 830	IG	1280	0.028	0.193	E0.003	E0.021
			1/26/01 1310	IG	1310	0.024	0.169	<0.005	<0.018
			1/26/01 2020	IG	1350	0.020	0.145	<0.005	<0.018
			1/27/01 1100	IG	1460	0.057	0.448	E0.004	E0.031
			2/1/01 1000	IG	1230	0.039	0.258	<0.005	<0.016
			2/8/01 1030	IG	1130	0.010	0.061	E0.002	E0.012
			2/15/01 1040	IG	1530	0.050	0.412	0.005	0.041
			2/22/01 800	IG	1230	0.011	0.073	<0.005	<0.016
			2/24/01 2350	IG	1370	0.010	0.074	<0.005	<0.018
			2/25/01 0300	IG	1410	0.011	0.084	<0.005	<0.019
			2/25/01 0800	IG	1440	0.014	0.109	<0.005	<0.019
			2/25/01 1200	IG	1520	0.016	0.131	<0.005	<0.020
			2/25/01 1620	IG	1650	0.012	0.107	<0.005	<0.022
			2/25/01 2000	IG	1710	0.011	0.101	E0.004	E0.037
			2/25/01 2350	IG	1720	0.012	0.111	<0.005	<0.023
			2/26/01 0340	IG	1710	0.012	0.111	<0.005	<0.023
8	McHenry Storm drain at Bodem Street at Modesto	373847120590801	1/25/01 1800	AS	1.56	0.506	0.004	<0.050	<0.001
			1/25/01 1900	AS	72.9	0.947	0.372	0.023	0.009
			1/25/01 2000	AS	44.8	0.922	0.222	0.035	0.008
			1/25/01 2100	AS	23.3	0.708	0.089	0.033	0.004
			1/25/01 2200	AS	7.25	0.691	0.027	0.031	0.001
			1/25/01 2300	AS	4.35	0.727	0.017	0.033	0.001
			1/26/01 0000	AS	2.56	0.756	0.010	0.018	<0.001
			1/26/01 0100	AS	1.89	0.761	0.008	0.023	<0.001
			1/26/01 0200	AS	1.21	0.823	0.005	0.033	<0.001

Table 3. Environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for water quality sampling sites in the San Joaquin River Basin, California—Continued

Site number	Site name	Site identification number	Date and time	Collection method	Streamflow (ft^3/s)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rates (lb a.i/day)	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i/day)
9	Tuolumne River at Shiloh Road Bridge near Grayson	11290200	1/4/01 1350	IG	E430	E0.005	E0.012	E0.004	E0.009
			1/8/01 1630	IG	E595	0.039	0.125	<0.005	<0.005
			1/11/01 1240	IG	E602	0.135	0.438	0.009	0.029
			1/18/01 1340	IG	E482	E0.005	E0.013	0.008	0.021
			1/26/01 0500	IG	E519	0.035	0.098	0.007	0.020
			1/26/01 0910	IG	E603	0.201	0.653	0.007	0.023
			1/26/01 1500	IG	E592	0.108	0.344	0.008	0.026
			1/26/01 1820	IG	E631	0.123	0.418	0.010	0.034
			1/27/01 0200	IG	E646	0.026	0.090	E0.005	E0.017
			1/27/01 0930	IG	E650	0.022	0.077	0.005	0.018
			1/27/01 1330	IG	E688	0.022	0.082	0.006	0.022
			1/27/01 2100	IG	E756	0.035	0.143	0.006	0.024
			1/28/01 0900	IG	E657	0.027	0.096	E0.005	E0.018
			2/1/01 1240	IG	E458	0.008	0.020	E0.002	E0.005
			2/8/01 0950	IG	E433	<0.005	<0.003	E0.002	E0.004
			2/15/01 0950	IG	E1040	E0.005	E0.028	<0.005	<0.008
			2/21/01 1800	IG	E1300	0.007	0.049	<0.005	<0.011
			2/22/01 1040	IG	E1640	E0.004	E0.035	<0.005	<0.013
			2/24/01 2200	IG	E3510	0.006	0.113	<0.005	<0.028
			2/25/01 0200	IG	E3420	E0.005	E0.092	<0.005	<0.028
			2/25/01 0700	IG	E3400	0.006	0.110	<0.005	<0.027
			2/25/01 1100	IG	E3460	E0.004	E0.075	<0.005	<0.028
			2/25/01 1510	IG	E3550	E0.004	E0.077	<0.005	<0.029
			2/25/01 1900	IG	E3590	E0.004	E0.077	<0.005	<0.029
			2/25/01 2310	IG	E3700	0.006	0.120	<0.005	<0.030
			2/26/01 0300	IG	E3810	E0.005	E0.103	<0.005	<0.031
			2/26/01 1100	IG	E3790	E0.003	E0.061	<0.005	<0.031

Table 3. Environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for water quality sampling sites in the San Joaquin River Basin, California—Continued

Site number	Site name	Site identification number	Date and time	Collection method	Streamflow (ft^3/s)	Diazinon concentration (μg/L)	Diazinon instantaneous loading rates (lb a.i/day)	Chlorpyrifos concentration (μg/L)	Chlorpyrifos instantaneous loading rate (lb a.i/day)
12	Stanislaus River at Caswell State Park near Ripon	374209121103800	1/4/01 1520	BG	E360	0.005	0.010	0.038	0.074
			1/11/01 1330	BG	E445	0.051	0.122	0.012	0.029
			1/18/01 1430	BG	E366	0.018	0.035	E0.002	E0.004
			1/26/01 1010	BG	E407	0.067	0.147	0.006	0.013
			1/26/01 1930	BG	E413	0.054	0.120	0.006	0.013
			1/27/01 000	BG	E439	0.072	0.170	0.007	0.017
			1/27/01 0300	BG	E466	0.053	0.133	0.007	0.018
			1/27/01 0700	BG	E479	0.081	0.209	0.006	0.015
			1/27/01 1020	BG	E475	0.083	0.212	0.007	0.018
			1/27/01 2000	BG	E437	0.058	0.137	0.006	0.014
			2/1/01 1320	BG	E348	0.006	0.011	<0.005	<0.003
			2/8/01 0850	BG	E343	<0.005	<0.003	<0.005	<0.003
			2/15/01 0900	BG	E362	0.007	0.014	<0.005	<0.003
			2/22/01 1120	BG	E367	0.007	0.014	<0.005	<0.003
			2/24/01 2310	BG	E407	0.026	0.057	<0.005	<0.003
			2/25/01 0300	BG	E415	0.018	0.040	<0.005	<0.003
			2/25/01 0800	BG	E428	0.017	0.039	<0.005	<0.003
			2/25/01 1200	BG	E491	0.026	0.069	<0.005	<0.004
			2/25/01 1600	BG	E581	0.014	0.044	0.011	0.034
			2/26/01 0010	BG	E577	0.027	0.084	E0.002	E0.006
			2/26/01 1000	BG	E501	0.010	0.027	<0.005	<0.004
13	San Joaquin River near Vernalis	11303500	1/4/01 1440	IG	2020	E0.003	E0.033	<0.005	<0.016
			1/8/01 1720	IG	2120	E0.004	E0.046	E0.003	E0.034
			1/9/01 0900	IG	2290	0.024	0.296	<0.005	<0.019
			1/9/01 1450	IG	2290	0.041	0.506	E0.003	E0.037
			1/10/01 0915	IG-t	2280	0.014	0.172	<0.004	<0.025
			1/11/01 1300	IG	2620	0.031	0.438	E0.004	E0.056
			1/12/01 1105	IG-t	2840	0.044	0.673	<0.004	<0.031
			1/13/01 1005	IG-t	2970	0.039	0.624	<0.004	<0.032

Table 3. Environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for water quality sampling sites in the San Joaquin River Basin, California—Continued

Site number	Site name	Site identification number	Date and time	Collection method	Streamflow (ft^3/s)	Diazinon concentration (μg/L)	Diazinon instantaneous loading rates (lb a.i/day)	Chlorpyrifos concentration (μg/L)	Chlorpyrifos instantaneous loading rate (lb a.i/day)
13	San Joaquin River near Vernalis—continued	11303500	1/14/01 1130	IG-t	3050	0.029	0.477	<0.004	<0.033
			1/15/01 1030	IG-t	3030	0.020	0.326	<0.004	<0.033
			1/16/01 1545	IG-t	2940	0.021	0.333	0.010	0.158
			1/18/01 0940	IG	2560	0.019	0.262	0.006	0.083
			1/19/01 1330	IG-t	2480	0.007	0.094	0.016	0.214
			1/23/01 1515	IG-t	2260	0.017	0.207	0.008	0.097
			1/26/01 0710	IG	2390	0.020	0.258	0.006	0.077
			1/26/01 1100	IG	2440	0.028	0.368	0.007	0.092
			1/26/01 1345	IG-t	2460	0.043	0.570	0.018	0.239
			1/26/01 1710	IG	2490	0.104	1.400	0.009	0.121
			1/26/01 2030	IG	2520	0.073	0.991	0.008	0.109
			1/27/01 0040	IG	2540	0.168	2.300	E0.004	E0.055
			1/27/01 0400	IG	2570	0.172	2.380	0.007	0.097
			1/27/01 0800	IG	2610	0.201	2.830	0.007	0.098
			1/27/01 1710	P-t	2750	0.141	2.089	<0.004	<0.030
			1/27/01 1900	IG	2780	0.206	3.080	0.006	0.090
			1/28/01 0200	IG	2830	0.235	3.580	0.005	0.076
			1/28/01 0950	IG	2840	0.200	3.060	0.010	0.153
			1/28/01 1650	P-t	2800	0.170	2.565	0.015	0.226
			1/28/01 2230	IG	2770	0.220	3.283	0.007	0.104
			1/29/01 0900	IG	2740	0.224	3.307	0.005	0.074
			1/29/01 2020	IG	2680	0.185	2.670	0.006	0.087
			1/30/01 0900	IG	2600	0.141	1.980	0.006	0.084
			1/30/01 1800	IG	2550	0.126	1.730	E0.004	E0.055
			1/31/01 0800	IG-t	2480	0.058	0.775	<0.004	<0.027
			2/1/01 0900	IG	2400	0.035	0.452	<0.005	<0.019
			2/4/01 1200	IG-t	2180	0.025	0.294	<0.004	<0.023

Table 3. Environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for water quality sampling sites in the San Joaquin River Basin, California—Continued

Site number	Site name	Site identification number	Date and time	Collection method	Streamflow (ft³/s)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rates (lb a.i/day)	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i/day)
13	San Joaquin River near Vernalis—continued	11303500	2/6/01 1005	IG-t	2140	0.024	0.277	0.013	0.150
			2/8/01 1300	IG	2110	0.008	0.091	E0.002	E0.023
			2/11/01 1315	IG-t	2270	0.025	0.306	<0.004	<0.024
			2/12/01 0845	IG-t	2440	0.026	0.342	<0.004	<0.026
			2/12/01 1730	IG	2500	0.028	0.377	E0.002	E0.027
			2/13/01 1230	IG-t	2760	<0.004	<0.030	<0.004	<0.030
			2/13/01 1710	IG	2850	0.117	1.800	0.012	0.184
			2/14/01 0845	IG-t	2900	0.024	0.375	<0.004	<0.031
			2/14/01 1700	IG	2890	0.019	0.296	<0.005	<0.023
			2/15/01 0945	IG-t	2890	0.024	0.374	<0.004	<0.031
			2/15/01 1320	IG	2890	0.024	0.374	<0.005	<0.023
			2/16/01 0900	IG-t	2980	0.014	0.225	0.014	0.225
			2/17/01 0920	IG-t	2940	0.006	0.095	<0.004	<0.032
			2/20/01 0930	IG-t	2790	0.007	0.105	<0.004	<0.030
			2/21/01 1700	IG	2700	0.012	0.175	<0.005	<0.022
			2/22/01 600	IG	2960	0.012	0.191	<0.005	<0.024
			2/22/01 1150	IG	3080	0.010	0.166	<0.005	<0.025
			2/25/01 0900	IG	5380	0.013	0.377	<0.005	<0.043
			2/25/01 1300	IG	5430	0.010	0.293	<0.005	<0.044
			2/25/01 1730	IG	5580	0.011	0.331	<0.005	<0.045
			2/25/01 2110	IG	5720	0.010	0.308	<0.005	<0.046
			2/26/01 0110	IG	5860	0.007	0.221	<0.005	<0.047
			2/26/01 0500	IG	5970	0.009	0.289	<0.005	<0.048
			2/26/01 1200	IG	6040	0.013	0.423	<0.005	<0.049
			2/26/01 1800	IG	6000	0.010	0.323	<0.005	<0.048
			2/27/01 0700	IG	5810	0.006	0.188	<0.005	<0.047
			2/27/01 1740	IG	5680	0.007	0.214	<0.005	<0.046
			2/28/01 0730	IG	5450	0.010	0.294	<0.005	<0.044
			2/28/01 1830	IG	5320	0.012	0.344	<0.005	<0.043

Urban storm runoff samples were collected from a city storm drain in Modesto on an hourly basis beginning on January 25 at 6 p.m. and ending on January 26 at 2 a.m. using an autosampler outfitted with a pressure transducer that measured water depth (fig. 6I). The storm sampling at this location was designed to determine the occurrences and concentrations of pesticides in urban storm-water runoff and to compare the results with those of agricultural sites and precipitation.

The purpose of collecting precipitation samples was to encompass an area that included both urban and agricultural land use so that the occurrence and concentrations of diazinon and chlorpyrifos in the atmosphere could be compared. Precipitation samples were collected at eight locations (fig. 2: sites A–H). Agricultural site locations (sites A, D, F, and H) were chosen to give good spatial representation of almond and stone-bearing fruit orchards outside of Modesto. The urban sites (sites B, C, E, G) were placed throughout Modesto to give good spatial representation of the urban area. Sites E and F were unlike the other precipitation collecting sites because they had wet–dry autosamplers. These samplers have a sensory unit that detects both wet and dry conditions. During dry periods, a container remains open to collect dry deposition from the atmosphere and, at the onset of precipitation, the apparatus closes the dry deposition collection container and opens a container for collecting precipitation. Two of these samplers were used in this study—one in an agricultural land-use area and one in an urban land-use area.

The sampling strategy for collecting precipitation was to set out the collecting apparatus at the locations before a forecasted storm event. The accumulated precipitation was then retrieved after the event. The total precipitation for time intervals of interest during storm periods was taken from a precipitation gage that collected hourly precipitation data located atop the Modesto Irrigation District office roof at 1231 Eleventh Street in downtown Modesto. Precipitation accumulations at each of the eight sites were calculated on the basis of the total volume of precipitation collected and the surface area of the collection unit. Of the three storms that were sampled for the precipitation segment of the study, only the January 23–26 storm was sampled at all eight sites.

SAMPLING AND ANALYTICAL METHODS

Sampling Methods

Samples from the January 23–26, 2001, and February 18–24, 2001, target storm periods at the river sites were collected in five different manners depending on the site and streamflow conditions. The five methods are (1) width- and depth-integrated using a D-77 isokinetic sampler with a Teflon nozzle bottle (Webb and others, 1999); (2) equally spaced, three-point integrated grab using a 3-L Teflon bottle strapped into a metal cage suspended by a rope; (3) midpoint grab using the same sampler; (4) grab sample from the bank using a 3-L Teflon bottle; and (5) directly pumped into a 1-L amber glass bottles using a peristaltic pump equipped with a stainless steel and Teflon inlet hose suspended in mid-channel. Most samples were collected as integrated grabs or midpoint grabs. In the first storm, samples were collected using both width- and depth-integrated and three-point integrated methods at the San Joaquin River near Vernalis and the Merced River at River Road sites. Samples were collected by both methods at these two sites within ten minutes of one another to check for sampling method variability. Samples from the Stanislaus River at Caswell State Park were collected from the right bank because this site does not have a bridge. The sample collection method for this site involved strapping a 3-L Teflon bottle into the cage sampler and tossing the sampler from the right bank into the main channel. All samples collected in a 3-L Teflon bottle from various methods described above were then directly poured into three separate sterile 1-L amber glass bottles, capped, and stored on ice.

The McHenry storm drain site was sampled using an autosampler equipped with Teflon tubing and a rack with twenty-four 1-L glass bottles. Discharge was determined from water-depth data that was collected using a pressure transducer attached to the autosampler, then converted to discharge using a depth-discharge relation provided by the City of Modesto staff.

Except for sites E and F (fig. 2), precipitation samples were collected using a 4-L amber glass bottle below a 31-cm diameter funnel enclosed in a 12-in. by 36-in. segment of plastic pipe. The collection apparatus was set out before a precipitation event; at the end of a precipitation event, the samples were capped, collected, and stored on ice. The sample volume was measured using a graduated cylinder at the USGS California District Laboratory in Sacramento, California (hereinafter referred to as the “USGS laboratory”). For samples collected by the wet–dry automatic samplers, the 27-cm diameter collection containers were connected to Teflon tubing and drained into a 4-L glass amber bottle that was collected and measured in the same manner as the other precipitation samples.

The 3-L Teflon sample-collection bottle was cleaned after use at each site using the following protocol. After sampling a site, the sample bottle was rinsed with deionized water. Approximately 30 mL of dilute Liquinox solution was then placed into the sample bottle, and it was capped and shaken. The Liquinox solution was then completely rinsed with deionized water followed by adding approximately 30 mL of methanol to the sample bottle, and it was capped and shaken. The methanol rinse was emptied into a waste container. The final step in the cleaning procedure was to rinse the sample bottle thoroughly with deionized water. At the next site, the sample bottle was rinsed three times with native water before collecting the sample. The autosampler used to collect storm-water runoff at McHenry storm drain was cleaned with Liquinox solution and rinsed with deionized water by the City of Modesto staff prior to deployment. The precipitation collection equipment—the 4-liter amber glass bottles, funnels, collection buckets, and Teflon tubing—was cleaned after each storm event at the USGS laboratory using the same cleaning protocol that was used for the 3-L Teflon sample collection bottles.

Analytical Methods

The samples collected for this study were stored on ice and shipped overnight for analysis to the National Water Quality Laboratory (NWQL) in Denver, Colorado, within three days of collection. Samples collected by the Toxics Program were analyzed at the USGS laboratory. Samples sent to the NWQL were analyzed for two suites of pesticides: USGS laboratory schedule 2001 and USGS laboratory schedule 1319. The samples for schedule 2001 are filtered prior to analysis, whereas the samples for schedule 1319 are not. A total of 220 environmental samples collected at the river sites were analyzed at NWQL. Of this total, 198 were analyzed for schedule 2001, whereas 22 samples at selected river sites were analyzed for both schedules 2001 and 1319. These 22 samples were generally selected on the rising limb of the hydrographs for the selected sites.

The samples analyzed for schedule 2001 were filtered, extracted, and analyzed at NWQL for 45 dissolved pesticides. These samples were filtered through a baked 0.7-micron glass-fiber filter. The dissolved pesticides were extracted by a solid-phase extraction (SPE) cartridge containing porous silica coated with a C-18 phase and preconditioned with methanol. The absorbed pesticides and degradates were removed from the cartridges by elution with ethyl acetate. Extracts of the effluent were analyzed by a capillary-column gas chromatograph/mass spectrometer (GC/MS) operated in the selected-ion monitoring mode (Zaugg and others, 1995).

The samples selected for laboratory schedule 1319 were analyzed for 11 pesticides at NWQL. This laboratory schedule involves using hexane to extract the pesticides from whole-water (unfiltered) with a separatory funnel. The extracts are then concentrated using a Kuderna-Danish apparatus and nitrogen gas (Wershaw and others, 1987). Following solvent reduction, the pesticides are analyzed by dual capillary-column gas chromatography with flame photometric detection (GC/FPD). Samples analyzed by the USGS laboratory were also filtered through a baked 0.7 micron glass-fiber filter. However, the USGS laboratory uses SPE cartridges with a C-8 bonded phase, not preconditioned, to isolate the pesticide from water. The cartridges are eluted with 9 mL of ethyl acetate and analyzed using a capillary-column GC/MS operated in full-scan mode (Orlando and others, 2003).

Table 4 lists the concentrations of diazinon and chlorpyrifos for sites that were chosen for analysis using laboratory schedules 2001 and 1319, as well as the relative percent difference (RPD) between the two analytical methods. The relative percent difference is used to describe the variability between the two analytical methods. An RPD could not be calculated for diazinon and chlorpyrifos values less than the laboratory reporting level. Theoretically, the whole-water samples (schedule 1319) should have higher concentrations than the filtered samples (schedule 2001) if the pesticides were partially associated with suspended sediments. This would particularly be expected in the case of chlorpyrifos as it readily sorbs to sediments. Comparison of reported concentrations from each method must take into account the differences in both reporting level and method performance. The diazinon and chlorpyrifos median recoveries from laboratory reagent water spike samples in schedule 1319 are 66 percent and 70 percent, compared with 93 percent and 84 percent for laboratory schedule 2001, respectively. The relative percent differences for these median recoveries are 34 percent for diazinon and 18 percent for chlorpyrifos. The chlorpyrifos concentrations reported by schedule 2001 for most samples listed in table 4 are below the higher schedule 1319 reporting level. For two samples with data reported from both methods, the chlorpyrifos data are comparable (within the expected method performance differences and variability). This is also the case for most of the diazinon concentrations reported by both methods. For several samples, the differences in diazinon concentrations reported by the two methods are substantially greater (>80 percent RPD) than expected on the basis of laboratory spike recovery differences. Interestingly, diazinon concentrations in schedule 2001 are all greater than schedule 1319, suggesting the amount of pesticide associated with suspended sediment in the whole water samples (schedule 1319) likely was small.

The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99 percent confidence that the analyte concentration is greater than zero. The MDL for laboratory schedule 2001 for diazinon and chlorpyrifos at NWQL is 0.003 μg /L with a 95 percent confidence level range of 0.0020 to 0.0036 for water year 2001. The MDL for laboratory schedule 1319 for water year 2001 is 0.010 μg /L for diazinon (95 percent confidence level range of 0.0098 to 0.0183) and 0.007 μg /L for chlorpyrifos (95 percent confidence level range of 0.0070 to 0.0131). Although the risk of reporting a false positive using the MDL is less than 1 percent, the probability of reporting a false negative is as much as 50 percent (that is, the analyte is reported as not present when it is present at the MDL) (Childress and others, 1999). To correct for the risk of reporting a false positive, NWQL uses a long-term method detection level for the MDL, which is based on a modification of the USEPA MDL procedure. NWQL sets a laboratory reporting level (LRL) at twice the MDL to reduce the probability of false negatives to less than one percent (Childress and others, 1999). These LRL values are reevaluated each year on the basis of the most recent quality control data and, consequently, may change from year to year. The LRL for both diazinon and chlorpyrifos for water year 2001 is 0.005 μg/L. Sample concentrations with a "<" (less than) qualifier are reported as less than the LRL (<0.005 μg/L) in table 3. Data reported as less than the LRL are those that were either not detected, failed the identification criteria, or were detected at a concentration less than the MDL when the risk of false positive exceeds 1 percent (Childress and others, 1999). However many of the concentrations reported as less than the LRL may actually be low-level detections near the MDL. For this study, half the MDL value (0.0015 μg/L) for both diazinon and chlorpyrifos was used for calculating instantaneous loads to have maximum information available for calculating loads and to be consistent with the method for calculating loads in a similar study in the same study area during water year 2000 (Kratzer and others, 2002).

Additionally, several diazinon and chlorpyrifos concentrations are reported as estimated, denoted by an "E" code in table 3. These samples have confirmed detections of the pesticides, but the concentrations are estimated because they are between the MDL and LRL or have some interference in the sample matrix (Childress and others, 1999). Laboratory schedule 2001 is considered an information-rich analytical method by NWQL, resulting in better qualitative identification. As a result, information-rich methods are not restricted to censoring all measurements below the MDL and, therefore, positively identified analytes below the MDL are reported as estimated ("E" remark code) if other quality control criteria are met (Childress and others, 1999). Several concentrations are reported with an "E" code below the MDL for chlorpyrifos in table 3.

Table 4. Comparison of diazinon and chlorpyrifos concentrations using laboratory schedules 1319 and 2001 for selected sites in the San Joaquin River Basin, California

[E, estimate; NA, not applicable; RPD, relative percent difference; µg/L, microgram per liter; <, less than]

Site identification number	Station name	Date and time	Laboratory schedule	Diazinon concentration (µg/L)	RPD	Chlorpyrifos concentration (µg/L)	RPD
11260815	San Joaquin River near Stevinson	1/26/01 1230	1319	0.212	30.7	<0.014	NA
			2001	0.289		0.005	
		1/26/01 2130	1319	0.140	37.7	<0.014	NA
			2001	0.205		0.007	
		2/25/01 1740	1319	0.031	22.8	<0.014	NA
			2001	0.039		<0.005	
11273500	Merced River at River Road Bridge near Newman	2/25/01 0700	1319	<0.020	NA	<0.014	NA
			2001	E0.004		E0.002	
		2/25/01 1510	1319	E0.004	40	<0.014	NA
			2001	0.006		E0.003	
11274538	Orestimba Creek at River Rd near Crows Landing	1/25/01 2200	1319	E0.010	66.7	<0.014	NA
			2001	0.020		E0.002	
		1/26/01 0200	1319	E0.008	22.2	<0.014	NA
			2001	0.010		<0.005	
		2/24/01 1430	1319	E0.003	150	<0.056	NA
			2001	0.021		<0.005	
		2/24/01 1930	1319	E0.012	34.4	<0.014	NA
			2001	0.017		<0.005	

Table 4. Comparison of diazinon and chlorpyrifos concentrations using laboratory schedules 1319 and 2001 for selected sites in the San Joaquin River Basin, California—*Continued*

Site identification number	Station name	Date and time	Laboratory schedule	Diazinon concentration (μg/L)	RPD	Chlorpyrifos concentration (μg/L)	RPD
11274570	San Joaquin River at Patterson Bridge near Patterson	1/26/01 2020	1319	E0.013	42.4	<0.014	NA
			2001	0.020		<0.005	
		2/25/01 0800	1319	E0.006	80	<0.014	NA
			2001	0.014		<0.005	
		2/25/01 1620	1319	E0.005	82.3	<0.014	NA
			2001	0.012		<0.005	
11290200	Tuolumne River at Shiloh Road Bridge near Grayson	1/26/01 0910	1319	0.160	22.7	E0.010	35.3
			2001	0.201		0.007	
		1/26/01 1820	1319	0.086	35.4	<0.014	NA
			2001	0.123		0.010	
		2/25/01 0700	1319	E0.006	0	<0.014	NA
			2001	0.006		<0.005	
		2/25/01 1510	1319	<0.020	NA	<0.014	NA
			2001	E0.004		<0.005	
11303500	San Joaquin River near Vernalis	1/27/01 0400	1319	0.130	27.8	<0.014	NA
			2001	0.172		0.007	
		2/25/01 900	1319	E0.01	26.1	<0.014	NA
			2001	0.013		<0.005	
		2/25/01 1730	1319	E0.007	44.4	<0.014	NA
			2001	0.011		<0.005	

Table 4. Comparison of diazinon and chlorpyrifos concentrations using laboratory schedules 1319 and 2001 for selected sites in the San Joaquin River Basin, California—*Continued*

Site identification number	Station name	Date and time	Laboratory schedule	Diazinon concentration (μg/L)	RPD	Chlorpyrifos concentration (μg/L)	RPD
374209121103800	Stanislaus River at Caswell State Park near Ripon	1/26/01 1010	1319	0.049	31	<0.014	NA
			2001	0.067		0.006	
		2/25/01 0800	1319	E0.012	34.4	<0.014	NA
			2001	0.017		<0.005	
		2/25/01 1600	1319	E0.010	33.3	E0.013	16.6
			2001	0.014		0.011	

The USGS laboratory method for determination of the MDL is based on the USEPA procedures (U.S. Environmental Protection Agency, 1997) and is described as the minimum concentration of a substance that can be measured and reported with 99 percent confidence that the analyte concentration is greater than zero. MDLs are compound, matrix, and method dependent; therefore, at the USGS laboratory, MDLs are estimated in the same matrices as most of the samples. In 2001 and 2002, the most common sample matrices were obtained from the Sacramento and San Joaquin Rivers; thus, MDLs are calculated in three different matrices (water from the Sacramento and San Joaquin Rivers and organic free water). For each MDL calculation, seven or eight replicate samples were spiked at a concentration of 10 ng/L and analyzed with an unspiked matrix sample. For San Joaquin River water, the MDL for diazinon and chlorpyrifos at the USGS laboratory was 0.0036 µg/L and 0.0042 µg/L, respectively, in water year 2001 (Kathryn Kuivila, U.S. Geological Survey, written communication, 2002).

In a linear regression using 21 replicate splits between NWQL and the USGS laboratory, NWQL values for diazinon were higher by 10 percent for the best fit line with an R^2 value of 0.97 (Kathryn Kuivila, U.S. Geological Survey, written communication, 2002). Therefore, diazinon concentrations for samples collected by the USGS Toxics Program at the San Joaquin River at Vernalis site during January and February 2001 were multiplied by 1.1 for use in this paper. A similar relation was found using 25 splits in a study by Kratzer in 1994 (Kratzer and Biagtan, 1997) where NWQL values were higher by 26 percent with a R^2 value of 0.98. The USGS laboratory MDL for diazinon (0.0036 µg/L) was also multiplied by 1.1, and half this value (0.0018 µg/L) was used in calculating loads for diazinon concentrations reported as less than the MDL.

A similar relationship could not be produced for chlorpyrifos because analytical replicate splits with detections above the USGS laboratory's MDL and NWQL's LRL were variable. In water years 2001 and 2002, a total of 39 replicate splits were analyzed for organophosphorus pesticides at both the USGS laboratory and NWQL. The analytical results of chlorpyrifos included four detections at both laboratories, five detections at only NWQL, and one detection at only the USGS laboratory. Although the detected concentrations for chlorpyrifos varied between the two laboratories, there was good agreement on nondetections in 29 of the 39 replicate splits. As a result, only those with chlorpyrifos concentrations below the USGS laboratory's MDL are used in this report. Table 3 lists several chlorpyrifos concentrations as less than the MDL (<0.004 µg/L) of the USGS laboratory. Half this value (0.002 µg/L) was used for the calculation of chlorpyrifos loads at the San Joaquin River near Vernalis site. Samples with no chlorpyrifos concentration values listed in table 3 are those whose values were above the MDL at the USGS laboratory and are not used in this report.

QUALITY CONTROL SAMPLES

Collection of quality control (QC) samples is necessary to evaluate the quality of the data. QC samples are collected, usually at the field site, in order to identify, quantify, and document bias and variability in data resulting from the collection, processing, shipping, and handling of samples by field and laboratory personnel (Wilde and others, 1998, p. 91). During the weekly sampling and the storm sampling events in January and February, 22 QC samples were collected out of a total of 251 (environmental and QC samples): 16 samples for standard QC sample testing (table 5) and 6 samples for comparison sampling methods (table 6). Of these 22 QC samples, 18 were field QC samples and 4 were laboratory QC samples. Four different types of field QC samples were collected in this study: field blanks, equipment blanks, split replicates, and sequential replicate samples that compared collection methods. The laboratory QC samples were laboratory-spiked environmental samples. All QC samples collected and reported in this study were analyzed at NWQL.

Table 5. Summary of quality control data on diazinon and chlorpyrifos concentrations for sites in the San Joaquin River Basin, California

[For replicates and spikes, first sample in each pair is the environmental sample, second sample is the quality control sample. E, estimate; NA, not applicable, cannot be calculated because of "less than" concentration; µg/L, microgram per liter; —, no data available; <, less than]

Site identification number	Site name	Date and time	Diazinon (µg/L)	Relative percent difference or percent recovery (diazinon)	Chlorpyrifos (µg/L)	Relative percent difference or percent recovery (chlorpyrifos)
REPLICATES						
11273500	Merced River at River Road Bridge near Newman	2/25/01 1100	E0.004	0	E0.003	NA
		2/25/01 1101	E0.004		<0.005	
11303500	San Joaquin River near Vernalis	1/26/01 1100	0.028	25	0.007	0
		1/26/01 1101	0.036		0.007	
		1/26/01 1710	0.104	12.2	0.009	11.7
		1/26/01 1711	0.092		0.008	
		2/15/01 1320	0.024	8.0	<0.005	NA
		2/15/01 1321	0.026		<0.005	
		2/25/01 1300	0.010	5.3	<0.005	NA
		2/25/01 1301	0.009		<0.005	
FIELD BLANKS						
11274538	Orestimba Creek at River Road near Crows Landing	1/18/01 1128	<0.005	NA	<0.005	NA
11260815	San Joaquin River near Stevinson	2/25/01 428	<0.005	NA	<0.005	NA
11273500	Merced River at River Road Bridge near Newman	2/25/01 2318	<0.005	NA	<0.005	NA

Table 5. Summary of quality control data on diazinon and chlorpyrifos concentrations for sites in the San Joaquin River Basin, California.—*Continued*

Site identification number	Site name	Date and time	Diazinon (µg/L)	Relative percent difference or percent recovery (diazinon)	Chlorpyrifos (µg/L)	Relative percent difference or percent recovery (chlorpyrifos)
373847120590801	McHenry storm drain at Bodem Street at Modesto	1/25/01 2108	<0.005	NA	<0.005	NA
374209121103800	Stanislaus River at Caswell State Park near Ripon	2/26/01 018	<0.005	NA	<0.005	NA
EQUIPMENT BLANKS						
373847120590801	McHenry storm drain at Bodem Street at Modesto	1/23/01 2358	<0.005	NA	<0.005	NA
		1/25/01 1308	<0.005	NA	<0.005	NA
SPIKES						
11303500	San Joaquin River near Vernalis	1/18/01 940	0.019	110.4	0.006	95.2
		1/18/01 943	0.135		0.106	
11290200	Tuolumne River at Shiloh Road Bridge near Grayson	2/25/01 200	E0.005	81.2	<0.005	78
		2/25/01 203	0.092		0.086	
		2/26/01 1100	E0.003	103.4	<0.005	95.9
		2/26/01 1103	0.120		0.111	
374209121103800	Stanislaus River at Caswell State Park, near Ripon	1/27/01 700	0.081	120.9	0.006	104.7
		1/27/01 703	0.208		0.116	

Table 6. Comparison of diazinon and chlorypyrifos concentrations using Equal Width Increment and Integrated Grab collection methods for selected sites in the San Joaquin River Basin, California

[E, estimate; EWI, equal width increment; IG, integrated grab; NA, not applicable; RPD, relative percent difference, µg/L, microgram per liter; <, less than.

Site identification number	Site name	Date and time	Collection method	Diazinon concentration (µg/L)	RPD	Chlorpyrifos concentration (µg/L)	RPD
11273500	Merced River at River Road Bridge near Newman	1/11/2001 1020	IG	0.021	9.1	E0.003	28.6
		1/11/2001 1030	EWI	0.023		E0.004	
		1/26/01 0710	IG	0.013	7.4	<0.005	NA
		1/26/01 0700	EWI	0.014		<0.005	
		1/26/01 1050	IG	0.014	25	<0.005	NA
		1/26/01 1100	EWI	0.018		<0.005	
		2/8/01 1120	IG	E0.004	NA	<0.005	NA
		2/8/01 1130	EWI	<0.005		E0.002	
11303500	San Joaquin River near Vernalis	1/11/01 1300	IG	0.028	16.3	0.007	54.5
		1/11/01 1310	EWI	0.033		E0.004	
		1/27/01 0800	IG	0.201	0.5	0.007	15.4
		1/27/01 0810	EWI	0.202	0.5	0.006	15.4

Field Quality Control Samples

Five field blank samples and two equipment blanks were processed throughout this study. Organic-free water was used as the blank solution to assess the degree of contamination introduced during field processing and handling, as well as laboratory handling of samples and equipment. The 3-L sample collection bottle was rinsed three times with organic-free water (instead of the native water rinse) after the standard cleaning procedure described in the sample processing section. The sample collection bottle was then filled with organic-free water and poured into a 1-L glass sample bottle and sent to NWQL with the environmental samples. There were no detections of diazinon and chlorpyrifos in any of the field and equipment blanks. The two equipment blanks were processed in the same manner as described above; however, the cleaning of the sampling equipment was done at the City of Modesto laboratory for the autosampler used at the McHenry storm drain site. Equipment blanks were completed prior to actual use of the equipment in the storm sampling to confirm the thoroughness of the cleaning procedure and to reduce the possibility of equipment contamination of field samples.

Five replicate samples were split from 3-L sample collection bottles at various sites to characterize the reproducibility of the complete sample processing and analytical process. The RPD between the environmental sample and the replicate is used to describe the variability in replicates (Kratzer and others, 2002). Four out of the five replicate samples had diazinon values above laboratory reporting limits with RPDs ranging from 0 to 25 percent and a median RPD of 5.3 percent. Only two of the five replicate samples had chlorpyrifos values above laboratory reporting limits with RPDs from 0 to 11.7 percent.

In the first target storm (January 23–26, 2001), samples were collected using both width- and depth-integrated and three-point integrated collection methods at the San Joaquin River near Vernalis and Merced River at River Road sites (table 6). These samples were collected as a QC check on the variability introduced by the different sampling methods used in this study. Four samples at the Merced River at River Road and two samples at the San Joaquin River near Vernalis were collected by both methods within ten minutes of one another. The RPD for diazinon concentrations ranged from 0.5 to 25 percent. The RPD for chlorpyrifos concentrations ranged from 15.4 to 54.5 percent. Thus, the RPDs for diazinon were within the range for replicate splits, while the RPDs for chlorpyrifos were outside the range for replicate splits. However, all the chlorpyrifos concentrations used for calculating the RPDs were very close to the detection level at which a small absolute difference in concentrations can result in a relatively high RPD (table 6). Generally, if streamflow at a site is well mixed, concentrations of dissolved constituents collected by different methods should not be significantly different (Martin and others, 1992).

Laboratory Quality Control

Four laboratory-spiked environmental samples were used to evaluate the recovery of diazinon and chlorpyrifos in the sample matrix. The four samples were collected in the same manner as replicates in the field. The samples were labeled as a spike with instructions to NWQL to add their spike mixture after filtering. Spike recoveries are calculated by subtracting the measured concentrations in the environmental sample from the measured concentrations in the spiked sample and dividing by the theoretical concentration added to the spiked sample. Recoveries in the four laboratory spiked samples ranged from 81.2 percent to 120.9 percent for diazinon and 78 percent to 104.7 percent for chlorpyrifos (table 5). In addition to the laboratory-spiked samples, NWQL measures a laboratory control spike in each analytical set of environmental samples. This laboratory control spike has the target pesticides spiked into pesticide-grade water (inorganic blank water) at the laboratory and extracted, processed, and analyzed in the same manner as environmental samples. During December 2000 through May 2001, NWQL ran 175 laboratory control spikes for laboratory schedule 2001. The median recovery for diazinon was 93 percent, with a 95 percent confidence interval of 74 to 118 percent. The median recovery for chlorpyrifos was 84 percent, with a 95 percent confidence interval of 59 to 111 percent (Bruce Darnell, National Water Quality Laboratory, written commun., 2002).

HYDROLOGY DURING THE STUDY PERIOD

During the dormant season, diazinon and chlorpyrifos transport in the San Joaquin River Basin is primarily a function of the amount and timing of application and storm runoff from application areas (Kratzer and others, 2002). The weekly sampling during nonstorm periods usually occurred during stable and relatively low streamflows (fig. 6). These weekly nonstorm sampling events occurred on January 4, 11, and 18, and on February 1, 8, 15, and 22. However, three of the seven weekly sampling dates (January 11, and February 15 and 22) occurred during or shortly after nontarget or target storms.

Four storm periods occurred during the dormant spray season: January 8–12 (2.86 in. at Modesto), January 23–26 (0.87 in. at Modesto), February 9–11 (0.60 in. at Modesto) and February 18–24 (1.81 in. at Modesto). The January 23–26 and February 18–24 storms were considered target storms and were sampled frequently throughout the storm hydrograph whereas the other two storm periods were considered nontarget storm periods. Though the storm that occurred during January 8–12 resulted in the highest precipitation during the study period, it was considered a nontarget storm because indications from the county agricultural advisors at the time suggested that most of the dormant spray had not been applied.

The next storm (January 23–26, 0.87 in. at Modesto) was considered a target storm period because of the additional time for dormant spray application. However the nontarget storm produced more runoff than the first target storm at the Merced River at River Road, Stanislaus River at Caswell State Park, and San Joaquin River near Vernalis sites. A relatively small nontarget storm occurred on February 9–11 (0.60 in. at Modesto). A reservoir release of approximately 600 ft^3/s occurred in the Merced River Basin during this same period, which explains much of the hydrograph rise at the Merced River at River Road and San Joaquin River near Patterson sites (fig. 6). In addition, a reservoir release of approximately 800 ft^3/s during February 14–18 in the Tuolumne River Basin accounts for much of the rise in the hydrographs for the Tuolumne River and San Joaquin River near Vernalis. Combined releases from the major reservoirs on the Merced, Tuolumne, and the Stanislaus Rivers increased from about 800 ft^3/s before February 8 to 1,300 ft^3/s on February 14, to 3,700 ft^3/s on February 22 through the end of the month. The traveltimes from these reservoir releases to the sampling sites generally range from one to three days. Thus, large reservoir releases of Sierra Nevada water show up as a new baseflow at these sampling sites from about February 23 through the rest of the month. This baseflow of “clean” water originating above the pesticide application area, serves to greatly dilute pesticide concentrations in the rivers during this period.

The storm water discharge at the McHenry storm drain (fig. 1: site 8) was sampled on an hourly basis beginning on January 25 at 6 p.m. and ending on January 26 at 2 a.m. A total of nine samples were collected during this period. The initial discharge of 1.6 ft^3/s at 6 p.m. rapidly increased to a discharge of 73 ft^3/s at 7 p.m. (fig. 6I).

The precipitation samples collected in this study were composite samples collected during the following three storm periods: January 8–12, January 23–26, and February 9–11. The precipitation totals for each of these storm periods at the Modesto precipitation gage were 2.86 inches, 0.87 inches, and 0.60 inches, respectively. These precipitation amounts reflect the total amount of precipitation recorded by the precipitation gage located on the roof of the MID office building in downtown Modesto. The precipitation amounts collected by the composite samplers were calculated on the basis of the volume collected and the surface area of the collection apparatus (table 7).

Table 7. Precipitation accumulations and summary of diazinon and chlorpyrifos concentrations and loads for composite precipitation samples collected at selected sites in the San Joaquin River Basin, California

[in., inches; µg/L, microram per liter; µg/ft², microgram per square foot; —, no sample taken]

Site letter	Site identification number	Site name	Composite precipitation period	Calculated precip-itation[1] (inches)	Diazinon concen-tration (µg/L)	Diazinon load (µg/ft²)	Chlorpy-rifos concen-tration (µg/L)	Chlorpy-rifos load (µg/ft²)
A	373228120551201	Precipitation Gage 4, TID lateral 3 Barnhardt Road near Turlock	1/23/2001–1/26/2001	0.44	0.491	0.05	0.052	0.06
B	373637121004601	Precipitation Gage 6, Wastewater Treatment Plant Rooftop at Modesto	1/23/2001–1/26/2001	0.48	0.908	0.86	0.086	0.10
C	373725120543701	Precipitation Gage 7, Cadoni Road Lift Station at Modesto	1/23/2001–1/26/2001	0.44	0.472	0.45	0.071	0.08
D	373750121092601	Precipitation Gage 3, MID Lateral 4 near Modesto	1/23/2001–1/26/2001	0.46	0.188	0.21	0.034	0.04
E	373834121000601	Wet/Dry Sampler 1 at MID Rooftop at Modesto	1/8/2001–1/12/2001	[2]—	0.151	[3]0.74	0.019	[3]0.09
			1/23/2001–1/26/2001	[4]0.62	0.544	0.80	0.063	0.09
			2/9/2001–2/12/2001	[5]0.45	0.030	0.03	E 0.002	0.002
F	373841120504801	Wet/Dry Sampler 2 at MID Gage, Albers Road near Turlock	1/23/2001–1/26/2001	0.64	0.870	1.3	0.148	.22
			2/9/2001–2/12/2001	0.57	0.175	0.23	0.050	0.07
G	374028120594301	Precipitation Gage 8, Bowen and Aloha Street at Modesto	1/23/2001–1/26/2001	0.45	0.486	0.54	0.057	0.06
H	374351121004701	Precipitation Gage 5, Tully Road near Modesto	1/23/2001–1/26/2001	0.46	0.675	0.76	0.105	0.12

[1]Calculated from sample volume collected (in liters) and the depth of precipitation (in inches) per liter for the 1.02-ft diameter funnel sampler at sites A–D, G, H (0.53 in./L) and for the 0.89-ftcm diameter wet/dry automatic sampler at sites E and F (0.70 in./L).

[2]Sample volume collected corresponds to only 0.61 in. precipitation, whereas Modesto precipitation gage at site recorded 2.86 in.

[3]Recorded precipitation (2.86 in.) was adjusted to a calculated precipitation (2.09 in.) using the average calculated precipitation/recorded precipitation ratio from 1/23–1/26 (0.71 in.) and 2/9–2/12 (0.75 in.) events at site E.

[4]Sample volume collected corresponds to only 0.62 in. precipitation, whereas Modesto precipitation gage at site recorded 0.87 in. To be consistent with other sites, the calculated precipitation is used to calculate loads instead of the recorded precipitation.

[5]Sample volume collected corresponds to only 0.45 in.precipitation, whereas Modesto precipitation gage at site recorded 0.60 in. To be consistent with other sites, the calculated precipitation is used to calculate loads instead of the recorded precipitation.

CONCENTRATIONS OF DIAZINON AND CHLORPYRIFOS

The concentrations of diazinon and chlorpyrifos in the samples collected during this study are presented in tabular form (table 3) and shown graphically (figs. 7, 8, and 9). Although the urban storm runoff site, McHenry storm drain, is presented with the river sites in table 3 and in figures 7 and 8, it is discussed separately. The concentrations of diazinon and chlorpyrifos for the composite precipitation samples also are discussed separately (table 7 and fig. 9).

Diazinon

The highest concentrations of diazinon occurred during the rising limbs of storm runoff for both of the target storms that were sampled, January 23–26 and February 18–24. Of the 220 environmental river samples collected, 41 exceeded the proposed CMC of 0.08 μg /L for diazinon. Thirty-four of these "exceedances" occurred during the first target storm (January 23–26), three occurred during the second target storm (February 18–24), and four occurred during nonstorm periods. All river sites had exceedances except for Orestimba Creek at River Road and San Joaquin River near Patterson. The following samples exceeded the CMC: sixteen samples at the San Joaquin River near Vernalis; thirteen samples at San Joaquin River near Stevinson; and four samples at the Tuolumne River at Shiloh Road, Merced River at River Road, and Stanislaus River at Caswell State Park. Higher concentrations occurred during the first storm at all sites, except Orestimba Creek. Most samples collected during the second storm were diluted considerably by reservoir releases.

The storm runoff samples collected at the urban storm runoff site, McHenry storm drain, had the highest diazinon concentrations found in this study (fig. 7H and table 3). All nine samples collected at the McHenry storm drain exceeded the CMC. The lowest concentration collected was more than 6 times greater than the CMC and the highest concentration collected was nearly 12 times the CMC. The site was sampled on an hourly basis beginning at 6 p.m. on January 25 and ending at 2 a.m. on January 26. The concentrations nearly doubled from 0.506 μg/L at 6 p.m. to a maximum of 0.947 μg/L at 7 p.m. After dropping to 0.922 μg/L at 8 p.m., the diazinon concentrations on the falling limb of the storm hydrograph ranged from 0.691 μg/L to 0.823 μg/L. Other than the sharp increase on the rising limb, diazinon concentrations were essentially independent of flow. This same relation was found for this site in a February 1995 storm event (Kratzer, 1998).

During the January 23–26, 2001, storm event, composite precipitation samples were collected at four sites in the Modesto urban area and four sites in the agricultural areas surrounding Modesto (fig. 2, sites A–H). All precipitation samples exceeded the CMC. The highest diazinon concentrations at the agricultural sites occurred at sites east and north of Modesto (sites F and H, respectively) (fig. 9A and table 7). These concentrations were 0.870 and 0.675 μg/L, respectively. These high concentrations may reflect more recent localized applications near these sampling sites than at the other two agricultural sites. Site D had the lowest concentrations of the agricultural sites. This site is located west of Modesto in an area of less dense orchard land use. Concentration values for an area (agricultural or urban) were calculated as an average rather than as a weighted value of the distance each sampling site was from source. The average was selected because the concentration gradient away from an orchard, in the weighted value selection, would depend on various factors that are beyond the scope of the project objectives. In the averages method, however, a standard deviation is given as an indication of the variability for the calculated averages. The average and standard deviation concentrations for diazinon at the agricultural sites are 0.556 and 0.251 μg/L, respectively.

The concentrations in the precipitation at the urban sites were generally more uniform and slightly less than at the agricultural sites, with the exception of the sample at site B, the City of Modesto Wastewater Treatment Plant, which had the highest diazinon concentration (0.908 μg/L) at any of the eight precipitation sites. The average and standard deviation concentrations for diazinon at the urban sites are 0.603 and 0.178 μg/L, respectively. When the concentration at the Wastewater Treatment Plant is removed from the calculations, the average and standard deviation concentrations at the urban sites are 0.501 and 0.031 μg/L, respectively.

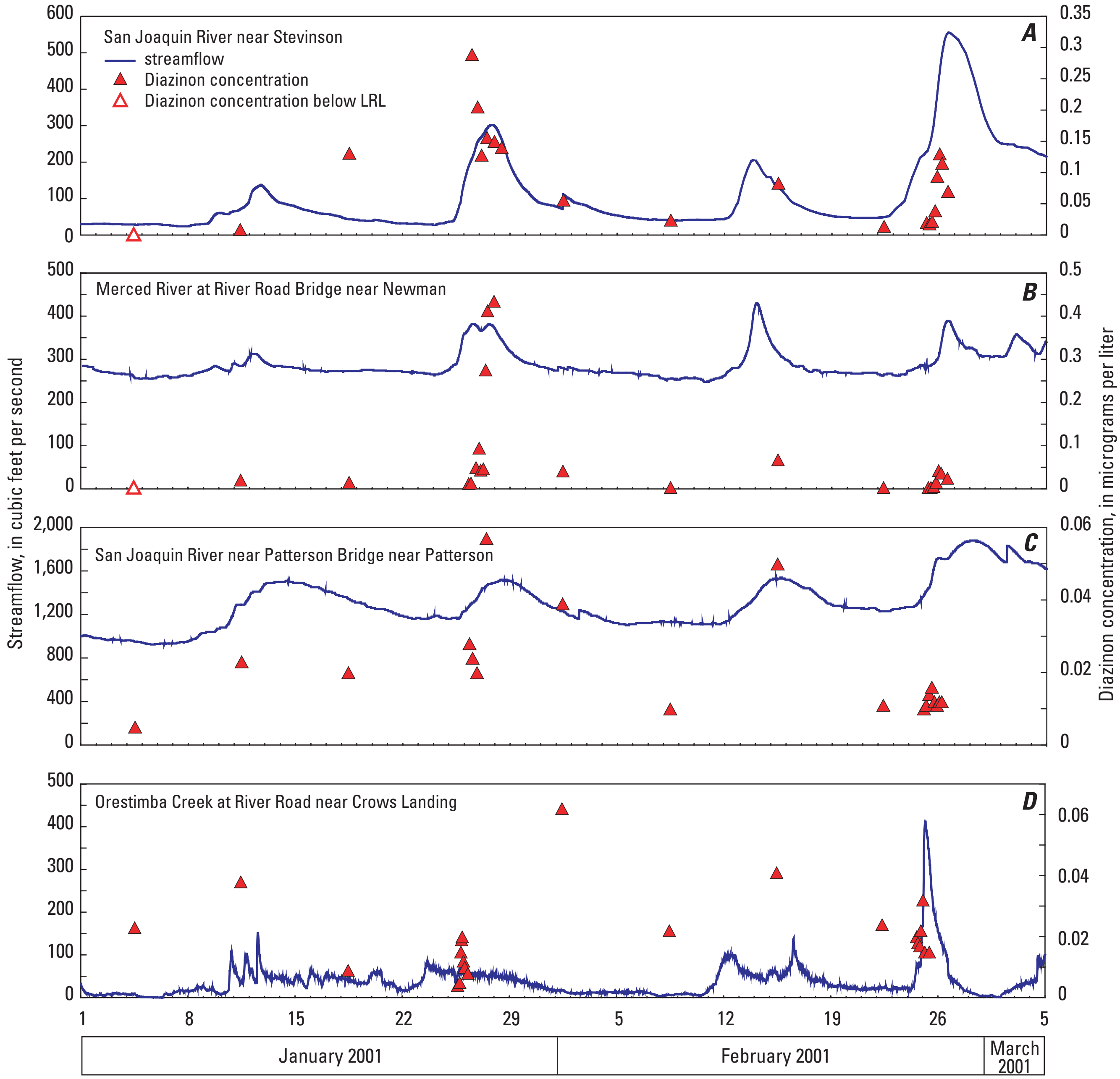
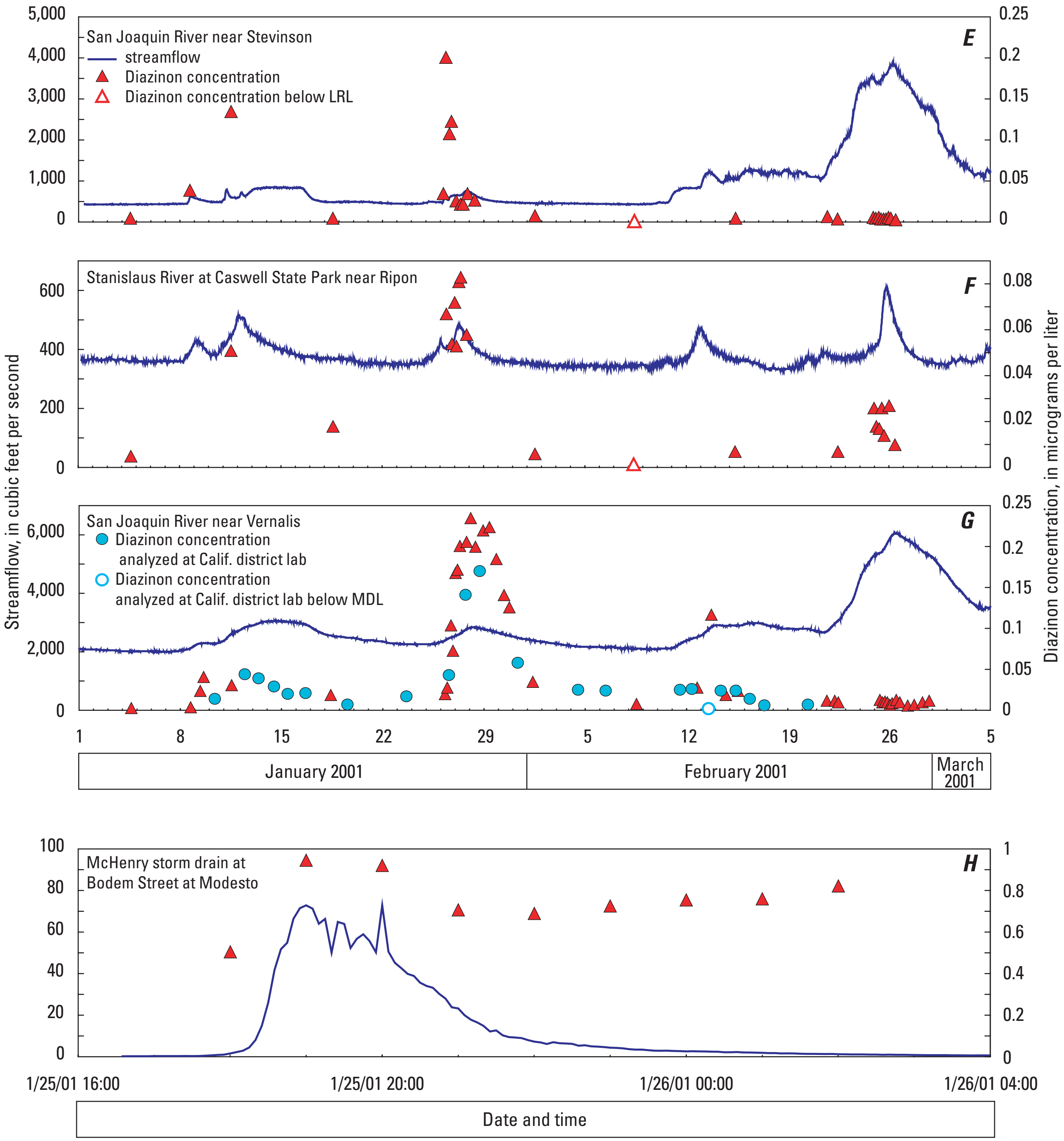


Figure 7. Streamflow and diazinon concentrations in the San Joaquin River Basin, California. ***A–G***. River sites. ***H***. McHenry storm drain site in Modesto, California.

(LRL, laboratory reporting limit; NWQL, National Water Quality Laboratory; MDL, method detection limit)



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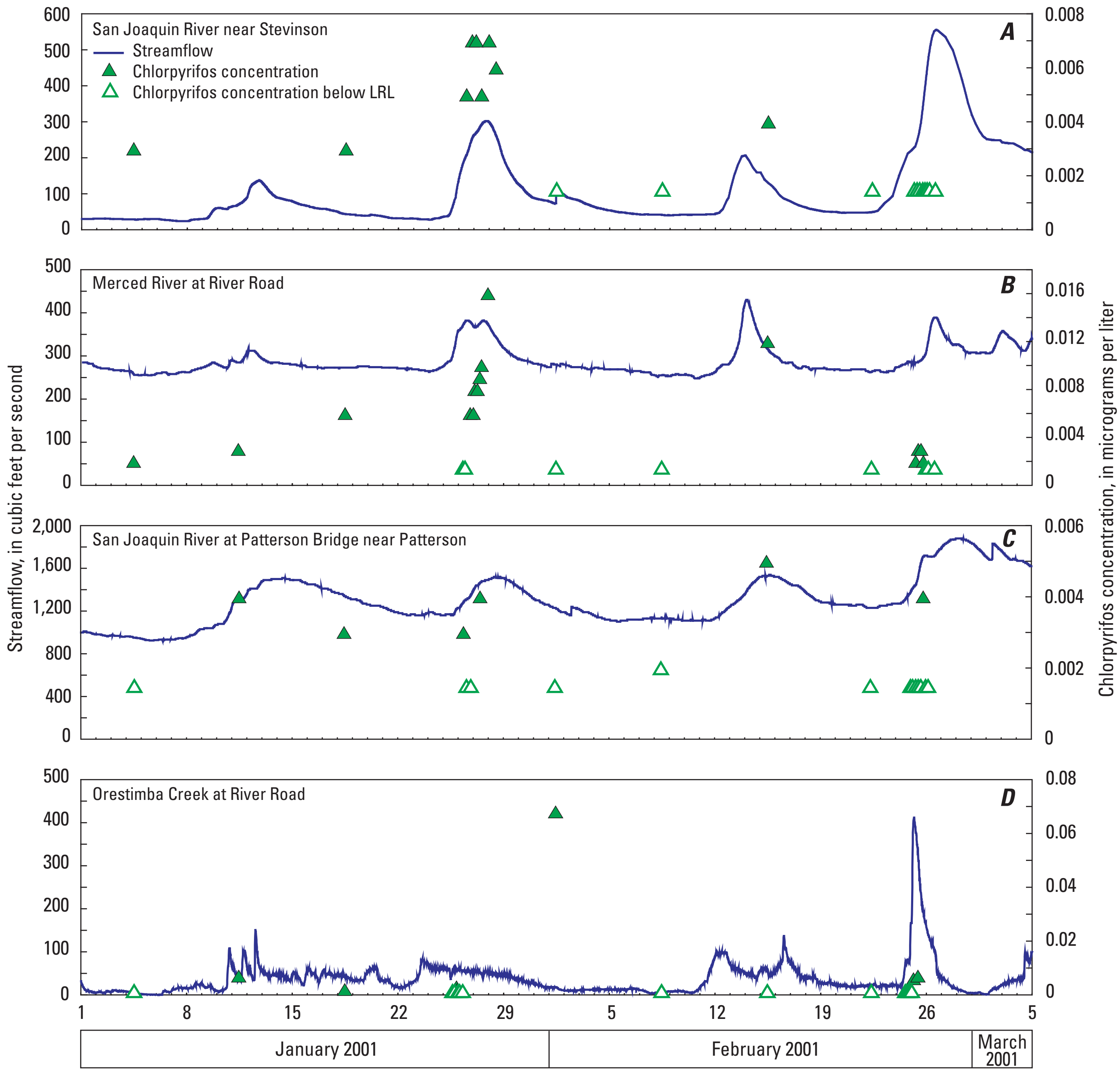
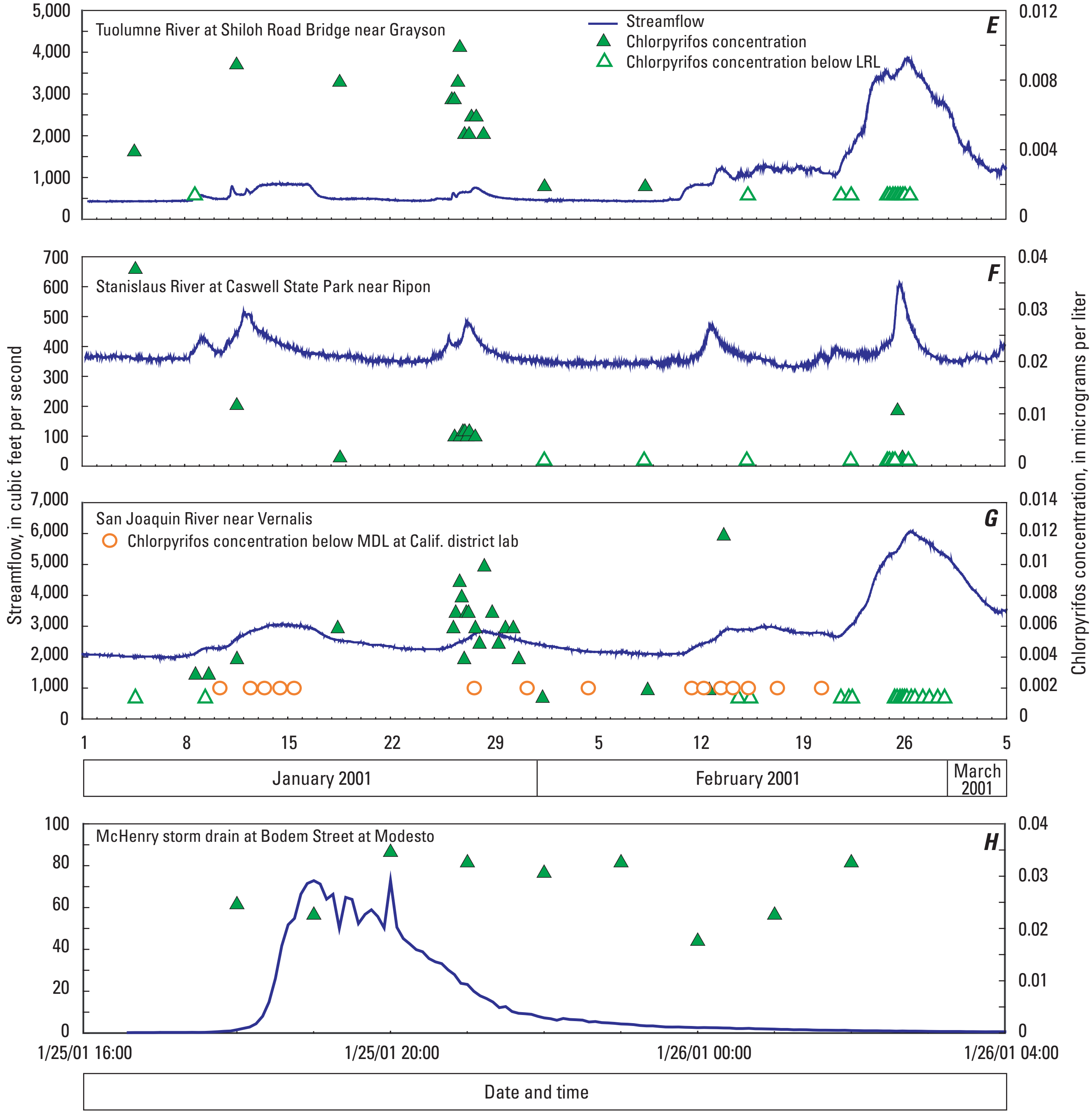


Figure 8. Streamflow and chlorpyrifos concentrations in the San Joaquin River Basin, California. ***A–G***. River sites. ***H***. McHenry storm drain site in Modesto, California.

(LRL, laboratory reporting limit; NWQL, National Water Quality Laboratory; MDL, method detection limit)



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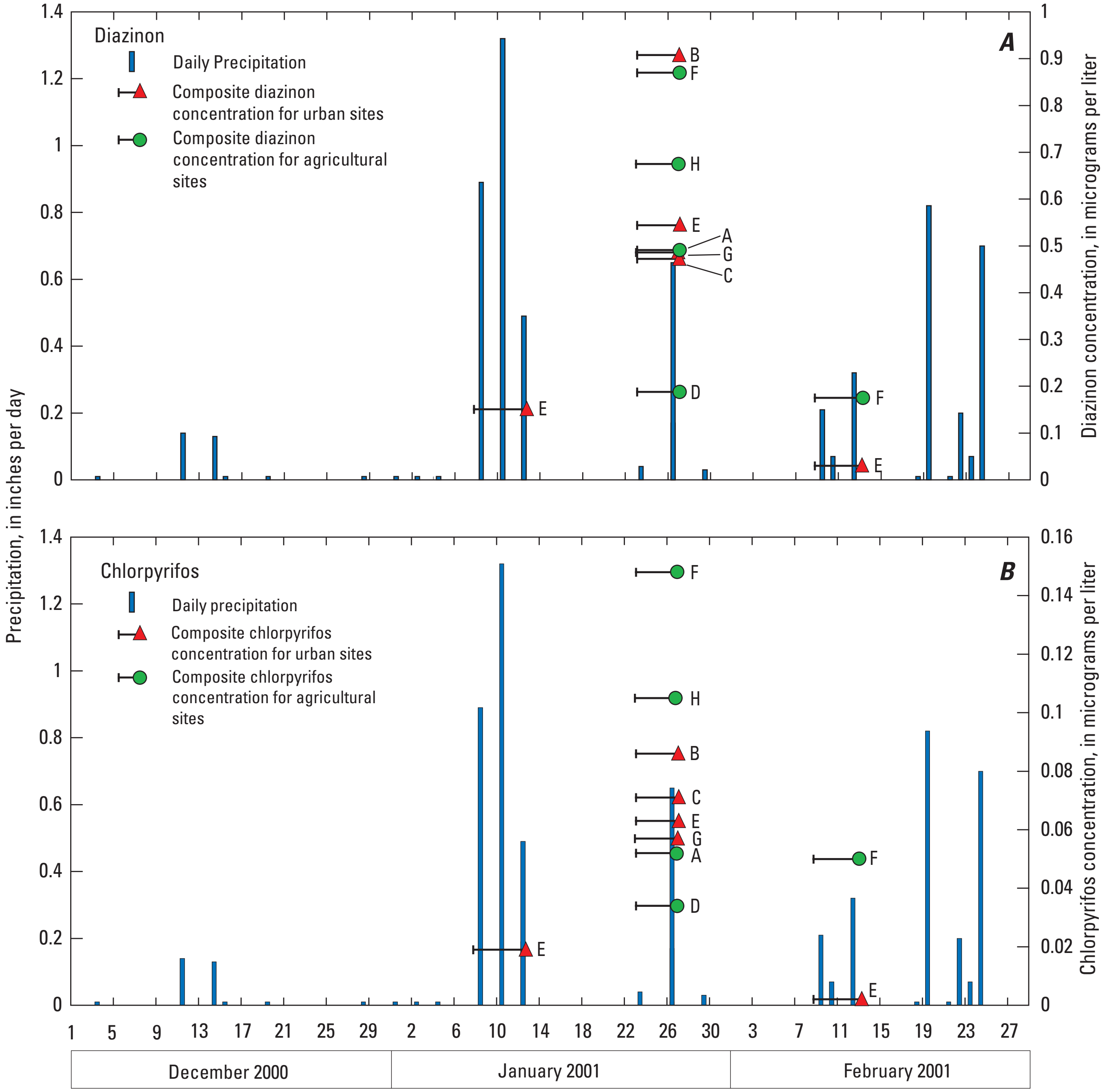


Figure 9. Daily precipitation at Modesto, California, December 2000–February 2001, and concentrations of composite precipitation samples collected in urban and agricultural areas in the San Joaquin River Basin, California. ***A***. Diazinon. ***B***. Chlorpyrifos.

The average diazinon concentration from the two precipitation sites in the McHenry storm drain basin (fig. 2: sites E and G), accounted for 68 percent of the flow-weighted average diazinon concentration in McHenry storm drain. Diazinon concentrations at the downtown Modesto site (site E) were much lower in storms before and after the January 23–26 storm (fig. 9A). The diazinon concentration at the site in the agricultural area east of Modesto was much lower in the storm after the January 23–26 storm (fig. 9A: site D). Two of the three samples from other storms exceeded the diazinon CMC. The higher precipitation concentrations for the January 23–26 storm may be due to the timing and amount of application just prior to this storm relative to the other two storms (fig. 5A).

Chlorpyrifos

Unlike diazinon, the highest concentrations of chlorpyrifos collected at the river sites did not occur during the two target storm events. Of the 220 environmental river samples collected, only two exceeded the proposed CMC of 0.02 μg/L. A concentration of 0.038 μg/L occurred on January 4 during the weekly sampling at the Stanislaus River at Caswell State Park site (fig. 8F and table 3), and a concentration of 0.068 μg/L occurred at the Orestimba Creek at River Road site during the weekly sampling on February 1 (fig. 8D and table 3). Though the remaining chlorpyrifos concentrations of samples collected were below the CMC, the concentrations at the river sites sampled on the rising limb of storm events were generally higher than those collected on the falling limb of a storm event or during routine weekly sampling.

The urban storm runoff site, McHenry storm drain, had a similar concentration pattern as for diazinon, but concentrations were more than one order of magnitude less (fig. 8H and table 3). Seven of the nine samples exceeded the CMC. The concentration was below the LRL in the first sample taken at 6 p.m. on January 25, and the maximum concentration (0.035 μg/L) occurred during the second peak flow at 8 p.m. The concentrations after 8 p.m. ranged from 0.018 to 0.033 μg/L. The concentration pattern was essentially independent of flow and was similar to the pattern for this site during a February 1995 storm event (Kratzer, 1998). However, the chlorpyrifos concentrations in the February 1995 storm event were about twice those found in this study.

The composite precipitation samples collected at the four sites in the Modesto urban area (fig. 2: sites B, C, E, and G) and the four sites in the agricultural area (sites A, D, F, and H) followed the same trend as the diazinon concentrations; that is, if the diazinon concentration at one site was high relative to the other sites, it was also high for the chlorpyrifos concentration relative to the other sites (fig. 9B and table 7). The highest precipitation concentration at the agricultural sites occurred at the sites east and north of Modesto (sites F and H, respectively). The average concentration for chlorpyrifos at these sites was 0.127 μg/L, and was more than twice the concentrations at the other two agricultural sites. These high concentrations may reflect more recent localized applications near these two sites than at the other two agricultural sites. Site D, had the lowest concentrations of all the agricultural sites. This site was located west of Modesto in an area of less dense orchard use. The average and standard deviation concentrations of chlorpyrifos at the agricultural sites are 0.085 and 0.045 μg/L, respectively.

The concentrations of chlorpyrifos in the precipitation at the urban sites were more consistent and slightly less than at the agricultural sites, with the exception of the sample from site B, the City of Modesto Wastewater Treatment Plant. As with diazinon, this site had the highest chlorpyrifos concentration (0.086 μg/L). It is unclear why the concentrations for both diazinon and chlorpyrifos in the precipitation sample at this site were unusually high. One possible explanation could be that there was an application to the trees and other plants in the Wastewater Treatment Plant nursery area near the sampling site before the storm event sampling took place. In addition, there is a large apartment complex near this site. It is also possible that the diazinon and chlorpyrifos residues detected in the rain were due to volatilization from fumigation activities at the complex. The average and standard deviation concentrations for chlorpyrifos at the urban sites are 0.069 and 0.011 μg/L, respectively. When the concentration at the Wastewater Treatment Plant is removed from the calculations, the average and standard deviation concentrations are 0.064 and 0.006 μg/L, respectively.

The average chlorpyrifos concentration from the two precipitation sites in the McHenry storm drain basin (fig. 2: sites E and G) had an average concentration in precipitation that was over 2.5 times higher than what was detected in the McHenry storm drain. As with diazinon, chlorpyrifos concentrations at the downtown Modesto site (site E) were much lower in the storm before and after the January 23–26 storm (fig. 9B). The chlorpyrifos concentration at the site in the agricultural area east of Modesto was much lower in the storm after the January 23–26 storm (fig. 9B: site D). One of three samples exceeded the CMC.

LOADS OF DIAZINON AND CHLORPYRIFOS

Instantaneous loads of diazinon and chlorpyrifos were calculated for each sample collected in this study (table 3 and figs. 10–12). For samples with concentrations less than the MDL, the concentration was set to half of the MDL to calculate instantaneous loads. A simple substitution of half the MDL produces less bias in the summary statistics for concentration at a site than the alternatives of zero or the MDL (Helsel, 1990). At the San Joaquin River near Vernalis, all instantaneous loads were connected and the following categories of loads were calculated from the area under the curves: target storms, nontarget storms, nonstorm, and baseline. Baseline loads were calculated for all sites. This was set to the loading rate on the true nonstorm, weekly sampling date of February 8 for all sites. This load was subtracted from the total load for the defined storm periods to calculate storm loads at each site. Loads for target storms were calculated for all sites except the San Joaquin River near Patterson. Insufficient samples were collected at this site to define the storm loads.

Attempts were made to use more robust methods to calculate loads. These methods involved the use of the load estimating programs, ESTIMATOR and LOADEST2. ESTIMATOR is a log-linear multiple regression model of a constituent against measured environmental variables that calculates daily, monthly, and annual loads (Cohn and others, 1989; Cohn and others, 1992). ESTIMATOR can only be used when the concentration data file for a site contains at least 25 observations per year for a minimum of a two-year period and at least 20 percent of the observations are above the detection limit. LOADEST2 uses a rating curve method to calculate loads and estimates the parameters of the rating curve by either the maximum-likelihood method or the linear attribution method (Crawford, 1996). Both methods assume that the rating-curve residual errors are normally distributed. It was not possible to use these two methods to calculate storm loads because the short-term nature of the data collected in this study does not meet the minimal data requirements of these programs.

The storm load was defined in this study as the total load minus the baseline load. To calculate a storm load at a site, the connected instantaneous load line was brought down to the baseline load line, and the area enclosed was digitized. The dashed lines that complete the storm loads (figs. 10 and 11) are called estimated storm loads. At the beginning of the storm load, this line is based on the beginning of the storm runoff hydrograph. At the end of the storm load, this line represents the estimated end of the storm hydrograph. This line is estimated for sites on the basis of the trend in the instantaneous loads, the storm hydrograph from the valley application areas, and the traveltimes between the sites. An estimated traveltime from the farthest upstream site, San Joaquin River near Stevinson site to the farthest downstream site, San Joaquin River near Vernalis, was considered in extending the load line for San Joaquin River near Vernalis (Kratzer and Biagtan, 1997).

Loads were divided by pesticide application and by drainage area to illustrate basins that have relatively higher or lower loading rates and yields (table 8). In this report, storm loads as related to application are based on the dry period preceding the storm. Thus, loads in the first target storm are related to the first dry period (December 1, 2000 to January 26, 2001), whereas loads in the second storm are related to the second dry period (January 27, 2001, to February 24, 2001). The significance of loading during the different periods (target storms, nontarget storms, nonstorm, and baseline loads) is best illustrated by the loading rate in pounds active ingredient per day (lb a.i./d). Maximum loading rates for each target storm are presented for all sites except San Joaquin River at Patterson where only maximum instantaneous loads are presented.

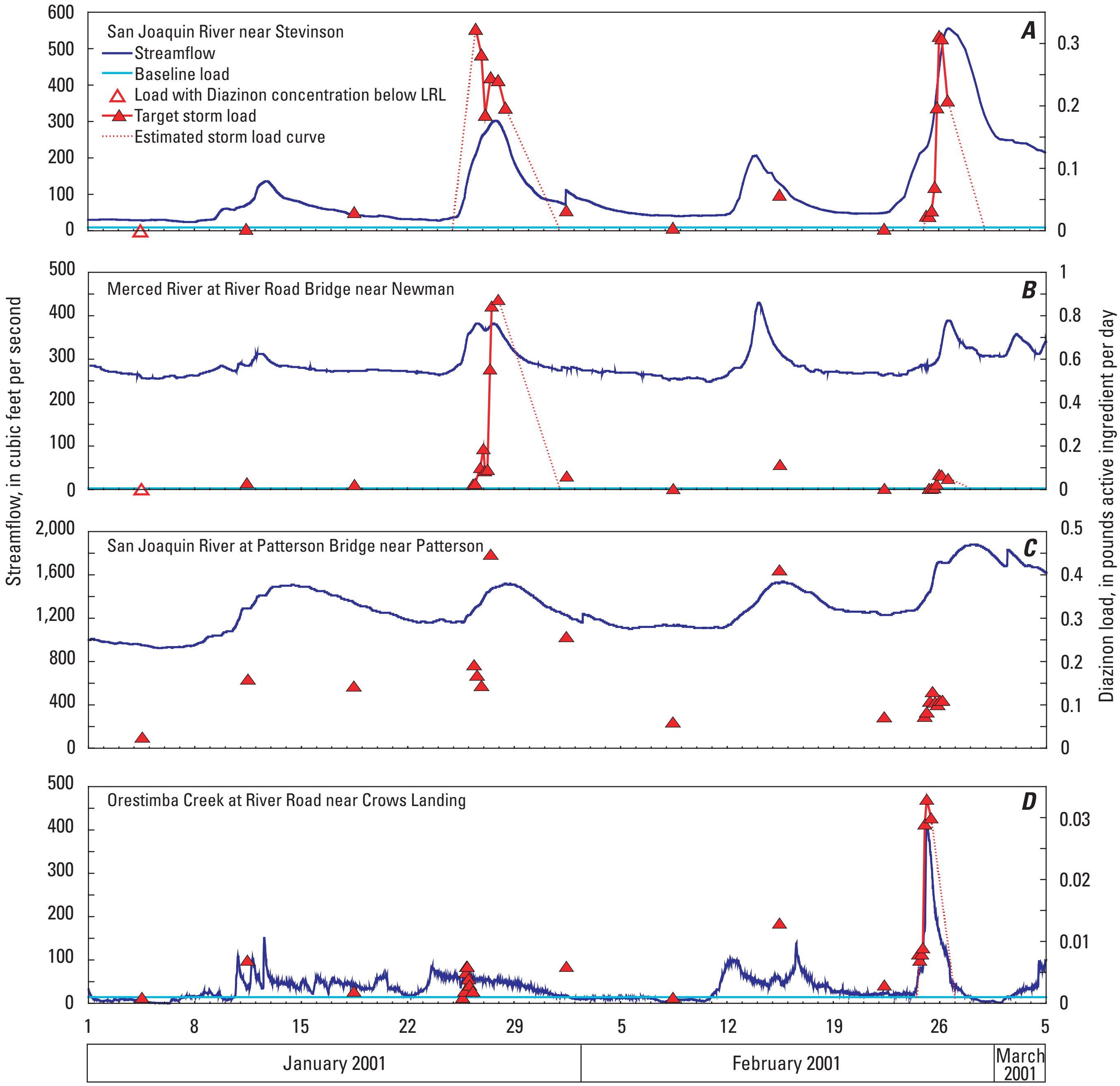
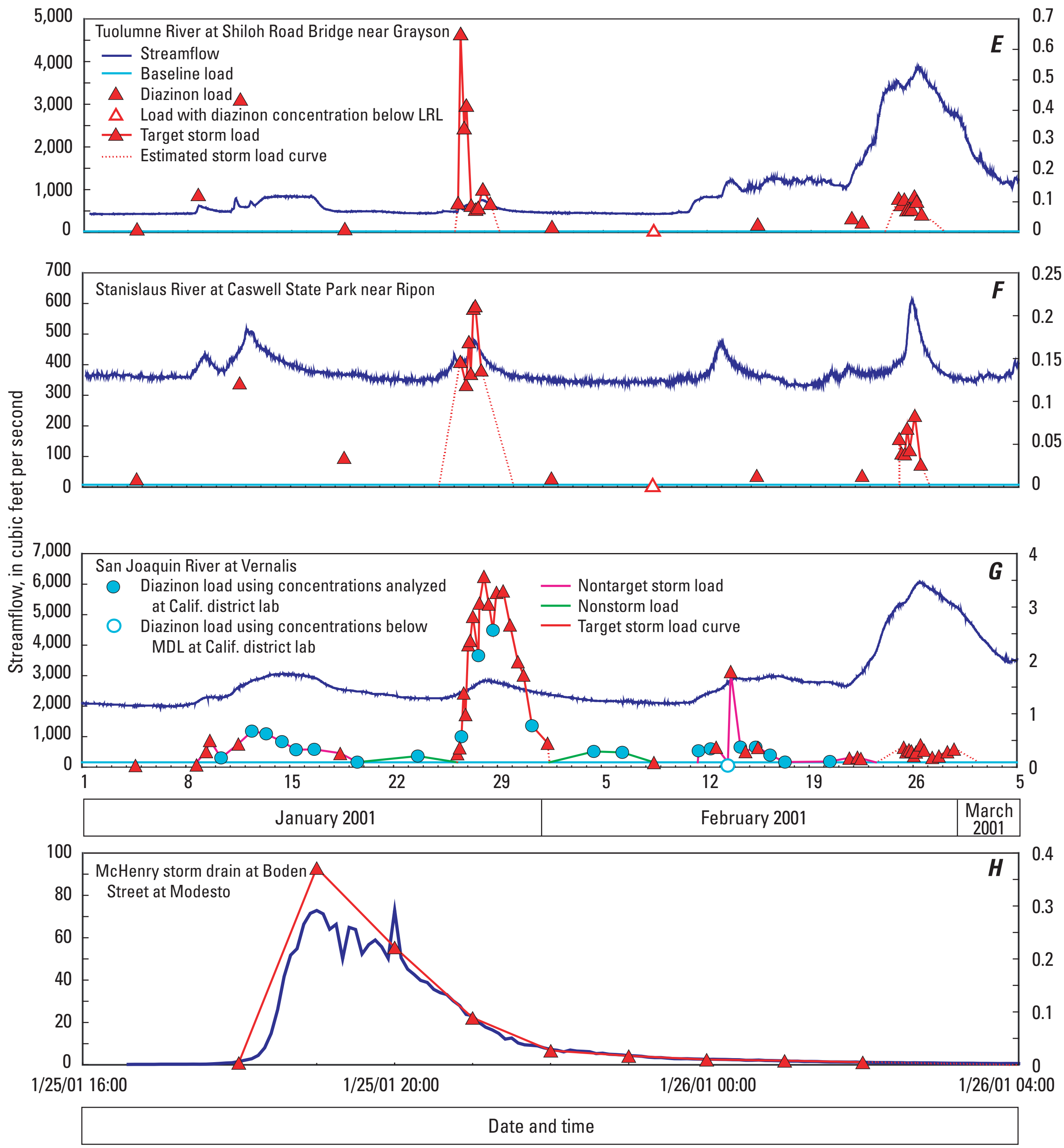


Figure 10. Streamflow and diazinon loads in the San Joaquin Rive Basin, California. ***A*—*G***. River sites. ***H,*** McHenry storm drain site in Modesto, California. (LRL, laboratory reporting limit,; NWQL, National Water Quality Laboratory, MDL, method detection limit)



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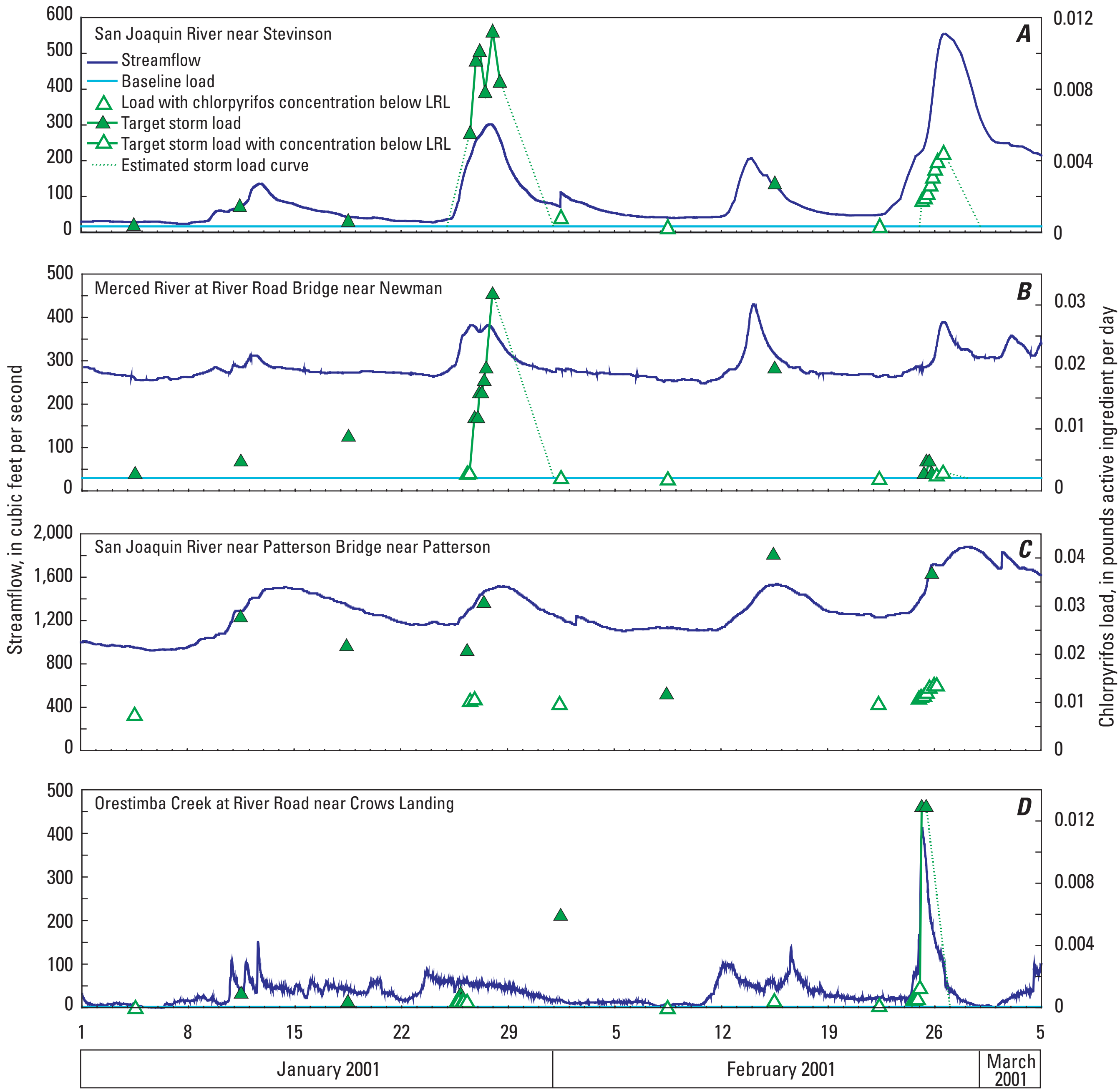

Figure 11. Streamflow and chlorpyrifos loads in the San Joaquin River Basin, California. ***A–G***. River sites. ***H***. McHenry storm drain site in Modesto, California. (LRL, laboratory reporting limit; NWQL, National Water Quality Laboratory; MDL, method detection limit)

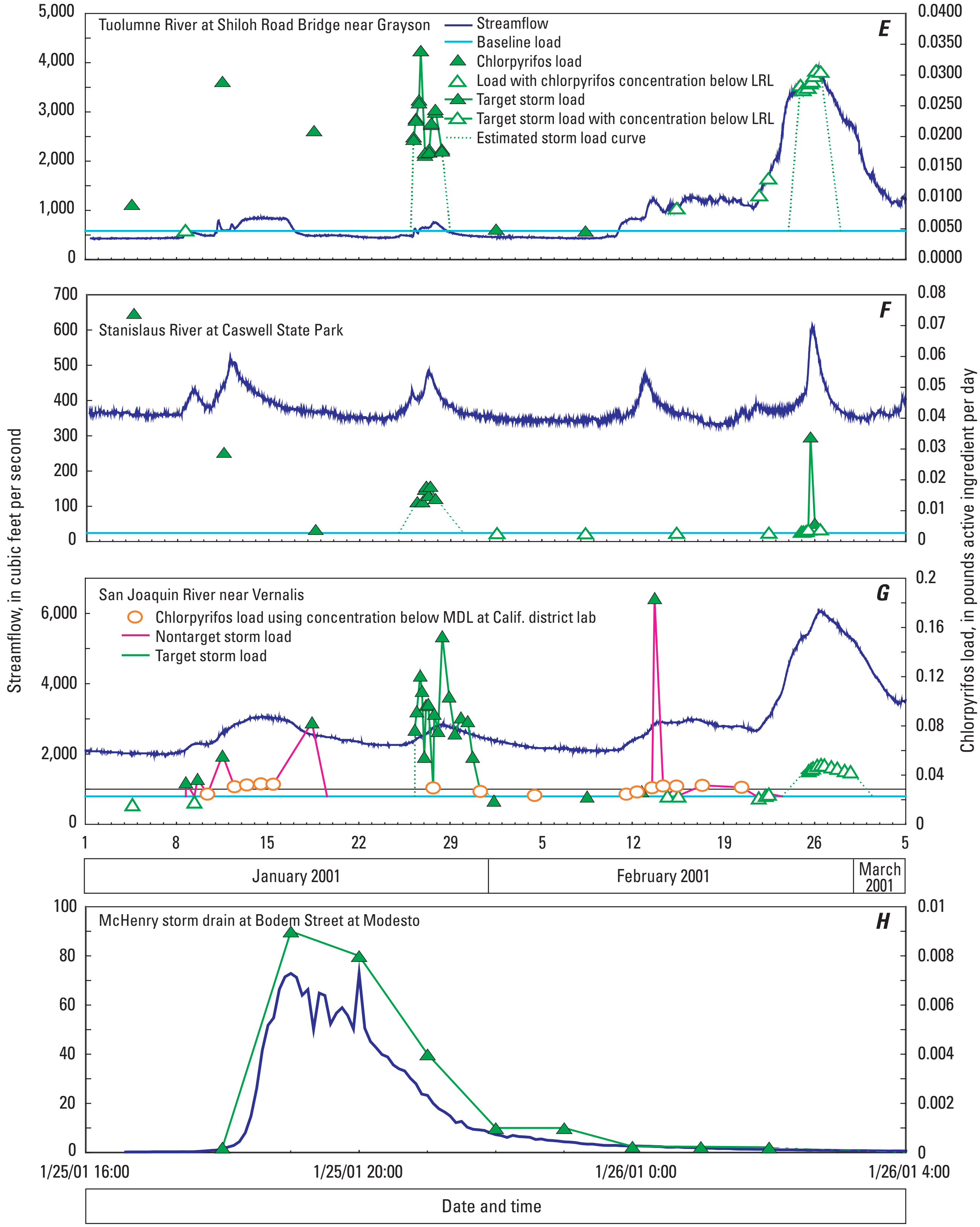

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Table 8. Diazinon and chlorpyrifos loading rates, loads, and yields in relation to agricultural applications for sites in the San Joaquin River Basin, California, January and February 2001

[See table 2 and figure 1B for basin names and locations. Value on top is diazinon, value in ( ) on bottom is chlorpyrifos. g/mi², grams per square mile; mi², square mile; inf, infinite; lb a.i., pound active ingredient; %, percent; NA, not applicable; <, less than]

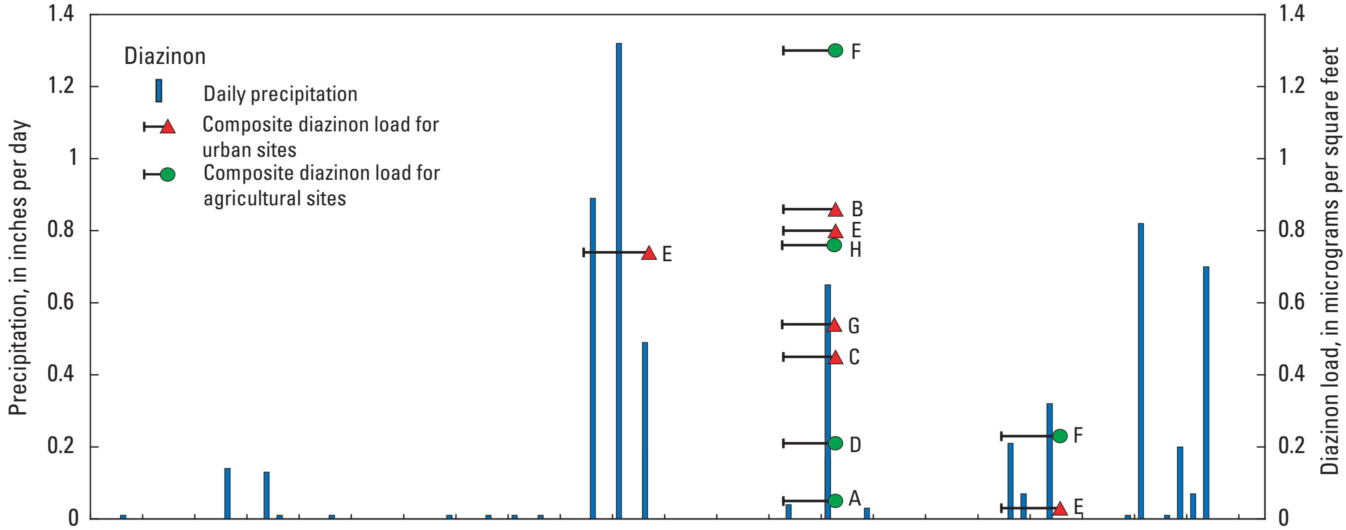
Basin	Site number	Site name	Basin valley area (mi²)	Dry Period 1, application (lb a.i.)	Baseline loading rate (lb a.i.)	Storm 1 load (lb a.i.)	Storm 1 load as % of Dry Period 1 application (percent)	Storm 1 yield, as load per valley basin area) (g/mi²)	Dry Period 2, application (lb a.i.)	Storm 2 load (lb a.i.)	Storm 2 load as % of Dry Period 2 application (percent)	Storm 2 yield, as load per valley basin area (g/mi²)	Total January and February load (lb a.i.)	Total January and February load, as % of application (percent)
A	1	San Joaquin River near Stevinson	218	78 (751)	0.005 (<0.001)	1.04 (0.034)	0.133 (0.004)	2.16 (0.071)	578 (2,539)	0.447 (0.015)	0.077 (<0.001)	0.930 (0.031)		
C	4	Merced River at River Road Bridge near Newman	245	1,193 (4,712)	0.005 (0.002)	2.35 (0.079)	0.197 (0.001)	4.35 (0.146)	701 (62)	0.058 (0.001)	0.008 (0.002)	0.107 (0.002)		
D	5	Orestimba Creek at River Road near Crows Landing	33	0 (0)	0.001 (<0.001)	0.004 (<0.001)	inf (inf)	0.055 (<0.014)	0 (0)	0.038 (0.013)	inf (inf)	0.522 (0.179)		
E	6	San Joaquin River at Patterson Bridge near Patterson	1,614	2,58 (5,538)	0.06 (0.012)				1,691 (2,545)					
G	8	McHenry storm drain at Bodem Street at Modesto	1.3	NA NA	NA NA	0.03 (0.001)	NA NA	10.4 (<0.349)	NA NA	NA	NA	NA		
F	10	Tuolumne River at Shiloh Road Bridge near Grayson	149	237(74)	<0.003 (0.004)	0.37 (0.044)	0.156 (0.059)	1.13 (0.134)	39.4 (378)	0.218 (0.067)	0.553 (0.018)	0.664 (0.204)		
H	12	Stanislaus River at Caswell State Park near Ripon	116	1,106 (122)	<0.003 (<0.003)	0.463 (0.026)	0.042 0.021	1.81 (0.102)	24 (324)	0.080 (0.008)	0.333 (0.002)	0.313 (0.031)		
K	13	San Joaquin River near Vernalis	2,273	6,566 (6,808)	0.091 (0.023)	11.6 (0.301)	0.176 (0.004)	2.31 (0.060)	2,300 (4,372)	0.988 (0.109)	0.043 (0.002)	0.197 (0.022)	23.8 (2.17)	0.268 (0.019)

Loading from atmospheric sources is a potentially important component in the overall contributions of contaminants to the San Joaquin River Basin. The atmosphere is a major pathway by which pesticides and other organic and inorganic compounds are transported and deposited in areas sometimes far removed from their sources (Majewski and Capel, 1995). Diazinon and chlorpyrifos loads from the precipitation collected at the urban and agricultural sites in the Modesto area were calculated on the basis of concentrations in the collected sample (μg/L) multiplied by the precipitation (inches) and a conversion factor (table 7). These loads are expressed in micrograms per square meter ($\mu g/ft^2$). Figures 12A and 12B illustrate the composite precipitation loads for diazinon and chlorpyrifos as well as the corresponding recorded precipitation totals at the downtown Modesto precipitation gage.

Diazinon

Instantaneous loads of diazinon at the river sites are closely related to streamflow (fig. 10). At all sites, the instantaneous diazinon storm loading rates (lb a.i./d) peaked during the rising limb of the storm hydrograph for both target storms (January 23–26 and February 18–24). The maximum storm loading rates at the river sites for the January target storm (not including the baseline loading rate) were 3.49 lb a.i./d at San Joaquin River near Vernalis, 0.871 lb a.i./d at Merced River near River Road, 0.650 lb a.i./d at Tuolumne River at Shiloh Road, 0.319 lb a.i./d at San Joaquin near Stevinson, 0.209 lb a.i./d at Stanislaus River at Caswell State Park, and less than 0.006 lb a.i./d at Orestimba Creek near River Road. The instantaneous storm loading rates for the February target storm were all less than or equal to 0.081 lb a.i/d, except for San Joaquin River near Vernalis (0.332 lb a.i./d), San Joaquin River near Stevinson (0.307 lb a.i./d), and Tuolumne River at Shiloh Road (0.117 lb a.i./d). For the first nontarget storm period (January 8–12), samples were collected during the weekly sampling on January 11 at all river sites and daily at the farthest downstream site, San Joaquin River near Vernalis, for the duration of the storm hydrograph. The instantaneous loading rates were less than 0.119 lb a.i./d, except for Tuolumne River at Shiloh Road (0.435 lb a.i./d) and San Joaquin River near Vernalis (0.347 lb a.i./d). For the second nontarget storm period (February 9–11), samples were collected during the weekly sampling on February 15 at all river sites and twice per day at the San Joaquin River near Vernalis for the duration of the storm hydrograph. The February 15 weekly samples had instantaneous loading rates less than or equal to 0.111 lb a.i./d, except at San Joaquin River near Patterson (0.448 lb a.i./d) and San Joaquin River near Vernalis (0.283 lb a.i./d). The highest instantaneous loading rate for this nontarget storm period at San Joaquin River near Vernalis was 1.71 lb a.i./d on February 13.

The total January and February 2001 diazinon loads were calculated only for the San Joaquin River near Vernalis. The total diazinon load in the San Joaquin River near Vernalis during January and February 2001 was 23.8 lb a.i. (table 8). This total includes, 1.06 lb a.i of nonstorm load, 4.35 lb a.i. of nontarget storm load, 5.82 lb a.i. of baseline load, and 12.6 lb a.i. of target storm load (fig. 10 and table 8). The first target storm (January 23–26, 2001) transported 11.6 lb a.i. of diazinon to Vernalis and the second target storm (February 18–24) transported 0.988 lb a.i. The 12.6 lb a.i. of diazinon transported during the two storms compares with 27.4 lb a.i. transported during two storms in January and February 1994 (Kratzer, 1999) and 8.17 lb a.i. in two storms in January and February 2000 (Kratzer and others, 2002).



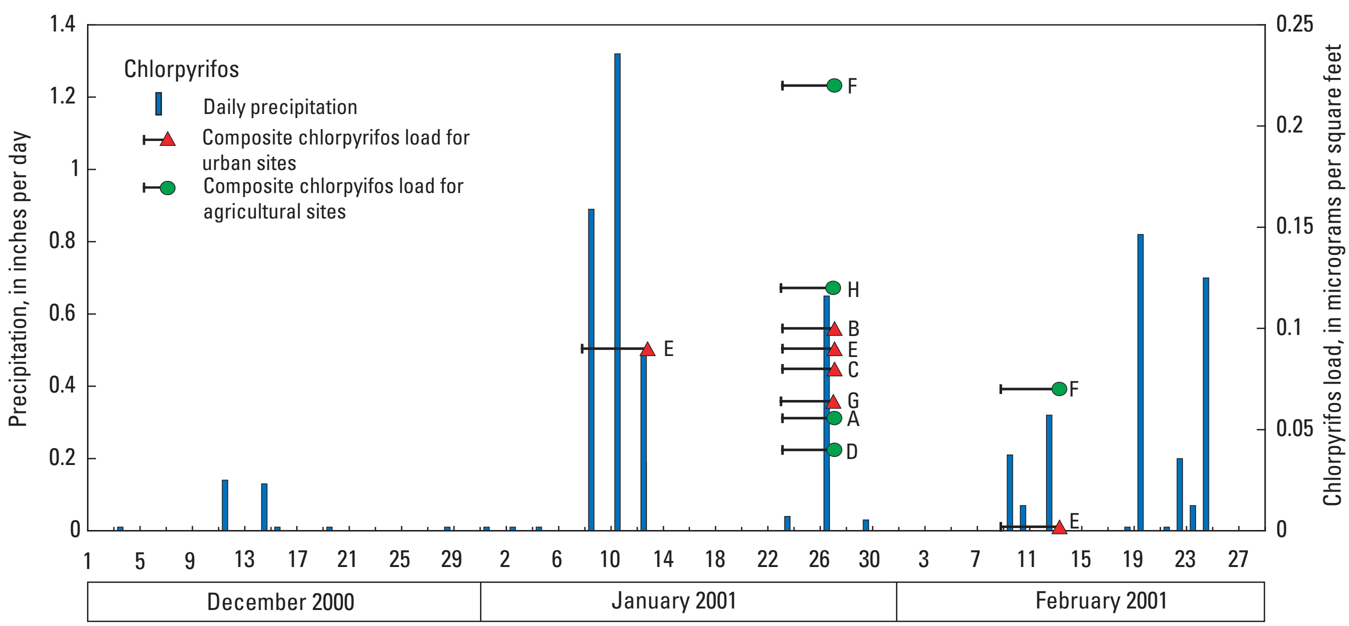


Figure 12. Daily precipitation at Modesto, California, December 2000–February 2001, and loads of composite precipitation samples collected in urban and agricultural areas in the San Joaquin River Basin, California. ***A***. Diazinon. ***B***. Chlorpyrifos.

Approximately 36 percent of the 11.6 lb a.i. diazinon load transported during the first target storm to San Joaquin River near Vernalis came from four sites: Merced River at River Road (2.35 lb a.i.), San Joaquin River near Stevinson (1.04 lb a.i.), Stanislaus River near Caswell State Park (0.463 lb a.i.), and Tuolumne River at Shiloh Road (0.370 lb a.i.). Approximately 79 percent of the 0.988 lb a.i diazinon load transported to Vernalis during the second target storm came from four sites: San Joaquin River near Stevinson (0.447 lb a.i), Tuolumne River at Shiloh Road (0.218 lb a.i.), Stanislaus River at Caswell State Park (0.080 lb a.i.), and Orestimba Creek at River Road (0.038 lb a.i.). These loads during runoff from the two target storms do not include the baseline loads of 1.20 lb a.i. at San Joaquin River near Vernalis, 0.045 lb a.i. at Merced River at River Road, 0.021 lb a.i. at Tuolumne River at Shiloh Road, 0.055 lb a.i. at San Joaquin River near Stevinson, 0.211 a.i. at Stanislaus River at Caswell State Park, and less than 0.003 lb a.i. at Orestimba Creek at River Road at River Road. The baseline loading rates in January through February 2001 were 30 to 77 percent less than in January through February 2000, except for San Joaquin River near Stevinson, which was 2.5 times more (table 8). The total load at San Joaquin River near Vernalis for January and February 2001 was 0.27 percent of dormant application. This compares with 0.17 percent during January through February 2000 at San Joaquin River near Vernalis (Kratzer and others, 2002).

The McHenry storm drain instantaneous loading rates follow the storm hydrograph very closely (fig. 10H, table 3). The maximum instantaneous load of 0.372 lb a.i./d occurred shortly before the peak of the storm hydrograph. The total load for the January 23–26 storm was 0.03 lb a.i. This load compares to a load of 0.024 lb a.i. during a February 1995 storm sampled at this site (Kratzer, 1998).

Figure 12A illustrates the diazinon loads from precipitation collected at urban and agricultural sites in the Modesto area. Composite precipitation samples were collected during the January 23–26 storm at all eight sites. The resulting loads, in $\mu g/ft^2$, are presented in table 7. The largest load for the urban locations was 0.86 $\mu g/ft^2$ at the Wastewater Treatment Plant (site B) and 0.80 $\mu g/ft^2$ collected by the wet–dry autosampler in downtown Modesto (site E). The largest load for the agricultural locations was 1.3 $\mu g/ft^2$ collected by the wet–dry auto sampler east of Modesto (site F) and 0.76 $\mu g/ft^2$ collected by the funnel sampler north of Modesto (site H).

Chlorpyrifos

As with diazinon, the instantaneous loads of chlorpyrifos at the river sites were usually closely related to streamflow. Two exceptions were the weekly nonstorm samples on January 4 at the Stanislaus River at Caswell State Park (fig. 11F) and on February 1 at Orestimba Creek at River Road (fig. 11D). The instantaneous chlorpyrifos loading rates usually peaked during the rising limb of the storm hydrograph for both target storms (January 23–26 and February 18–24). The maximum instantaneous loading rates at the river sites for the January target storm (not including the baseline loading rate) were 0.153 lb a.i./d at San Joaquin River near Vernalis, 0.030 lb a.i./d at Merced River near River Road and at Tuolumne River at Shiloh Road, and less than or equal to 0.015 lb a.i./d at Stanislaus River at Caswell State Park, San Joaquin River near Stevinson, and Orestimba Creek at River Road at River Road sites. The maximum instantaneous loading rates for the February target storm were all less than or equal to 0.031 at all sites. For the first nontarget storm period (January 8–12), samples were collected during the weekly sampling on January 11 at all river sites and daily at the San Joaquin River near Vernalis throughout the storm hydrograph. The instantaneous loading rates were all less than or equal to 0.028 lb a.i./d. For the second nontarget storm period (February 9–11), samples were collected on February 15 during the weekly sampling at all river sites and twice per day at the San Joaquin River near Vernalis throughout the storm hydrograph. Loading rates were less than or equal to 0.026 lb a.i./d at all sites with the exception of San Joaquin River at Patterson which had a instantaneous loading rate of 0.041 a.i./d. The highest instantaneous loading rate for this nontarget storm period at San Joaquin River near Vernalis was 0.161 lb a.i./d on February 13.

The total January and February 2001 chlorpyrifos loads were calculated only for the San Joaquin River near Vernalis. The total chlorpyrifos load in the San Joaquin River near Vernalis during January and February 2001 was 2.17 lb a.i. (table 8). This total includes 1.47 lb a.i. of baseline load, 0.291 lb a.i nontarget storm load, and 0.410 lb a.i. target storm load (fig. 11G and table 8). A nonstorm category was not considered for chlorpyrifos load as samples were either at or below the baseline loading rate.

The first target storm (January 23–26, 2001) transported 0.301 lb a.i. of chlorpyrifos to San Joaquin River near Vernalis and the second target storm (February 18–24, 2001) transported 0.109 lb a.i. The 0.410 lb a.i. of chlorpyrifos transported during the two target storms is almost 20 percent of the 2.17 lb a.i. of chlorpyrifos transported in two storms in January and February 2000 (Kratzer and others, 2002). Approximately 61 percent of the 0.301 lb a.i. chlorpyrifos transported during the first target storm to San Joaquin near Vernalis came from four sites: Merced River at River Road (0.079 lb a.i.), Tuolumne River at Shiloh Road (0.044 lb a.i.), San Joaquin River near Stevinson (0.034 lb a.i.), and Stanislaus River at Caswell State Park (0.026 lb a.i.). Approximately 61 percent of the 0.109 lb a.i. of chlorpyrifos transported to San Joaquin River near Vernalis during the second target storm came from the Tuolumne River at Shiloh Road (0.067 lb a.i.). Some of this chlorpyrifos in the Tuolumne River comes from the storm drains in the Modesto urban area. These loads from both target storms in January and February do not include the baseline loads of 0.303 lb a.i. at San Joaquin River near Vernalis, 0.028 lb a.i. at Tuolumne River at Shiloh Road, 0.021 lb a.i. at Stanislaus River at Caswell State Park, 0.018 lb a.i. at Merced River at River Road, 0.011 lb a.i. at San Joaquin River near Stevinson, and less than 0.003 lb a.i. at Orestimba Creek at River Road. The total load at San Joaquin River near Vernalis for January and February 2001 was 0.02 percent of dormant application. This is much lower than the 0.16 percent during January through February 2000 (Kratzer and others, 2002)

As with diazinon, the McHenry storm drain chlorpyrifos loading rates are closely related to the storm hydrograph (fig. 11H). The maximum instantaneous loading rate of 0.009 lb a.i. occurred shortly before the peak of the storm hydrograph, and instantaneous loading rates decreased to less than 0.001 lb a.i. at the end of the nine-hour sampling period. The total load in the McHenry storm drain produced by the January 23–26 storm period was 0.001 lb a.i. This load compares with a total load of less than 0.001 lb a.i. of chlorpyrifos during a February 1995 storm sampled at this site (Kratzer, 1998).

Figure 12B illustrates the chlorpyrifos loads from precipitation collected at urban and agricultural sites. Composite precipitation samples were collected during the January 23–26 storm at all eight sites. The resulting loads, in μg/ft^2, are listed in table 7. The largest loads for the urban locations were 0.10 μg/ft^2 collected by the funnel sampler at the Wastewater Treatment Plant (site B) and 0.09 μg/ft^2 collected by the wet–dry auto sampler in downtown Modesto (site E). The largest loads for the agricultural locations were 0.22 μg/ft^2 collected by the wet–dry auto sampler east of Modesto (site F) and 0.12 μg/ft^2 collected by the funnel sample north of Modesto (site H).

SUMMARY AND CONCLUSIONS

The agricultural application of diazinon and chlorpyrifos during December 2000 through February 2001 in the San Joaquin River Basin was 24 percent less and 3.2 times more, respectively, than that applied during the same time periods in 1999–2000. A total of seven river sites were sampled from 19 to 64 times each during January and February 2001. Samples were collected weekly during nonstorm periods and several times during storm runoff from a total of four storms. Of these four storms, two were defined to be target storms. These target storms had the greatest potential to produce runoff that would transport applied diazinon and chlorpyrifos. The two target storm periods were January 23–26, 2001 (0.87 in. at Modesto), and February 18–24, 2001 (1.81 in. at Modesto). The highest concentrations of diazinon and chlorpyrifos at the seven river sites occurred during storm runoff for diazinon and during weekly sampling for chlorpyrifos. Of the 220 environmental samples collected at river sites, 41 exceeded the proposed critical CMC of 0.08 μg/L for diazinon and only two exceeded the CMC of 0.02 μg/L for chlorpyrifos.

The total diazinon load in the San Joaquin River near Vernalis during the two target storms in January and February 2001 was 12.6 lb a.i. This compares with 8.17 lb a.i. during two storms in January and February 2000 and with 27.4 lb a.i. during two storms in January and February 1994. During the two target storms in January and February 2001, the main sources of diazinon in the San Joaquin River Basin were Merced River Basin (19.5 percent), San Joaquin River near Stevinson Basin (12.0 percent), Tuolumne River Basin (4.6 percent), and Stanislaus River Basin (4.3 percent). The total diazinon load in the San Joaquin River near Vernalis during January and February 2001 was 23.8 lb a.i. and was 0.27 percent of the December 1, 2000, through February 24, 2001, application. This compares with a total diazinon load of 19.6 lb a.i. during January and February 2000, which was 0.17 percent of the December 1, 1999, through February 14, 2000, application.

The total chlorpyrifos load in the San Joaquin River near Vernalis during the two target storms in January and February 2001 was 0.410 lb a.i. This compares with 2.17 lb a.i. transported in two storms in January and February 2000. The main sources of chlorpyrifos during the two target storms in 2001 were Tuolumne River Basin (27 percent), Merced River at River Road (20 percent), San Joaquin River near Stevinson (12 percent), Stanislaus River at Caswell State Park (8.3 percent), and Orestimba Creek at River Road (3.4 percent). The total chlorpyrifos load in the San Joaquin River near Vernalis during January and February 2001 was 2.17 lb a.i. and was 0.02 percent of the December 1, 2000, through the February 24, 2001, application. This compares with the total chlorpyrifos load of 5.68 lb a.i. during January and February 2000, which was 0.16 percent of the December 1999 through February 14, 2000, application.

The McHenry storm drain in Modesto was sampled nine times (hourly) during the January 23–26, 2001, storm. Composite precipitation samples were collected at eight sites during this same storm—four sites in the urban area and four sites in the outlying agricultural areas. Every sample collected from the McHenry storm drain during the January 23–26 storm event exceeded the CMC for diazinon; and seven of the nine samples exceeded the CMC for chlorpyrifos. All composite precipitation samples exceeded the CMC for both diazinon and chlorpyrifos.

The average diazinon concentration from the two precipitation sites in the McHenry storm drain basin (sites E and G), accounted for 68 percent of the flow-weighted average diazinon concentration in McHenry storm drain. Chlorpyrifos, however, had an average concentration in the precipitation that was over 2.5 times higher than what was detected in the McHenry storm drain. The contribution of the diazinon and chlorpyrifos concentrations in the precipitation to the concentrations in McHenry storm drain seems to be dependent on the physical and chemical properties of each pesticide. Diazinon is much more soluble than chlorpyrifos, which was reflected in the higher concentrations in McHenry storm drain. Chlorpyrifos has a greater tendency to sorb to suspended material and surfaces. No firm conclusions can be made on the basis of one storm event, but it appears that pesticides in precipitation significantly contribute to pesticide loads observed in runoff. However, a more detailed analysis of pesticide use before a sampling event is needed. The sampling of atmospheric deposition continued during 2002–2003 at six sites in the San Joaquin River Basin, including sites E and F.

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