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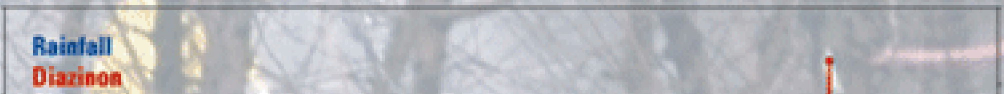
Diazinon and Chlorpyrifos Loads in the San Joaquin River Basin, California, January and February 2000

Water-Resources Investigations Report 02-4103



U.S. Department of the Interior
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Kratzer and others—Diazinon and Chlorpyrifos Loads in the San Joaquin River Basin, California, January and February 2000—WRIR 02-4103

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By Charles R. Kratzer[1], Celia Zamora[2], *and* Donna L. Knifong[1]

U.S. GEOLOGICAL SURVEY

Water Resources Investigations Report 02-4103

Prepared in cooperation with the

California Department of Pesticide Regulation

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CONVERSION FACTORS, VERTICAL DATUM, AND ABBREVIATIONS

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

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

$$°F = (1.8)°C + 32$$

Sea level: In this report "sea level" refers to the National Geodetic Vertical Datum of 1929 (NGVD of 1929)—a geodetic datum derived from a general adjustment of the first-order level nets of both the United States and Canada, formerly called Sea Level Datum of 1929.

Abbreviations and Acronyms

μg/L, microgram per liter
lb a.i., pound active ingredient
lb a.i./d, pound active ingredient per day
L, liter
mg/L, milligram per liter

CDPR, California Department of Pesticide Regulation
CMC, criterion maximum concentration
GC/MS, gas chromatograph with mass spectrometer
LRL, laboratory reporting level
MDL, method detection limit
NWQL, National Water Quality Laboratory
PCO, pest control operator
RPD, relative percentage difference
SPE, solid-phase extraction
TID5, Turlock Irrigation District lateral no. 5
USGS, U.S. Geological Survey

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ABSTRACT

The application of diazinon and chlorpyrifos on dormant orchards in 2000 in the San Joaquin River Basin was less than 21 percent of application in 1993 and 1994. A total of 13 sites were sampled weekly during nonstorm periods and more frequently during two storm periods. The sites included five major river and eight minor tributary sites. The highest concentrations of diazinon and chlorpyrifos occurred during the storm periods. Four samples from major river sites (Tuolumne River and two San Joaquin River sites) had diazinon concentrations greater than 0.08 microgram per liter, the concentration being considered by the state of California as its criterion maximum concentration for the protection of aquatic habitat. One sample from a major river site (San Joaquin River) exceeded the equivalent State guideline of 0.02 microgram per liter for chlorpyrifos. At the eight minor tributary sites, 24 samples exceeded the diazinon guideline and four samples exceeded the chlorpyrifos guideline. The total diazinon load in the San Joaquin River near Vernalis during January and February 2000 was 19.6 pounds active ingredient; of this, 8.17 pounds active ingredient was transported during two storms. In 1994, 27.4 pounds active ingredient was transported during two storms. The total chlorpyrifos load in the San Joaquin River near Vernalis during January and February 2000 was 5.68 pounds active ingredient; of this, 2.17 pounds active ingredient was transported during the two storms. During the frequently sampled February 2000 storm, the main sources of diazinon in the San Joaquin River Basin were the San Joaquin River near Stevinson Basin (25 percent), Tuolumne River Basin (14 percent), and the Stanislaus River Basin (10 percent). The main sources of chlorpyrifos in the San Joaquin River Basin were the San Joaquin River near Stevinson Basin (17 percent), Tuolumne River Basin (13 percent), and the Merced River Basin (11 percent). The total January and February diazinon load in the San Joaquin River near Vernalis was 0.17 percent of dormant application; total January and February chlorpyrifos load was 0.16 percent of dormant application.

INTRODUCTION

The organophosphorus insecticides diazinon and chlorpyrifos are widely used in agricultural and urban areas. They are applied to several crops in the agriculturally dominated San Joaquin River Basin. The most intense application period for diazinon is January and February when it is applied on dormant stone-fruit orchards to control wood-boring insects. Most of this use of diazinon is on almond orchards. Chlorpyrifos is also used as a dormant spray on almonds in January and February and extensively on alfalfa in March and on walnuts and almonds in May through July (Panshin and others, 1998).

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 (milligram per liter) at 20°C and may sorb to sediments moderately, but should not significantly bioconcentrate in aquatic organisms (Howard, 1991). Hydrolysis, biodegradation, and volatilization may be significant fate processes for diazinon in natural waters. Hydrolysis half-life (at 20°C) is 185 days at pH 7.4 (Howard, 1991).

Chlorpyrifos usually persists for about 9 to 17 weeks in soil, 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 (Howard, 1991). Unlike diazinon, chlorpyrifos has a 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. Hydrolysis half-life (at 20°C) is about 44 to 117 days near pH 7 (Howard, 1991). Biodegradation and volatilization are probably less significant fate processes, especially as concentrations of suspended sediment increases.

Several studies have evaluated diazinon and(or) chlorpyrifos transport during January and February storms in the San Joaquin Basin. The studies can be grouped by their spatial coverage of the basin. Some studies only monitored the basin outlet at Vernalis (Kuivila and Foe, 1995; MacCoy and others, 1995), whereas other studies monitored only one subbasin upstream of Vernalis (Ganapathy and others, 1997; Poletika and Robb, 2000). Some studies monitored at Vernalis and at one to three subbasins upstream (Domagalski and others, 1997; Kratzer, 1998; Bennett and others, 1998; Panshin and others, 1998), whereas other studies monitored at Vernalis and at more than three subbasins upstream (Ross and others, 1996; Kratzer, 1999). Besides Vernalis, the most frequently monitored sites have been on Orestimba Creek and the Merced River (fig. 1, sites 17, 7, and 6).

Several studies also have been completed on the toxicity of diazinon and chlorpyrifos in the San Joaquin Basin. The most commonly used guidelines in California for short-term exposure (criterion maximum concentration or CMC) in terms of concentrations are 0.08 μg/L (microgram per liter) for diazinon and 0.02 μg/L for chlorpyrifos (Siepmann and Finlayson, 2000). The corresponding guidelines for longer-term exposure (criterion continuous concentration) are 0.05 μg/L for diazinon and 0.014 μg/L for chlorpyrifos.

The purpose of this report is to describe the loads of diazinon and chlorpyrifos in the San Joaquin Basin during January and February 2000. Loads, storm and nonstorm related, are compared with applications and storm runoff. The study design was to sample two storms with the greatest potential for transporting diazinon and chlorpyrifos. The format and analysis used in this report is similar to a 1994 study in the same area (Kratzer, 1999). Several comparisons will be made in this report to the diazinon loads in 1994. The Kratzer (1999) paper should be referred to for additional information on diazinon transport in the San Joaquin Basin.

The authors wish to thank George Nichol, Philip Crader, Christina Pali, Thomas King, and Jamie Lu of the Central Valley Regional Water Quality Control Board staff and Christopher Eacock of the U.S. Bureau of Reclamation for their assistance in storm sampling. We especially thank Shakoora Azimi of the Regional Board staff for enlisting and organizing the storm sampling assistance from the above individuals.

STUDY AREA

The basin for the perennial San Joaquin River drains 7,345 mi^2 (square mile), of which 4,299 mi^2 are in the Sierra Nevada, 2,244 mi^2 are in the San Joaquin Valley, and 802 mi^2 are in the Coast Ranges (fig. 1 and table 1). Almost all of the agricultural application of diazinon and chlorpyrifos is in the San Joaquin Valley part of the study area. According to U.S. Geological Survey (USGS) streamflow data for 1951–1995 (U.S. Geological Survey, accessed May 15, 2001), 66 percent of the average streamflow in the perennial San Joaquin River comes from the three major east-side river basins: the Merced River (15 percent), the Tuolumne River (30 percent), and the Stanislaus River (21 percent). The remaining streamflow in the San Joaquin River comes from the Bear Creek Basin; Mud and Salt Sloughs, and ephemeral creeks that drain from the west; drainage canals that flow directly to the San Joaquin River; and occasionally from the upper San Joaquin River above Bear Creek during especially high flows.

A total of 13 sites were sampled between 8 and 36 times each in January and February 2000 during this study (fig. 1 and table 1). These sites include two sites on the mainstem of the San Joaquin River (fig. 1, sites 1 and 17), basin outlet sites on the three major east-side tributaries (sites 6, 14, and 16), two drainage canals in the Merced River Basin (sites 3 and 4), two creek sites in the Tuolumne River Basin (sites 10 and 11), two west-side creeks (sites 7 and 9), and two drainage canals flowing directly to the San Joaquin River (sites 2 and 8). The San Joaquin River sites include the basin outlet near Vernalis and the upstream boundary of the perennial San Joaquin River near Stevinson. The drainage canals in the Merced River Basin are Highline Canal, which drains an exclusively agricultural area, and Livingston Canal, which drains both urban and agricultural areas. The creek sites (Dry Creek) in the Tuolumne River Basin are upstream and downstream of the Modesto urban area. The west-side creeks (Orestimba and Del Puerto Creeks) and drainage canal (Newman Wasteway) exclusively drain agricultural areas, whereas the east-side drainage canal (Turlock Irrigation District lateral no. 5 or TID5) receives both agricultural drainage and treated wastewater from the city of Turlock.

The water-quality sampling sites on the Merced, Tuolumne, and Stanislaus Rivers (fig. 1, sites 6, 14, and 16, respectively) are downstream of gaging stations (sites 5, 13, and 15, respectively). Streamflows at the water-quality sampling sites were estimated using traveltimes in the tributaries from the gaging stations

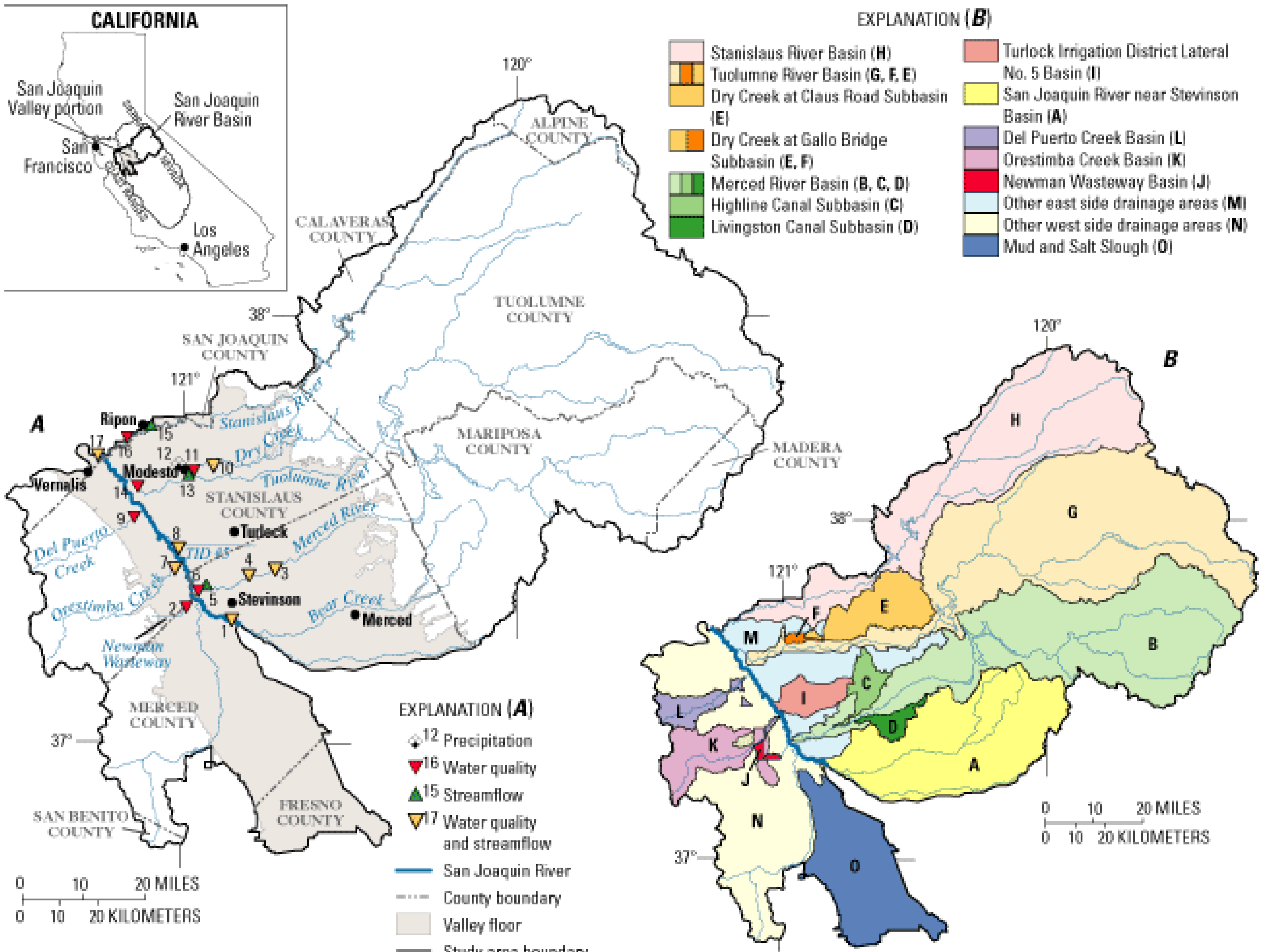

Figure 1. Location of (***A***) data sites and (***B***) drainage basins in the San Joaquin River Basin, California.

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

[See figure 1 for site locations]

Site number	Site name	Site identification number	Site location (unless otherwise noted: river miles from San Joaquin River; river miles from Vernalis	Data at site		
				Precipitation	Streamflow	Water quality
1	San Joaquin River near Stevinson	11260815	[1]60.5		X	X
2	Newman Wasteway at Highway 33, near Gustine	371903120585400	1.0; 48.2			X
3	Livingston Canal at Livingston Treatment Plant, near Livingston	372424120432800	21.6; 67.3		X	X
4	Highline Canal Spill near Hilmar	372323120481700	15.5; 61.2		X	X
5	Merced River near Stevinson	11272500	4.8; 50.5		X	
6	Merced River at River Road Bridge, near Newman	11273500	1.1; 46.8			X
7	Orestimba Creek at River Road, near Crows Landing	11274538	1.0; 37.7		X	X
8	Turlock Irrigation District Lateral no. 5, near Patterson	11274560	0.2; 31.3		X	X
9	Del Puerto Creek at Vineyard Road, near Patterson	11274653	1.0; 21.7			X
10	Dry Creek at Claus Road Bridge, at Modesto	373925120550701	[2]5.5; 21.9; 33.1		X	X
11	Dry Creek at Gallo Bridge below Highway 132, at Modesto	373811120590001	[2]0.8; 17.2; 28.4			X
12	Modesto Irrigation District office rooftop, 1231 11th Street, Modesto	Not applicable	Not applicable	X		
13	Tuolumne River at Modesto	11290000	16.2; 27.4		X	
14	Tuolumne River at Shiloh Road Bridge, near Grayson	11290200	3.6; 14.8			X
15	Stanislaus River at Ripon	11303000	15.7; 18.2		X	
16	Stanislaus River at Caswell State Park, near Ripon	374209121103800	8.5; 11.0			X
17	San Joaquin River near Vernalis	11303500	[1]0.0		X	X

[1]River miles from Vernalis.

[2]River miles from Tuolumne River; river miles from San Joaquin River; river miles from Vernalis.

(Kratzer and Biagtan, 1997). Precipitation in the study area is represented in this report by a site in downtown Modesto (site 12).

APPLICATION OF DIAZINON AND CHLORPYRIFOS

Most of the agricultural application of diazinon and chlorpyrifos in December through February is on dormant orchards of several stone fruits and nuts in the San Joaquin Basin, primarily almonds (Panshin and others, 1998). This is generally the most intense agricultural application period for diazinon in the San Joaquin Basin. The agricultural application of chlorpyrifos in the basin is more spread out over the year, with intense applications on alfalfa in March and intense in-season applications on almonds and walnuts during May through July. Both diazinon and chlorpyrifos are applied in urban areas, primarily for structural pest control (Kratzer, 1998).

The application data presented in this report is from records maintained by the California Department of Pesticide Regulation (CDPR). The agricultural application data are reported by day of use, crop use, and area of use to the square mile. The agricultural application of diazinon and chlorpyrifos is presented for the two relatively dry periods that preceded the two storm periods sampled in this study (figs. 2 and 3, respectively). The agricultural application 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 representing low [less than 40 lb a.i. (pounds active ingredient) per mi^2], medium (40–100 lb a.i. per mi^2), and high (greater than 100 lb a.i. per mi^2) application areas. The only urban applications reported to CDPR are those by licensed pest control operators (PCO) by county. Household use, daily use, and place of use (except for county) are not reported. Most of the urban area within the study area is in Stanislaus and Merced Counties (fig. 1). Urban applications reported in this report are only for those two counties.

The agricultural application of diazinon and chlorpyrifos during the dry periods was geographically dispersed across the study area. This is very different from the agricultural application of diazinon in 1993–1994 when some areas had especially heavy application (Kratzer, 1999). The agricultural application amounts of both diazinon and chlorpyrifos during December 1999 through February 2000 (table 2) were drastically reduced from those of roughly the same periods in 1992 through 1994 (Panshin and others, 1998; Kratzer, 1999; California Department of Pesticide Regulation, 2000, 2001). During December 1999 through February 2000, about 11,700 lb a.i. of diazinon was applied to agricultural areas in the San Joaquin Basin compared to about 83,000 lb a.i. in 1992–1993 and 56,100 lb a.i. in 1993–1994. The most drastic reduction was the reported use in the Tuolumne River Basin: about 6,600 lb a.i. in 1993–1994 and less than 400 lb a.i. in 1999–2000. During December 1999 through February 2000, about 3,500 lb a.i. chlorpyrifos was applied to agricultural areas in the San Joaquin Basin compared to about 27,000 lb a.i. in 1992–1993.

Urban applications by PCOs is reported by month only, so the December and January application data are shown in dry period 1 (table 2), and February application data are shown in dry period 2 as approximations. The overall urban applications for Merced and Stanislaus Counties during the dormant spray period were 1.94 and 1.41 times greater than the reported agricultural applications of diazinon and chlorpyrifos, respectively (table 2). The Modesto urban area accounts for about 62 percent of the population in Stanislaus County (Gronberg and others, 1998). Thus, although the Dry Creek Basin had little or no reported agricultural applications of diazinon and chlorpyrifos, there was probably a relatively large amount of urban application. Likewise, the Livingston Canal and TID5 basins probably had relatively large urban applications. Because of the lack of reporting detail on urban applications, it was not possible to provide the same level of analysis made for agricultural application data.

SAMPLING DESIGN AND METHODOLOGY

Sampling Design

The primary transport mechanism for diazinon and chlorpyrifos to streams in the San Joaquin Basin during January and February is runoff from winter storms. Because the pesticides should stay on the trees following application to be effective, most application occurs during extended dry periods in January and February (fig. 4). Two storm periods were sampled during January and February 2000 following most of the application of diazinon and chlorpyrifos on dormant orchards. The storm periods were January 23–25, 2000, and February 9–14, 2000, which resulted in 2.66 and 2.44 in. (inch), respectively, of rain at Modesto (fig. 1, site 12). These storm periods were preceded by two relatively dry periods that were suitable for dormant spray application: December 1, 1999, to January 22, 2000, and January 26 to February 8, 2000. In this report, the “dry period” includes all periods of applications, including the period when storm runoff is sampled. In other words, although January 25 was a rainy day during a storm period (January 23–25), it is considered part of dry period 1 because runoff from January 25 was captured in the first storm sampling.

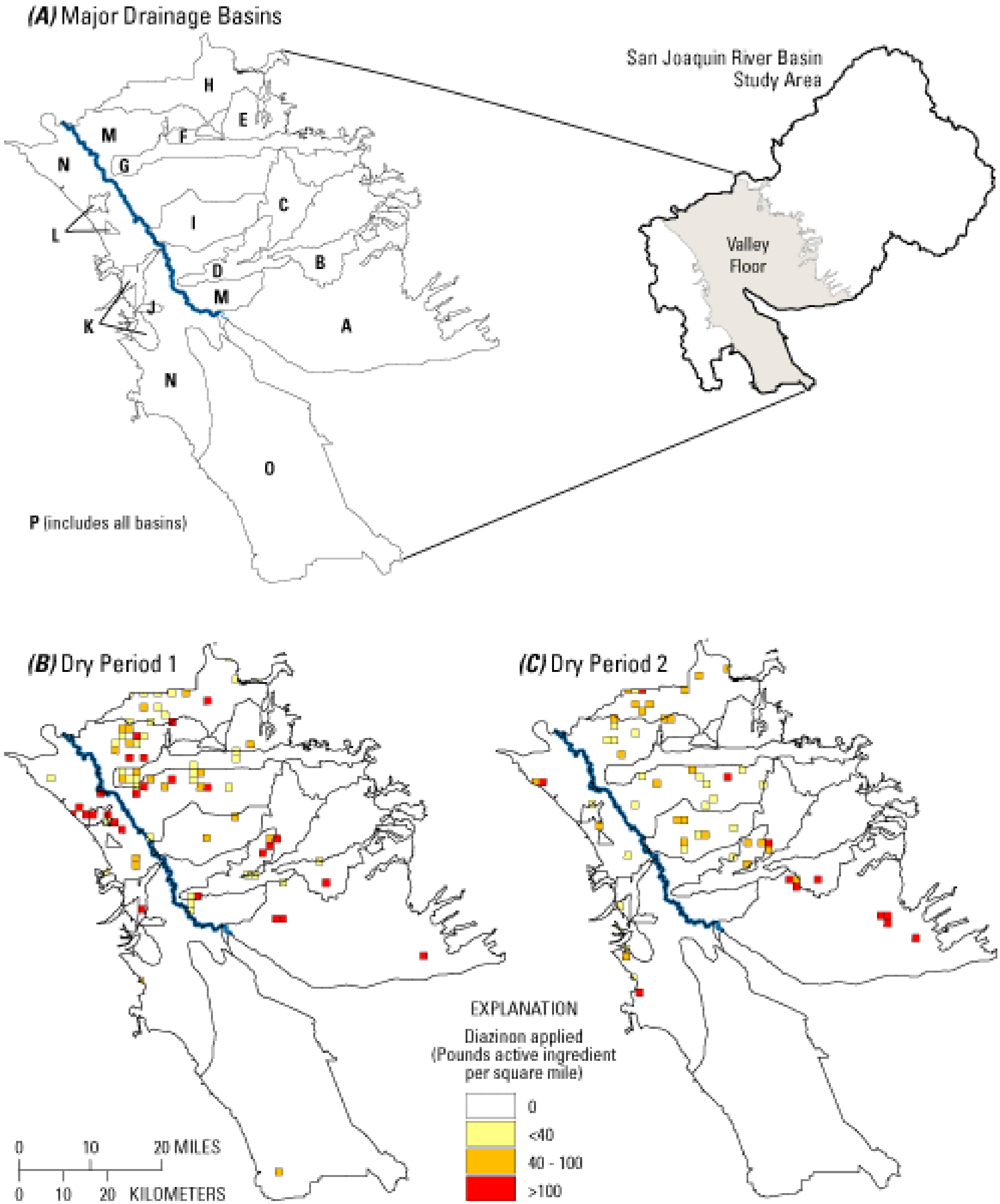

Figure 2. Diazinon application in (***A***) major drainage basins during (***B***) dry period 1 (December 1, 1999 to January 25, 2000) and (***C***) dry period 2 (January 26, 2000 to February 14, 2000) in the San Joaquin Valley part of the San Joaquin River Basin, California. <, less than; >, greater than.

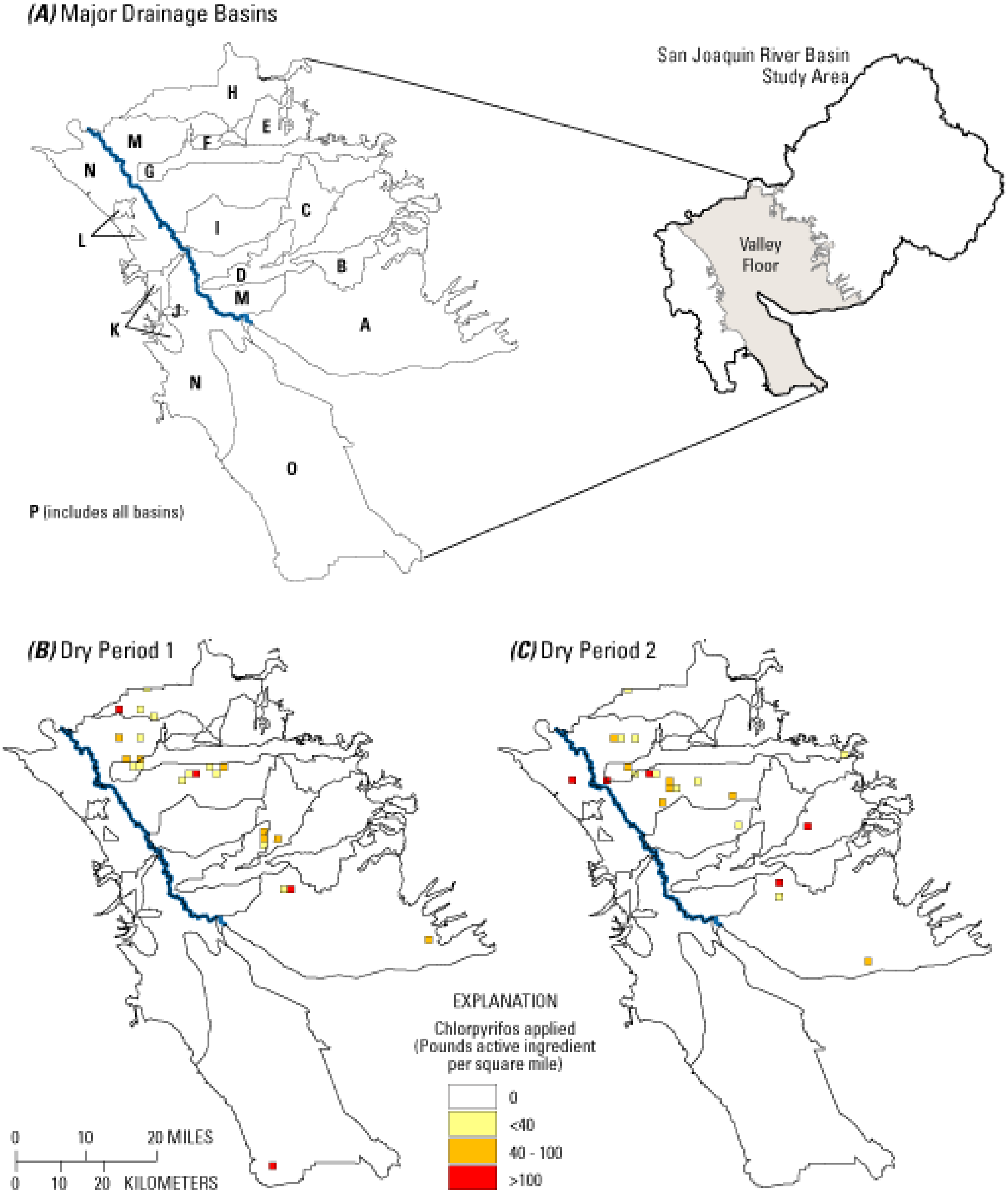

Figure 3. Chlorpyrifos application in (***A***) major drainage basins during (***B***) dry period 1 (December 1, 1999 to January 25, 2000), and (***C***) dry period 2 (January 26, 2000 to February 14, 2000) in the San Joaquin Valley part of the San Joaquin River Basin, California. <, less than; >, greater than.

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

[See figure 1 for basin areas and locations. Dry period 1: December 1, 1999 to January 25, 2000; dry period 2: January 26, 2000 to February 14, 2000]

Basin	Basin, subbasin or site name	Total basin area (square mile)	Valley basin area (square mile)	Almond orchard area (square mile)	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 Basin	818	413	44.5	489	1,789	217	227
B	Livingston Canal Subbasin	43.7	42.5	12.2	375	240	0	0
C	Highline Canal Subbasin	63.5	63.5	27.7	142	193	83	0
D	Merced River at River Road Bridge	1,397	259	80.1	1,039	625	284	314
E	Dry Creek at Claus Road Bridge	201	55.4	6.7	53	0	0	0
F	Dry Creek at Gallo Bridge	212	66.3	7.0	53	0	0	0
G	Tuolumne River at Shiloh Road Bridge	1,862	150	21.0	350	1	52	441
H	Stanislaus River at Caswell State Park	1,144	116	18.0	417	577	201	5
I	Turlock Irrigation District Lateral no. 5	86.4	86.4	12.2	104	326	0	28
J	Newman Wasteway at Hwy 33	8.8	7.7	2.7	5	0	0	0
K	Orestimba Creek at River Road	195	33.3	5.6	627	10	0	0
L	Del Puerto Creek at Vineyard Road	81.0	8.4	0.2	204	13	0	0
M	San Joaquin River (other east side areas)	369	354	73.5	2,046	744	463	1,011
N	San Joaquin River (other west side areas)	890	334	18.0	1,609	638	0	140
O	Mud and Salt Slough Basin	492	484	2.0	80	0	162	0
P	San Joaquin River near Vernalis	7,345	2,245	278	6,970	4,732	1,379	2,165
	Merced County	1,971	1,381	133	3,272[1]	1,538[2]	1,010	652
	Stanislaus County	1,514	851	141	10,410	7,467	2,175	1,144

[1]County application by licensed pest control operators is reported by month only (December 1999 and January 2000 data is shown for dry period 1).

[2]County application by licensed pest control operators is reported by month only (February 2000 data is shown for dry period 2).

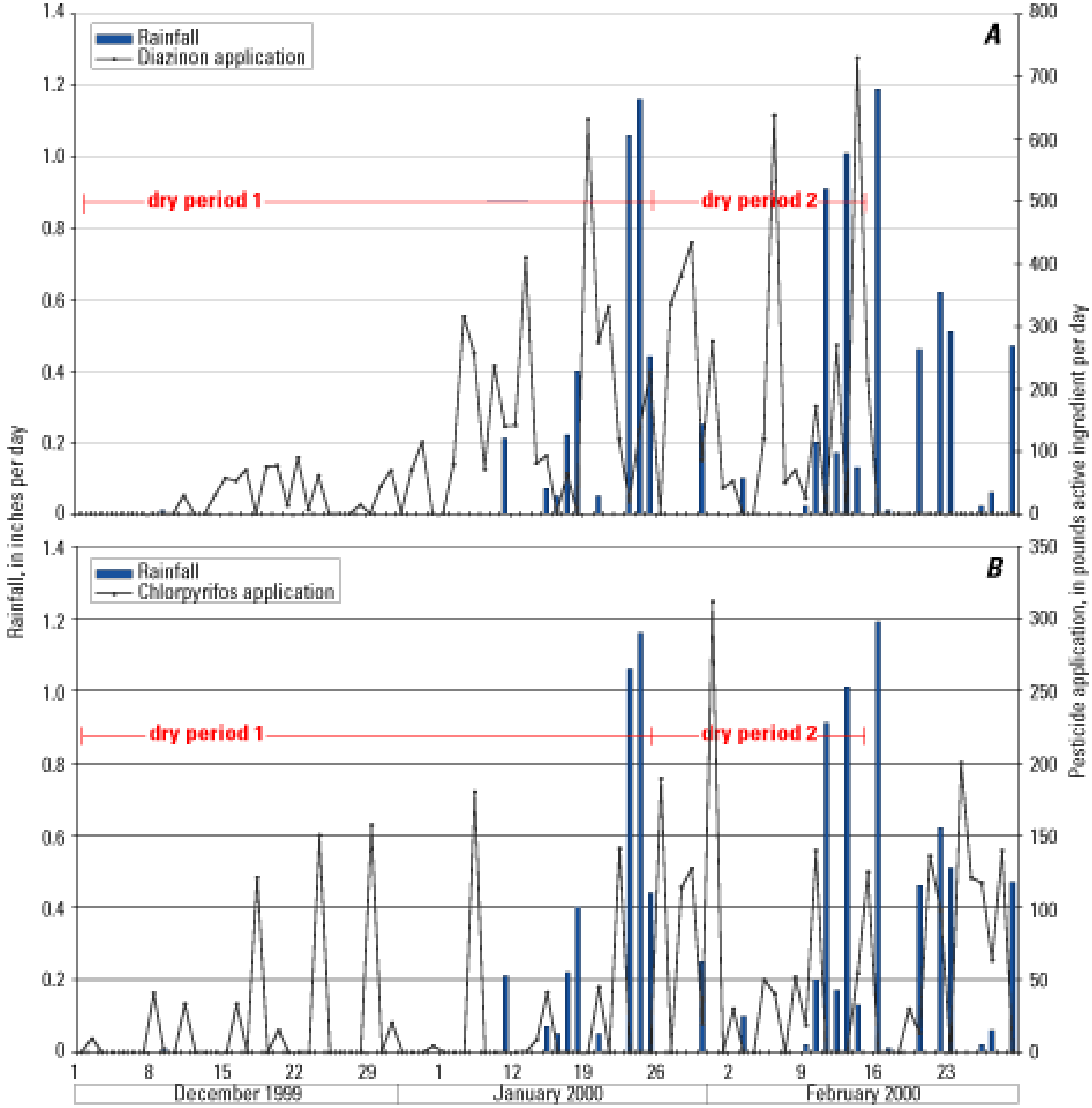

Figure 4. Daily rainfall at Modesto and (***A***) diazinon and (***B***) chlorpyrifos applications in the San Joaquin River Basin, California, December 1999 through February 2000.

The sampling strategy was to collect several samples at each site throughout the storm runoff hydrograph. In addition, each site was sampled weekly during January and February when there was not a relatively large storm. This allows for a determination of the nonstorm transport of diazinon and chlorpyrifos during the dormant spray season. Sampling during the storm runoff hydrograph was easier to accomplish at the major river sites than at the relatively small, flashy agricultural drains and creeks. The major river sites have upstream sites with real time streamflow data, so the runoff can be seen before it gets to the sampling sites. Several of the drains and creeks do not have real time streamflow data, and sampling times are based on neighboring sites with real time data. This includes Newman Wasteway, Livingston Canal, Highline Canal, TID5, and Del Puerto Creek (fig. 1, sites 2, 3, 4, 8, and 9, respectively). The timing of sample collection relative to storm runoff hydrographs at the major river sites provided generally good coverage of the hydrographs, especially the rising limb where higher concentrations were expected (fig. 5). The storm on January 23–25 was only partially sampled because it did not appear to be producing very much runoff. Except for one sample at Del Puerto Creek (table 3), samples were only collected from the major river sites. Two to three samples were collected throughout the hydrograph, except at Vernalis, where eight samples were collected.

The difficulty in timing sample collection at drain sites is best illustrated by Livingston Canal (fig. 5*B*). Like the other drain and creek sites, Livingston Canal was not sampled during the January 23–25 storm and did not respond hydrologically during the frequently sampled February 9–14 storm. The storm hydrograph response during the February 9–14 storm at Highline Canal and TID5 was much better than at Livingston Canal, although the sampling missed most of the rising limb on Highline Canal on February 13. The success of capturing storm runoff at the Newman Wasteway and Del Puerto Creek sites is unknown because these sites do not have continuous streamflow records.

Sample Processing and Laboratory Methods

Samples were collected during this study using five methods, depending on the site and streamflow conditions: width- and depth-integrated using a D-77 isokinetic sampler with a Teflon nozzle and 3-L (liter) Teflon bottle (Shelton, 1994); an equally spaced, three-point integrated surface grab using a 3-L Teflon bottle strapped into a metal cage suspended from a rope; a midpoint surface grab using the same sampler; a grab sample from the bank using the 3-L Teflon bottle; and a sample pumped from the bank using a pump with a Teflon line. Most samples were collected as integrated grabs or midpoint grabs (table 3). Early samples at the San Joaquin River near Vernalis site were the only width- and depth-integrated samples. Samples collected at the Stanislaus River, Highline Canal, and the Dry Creek at Claus Road sites were bank grabs. The Stanislaus River site does not have a bridge so the samples were collected from the right bank (facing downstream). The Dry Creek at Claus Road samples were collected from the right bank just upstream of a storm drain to avoid any influence from the Modesto urban area on the water quality of the samples. If the streamflow at a site is well mixed, there is usually no significant difference in concentrations of dissolved constituents collected by different methods (Martin and others, 1992). This should be evaluated in the future at these sampling sites under a variety of streamflow conditions.

The 3-L Teflon sample-collection bottle was cleaned between each site using the following protocol. After sampling at a site, the sample bottle was rinsed with deionized water, and about a tablespoon of dilute Liquinox solution was put into the sample bottle and swished around. The Liquinox solution then was completely rinsed out with deionized water. The sample bottle then was rinsed thoroughly with organic-free water. At the next site, the sample bottle was rinsed three times with native water before collecting the sample.

All samples were analyzed for specific conductance at the USGS laboratory in Sacramento, California. Streamflow measurements were made when possible at the Del Puerto Creek and Newman Wasteway sites. All samples for pesticide analyses were stored on ice and shipped within 3 days of collection to the National Water Quality Laboratory (NWQL) in Denver, Colorado. All pesticide samples were filtered, extracted, and analyzed for 45 dissolved pesticides (USGS laboratory schedule 2001) at the NWQL (Zaugg and others, 1995). The samples were filtered through a baked 0.7-micrometer glass-fiber filter. The dissolved pesticides were extracted by solid-phase extraction (SPE) cartridges containing porous silica coated with a C-18 phase and preconditioned with methanol. The adsorbed pesticides and metabolites were removed from the cartridges by elution with hexane-isopropanol (3:1). Extracts of the eluant were analyzed by a capillary-column gas chromatograph/mass spectrometer (GC/MS) operated in the selected-ion monitoring mode (Zaugg and others, 1995).

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 concentration is greater than zero. The MDL for diazinon at the NWQL is 0.002 μg/L; chlorpyrifos has a MDL of 0.004 μg/L. 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). The NWQL sets a laboratory reporting level (LRL) at twice the MDL to reduce the probability of false negatives to less than 1 percent (Childress and others, 1999). For this study, concentrations are reported at the MDL instead of the LRL to have the maximum information available for calculating loads. Many of the concentrations reported as less than the MDL may actually be low-level detections near the MDL.

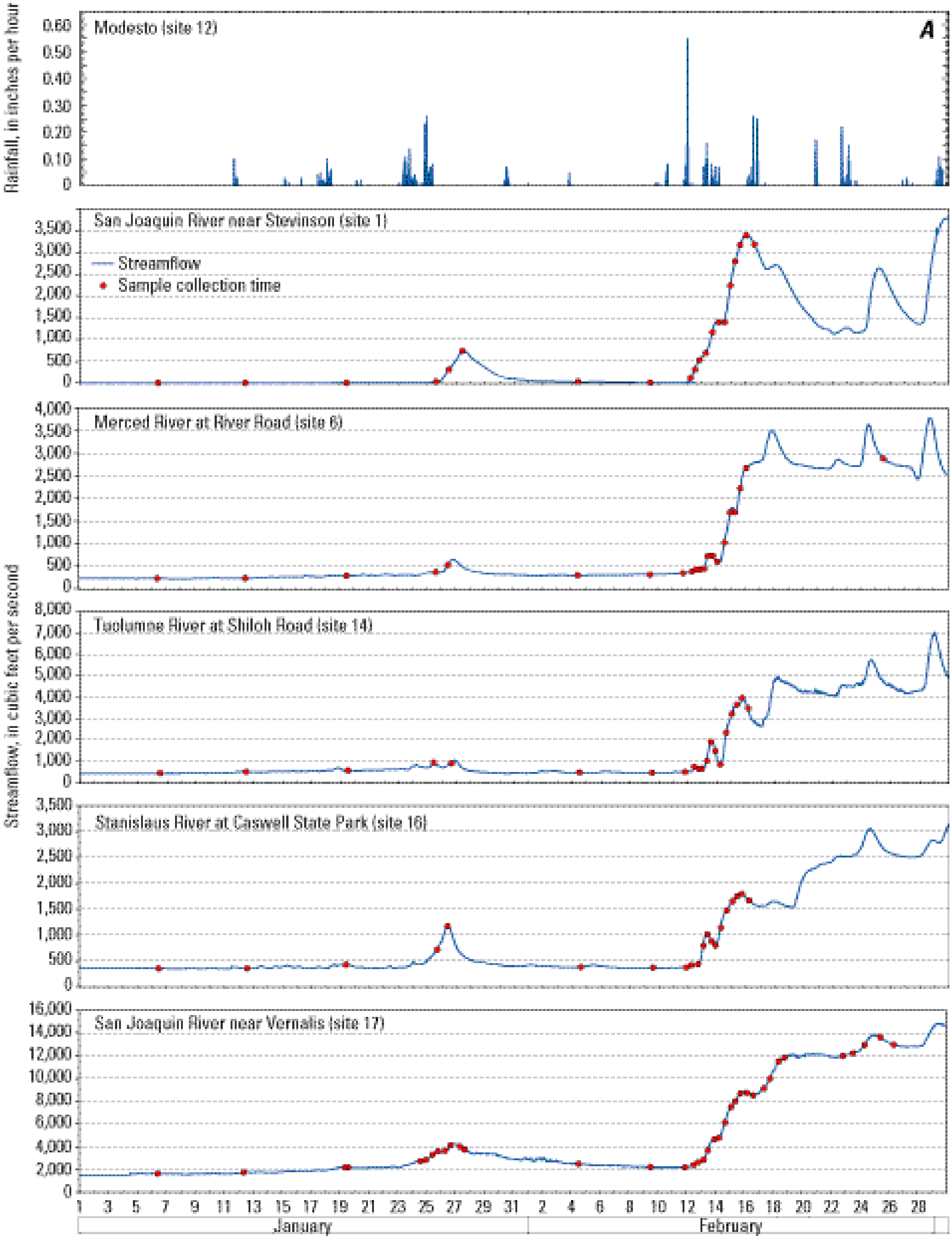

Figure 5. Hourly rainfall at Modesto, California, and streamflow and sample collection times at (***A***) major river sites in the San Joaquin River Basin, California. *Continued*.

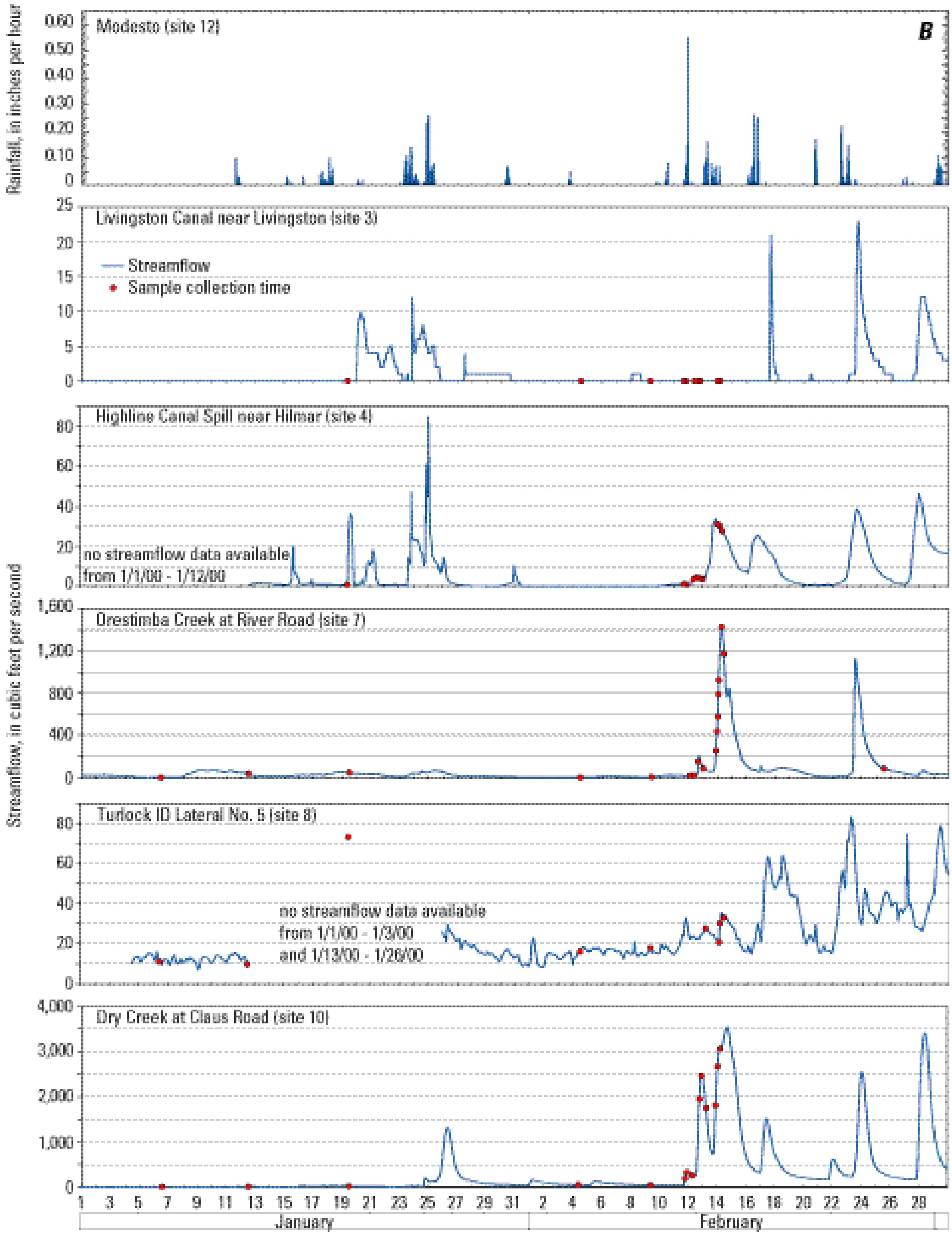

Figure 5. Hourly rainfall at Modesto, California, and streamflow and sample collection times at (***B***) minor tributary sites in the San Joaquin River Basin, California.

Table 3. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California

[See figure 1 for site locations. Streamflow is in cubic feet per second. IG, integrated grab; MG, midpoint grab; BG, bank grab; EWI, equal-width increment (width- and depth-integrated); P, pumped; E, estimate; QE, qualitative estimate; NA, not available. lb a.i./d, pound active ingredient per day; µg/L, microgram per liter; <, less than]

Site number	Site name	Site identification number	Date and time (month/day/year 24-hour time)	Collection method	Streamflow	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (lb a.i./d)
1	San Joaquin River near Stevinson	11260815	01/06/2000 0930	IG	2.9	<0.004	<0.001	<0.002	<0.001
			01/12/2000 1020	IG	2.6	<0.004	<0.001	0.006	<0.001
			01/19/2000 1020	IG	5.1	<0.004	<0.001	0.009	<0.001
			01/25/2000 1520	IG	31	0.006	0.001	0.016	0.003
			01/26/2000 1200	IG	308	QE 0.013	0.022	QE 0.15	0.249
			01/27/2000 1040	IG	732	0.014	0.055	0.026	0.103
			02/04/2000 0940	IG	25	0.007	<0.001	0.047	0.006
			02/09/2000 0950	IG	13	<0.030	0.001	0.027	0.002
			02/12/2000 0520	IG	127	0.073	0.050	0.064	0.044
			02/12/2000 1205	IG	320	0.011	0.019	0.088	0.153
			02/12/2000 2015	IG	533	0.004	0.011	0.054	0.155
			02/13/2000 0600	IG	686	0.005	0.018	0.065	0.240
			02/13/2000 1700	IG	1,170	0.006	0.038	0.043	0.271
			02/14/2000 0250	MG	1,390	0.006	0.045	0.033	0.247
			02/14/2000 1300	MG	1,400	0.008	0.060	0.042	0.309
			02/14/2000 2300	MG	2,240	0.006	0.072	0.032	0.386
			02/15/2000 0700	MG	2,790	0.004	0.060	0.019	0.286
			02/15/2000 1500	MG	3,170	E 0.004	0.068	0.018	0.307
			02/16/20000 030	MG	3,390	0.004	0.073	0.016	0.292
			02/16/2000 1430	MG	3,190	0.004	0.069	0.015	0.258
2	Newman Wasteway at Highway 33, near Gustine	371903120585400	01/06/2000 1130	IG	1.5	<0.004	<0.001	<0.002	<0.001
			01/12/2000 1350	IG	1.3	<0.004	<0.001	0.020	<0.001
			01/19/2000 1220	IG	2.9	E 0.004	<0.001	0.056	<0.001
			02/04/2000 1140	IG	1.4	0.019	<0.001	0.082	<0.001
			02/09/2000 1140	IG	1.3	0.005	<0.001	E 0.003	<0.001
			02/12/2000 0500	IG	2.1	0.005	<0.001	0.010	<0.001
			02/13/2000 0000	IG	51	0.017	0.005	0.029	0.008
			02/14/2000 0300	IG	E150	0.030	0.024	0.112	0.091
			02/14/2000 0720	IG	E150	0.037	0.030	0.154	0.124

Table 3. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California—*Continued*

Site number	Site name	Site identification number	Date and time (month/day/year 24-hour time)	Collection method	Streamflow	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (lb a.i./d)
3	Livingston Canal at Livingston Treatment Plant, near Livingston	372424120432800	01/19/2000 0900	MG	0.05	E 0.003	<0.001	E 0.004	<0.001
			02/04/2000 1320	MG	0.05	0.010	<0.001	0.076	<0.001
			02/09/2000 0900	MG	0.05	0.005	<0.001	0.064	<0.001
			02/11/2000 1600	MG	0.05	0.007	<0.001	0.086	<0.001
			02/11/2000 1950	MG	0.05	0.007	<0.001	0.090	<0.001
			02/12/2000 1010	MG	0.05	0.009	<0.001	0.084	<0.001
			02/12/2000 1600	MG	0.05	0.010	<0.001	0.084	<0.001
			02/12/2000 1900	MG	0.05	0.007	<0.001	0.024	<0.001
			02/14/2000 0000	MG	0.05	0.012	<0.001	0.083	<0.001
			02/14/2000 0330	MG	0.05	0.011	<0.001	0.087	<0.001
4	Highline Canal Spill near Hilmar	372323120481700	01/19/2000 0930	BG	0.6	0.004	<0.001	0.006	<0.001
			02/11/2000 1700	BG	0.05	E 0.003	<0.001	0.011	<0.001
			02/11/2000 2030	BG	0.05	0.005	<0.001	0.014	<0.001
			02/12/2000 0940	BG	0.05	0.005	<0.001	0.011	<0.001
			02/12/2000 1455	BG	0.05	E 0.003	<0.001	0.012	<0.001
			02/12/2000 1800	BG	2.5	0.005	<0.001	0.011	<0.001
			02/13/2000 0100	BG	4.8	0.008	<0.001	0.070	0.002
			02/14/2000 0030	BG	13	0.011	<0.001	0.126	0.009
			02/14/2000 0400	BG	25	0.010	0.001	0.114	0.015
			02/14/2000 0800	BG	33	0.009	0.002	0.122	0.022
6	Merced River at River Road Bridge, near Newman	11273500	01/06/2000 1000	IG	229	<0.004	0.002	<0.002	0.001
			01/12/2000 1100	IG	231	<0.004	0.002	0.006	0.007
			01/19/2000 1050	IG	289	E 0.003	0.005	0.007	0.011
			01/25/2000 1440	IG	361	0.005	0.010	0.042	0.082
			01/26/2000 1100	IG	528	0.007	0.020	0.010	0.028
			02/04/2000 1020	IG	296	<0.004	0.003	0.005	0.008
			02/09/2000 1010	IG	316	<0.004	0.003	0.004	0.007
			02/11/2000 1730	IG	352	<0.004	0.004	E 0.004	0.008
			02/12/2000 0800	IG	384	0.006	0.010	0.007	0.014
			02/12/2000 1515	IG	426	0.005	0.011	0.007	0.016
			02/12/2000 2100	IG	424	E 0.003	0.007	0.006	0.014
			02/13/2000 0350	IG	446	E 0.003	0.007	0.005	0.012
			02/13/2000 1000	IG	726	0.007	0.027	0.008	0.031
			02/13/2000 1800	IG	731	0.012	0.047	0.012	0.047

Table 3. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California—*Continued*

Site number	Site name	Site identification number	Date and time (month/day/year 24-hour time)	Collection method	Streamflow	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (lb a.i./d)
6	Merced River at River Road Bridge, near Newman—*Continued*	11273500	02/14/2000 0150	IG	604	0.011	0.036	0.014	0.046
			02/14/2000 1345	IG	1,022	0.011	0.061	0.014	0.077
			02/14/2000 2330	IG	1,690	0.010	0.091	0.014	0.127
			02/15/2000 0710	IG	1,695	0.005	0.046	0.008	0.073
			02/15/2000 1600	IG	2,220	0.005	0.060	0.008	0.108
			02/16/2000 0150	IG	2,673	E 0.004	0.058	0.007	0.101
			02/25/2000 1300	IG	2,880	0.004	0.062	E 0.003	0.047
7	Orestimba Creek at River Road, near Crows Landing	11274538	01/06/2000 1030	IG	3	<0.004	<0.001	0.006	<0.001
			01/12/2000 1230	IG	36	<0.004	<0.001	0.183	0.035
			01/19/2000 1140	IG	49	0.006	0.002	0.033	0.009
			02/04/2000 1100	IG	3	0.008	<0.001	0.072	0.001
			02/09/2000 1110	IG	6	0.004	<0.001	0.020	<0.001
			02/12/2000 0300	IG	19	E 0.004	<0.001	0.018	0.002
			02/12/2000 0840	IG	22	<0.004	<0.001	0.026	0.003
			02/12/2000 1600	IG	149	0.004	0.003	0.028	0.022
			02/13/2000 0130	IG	88	<0.004	<0.001	0.015	0.007
			02/13/2000 2130	P	252	0.004	0.005	0.067	0.091
			02/13/2000 2321	P	408	0.011	0.024	0.300	0.659
			02/14/2000 0030	P	577	E 0.003	0.009	0.084	0.261
			02/14/2000 0130	P	786	0.008	0.034	0.101	0.428
			02/14/2000 0230	P	923	0.008	0.040	0.059	0.293
			02/14/2000 0650	P	1,420	<0.004	0.015	0.007	0.054
			02/14/2000 1100	P	1,170	0.006	0.038	0.011	0.069
			02/25/2000 1200	IG	88	<0.004	<0.001	<0.002	<0.001
8	Turlock Irrigation District Lateral no. 5, near Patterson	11274560	01/06/2000 1040	MG	21	0.007	<0.001	0.018	0.002
			01/12/2000 1320	MG	21	0.007	<0.001	0.029	0.003
			01/19/2000 1120	MG	73	0.011	0.004	0.034	0.013
			02/04/2000 1040	MG	29	0.006	<0.001	0.056	0.009
			02/09/2000 1040	MG	33	0.005	<0.001	0.029	0.005
			02/13/2000 0235	MG	52	<0.008	0.001	<0.060	0.008
			02/14/2000 0017	MG	41	0.009	0.002	0.069	0.015
			02/14/2000 0430	MG	61	0.013	0.004	0.060	0.020
			02/14/2000 0800	MG	68	0.010	0.004	0.046	0.017

Table 3. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California—*Continued*

Site number	Site name	Site identification number	Date and time (month/day/year 24-hour time)	Collection method	Streamflow	Chlorpyrifos concentration (μg/L)	Chlorpyrifos instantaneous loading rate (lb a.i./d)	Diazinon concentration (μg/L)	Diazinon instantaneous loading rate (lb a.i./d)
9	Del Puerto Creek at Vineyard Road, near Patterson	11274653	01/06/2000 1240	IG	4.7	<0.004	<0.001	0.385	0.010
			01/12/2000 1000	IG	1.8	<0.008	<0.001	1.06	0.010
			01/19/2000 1400	IG	6.4	0.005	<0.001	0.182	0.006
			01/24/2000 1700	IG	16	0.007	<0.001	0.075	0.006
			02/12/2000 0100	IG	38	0.009	0.002	0.834	0.002
			02/12/2000 0700	IG	11	0.009	0.001	0.236	0.014
			02/12/2000 1400	IG	NA	<0.004	NA	E 0.017	NA
			02/13/2000 0200	IG	25	<0.004	<0.001	0.008	0.001
			02/13/2000 2030	MG	NA	E 0.003	NA	0.021	NA
			02/14/2000 0100	IG	NA	<0.004	NA	<0.002	NA
			02/14/2000 0600	IG	NA	<0.004	NA	<0.002	NA
10	Dry Creek at Claus Road Bridge, at Modesto	373925120550701	01/06/2000 1330	BG	0.9	0.005	<0.001	<0.002	<0.001
			01/12/2000 1300	BG	3.7	E 0.003	<0.001	0.015	<0.001
			01/19/2000 1130	BG	15	0.008	<0.001	0.016	0.001
			02/04/2000 0950	BG	46	<0.004	<0.001	0.010	0.002
			02/09/2000 1050	BG	35	<0.004	<0.001	0.009	0.002
			02/11/2000 2000	BG	183	0.010	0.010	0.347	0.342
			02/11/2000 2330	BG	323	0.025	0.044	0.126	0.219
			02/12/2000 0745	BG	252	E 0.003	0.004	0.021	0.029
			02/12/2000 2000	BG	1,950	E 0.003	0.032	0.018	0.189
			02/12/2000 2300	BG	2,460	0.004	0.053	0.018	0.239
			02/13/2000 0730	BG	1,690	0.005	0.046	0.020	0.182
			02/13/2000 2230	BG	1,620	0.005	0.044	0.017	0.148
			02/14/2000 0210	MG	2,700	0.006	0.087	0.016	0.233
			02/14/2000 0610	MG	3,070	0.004	0.066	0.012	0.215
11	Dry Creek at Gallo Bridge below Highway 132, at Modesto	373811120590001	01/06/2000 1400	MG	NA	0.005	NA	0.047	NA
			01/12/2000 1230	MG	NA	0.020	NA	0.352	NA
			01/19/2000 1100	MG	NA	0.011	NA	0.042	NA
			02/04/2000 1040	MG	NA	0.005	NA	0.029	NA
			02/09/2000 1110	MG	NA	<0.004	NA	0.010	NA
			02/12/2000 0405	MG	NA	0.008	NA	0.052	NA
			02/12/2000 1040	MG	NA	0.004	NA	0.025	NA
			02/14/2000 0120	MG	NA	0.004	NA	0.017	NA

Table 3. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California—*Continued*

Site number	Site name	Site identification number	Date and time (month/day/year 24-hour time)	Collection method	Streamflow	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (lb a.i./d)
14	Tuolumne River at Shiloh Road Bridge, near Grayson	11290200	01/06/2000 1230	MG	413	<0.004	0.004	0.005	0.011
			01/12/2000 1130	MG	479	0.007	0.018	0.064	0.165
			01/19/2000 1200	MG	548	0.004	0.012	0.017	0.050
			01/25/2000 1000	MG	756	0.018	0.073	0.092	0.375
			01/26/2000 1510	MG	886	QE 0.011	0.053	QE 0.012	0.057
			02/04/2000 1130	MG	455	0.008	0.020	0.020	0.049
			02/09/2000 1150	MG	449	<0.004	0.005	E 0.003	0.007
			02/11/2000 1830	MG	476	E 0.003	0.008	0.020	0.051
			02/12/2000 0945	MG	703	0.008	0.030	0.073	0.276
			02/12/2000 1800	MG	657	0.006	0.021	0.043	0.152
			02/12/2000 2350	MG	642	0.005	0.017	0.020	0.069
			02/13/2000 0700	MG	1,007	0.004	0.022	0.021	0.114
			02/13/2000 1400	MG	1,894	0.006	0.061	0.032	0.327
			02/13/2000 2100	MG	1,480	0.006	0.048	0.030	0.239
			02/14/2000 0430	MG	833	0.008	0.036	0.031	0.139
			02/14/2000 1500	MG	2,326	0.006	0.075	0.018	0.226
			02/15/2000 0030	MG	3,209	0.005	0.086	0.011	0.190
			02/15/2000 0830	MG	3,641	E 0.004	0.078	0.010	0.196
			02/15/2000 1700	MG	3,950	E 0.003	0.064	0.007	0.149
			02/16/2000 0315	MG	3,499	E 0.003	0.057	0.007	0.132
16	Stanislaus River at Caswell State Park, near Ripon	374209121103800	01/06/2000 1100	BG	355	<0.004	0.004	<0.002	0.002
			01/12/2000 1400	BG	357	0.004	0.008	0.013	0.025
			01/19/2000 1000	BG	424	E 0.004	0.009	0.016	0.037
			01/25/2000 1640	BG	717	0.007	0.027	0.030	0.116
			01/26/2000 0920	BG	1,173	0.010	0.063	0.019	0.120
			02/04/2000 1430	BG	387	<0.004	0.004	0.014	0.029
			02/09/2000 1350	BG	364	<0.004	0.004	E 0.004	0.008
			02/11/2000 2100	BG	375	E 0.003	0.006	0.013	0.026
			02/12/2000 0540	BG	417	0.007	0.016	0.037	0.083
			02/12/2000 1600	BG	435	E 0.004	0.009	0.015	0.035
			02/13/2000 0105	BG	798	0.005	0.021	0.029	0.125
			02/13/2000 0800	BG	1,016	0.006	0.033	0.035	0.192
			02/13/2000 1500	BG	885	0.005	0.024	0.054	0.257
			02/13/2000 2200	BG	802	0.004	0.017	0.036	0.156
			02/14/2000 0600	BG	1,141	0.006	0.037	0.042	0.258

Table 3. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California—*Continued*

Site number	Site name	Site identification number	Date and time (month/day/year 24-hour time)	Collection method	Streamflow	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (lb a.i./d)
16	Stanislaus River at Caswell State Park, near Ripon—*Continued*	374209121103800	02/14/2000 1615	BG	1,475	0.006	0.048	0.028	0.215
			02/15/2000 0150	BG	1,650	0.006	0.053	0.016	0.142
			02/15/2000 0900	BG	1,746	E 0.003	0.028	0.014	0.132
			02/15/2000 1745	BG	1,794	<0.004	0.019	0.007	0.068
			02/16/2000 0425	BG	1,671	<0.004	0.018	0.007	0.063
17	San Joaquin River near Vernalis	11303500	01/06/2000 1000	EWI	1,620	E 0.003	0.026	<0.002	0.009
			01/12/2000 0850	EWI	1,730	0.004	0.047	0.017	0.158
			01/19/2000 0900	EWI	2,180	0.005	0.059	0.030	0.352
			01/19/2000 1440	EWI	2,170	0.004	0.047	0.027	0.316
			01/24/2000 1500	EWI	2,740	0.008	0.118	0.053	0.782
			01/25/2000 0010	EWI	3,230	0.008	0.139	0.056	0.975
			01/25/2000 1100	EWI	3,290	0.010	0.177	0.062	1.099
			01/25/2000 2000	EWI	3,580	0.012	0.231	0.094	1.813
			01/26/2000 0730	EWI	3,600	0.009	0.175	0.061	1.183
			01/26/2000 1730	EWI	4,100	0.009	0.199	0.031	0.685
			01/27/2000 0820	EWI	4,080	0.009	0.198	0.027	0.594
			01/27/2000 1600	EWI	3,750	0.006	0.121	0.016	0.323
			02/04/2000 1330	EWI	2,490	0.006	0.080	0.019	0.255
			02/09/2000 1310	EWI	2,190	<0.004	0.024	0.010	0.118
			02/11/2000 2200	EWI	2,190	E 0.003	0.035	0.021	0.248
			02/12/2000 1230	EWI	2,390	<0.010	0.064	0.015	0.193
			02/12/2000 2100	EWI	2,620	E 0.002	0.028	0.025	0.353
			02/13/2000 0530	EWI	2,860	0.012	0.185	0.075	1.156
			02/13/2000 1200	EWI	3,680	E 0.012	0.238	0.030	0.595
			02/13/2000 2300	IG	4,640	0.005	0.125	0.036	0.900
			02/14/2000 0650	IG	4,770	0.016	0.411	0.036	0.925
			02/14/2000 1700	IG	6,140	<0.010	0.165	0.054	1.786
			02/15/2000 0230	IG	7,500	E 0.009	0.364	0.055	2.222
			02/15/2000 1000	IG	8,000	E 0.003	0.129	0.016	0.690
			02/15/2000 1815	IG	8,690	E 0.004	0.187	0.018	0.843
			02/16/2000 5450	IG	8,770	E 0.003	0.142	0.016	0.756
			02/16/2000 1600	IG	8,520	0.005	0.230	0.015	0.689
			02/17/2000 0930	P	9,120	0.005	0.246	0.019	0.934

Table 3. Summary of environmental data collected on diazinon and chlorpyrifos concentrations and instantaneous loading rates for sites in the San Joaquin River Basin, California—*Continued*

Site number	Site name	Site identification number	Date and time (month/day/year 24-hour time)	Collection method	Streamflow	Chlorpyrifos concentration (µg/L)	Chlorpyrifos instantaneous loading rate (lb a.i./d)	Diazinon concentration (µg/L)	Diazinon instantaneous loading rate (lb a.i./d)
17	San Joaquin River near Vernalis—*Continued*	11303500	02/17/2000 1930	IG	9,980	0.005	0.269	0.011	0.591
			02/18/2000 1005	IG	11,500	E 0.004	0.248	0.008	0.496
			02/18/2000 1930	IG	11,800	0.004	0.254	0.008	0.509
			02/22/2000 2040	IG	12,000	0.004	0.323	0.006	0.388
			02/23/2000 1340	IG	12,200	0.004	0.263	0.008	0.526
			02/24/2000 0900	IG	12,900	E 0.004	0.278	0.009	0.626
			02/25/2000 1030	IG	13,600	E 0.003	0.220	0.007	0.513
			02/26/2000 0920	IG	13,000	<0.004	0.140	0.006	0.420

Several concentrations of diazinon and chlorpyrifos are reported with an E (for estimate) in table 3. These samples have confirmed detections of the pesticides, but the concentrations are estimated because they are below the MDL or have some interference in the sample matrix. A few samples have MDLs higher than the normal 0.002 and 0.004 μg/L concentrations for diazinon and chlorpyrifos, respectively. The MDLs were raised for these samples by the NWQL because of interference in the sample matrix, small sample volume, or a laboratory process failure indicated by the laboratory quality-control samples (Ronald Brenton, U.S. Geological Survey, written commun., 2001).

Two samples are reported with a QE (for qualitative estimate) in table 3. These samples were compromised at the NWQL, making quantitative determination of analytes inaccurate. After being extracted and eluted, the caps on these samples were not sufficiently tightened while the samples were waiting to be run through the GC/MS. Some of the pesticide could have volatilized during this time, resulting in low reported concentrations (Chris Lindley, U.S. Geological Survey, written commun., 2000). This would be more of a problem for diazinon than for chlorpyrifos because of its greater volatility. The qualitative determinations of diazinon and chlorpyrifos are reported in table 3.

Quality-Control Samples

During the weekly and storm sampling in January and February, 25 quality-control samples were a subset of the 230 total samples collected (table 3). These quality-control samples included replicate samples to evaluate the variability in concentrations (n = 13), field blanks to evaluate possible contamination (n = 6), and laboratory-spiked environmental samples to evaluate the recovery of diazinon and chlorpyrifos in the sample matrix (n = 6).

Replicates were usually split from the sample collection bottle by shaking and pouring into separate sample bottles. The replicate collected at Orestimba Creek on February 14 was a sequential replicate pumped from the bank. The relative percentage difference (RPD) between environmental sample and replicate is used to describe the variability in replicates. The 13 replicates for diazinon and chlorpyrifos both had RPDs ranging from 0 to 33.3 percent (table 4), with a median RPD of 5 percent for diazinon and 22 percent for chlorpyrifos.

Field blanks were collected by rinsing the sample collection bottle three times with organic-free water (instead of native water) after rinsing out the Liquinox solution with deionized water. The sample collection bottle then was filled with organic-free water and poured into 1-L amber glass sample bottles and sent to the NWQL with environmental samples. All field blanks were less than detection for diazinon and chlorpyrifos, except for the January 12 detection of 0.003 μg/L, which is slightly above the 0.002 μg/L detection level (table 4). In 175 field blanks sent to the NWQL from surface-water sites as part of the National Water-Quality Assessment Program during 1992–1995, there were four detections of diazinon and one detection of chlorpyrifos (Martin and others, 1999). Considering the levels of diazinon in the environmental samples in this study, the one low-level detection in a field blank was not of concern.

Spiked samples were collected the same way as replicates in the field. One of the samples was labeled as a spike with instructions to the NWQL to add their spike mixture after filtering. Recovery was calculated by subtracting the measured concentrations in the environmental sample from the measured concentrations in the spiked sample and then dividing by the theoretical concentrations added to the spiked sample. Recoveries in the six laboratory spiked samples ranged from 91.6 to 121.0 percent for diazinon and 97.1 to 118.4 percent for chlorpyrifos (table 4). In addition to the laboratory spiked samples, the 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 blank water at the laboratory and extracted, processed, and analyzed like environmental samples. In calendar year 2000, the NWQL ran 451 laboratory control spikes for schedule 2001. The median recovery for diazinon was 95 percent, with a 95-percent confidence interval of 76 to 120 percent. The median recovery for chlorpyrifos was 90 percent, with a 95-percent confidence interval of 63 to 120 percent (Bruce Darnel, National Water Quality Laboratory, written commun., 2001).

HYDROLOGY DURING THE STUDY

Diazinon and chlorpyrifos transport during the dormant spray season in the San Joaquin Basin is primarily a function of the amount and timing of application and storm runoff from application areas (figs. 2, 3, and 5). As expected, the weekly sampling during nonstorm periods was at stable and relatively low streamflows (fig. 5). However, three (January 12, January 19, and February 4) of the five nonstorm sampling dates were after relatively small storms. Rainfall at Modesto preceding these sampling dates was 0.21 in. on January 11, 0.62 in. on January 17 and 18, and 0.10 in. on February 3. Only the January 6 and February 9 nonstorm sampling dates were truly nonstorm periods. Two larger-magnitude storm periods—January 23–25, 2000 (2.66 in. at Modesto), and February 9–14, 2000 (2.44 in. at Modesto)—occurred

Table 4. Summary of quality-control data on diazinon and chlorpyrifos concentrations for sites in the San Joaquin River Basin, California

[NA, not applicable—cannot be calculated because of "less than" concentration; µg/L, microgram per liter; E, estimate; <, less than]

Site identification number	Site name	Date and time (month/day/year 24-hour time)	Chlorpyrifos (µg/L)	Relative percent difference OR percent recovery (chlorpyrifos)	Diazinon (µg/L)	Relative percent difference OR percent recovery (diazinon)
REPLICATES:						
11303500	San Joaquin River near Vernalis	01/19/2000 0900	0.005		0.030	
		01/19/2000 0901	0.005	0.0	0.035	15.4
		02/13/2000 2300	0.005		0.036	
		02/13/2000 2308	0.007	33.3	0.035	2.8
374209121103800	Stanislaus River at Caswell State Park, near Ripon	02/09/2000 1350	<0.004		E 0.004	
		02/09/2000 1351	<0.004	NA	0.004	0.0
		02/12/2000 1600	E 0.004		0.015	
		02/12/2000 1608	E 0.004	0.0	0.015	0.0
11290200	Tuolumne River at Shiloh Road Bridge, near Grayson	02/13/2000 1400	0.006		0.032	
		02/13/2000 1408	0.008	28.6	0.033	3.1
11273500	Merced River at River Road Bridge, near Newman	02/13/2000 0350	E 0.003		0.005	
		02/13/2000 0405	0.004	28.6	0.007	33.3
11260815	San Joaquin River near Stevinson	02/14/2000 0250	0.006		0.033	
		02/14/2000 0258	0.007	15.4	0.031	6.3
11274538	Orestimba Creek at River Road, near Crows Landing	02/14/2000 0130	0.008		0.101	
		02/14/2000 0138	E 0.008	0.0	0.081	22.0
11274653	Del Puerto Creek at Vineyard Road, near Patterson	02/13/2000 0200	<0.004		0.009	
		02/13/2000 0208	0.004	NA	0.009	0.0
371903120585400	Newman Wasteway at Highway 33, near Gustine	01/06/2000 1130	<0.004		<0.002	
		01/06/2000 1131	<0.004	NA	<0.002	NA
		02/13/2000 0000	0.017		0.029	
		02/13/2000 0008	0.016	6.1	0.026	10.9
373925120550701	Dry Creek at Claus Road Bridge, at Modesto	02/12/2000 2000	E 0.003		0.018	
		02/12/2000 2008	E 0.004	28.6	0.014	25.0
372424120432800	Livingston Canal at Livingston Treatment Plant, near Livingston	02/12/2000 1010	0.009		0.084	
		02/12/2000 1018	0.012	28.6	0.081	3.6
BLANKS:						
374209121103800	Stanislaus River at Caswell State Park, near Ripon	02/13/2000 1508	<0.004		<0.002	
11273500	Merced River at River Road Bridge, near Newman	01/12/2000 1108	<0.004		E 0.003	
		02/13/2000 1808	<0.004		<0.002	
11260815	San Joaquin River near Stevinson	02/09/2000 0958	<0.004		<0.002	
11274538	Orestimba Creek at River Road, near Crows Landing	02/04/2000 1108	<0.004		<0.002	
		02/12/2000 0848	<0.004		<0.002	

Table 4. 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 (month/day/year 24-hour time)	Chlorpyrifos (μg/L)	Relative percent difference OR percent recovery (chlorpyrifos)	Diazinon (μg/L)	Relative percent difference OR percent recovery (diazinon)
SPIKES[1]:						
374209121103800	Stanislaus River at Caswell State Park,	02/04/2000 1430	<0.004		0.014	
	near Ripon	02/04/2000 1433	0.143	101.4	0.154	100.7
371903120585400	Newman Wasteway at Highway 33,	02/14/2000 0720	0.037		0.154	
	near Gustine	02/14/2000 0713	0.206	114.8	0.324	115.6
11274560	Turlock Irrigation District Lateral no. 5,	02/14/2000 0430	0.013		0.060	
	near Patterson	02/14/2000 0433	0.221	118.4	0.273	121.0
373811120590001	Dry Creek at Gallo Bridge below	02/09/2000 1110	<0.004		0.010	
	Highway 132, at Modesto	02/09/2000 1113	0.133	100.0	0.130	91.6
372323120481700	Highline Canal Spill near Hilmar	02/12/2000 1800	0.005		0.011	
		02/12/2000 1803	0.144	97.1	0.150	97.2
372424120432800	Livingston Canal at Livingston Treatment	02/12/2000 1900	0.007		0.024	
	Plant, near Livingston	02/12/2000 1903	0.175	101.8	0.192	101.8

[1]First sample in each pair is the environmental sample; second sample is the spike.

during the dormant spray period. Rain before January 23 produced little runoff, and rain after February 14 occurred after most of the dormant spray had been applied and presumably already transported by the February 9–14 storm. The combined releases from the major reservoirs on the Merced, the Tuolumne, and the Stanislaus Rivers also increased from about 1,000 ft^3/s (cubic foot per second) before February 14 to about 4,000 ft^3/s on February 14, to over 6,000 ft^3/s on February 15–16, to over 8,000 ft^3/s on February 17 through the end of the month and beyond. In addition, smaller reservoirs upstream of the San Joaquin River near Stevinson in the Bear Creek Basin increased releases on average from less than 100 ft^3/s before February 12 to about 2,000 ft^3/s during February 12–17, dropping to about 500 to 2,000 ft^3/s during the rest of February. The traveltimes from these reservoir releases to the sampling sites are generally about 1 to 3 days. Thus, these large reservoir releases of Sierra Nevada water show up as a new baseflow at the sampling sites from about February 17 through the rest of the month (fig. 5*A*). This baseflow of “clean” water—originating above the pesticide application area—serves to greatly dilute pesticide concentrations in the rivers during this period.

Although the total rainfall at Modesto during the first storm period was slightly greater than during the second storm period (2.66 and 2.44 in., respectively), there was much less runoff in the valley from application areas (fig. 5*A*). The first storm period followed an extremely dry December and early January (fig. 4), and most of the rainfall infiltrated instead of running off. The second storm period produced more runoff because of higher antecedent soil moisture. The greatest runoff following the first storm period occurred in the Stanislaus River and the San Joaquin River near Stevinson basins, with lesser amounts in the Merced River and the Tuolumne River basins, and much lesser amounts in the Orestimba Creek Basin. Following the second storm period, the greatest runoff occurred in the Tuolumne River, the San Joaquin River near Stevinson, and the Merced River basins, with lesser amounts in the Stanislaus River and the Orestimba Creek basins (fig. 5). However, most of the runoff in the San Joaquin River near Stevinson Basin during both periods appears to be from reservoir releases instead of valley runoff. The later part of the runoff in the Orestimba Creek Basin during the second storm also was from the Coast Ranges and not from valley runoff on the basis of gaged streamflows for Orestimba Creek in the Coast Ranges.

CONCENTRATIONS OF DIAZINON AND CHLORPYRIFOS

The concentrations of diazinon and chlorpyrifos in the samples collected during storm and nonstorm periods in January and February are presented in table 3. The concentrations are presented graphically along with the continuous streamflow for all sites, except Del Puerto Creek and Newman Wasteway, in figures 6 and 7.

Diazinon

As expected, the highest diazinon concentrations at the major river sites occurred during the rising limb of storm runoff (fig. 6*A*). Concentrations were considerably lower than in 1994 (Kratzer, 1999), however, and only four samples at major river sites exceeded the proposed CMC of 0.08 μg/L. Three of these four exceedances of the CMC occurred during runoff from the first storm at the San Joaquin River near Stevinson, the Tuolumne River at Shiloh Road, and the San Joaquin River near Vernalis. The fourth exceedance occurred during runoff from the second storm at the San Joaquin River near Stevinson. At all major river sites, except the Stanislaus River, the highest concentration occurred on the rising limb of runoff from the first storm. The highest concentration at the Stanislaus River site occurred on the rising limb of runoff from the second storm. Nonstorm samples had relatively low concentrations at all major river sites, except for the January 12 weekly sample from the Tuolumne River. This sample was collected 1 day after a relatively small storm, so some storm runoff probably contributed to this weekly nonstorm sample. At all the major river sites, the concentrations in samples collected during runoff from the second storm peaked on the rising limb and decreased in later samples. This also was true at the Vernalis site for the first storm. The samples collected at Vernalis after February 18 had relatively low diazinon concentrations due to the effect of dilution from reservoir releases.

Most of the highest diazinon concentrations at the minor tributary sites also were during storm events (fig. 6*B*). A total of 24 samples at minor tributary sites exceeded the proposed CMC of 0.08 μg/L; 16 of these are shown in figure 6*B* and table 3, and 8 are at sites without continuous streamflow gages (Del Puerto Creek and Newman Wasteway) and are, therefore, only tabulated (table 3). The first three weekly, nonstorm samples collected at Del Puerto Creek exceeded the short-term guideline, especially the sample on January 12. Because of a small storm on January 11, samples collected on January 12 probably contained some storm runoff and diazinon concentrations were relatively high in Del Puerto Creek, Orestimba Creek, and Dry Creek at Gallo Bridge (table 3). The influence of the Modesto urban area was apparent in the differences between concentrations at the upper (Claus Road) and lower (Gallo Bridge) sites on Dry Creek during low-flow periods. The streamflow shown in figure 6*B* is only for the upstream site at Claus Road and does not show the contribution of urban runoff to the Gallo Bridge site. The highest concentration in Orestimba Creek occurred on the rising limb of runoff from the second storm at a streamflow of about 400 ft^3/s, before most of the diluting streamflows from the Coast Ranges made it to the River Road sampling site. Several samples collected during the second storm at the Highline and Livingston Canal sites had concentrations exceeding the 0.08 μg/L guideline. The Livingston Canal exceedances occurred at flows less than 0.1 ft^3/s and do not represent any significant storm runoff. The Highline Canal exceedances occurred during the rising limb of runoff from the second storm.

Chlorpyrifos

The highest chlorpyrifos concentrations at the major river sites occurred during storm runoff (fig. 7*A*). Only one sample at major river sites exceeded the proposed CMC of 0.02 μg/L (table 3). This sample was collected on the rising limb of runoff from the second storm at the San Joaquin River near Stevinson site and had a chlorpyrifos concentration of 0.073 μg/L. This was the first sample collected during the second storm and a sample collected 6.75 hours later had a concentration of only 0.011 μg/L. The highest nonstorm concentrations at the major river sites occurred in the Tuolumne River on January 12 and February 4 following minor storms on January 11 and February 3, respectively. These smaller storms could generate urban runoff in Modesto, which could explain the higher chlorpyrifos concentrations.

Most of the highest concentrations at the minor tributary sites also occurred during storm runoff (fig. 7*B*). Only three samples at minor tributary sites exceeded the proposed CMC of 0.02 μg/L, one at Dry Creek at Claus Road and two at Newman Wasteway (table 3). All of these samples were collected during runoff from the second storm. The Dry Creek at Gallo Bridge sample on January 12 had a concentration of 0.020 μg/L a day after a relatively small storm. This site receives significant urban runoff from storm drains in Modesto, which have in the past contained chlorpyrifos concentrations of 0.06 to 0.3 μg/L (Kratzer, 1998). This

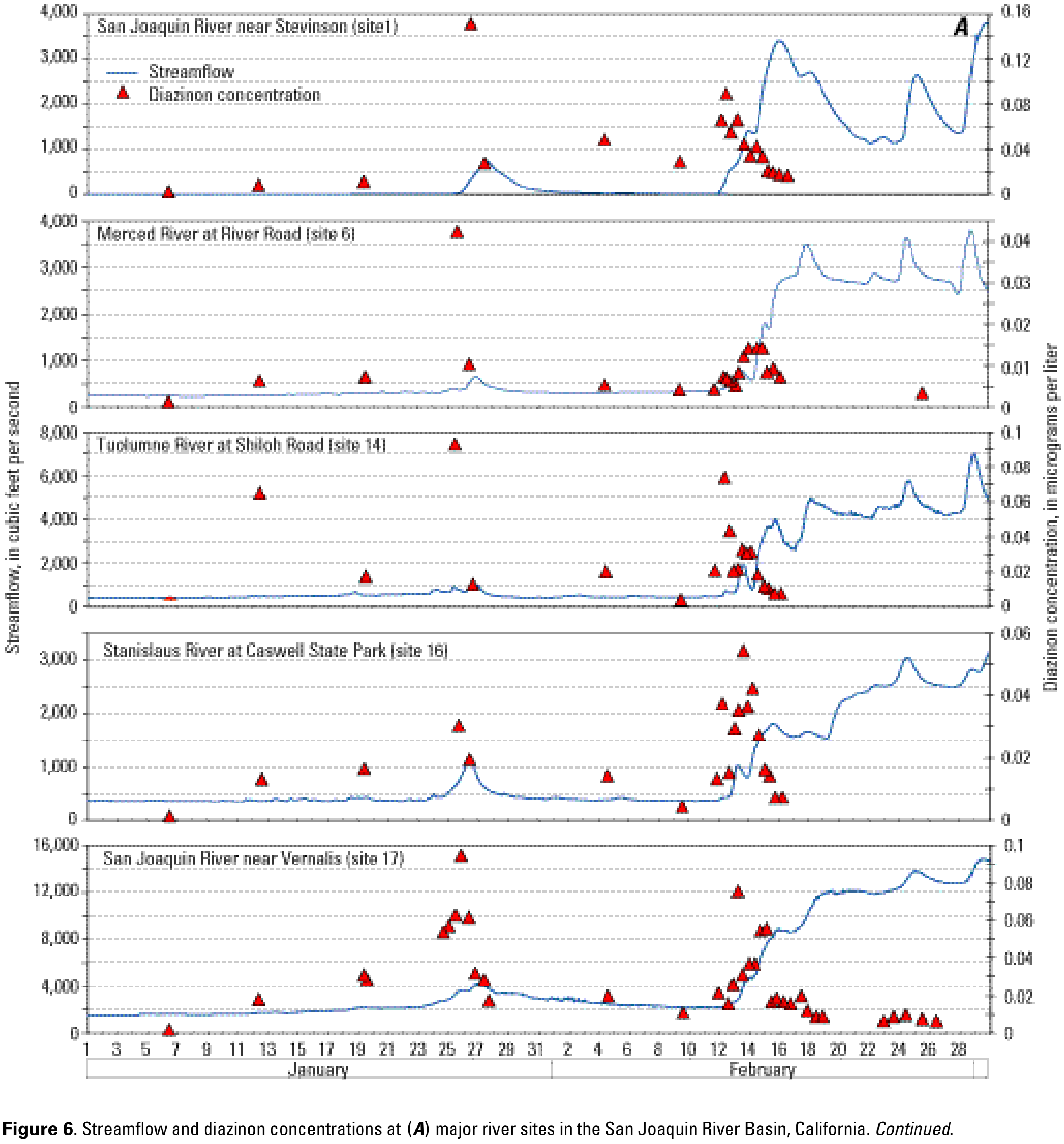

Figure 6. Streamflow and diazinon concentrations at (***A***) major river sites in the San Joaquin River Basin, California. *Continued.*

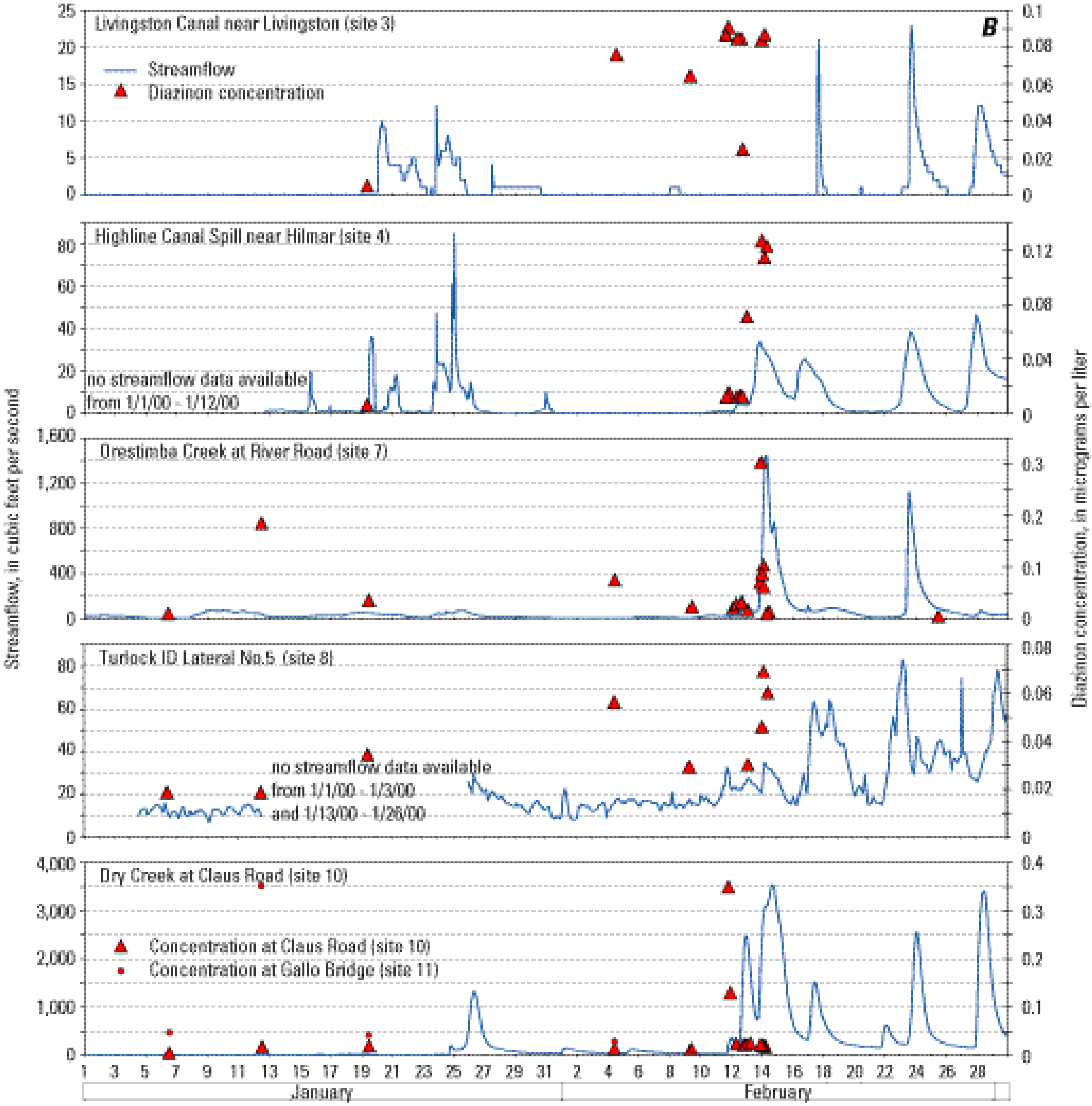

Figure 6. Streamflow and diazinon concentrations at (***B***) minor tributary sites in the San Joaquin River Basin, California.

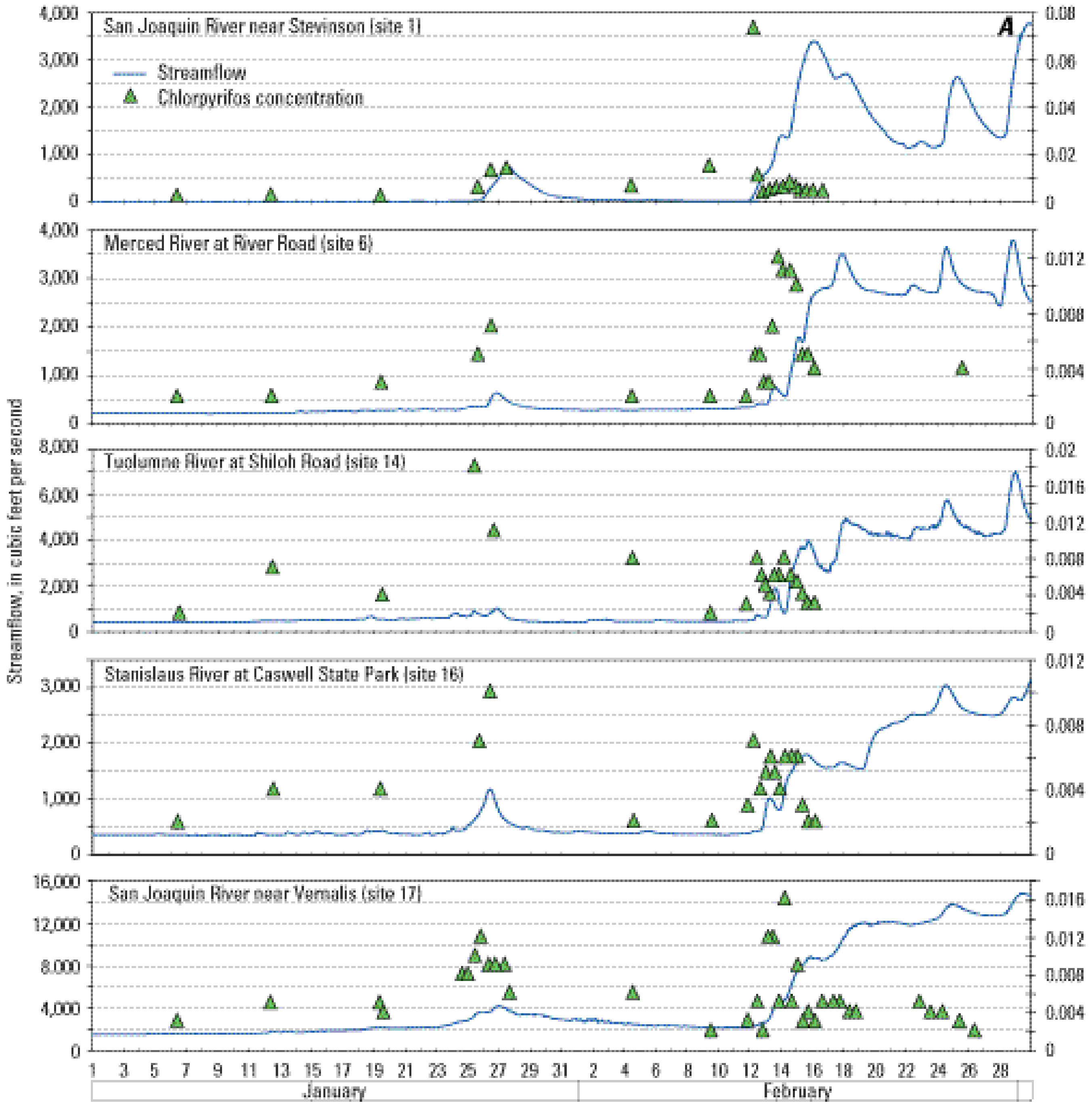

Figure 7. Streamflow and chlorpyrifos concentrations at (***A***) major river sites in the San Joaquin River Basin, California. *Continued*.

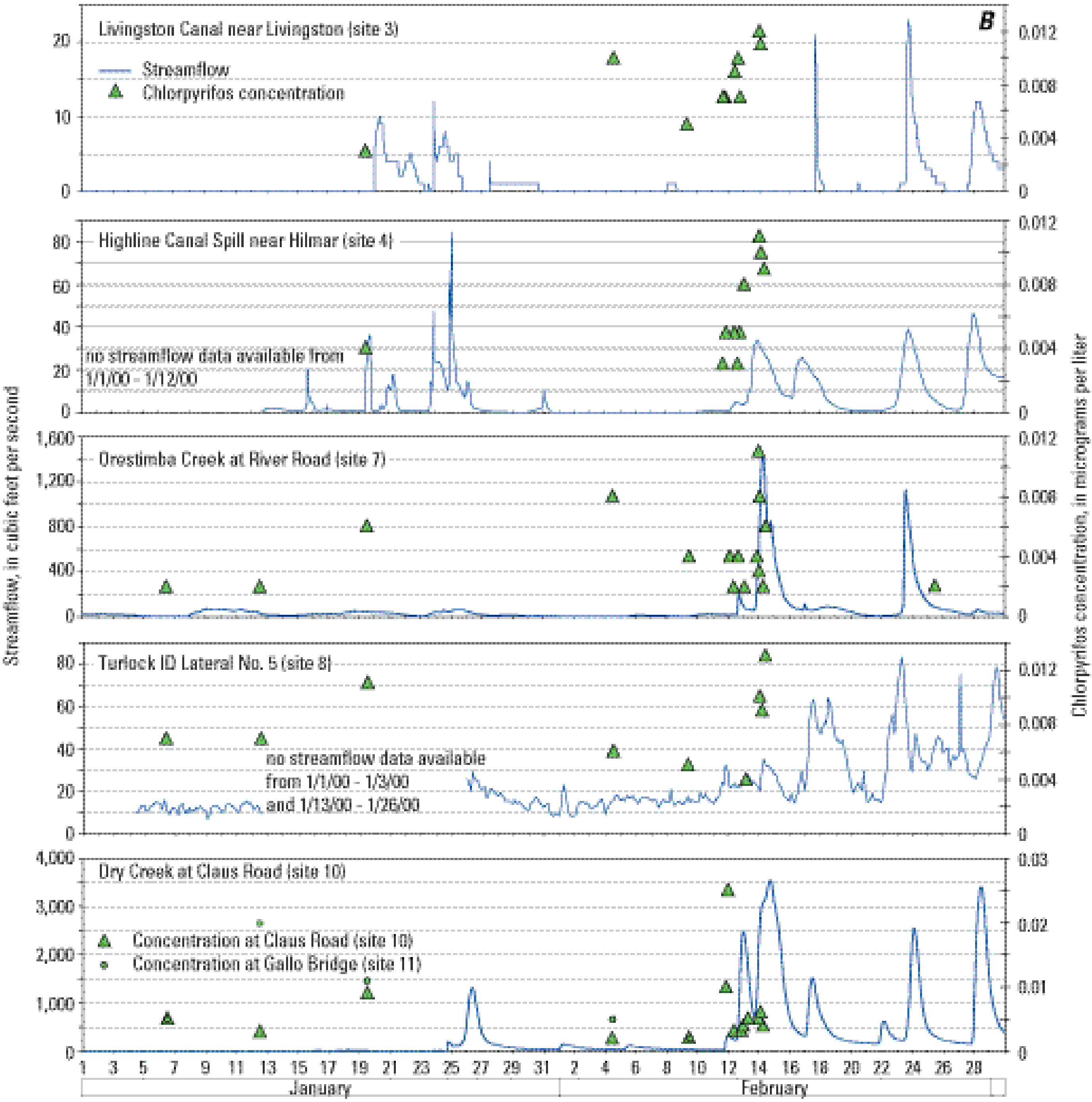

Figure 7. Streamflow and chlorpyrifos concentrations at (***B***) minor tributary sites in the San Joaquin River Basin, California.

would explain the relatively high concentration at Dry Creek at Gallo Bridge, the high concentration in the Tuolumne River, and the relatively low concentration at the upstream Claus Road site, which is above the Modesto urban runoff.

LOADS OF DIAZINON AND CHLORPYRIFOS

Instantaneous loads of diazinon and chlorpyrifos were calculated for each sample collected in January and February that had a streamflow measurement (table 3). No instantaneous loads are presented for Dry Creek at Gallo Bridge because streamflow was not measured. For samples with concentrations less than the MDL, the concentration was set to half the MDL to calculate an instantaneous load. Instead of using more robust methods to fit values to the less than MDL, 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). It was beyond the scope of this study to evaluate the possibility of using more robust methods. The instantaneous loads are presented graphically with continuous streamflow for all other sites except Del Puerto Creek and Newman Wasteway (figs. 8 and 9). At the major river sites, and the Dry Creek at Claus Road and the Orestimba Creek at River Road (table 3), the instantaneous loads were connected, and the total load during the second storm was calculated as the area under the load curve. The loading rate on the true nonstorm sampling date of February 9 was considered a baseline nonstorm loading rate at each site. This load was subtracted from the total load during the storm to calculate storm loads at each site. Loads for the first storm (storm 1) and for all of January and February were calculated only for the San Joaquin River near Vernalis site.

To calculate a total storm load at a site, the connected instantaneous load line was brought down to the x-axis, and the area was digitized. The dashed lines that complete the storm loads is called estimated storm load in figures 8 and 9. 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 contributing to load from the February 9–14 storm. This line is estimated for sites based on the trend in the instantaneous loads, the storm hydrograph from valley application areas, and traveltimes between sites. The later parts of the February 9–14 storm hydrograph at the major east-side tributaries (Merced, Tuolumne, and Stanislaus Rivers) and in Orestimba Creek were from areas outside of the valley application area (fig. 5). These flows were not considered in the drawing of the estimated load line. The contribution of Dry Creek to storm runoff from valley application areas in the Tuolumne River Basin was considered, along with the traveltime to the Tuolumne River at Shiloh site, in extending the estimated load line for Dry Creek (Kratzer and Biagtan, 1997). An estimated traveltime from the San Joaquin River near Stevinson site to the San Joaquin River near Vernalis was considered in extending the load line for Vernalis. For all sites, the storm-load time period was the same for diazinon and chlorpyrifos loads in the second storm (storm 2). Calculating total January and February loads at Vernalis required creating another category of loads, other nonstorm loads—nonstorm loads above the baseline, but not during the two frequently sampled storms.

Loads were calculated as a percentage of applied pesticide and as a percentage of drainage area (or yield) to illustrate basins with relatively higher or lower loading rates. In this report, storm loads as related to application are based on the dry period preceding the storm. Thus, loads in the first storm are related to application during the first dry period (December 1, 1999 to January 25, 2000), whereas loads in the second storm are related to application during the second dry period (January 26, 2000 to February 14, 2000). The total January and February loads calculated for Vernalis includes all loads (storm 1, storm 2, and baseline and other nonstorm). This load related to application or to basin area is a combination of the corresponding values for storm 1, storm 2, and baseline and other nonstorm loads. Comparisons of loading during the different periods (storm 1, storm 2, and baseline and other nonstorm) is facilitated by expressing the loading as a rate, for example, pounds active ingredient per day (lb a.i./d).

Diazinon

Instantaneous loads of diazinon at the major river sites are very closely related to streamflow (figs. 8*A* and 8*B*). For the two true nonstorm sampling dates of January 6 and February 9, instantaneous loading rates at all sites were less than 0.012 lb a.i./d, except for Vernalis on February 9 (0.118 lb a.i./d) (table 3). For the sites upstream of Vernalis, all samples collected outside of the two storm periods had instantaneous loading rates less than 0.051 lb a.i./d, except for the January 12 sample for the Tuolumne River (0.165 lb a.i./d) (table 3). At all the major river sites, storm loading rates (pounds active ingredient per day) peaked during the rising limb of the storm hydrographs. The maximum instantaneous diazinon storm loading rate at the major river sites (not including the baseline loading rate) was 0.120 lb a.i./d in the Merced River, 0.250 lb a.i./d in the

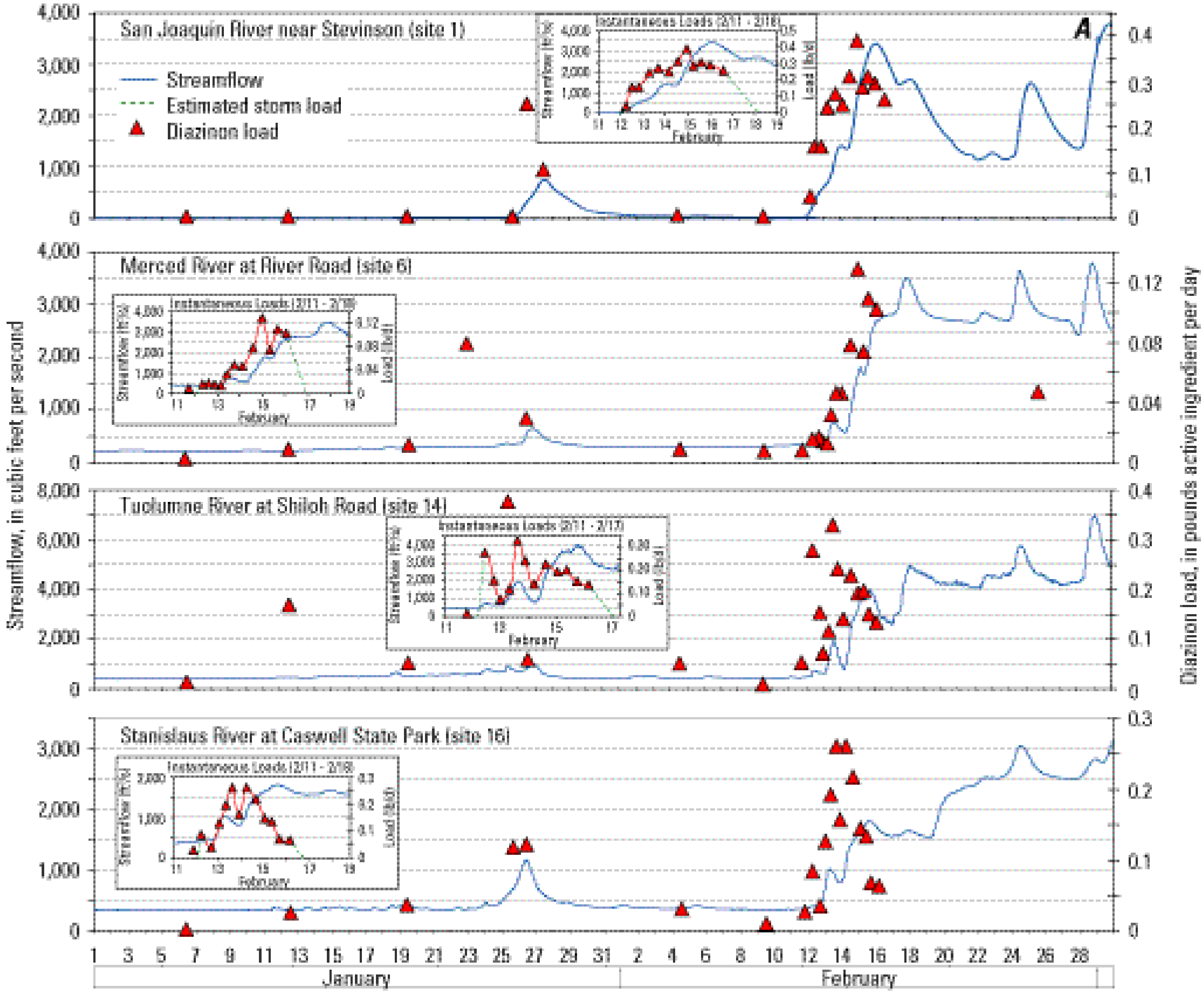

Figure 8. Streamflow and instantaneous diazinon loads at (***A***) major river sites in the San Joaquin Valley part of the San Joaquin River, California. Site numbers refer to figure 1 and table 3. ft^3/s, cubic foot per second; lb/d, pound per day. *Continued.*

Stanislaus River, 0.368 lb a.i./d in the Tuolumne River, 0.384 lb a.i./d in the San Joaquin River near Stevinson, and 2.10 lb a.i./d in the San Joaquin River near Vernalis.

Instantaneous loading rates at Livingston Canal, Highline Canal, and TID5 were very small, with the highest rate being 0.022 lb a.i./d near the peak runoff from the second storm at the Highline Canal site (fig. 8*C*). Nonstorm loading rates at the minor tributary sites were generally much lower than storm rates. The two exceptions to this were during the January 12 sampling at Orestimba Creek (0.035 lb a.i./d) and the January 19 sampling at TID5 (0.013 lb a.i./d) (table 3). Both of these nonstorm sampling dates followed relatively small storms. Otherwise, the nonstorm loading rates at the minor tributary sites were all below 0.011 lb a.i./d (table 3). The instantaneous loading rates at Orestimba Creek and Dry Creek at Claus Road varied greatly over a short period during runoff from the second storm, a function of both the rapidly changing streamflow and concentrations (fig. 6*B*). The maximum storm loading rate in Orestimba Creek was 0.66 lb a.i./d and in Dry Creek at Claus Road was 0.34 lb a.i./d (fig. 8*A*).

The total diazinon load in the San Joaquin River near Vernalis during January and February 2000 was 19.6 lb a.i. (table 5). Of this total, 5.78 lb a.i. was non-storm, baseline load, assuming a zero baseline prior to the rainfall on January 11 and a baseline loading rate of

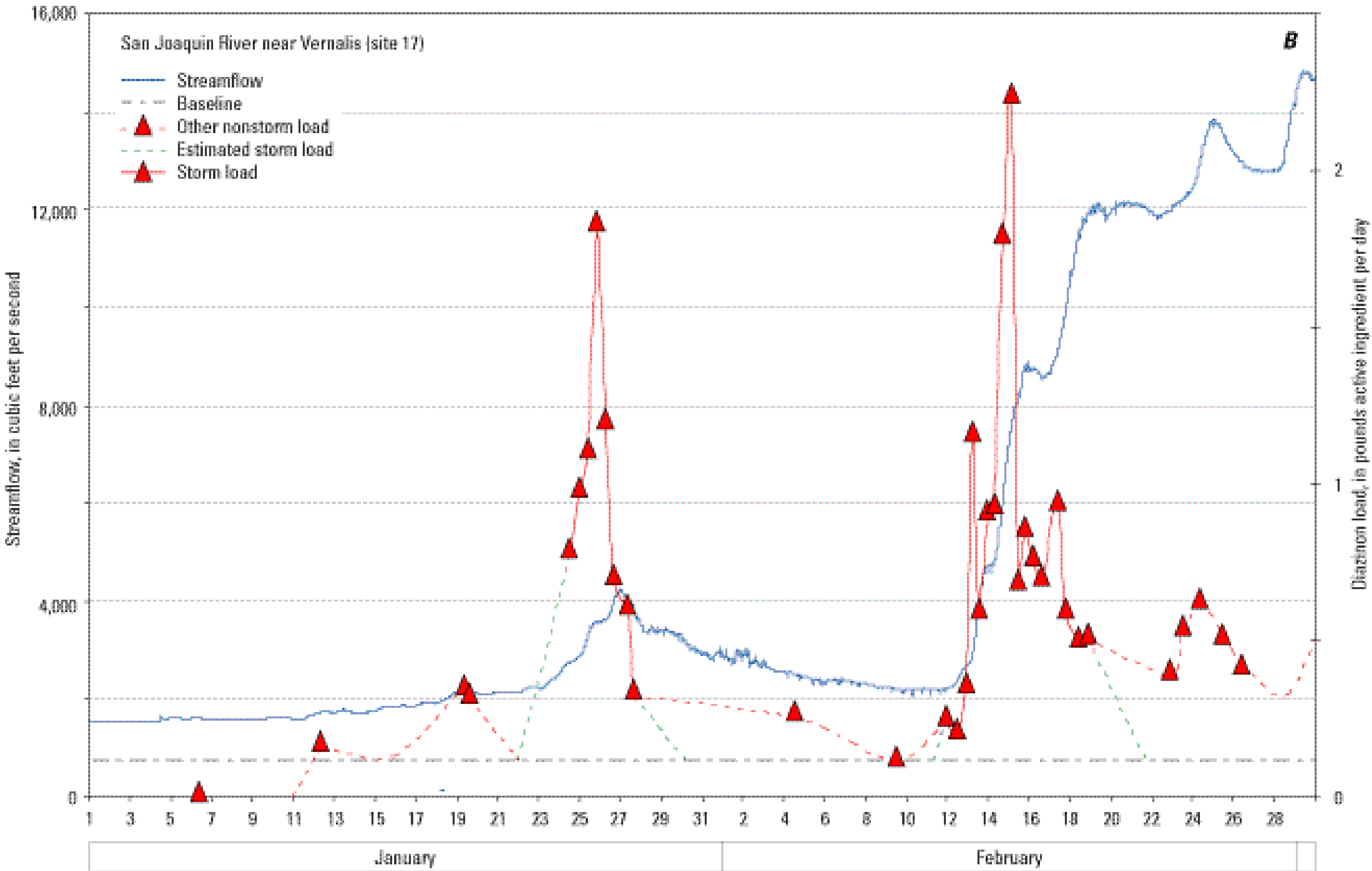

Figure 8. Streamflow and instantaneous diazinon loads at (***B***) San Joaquin River near Vernalis in the San Joaquin Valley part of the San Joaquin River, California. Site numbers refer to figure 1 and table 3. *Continued.*

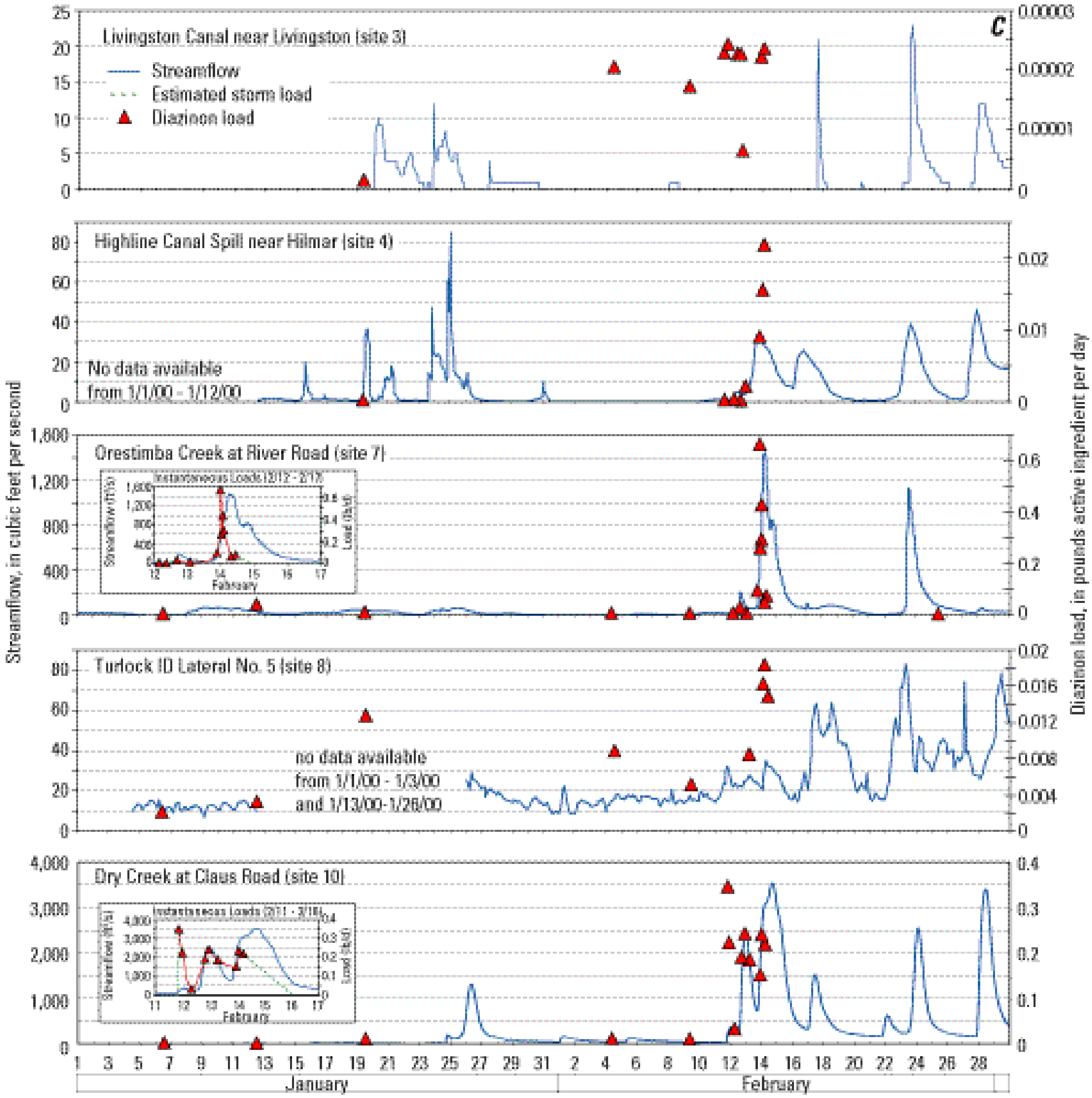

Figure 8. Streamflow and instantaneous diazinon loads at (***C***) minor tributary sites in the San Joaquin Valley part of the San Joaquin River, California. Site numbers refer to figure 1 and table 3. ft^3/s, cubic foot per second; lb/d, pound per day.

0.118 lb a.i./d for the rest of January and February (fig. 8*B*). This baseline was defined by the instantaneous loading rate on the nonstorm February 9 sampling. Another 5.66 lb a.i. of the total January and February load at Vernalis is shown as other nonstorm load (fig. 8*B*). For the Merced River, the Tuolumne River, the Stanislaus River, the San Joaquin River near Stevinson, the Orestimba Creek, and the Dry Creek at Claus Road sites, the storm loads for the second storm only are shown in table 5 and figure 8; instantaneous loads for the other minor tributary sites are shown in figure 8*C* and table 3.

The first storm transported 2.97 lb a.i. diazinon to Vernalis and the second storm 5.20 lb a.i. (table 5). The 8.17 lb a.i. transported during the two storms in 2000 is less than one-third of the 27.4 lb a.i. transported during two storms in January and February 1994 (Kratzer, 1999). About 57 percent of the 5.20 lb a.i. diazinon load at Vernalis during storm 2 came from the San Joaquin River near Stevinson (1.30 lb a.i.), the Tuolumne River (0.72 lb a.i.), the Stanislaus River (0.53 lb a.i.), the Merced River (0.23 lb a.i.), and Orestimba Creek (0.17 lb a.i.). These loads during runoff from storm 2 do not include baseline loads of 1.22 lb a.i. at Vernalis, 0.01 lb a.i. at Stevinson, 0.03 lb a.i. in the Tuolumne River, 0.04 lb a.i. in the Stanislaus River, and 0.03 lb a.i. in the Merced River. These baseline loads are about half of the baseline loads reported in January and February 1994 (Kratzer, 1999). The load at Vernalis as a percentage of application during the dry periods preceding the storms was 0.04 and 0.11 percent, respectively. This is similar to the 0.05 percent calculated during two storms in January and February 1994 (Kratzer, 1999). For the second storm, this percentage ranged from 0.04 in the Merced River Basin to infinite in the Dry Creek Basin. Both the Dry Creek and Tuolumne River Basins had diazinon runoff with essentially no reported agricultural use. However, there was probably considerable urban application in Modesto and other urban areas (table 2). For the entire months of January and February, the diazinon load at Vernalis was 0.17 percent of the December 1, 1999, through February 14, 2000, agricultural application (table 5).

The diazinon yields during storm 2 were highest in the Dry Creek at Claus Road Basin (table 5). The Orestimba, the Tuolumne, and the Stanislaus Basins were next highest, with most of the Tuolumne load coming from the Dry Creek Basin. The Merced Basin had the least diazinon yield during storm 2. The 2.97 lb a.i. of storm 1 load in the San Joaquin River near Vernalis occurred over 5.75 days for a loading rate of 0.52 lb a.i./d (fig. 8*A*). The corresponding loading rate for storm 2 (5.20 lb a.i. in 10.25 days) is 0.51 lb a.i./d; for baseline nonstorm (5.78 lb a.i. in 49 days), 0.12 lb a.i./d; and for other nonstorm (5.66 lb a.i. in 33 days), 0.17 lb a.i./d. Thus, the two frequently sampled storms had much higher loading rates than the nonstorm periods.

Chlorpyrifos

Similar to diazinon, the instantaneous loads of chlorpyrifos at the major river sites are closely related to streamflow (figs. *9A* and *9B*). For the two true nonstorm sampling dates of January 6 and February 9, instantaneous loading rates at upstream sites were less than 0.005 lb a.i./d, and Vernalis was 0.026 and 0.024 lb a.i./d, respectively (table 3). For the sites upstream of Vernalis, all samples collected outside of the two storm periods had instantaneous loading rates less than 0.009 lb a.i./d, except for the January 12, January 19, and February 4 samples for the Tuolumne River (0.018, 0.012, and 0.020 lb a.i./d, respectively) (table 3). At all the major river sites, storm loading rates (pounds active ingredient per day) peaked during the rising limb of the storm hydrographs. The maximum instantaneous chlorpyrifos storm loading rate at the major river sites (not including the baseline loading rate) was 0.059 lb a.i./d in the Stanislaus River, 0.072 lb a.i./d in the San Joaquin River near Stevinson, 0.081 lb a.i./d in the Tuolumne River, 0.088 lb a.i./d in the Merced River, and 0.387 lb a.i./d in the San Joaquin River near Vernalis.

Instantaneous loading rates in the Livingston Canal, Highline Canal, and TID5 were very small, with the highest being 0.004 lb a.i./d on January 19 and February 14 in TID5 (fig. 9*C*). Nonstorm loading rates at the minor tributary sites generally were much lower than storm rates. Other than the January 19 and February 14 samples at TID5, all other nonstorm instantaneous loads at minor tributary sites were 0.002 lb a.i./d or less (table 3). The instantaneous loading rates at Orestimba Creek and Dry Creek at Claus Road varied greatly over a short period during runoff from the second storm. This was primarily a function of the rapidly changing streamflow (fig. 8*B*). The maximum loading rate in Orestimba Creek was 0.040 lb a.i./d, and in Dry Creek at Claus Road it was 0.087 lb a.i./d (table 3).

The total chlorpyrifos load in the San Joaquin River near Vernalis during January and February 2000 was 5.68 lb a.i. (in parentheses, table 5). Of this total, 1.44 lb a.i. was nonstorm, baseline load, assuming a baseline loading rate of 0.024 lb a.i./d for January and February (fig. 9*B*). This baseline was defined by the instantaneous loading rate on the nonstorm February 9 sampling. Another 2.07 lb a.i. of the total January and February load at Vernalis is shown as other nonstorm load. For the Merced River, the Tuolumne River, the Stanislaus River, the San Joaquin River near Stevinson, Orestimba Creek, and the Dry Creek sites, the storm loads for the second storm only are shown in table 5and figure 9; instantaneous loads for the other minor tributary sites are shown in figure 9*C* and table 3.

The first storm transported 0.68 lb a.i. chlorpyrifos to Vernalis and the second storm 1.49 lb a.i. About 50 percent of the 1.49 lb a.i. chlorpyrifos load at Vernalis during storm 2 came from the San Joaquin River near Stevinson (0.26 lb a.i.), the Tuolumne River (0.20 lb a.i.), the Merced River (0.17 lb a.i.), the Stanislaus River (0.09 lb a.i.), and Orestimba Creek

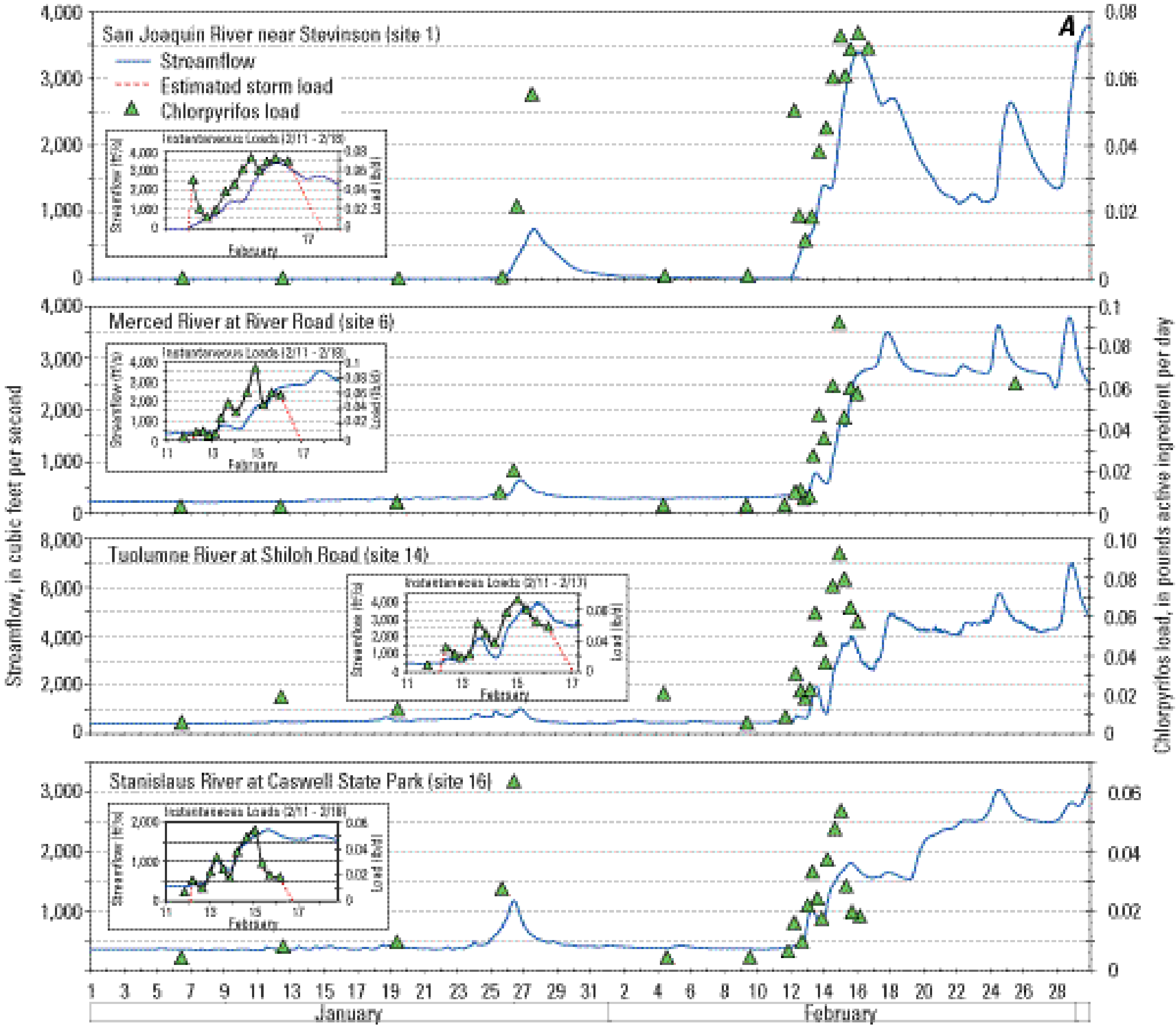

Figure 9. Streamflow and instantaneous chlorpyrifos loads at *(A)* major river sites in the San Joaquin Valley part of the San Joaquin River, California. Site numbers refer to figure 1 and table 3. ft^3/s, cubic foot per second; lb/d, pound per day. *Continued.*

(0.02 lb a.i.) (table 5). These storm loads during runoff from storm 2 do not include baseline loads of 0.25 lb a.i. at Vernalis, 0.01 lb a.i. at Stevinson, 0.02 lb a.i. in the Tuolumne River, 0.01 lb a.i. in the Merced River, and 0.02 lb a.i. in the Stanislaus River. The load at Vernalis as a percentage of application during the dry periods preceding the storms was 0.05 and 0.07 percent, respectively. For the second storm, this percentage ranged from 0.05 in the Tuolumne and Merced River Basins to infinite in the Orestimba Creek and Dry Creek Basins. These basins had chlorpyrifos runoff with essentially no reported agricultural use. However, as with diazinon, there was probably considerable urban application in Modesto and other urban areas (table 2). For the entire months of January and February, the chlorpyrifos load at Vernalis was 0.16 percent of the December 1, 1999 to February 14, 2000, application (table 5).

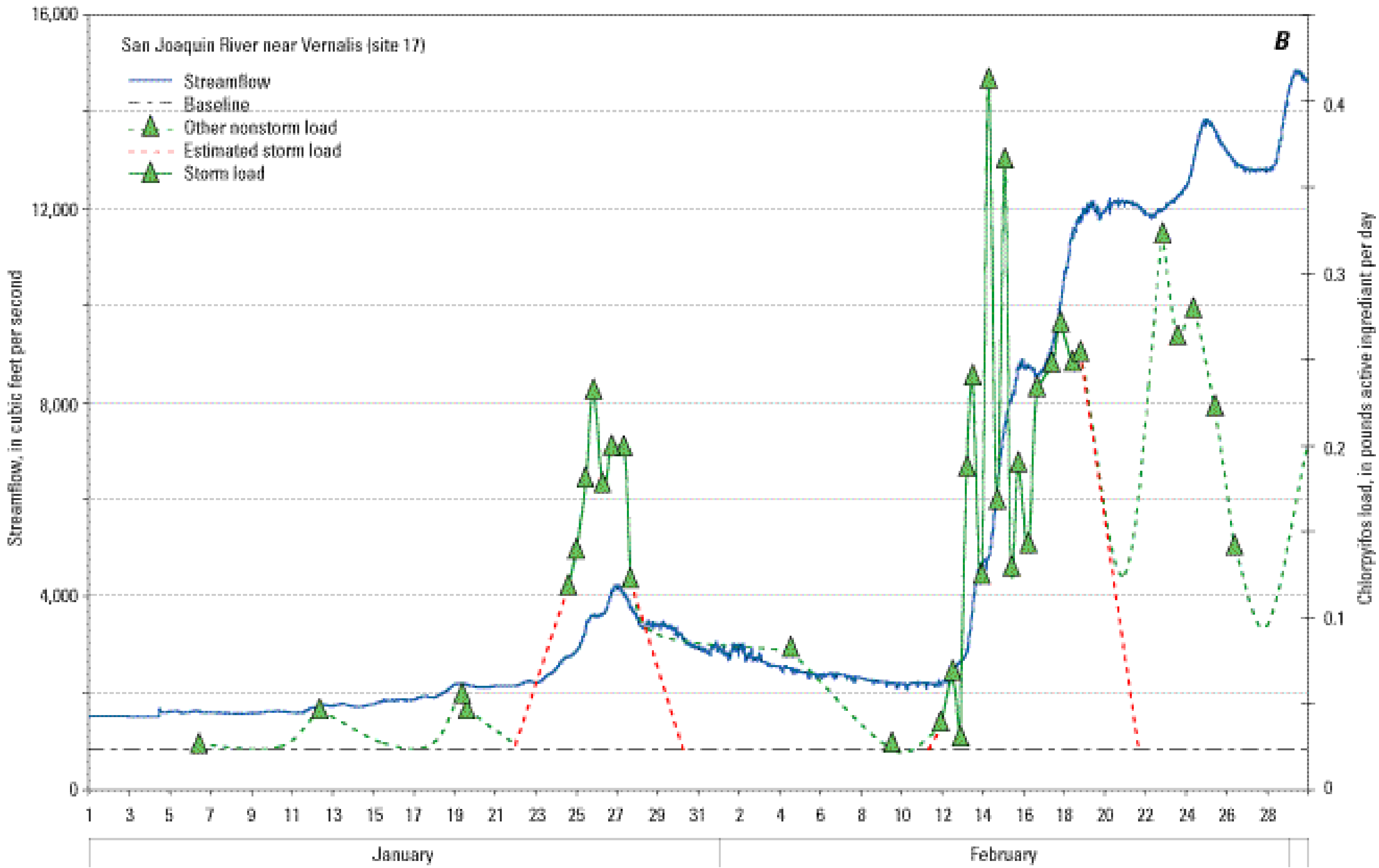

Figure 9. Streamflow and instantaneous chlorpyrifos loads at (***B***) San Joaquin River near Vernalis in the San Joaquin Valley part of the San Joaquin River, California. Site numbers refer to figure 1 and table 3. *Continued.*

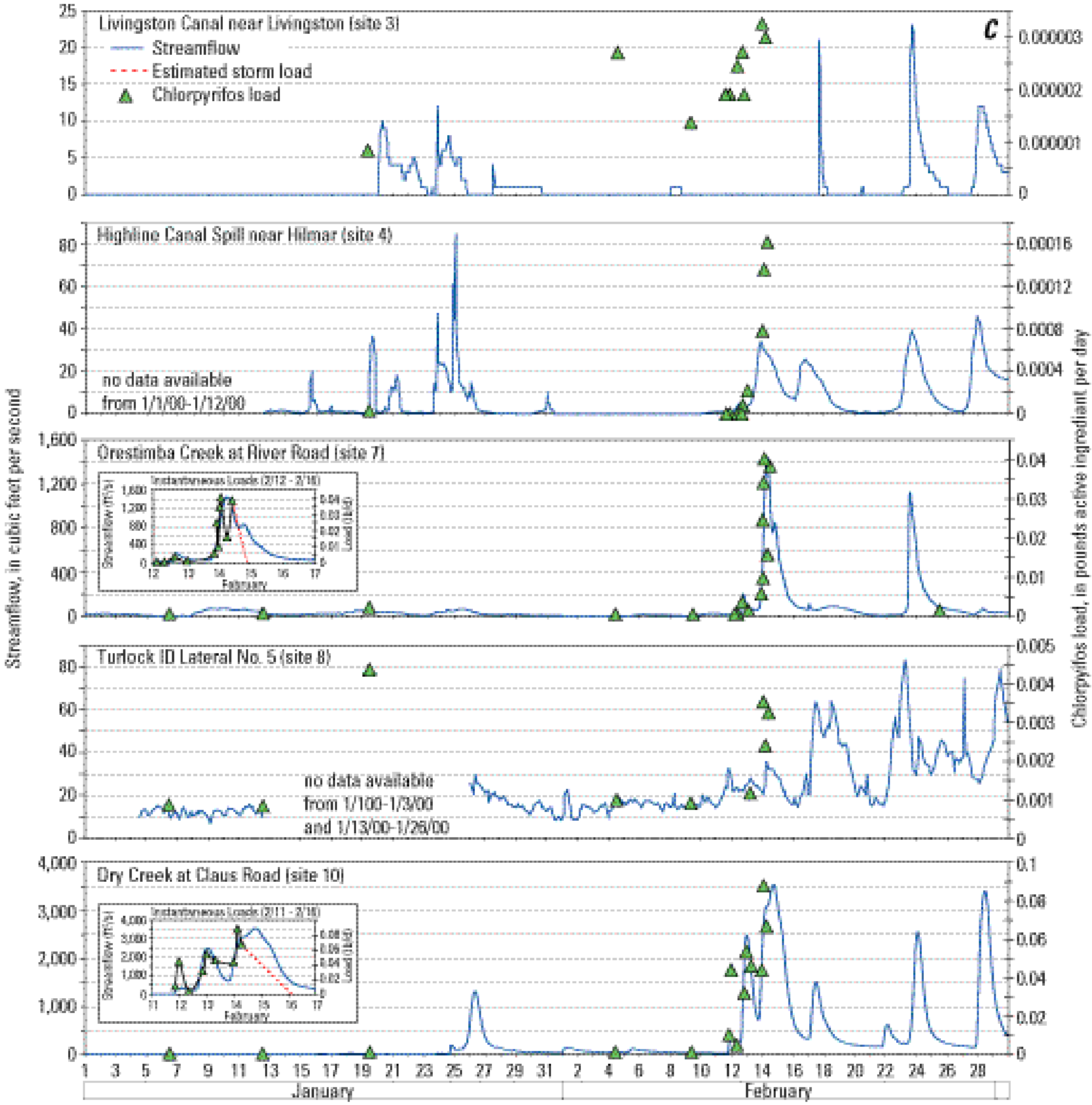

Figure 9. Streamflow and instantaneous chlorpyrifos loads at (***C***) minor tributary sites in the San Joaquin Valley part of the San Joaquin River, California. Site numbers refer to figure 1 and table 3. ft^3/s, cubic foot per second; lb/d, pound per day.

Dry Creek at Claus Road basin produced the highest yield of chlorpyrifos during storm 2 (table 5). The Tuolumne Basin had the second highest yield due to the Dry Creek loads. The 0.68 lb a.i. of storm 1 load in the San Joaquin River at Vernalis occurred over 8.25 days for a loading rate of 0.08 lb a.i./d (fig. 9*B*). The corresponding loading rate for storm 2 (1.49 lb a.i. in 10.25 days) is 0.15 lb a.i./d; for baseline nonstorm (1.44 lb a.i. in 60 days), 0.02 lb a.i./d; and for other nonstorm (2.07 lb a.i. in 41.5 days), 0.05 lb a.i./d. Thus, the loading rates were greater during the two frequently sampled storms than during the rest of January and February.

Table 5. Summary of diazinon and chlorpyrifos loads and yields in relation to agricultural applications for sites in the San Joaquin River Basin, Calfornia

[See table 2 and figure 1 for basin names and locations. Basin area (valley) is in square miles. Value on top is diazinon, value in ( ) on bottom is chlorpyrifos. g/mi^2, grams per square mile; inf, infinite; lb a.i., pound active ingredient; %, percent; —, no data]

Basin	Basin name	Basin area (valley)	Dry period 1 application, in lb a.i.	Storm 1 load, in lb a.i.	Load as % of application, in percent	Storm 1 yield, (load per valley basin area), in g/mi^2	Dry period 2 application, in lb a.i.	Storm 2 load, in lb a.i.	Load as % of application, in percent	Storm 2 yield, (load per valley basin area), in g/mi^2	Total January and February load, in lb a.i.	Total January and February load, as % of application, in percent
A	San Joaquin River near Stevinson	413	489 (217)	— —	— —	— —	1,789 (227)	1.30 (0.26)	0.07 (0.11)	1.43 (0.29)	— —	— —
D	Merced River at River Road Bridge	259	1,039 (284)	— —	— —	— —	625 (314)	0.23 (0.17)	0.04 (0.05)	0.40 (0.30)	— —	— —
E	Dry Creek at Claus Road Bridge	55.4	53 (0)	— —	— —	— —	0 (0)	0.59 (0.15)	inf (inf)	4.84 (1.23)	— —	— —
G	Tuolumne River at Shiloh Road Bridge	150	350 (52)	— —	— —	— —	1 (441)	0.72 (0.20)	72 (0.05)	2.18 (0.61)	— —	— —
H	Stanislaus River at Caswell State Park	116	417 (201)	— —	— —	— —	577 (5)	0.53 (0.09)	0.09 (1.8)	2.07 (0.35)	— —	— —
K	Orestimba Creek at River Road	33.3	627 (0)	— —	— —	— —	10 (0)	0.17 (0.02)	1.7 (inf)	2.32 (0.27)	— —	— —
P	San Joaquin River near Vernalis	2,245	6,970 (1,379)	2.97 (0.68)	0.04 (0.05)	0.60 (0.14)	4,732 (2,165)	5.20 (1.49)	0.11 (0.07)	1.05 (0.30)	19.6 (5.68)	0.17 (0.16)

SUMMARY AND CONCLUSIONS

The application of diazinon and chlorpyrifos during December 1999 through February 2000 in the San Joaquin River Basin (San Joaquin Basin) was less than 21 percent of that applied during the same periods in 1992 through 1994. A total of 13 sites were sampled from 8 to 36 times each during January and February 2000. Samples were collected weekly during nonstorm periods and several times during storm runoff from one or two storms. The two main storm periods sampled included January 23–25 (2.66 inches rain at Modesto) and February 9–14 (2.44 inches rain at Modesto). Although there was slightly more rain during the first storm period, due to antecedent soil moisture, there was considerably more storm runoff from the valley application areas during the second storm.

The highest concentrations of diazinon and chlorpyrifos occurred during storm runoff. Only four samples at major river sites exceeded the proposed critical maximum concentration (CMC) of 0.08 μg/L (microgram per liter) for diazinon. At the minor tributary sites, 24 samples exceeded the diazinon guideline, although only three of these occurred at flows over 100 ft^3/s (cubic foot per second). Only one sample at major river sites and four samples at minor tributary sites exceeded the proposed CMC of 0.02 μg/L for chlorpyrifos.

The diazinon load in the San Joaquin River at Vernalis during the two storms in January and February 2000 was 8.17 lb a.i. (pound active ingredient), which is less than one-third of the 27.4 lb a.i. during two storms in January and February 1994. During the February 2000 storm, the main sources of diazinon in the San Joaquin Basin were the San Joaquin River near Stevinson Basin (25 percent), the Tuolumne River Basin (14 percent), and the Stanislaus River Basin (10 percent). The total diazinon load in the San Joaquin River at Vernalis during January and February 2000 was 19.6 lb a.i. This total diazinon load at Vernalis was 0.17 percent of the December 1, 1999, through February 14, 2000, application.

During the February 2000 storm, the main sources of chlorpyrifos in the San Joaquin Basin were the San Joaquin River near Stevinson Basin (17 percent), theTuolumne River Basin (13 percent), and the Merced River Basin (11 percent). The total chlorpyrifos load in the San Joaquin River at Vernalis during January and February 2000 was 5.68 lb a.i. This total chlorpyrifos load at Vernalis was 0.16 percent of the December 1, 1999, through February 14, 2000, application.

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