

Occurrence and Distribution of Dissolved Pesticides in the San Joaquin River Basin, California

Water-Resources Investigations Report 98-4032

National Water-Quality Assessment Program

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By Sandra Y. Panshin, Neil M. Dubrovsky, JoAnn M. Gronberg, *and* Joseph L. Domagalski

U.S. GEOLOGICAL SURVEY

Water-Resources Investigations Report 98-4032

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

6440-46

Sacramento, California
1998



U.S. DEPARTMENT OF THE INTERIOR
BRUCE BABBITT, Secretary

U.S. GEOLOGICAL SURVEY
Thomas J. Casadevall, Acting Director



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FOREWORD

The mission of the U.S. Geological Survey (USGS) is to assess the quantity and quality of the earth resources of the Nation and to provide information that will assist resource managers and policymakers at Federal, State, and local levels in making sound decisions. Assessment of water-quality conditions and trends is an important part of this overall mission.

One of the greatest challenges faced by water-resources scientists is acquiring reliable information that will guide the use and protection of the Nation's water resources. That challenge is being addressed by Federal, State, interstate, and local water-resource agencies and by many academic institutions. These organizations are collecting water-quality data for a host of purposes that include: compliance with permits and water-supply standards; development of remediation plans for specific contamination problems; operational decisions on industrial, wastewater, or water-supply facilities; and research on factors that affect water quality. An additional need for water-quality information is to provide a basis on which regional- and national-level policy decisions can be based. Wise decisions must be based on sound information. As a society we need to know whether certain types of water-quality problems are isolated or ubiquitous, whether there are significant differences in conditions among regions, whether the conditions are changing over time, and why these conditions change from place to place and over time. The information can be used to help determine the efficacy of existing water-quality policies and to help analysts determine the need for and likely consequences of new policies.

To address these needs, the U.S. Congress appropriated funds in 1986 for the USGS to begin a pilot program in seven project areas to develop and refine the National Water-Quality Assessment (NAWQA) Program. In 1991, the USGS began full implementation of the program. The NAWQA Program builds upon an existing base of water-quality studies of the USGS, as well as those of other Federal, State, and local agencies. The objectives of the NAWQA Program are to:

- Describe current water-quality conditions for a large part of the Nation's freshwater streams, rivers, and aquifers.
- Describe how water quality is changing over time.

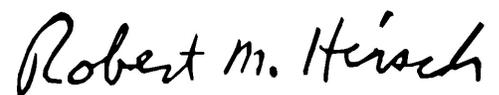
- Improve understanding of the primary natural and human factors that affect water-quality conditions.

This information will help support the development and evaluation of management, regulatory, and monitoring decisions by other Federal, State, and local agencies to protect, use, and enhance water resources.

The goals of the NAWQA Program are being achieved through ongoing and proposed investigations of 60 of the Nation's most important river basins and aquifer systems, which are referred to as study units. These study units are distributed throughout the Nation and cover a diversity of hydrogeologic settings. More than two-thirds of the Nation's freshwater use occurs within the 60 study units and more than two-thirds of the people served by public water-supply systems live within their boundaries.

National synthesis of data analysis, based on aggregation of comparable information obtained from the study units, is a major component of the program. This effort focuses on selected water-quality topics using nationally consistent information. Comparative studies will explain differences and similarities in observed water-quality conditions among study areas and will identify changes and trends and their causes. The first topics addressed by the national synthesis are pesticides, nutrients, volatile organic compounds, and aquatic biology. Discussions on these and other water-quality topics will be published in periodic summaries of the quality of the Nation's ground and surface water as the information becomes available.

This report is an element of the comprehensive body of information developed as part of the NAWQA Program. The program depends heavily on the advice, cooperation, and information from many Federal, State, interstate, Tribal, and local agencies and the public. The assistance and suggestions of all are greatly appreciated.



Robert M. Hirsch
Chief Hydrologist

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CONVERSION FACTORS, VERTICAL DATUM, ABBREVIATIONS, AND ACRONYMS

Multiply	By	To obtain
inch (in.)	25.4	millimeter
foot (ft)	0.3048	meter
acre	4,047	square meter
square mile (mi ²)	2.590	square kilometer
pound (lb)	0.4536	kilogram

Temperature is given in degrees Celsius (°C), which can be converted to degrees Fahrenheit (°F) by the following equation: °F = 1.8(°C) + 32

Vertical Datum

Sea level: In this report, "sea level" refers to the National Geodetic Vertical Datum 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.

Water Quality Units

Concentrations of constituents in water samples are given in either milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g/L}$). Milligrams per liter is equivalent to “parts per million” and micrograms per liter is equivalent to “parts per billion.”

Abbreviations:

a. i.	active ingredient
K_{oc}	organic-carbon-normalized adsorption coefficient
mi	mile
L	liter
lb	pound
mg	milligram
mg/L	milligram per liter
$\mu\text{g/L}$	microgram per liter

Acronyms:

CCID	Central California Irrigation District
GC/MS	gas chromatography/mass spectrometry
HPLC	high-performance liquid chromatography
MDL	method detection limit
NAWQA	National Water-Quality Assessment Program
USGS	U.S. Geological Survey

OCCURRENCE AND DISTRIBUTION OF DISSOLVED PESTICIDES IN THE SAN JOAQUIN RIVER BASIN, CALIFORNIA

By Sandra Y. Panshin, Neil M. Dubrovsky, JoAnn M. Gronberg, and Joseph L. Domagalski

ABSTRACT

The effects of pesticide application, hydrology, and chemical and physical properties on the occurrence of pesticides in surface water in the San Joaquin River Basin, California, were examined. The study of pesticide occurrence in the highly agricultural San Joaquin–Tulare Basins is part of the National Water-Quality Assessment Program of the U.S. Geological Survey. One hundred forty-three water samples were collected throughout 1993 from sites on the San Joaquin River and three of its tributaries: Orestimba Creek, Salt Slough, and the Merced River. Of the 83 pesticides selected for analysis in this study, 49 different compounds were detected in samples from the four sites and ranged in concentration from less than the detection limit to 20 micrograms per liter. All but one sample contained at least one pesticide, and more than 50 percent of the samples contained seven or more pesticides. Six compounds were detected in more than 50 percent of the samples: four herbicides (dacthal, EPTC, metolachlor, and simazine) and two insecticides (chlorpyrifos and diazinon). None of the measured concentrations exceeded U.S. Environmental Protection Agency drinking water criteria, and many of the measured concentrations were very low. The concentrations of seven pesticides exceeded criteria for the protection of freshwater aquatic life: azinphos-methyl, carbaryl, chlorpyrifos, diazinon, diuron, malathion, and trifluralin. Overall, some criteria for protection of aquatic life were exceeded in a total of 97 samples.

Factors affecting the spatial patterns of occurrence of the pesticides in the different subbasins included the pattern of application and hydrology. Seventy percent of pesticides with known application were detected. Overall, 40 different pesticides were detected in Orestimba Creek, 33 in Salt Slough, and 26 in the Merced River. Samples from the Merced River had a relatively low number of detections, despite the high number (35) of pesticides applied, owing to the generally low percentage of irrigation return flow and contribution of pesticide-free streamflow from reservoir releases. Irrigation return flows in the Orestimba Creek and Salt Slough subbasins generally contained more pesticides at higher concentrations. In addition, the distribution of seven pesticides (alachlor, cyanazine, dacthal, fonofos, molinate, napropamide, and trifluralin) in the subbasins showed a direct spatial correspondence between occurrence and application rates.

Temporal patterns of occurrence also were affected by patterns of application and hydrology. Most pesticides showed a clear correspondence between the times of their application and their occurrence. Fourteen pesticides had maximum application and concentrations during the summer irrigation season. However, several pesticides exhibited maximum concentrations during winter storms, although maximum application occurred at some other time of year—the result of differences in precipitation and streamflow between seasons. In some subbasins, precipitation runoff was more effective than irrigation return flows at

transporting pesticides from the site of application to the stream. Also, during autumn, when there was neither precipitation nor irrigation, the transport of pesticides to streams was limited.

The effect of chemical and physical properties on the occurrence of pesticides was examined for the San Joaquin River Basin as a whole. The runoff potential of each pesticide, calculated from the solubility, water-soil organic carbon partition coefficient K_{oc} , and hydrolysis half-life, is generally consistent with the frequency of detection of pesticides in surface water in relation to the amount applied. These three properties each were generally, and weakly, correlated with the relative load of the pesticides in surface water.

Pesticide occurrence and concentrations at the mouth of the basin (the San Joaquin River near Vernalis) were compared with pesticide occurrence and concentrations in the three subbasins to evaluate how well sampling at the mouth of the basin reflects conditions in the subbasins. This evaluation shows that if the objective of the monitoring is to describe the maximum concentrations of pesticides in the basin, sampling at the integrator site at the mouth of the basin is insufficient, and sampling at small indicator subbasins is required. If the objectives of the monitoring are to identify which pesticides occur in surface water in the basin and to provide a gross indication of the concentration levels of the most commonly occurring pesticides, then sampling at the basin mouth integrator site may be sufficient.

INTRODUCTION

The San Joaquin Valley is one of the most important agricultural areas in the United States. Most of the valley floor is agricultural land, and its agricultural history dates back to the 1870s. The combination of seasonal abundant water and the long growing season results in an exceptionally productive agricultural economy in the San Joaquin Valley. In 1987, California produced 10.2 percent of the total value of agricultural production in the United States, 49 percent of which was generated in the San Joaquin Valley (San Joaquin Valley Drainage Program, 1990). In 1987, gross sales

from agricultural products from the San Joaquin Valley totaled \$6.82 billion. Crops accounted for \$4.45 billion of the valley output, and livestock and related products accounted for \$2.37 billion. Many pesticides are applied to crops in the valley. In 1993, a total of 16.6 million lb active ingredient (a. i.) of pesticides (1,800 different compounds) was applied to agricultural land in the San Joaquin River Basin, with an additional 3 million lb a. i. of nonagricultural application (California Department of Pesticide Regulation, 1994).

The occurrence of these pesticides and their effect on the water quality of the San Joaquin River has been studied by several scientists (Foe and Connor, 1991; Foe, 1995; Kuivila and Foe, 1995; MacCoy and others, 1995; Ross and others, 1996; Domagalski, 1997a, b). All of these studies detected the presence of pesticides in water samples from the San Joaquin River and its tributaries. Three studies (Foe and Conner, 1991; Foe, 1995; Kuivila and Foe, 1995) demonstrated that water in the San Joaquin River is sometimes toxic to *Ceriodaphnia dubia*, a water flea. Foe (1995) examined the seasonality of pesticide concentrations, *Ceriodaphnia* mortality, and pesticide applications to different crops. He was able to identify the pesticides most likely responsible for the toxicity of the water at different times of the year and to associate these pesticides with the crops to which they were applied. This link between agricultural pesticide use and toxicity to aquatic organisms underscores the importance of understanding the factors that cause pesticide transport to streams. A thorough understanding of the relation between agricultural pesticide use and pesticide occurrence in surface water also will be necessary to achieve the objective of the elimination of toxicity in the San Joaquin River above baseline conditions established by the State Water Resources Control Board (California State Water Resources Control Board, 1991) and the Central Valley Regional Water Quality Control Board (1991).

Purpose and Scope

The purpose of this report is to examine the spatial and temporal variability of dissolved pesticide occurrence and concentrations in surface water within the San Joaquin River Basin and, to the extent possible, determine the sources and transport mechanisms responsible for their presence. Data were collected on the concentrations of 83 pesticides in surface-water

samples from four sites within the San Joaquin River Basin (fig. 1) throughout 1993. One of these sites, the San Joaquin River near Vernalis, was chosen because it is at the mouth of the San Joaquin River and characterizes water quality in the basin as a whole. The other three sites—Orestimba Creek at River Road near Crows Landing, Salt Slough at Highway 165 near Stevinson, and the Merced River at River Road near Newman—are located in subbasins, each designed to characterize one type of physiography, localized pesticide application, and specific land use. These differences in subbasin characteristics, along with the resulting differences in pesticide application, allow a detailed examination of the factors leading to the transport of pesticides to streams. Pesticide occurrence and concentration data from the San Joaquin River is compared with data from the other three sites to evaluate consistency between what is observed at the San Joaquin River site and what is observed in the subbasins. This study is just one part of an integrated study of the quality of surface water, ground water, and aquatic ecosystems by the San Joaquin–Tulare Basins study team of the U.S. Geological Survey’s (USGS) National Water-Quality Assessment (NAWQA) Program. NAWQA began in 1991 and is intended to give an overall view of the quality of the Nation’s water resources.

Description of the Study Area

The San Joaquin–Tulare Basins NAWQA study unit covers approximately 31,200 mi² in central California. The study unit includes the western slope of the Sierra Nevada to the east, the San Joaquin Valley, and the eastern slope of the Coast Ranges to the west. Although the study unit consists of the entire drainage basin, this study focused on that part of the San Joaquin Valley that lies within the San Joaquin River Basin, specifically the perennial reach of the San Joaquin River. This study area was selected for two reasons: (1) the perennial San Joaquin River is the only surface water to exit the basin during most years; and (2) the water quality of the San Joaquin River influences the water quality of the Sacramento–San Joaquin Delta, which is the source of the drinking water for millions of people in southern California.

The San Joaquin Valley has an arid-to-semiarid climate characterized by hot summers and mild winters, with average temperatures in degrees Fahrenheit

ranging from the low 40s during the winter to the mid-80s during the summer. The eastern slope of the Coast Ranges, and the valley, are in the rain shadow of the Coast Ranges. The large amounts of precipitation that fall on the western slope of the Sierra Nevada are the major source of water entering the basin. Monthly and annual precipitation in the study unit is highly variable. Most of the precipitation (88 percent) falls during November through April; January is the peak precipitation month (for example, the mean monthly precipitation from 1961 to 1990 is compared with the monthly precipitation in 1993 for the city of Modesto in fig. 2). Total precipitation in 1993 was high when compared with the yearly average for 1961–90 (16.57 in. versus 12.10 in.). Further, 1993 was classified as a wet year according to the index used by the California State Water Resources Control Board (Gary Hester, oral commun., 1996).

The bedrock geology of the areas adjacent to the east and west sides of the San Joaquin Valley contrasts sharply with, and has a profound influence on, the characteristics of the sediments in the valley. The Sierra Nevada east of the valley in the study area, is composed primarily of granitic rocks and an associated foothill belt of marine and metavolcanic rocks. The soils and sediments in the eastern part of the valley are derived primarily from the Sierra Nevada and are generally permeable, medium- to coarse-grained sands. The Coast Ranges west of the study area are primarily marine and continental sedimentary rocks, with a core of ultramafic rocks. As a result, the soils and sediments of the western part of the valley tend to have a higher clay content and a lower permeability compared with the eastern part of the valley.

The Coast Ranges, Sierra Nevada, and foothills of the Sierra Nevada are predominantly forested land, whereas the valley floor is predominantly agricultural land. In 1987, about 10.5 million acres in the San Joaquin Valley was farmland. Major products include livestock and livestock products, fruits and nuts, cotton, vegetables, hay and grains, and other crops (San Joaquin Valley Drainage Program, 1990).

The surface-water hydrology of the San Joaquin–Tulare Basins study unit has been significantly modified by development of water resources. Almost every tributary and drainage into the San Joaquin River has been altered by a network of canals, drains, and wasteways. Almost every major river entering the valley from the Sierra Nevada has one or more

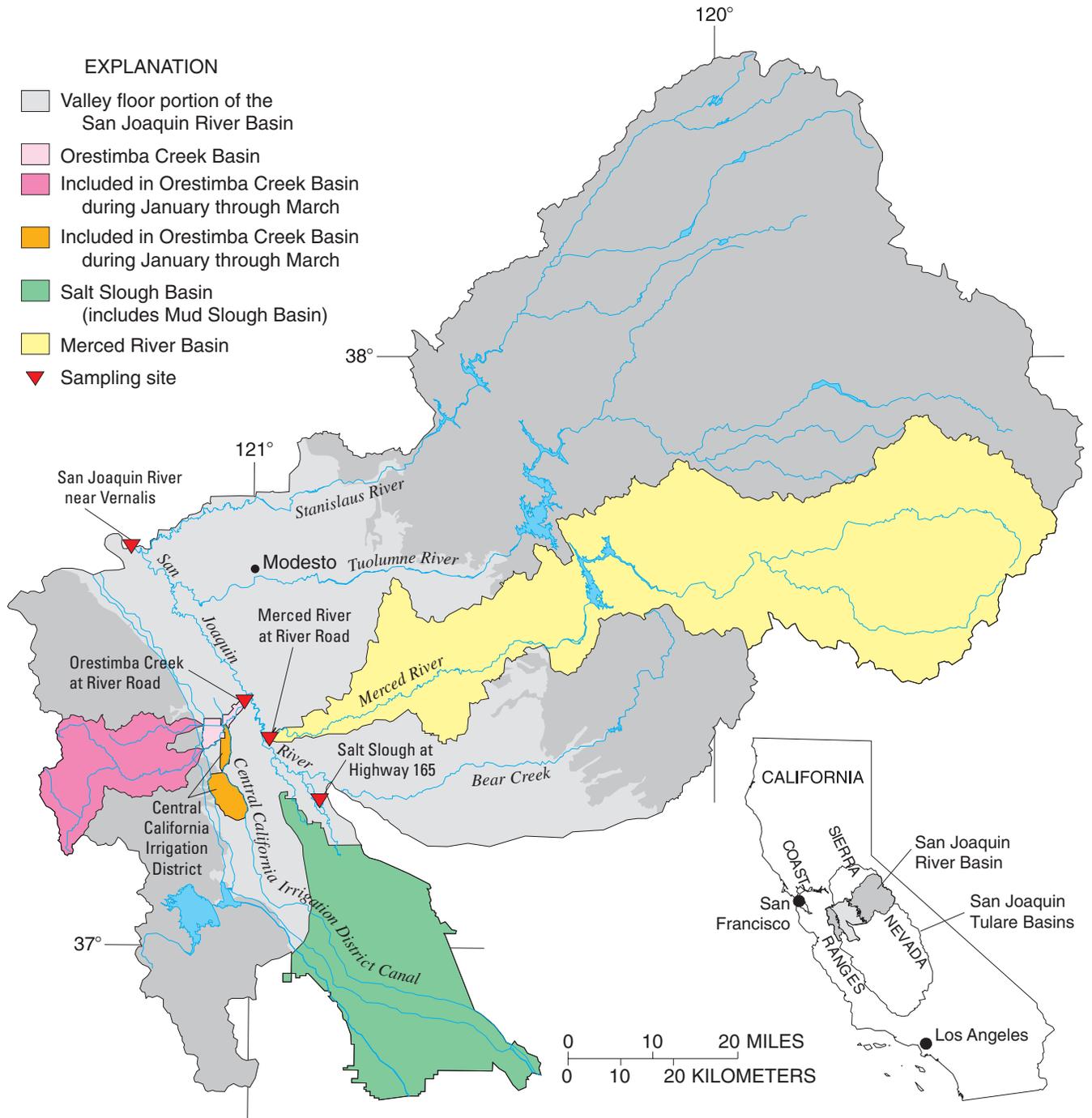


Figure 1. Study area, basin boundaries, and sampling site locations, San Joaquin River Basin, California.

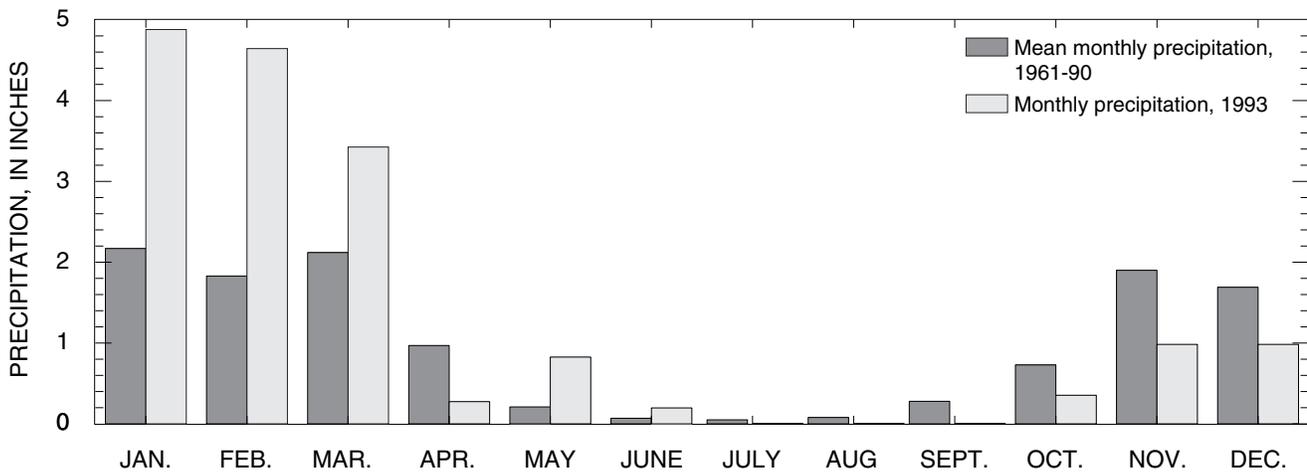


Figure 2. Precipitation for the city of Modesto, California: mean monthly for 1961 through 1990, and 1993 monthly.

reservoirs. Most streamflow in the San Joaquin River is contributed by its major eastern tributaries—the Stanislaus, Tuolumne, and Merced rivers. The western tributaries are primarily ephemeral and contribute only a small part of the San Joaquin River streamflow, except sometimes during the irrigation season.

STUDY APPROACH

Spatial Design: Selection of Subbasins

Samples of surface water for determining the dissolved pesticides were collected at four sites, termed “intensive fixed sites” (Gilliom and others, 1995). The San Joaquin River near Vernalis site was chosen because it receives streamflow from the entire basin and, hence, characterizes water quality in the basin as a whole. Such a site is called an “integrator site” (Gilliom and others, 1995) because it integrates the effects of hydrology, land use, pesticide application, and other factors for the entire heterogeneous basin. Additional sites were selected to represent three subbasins. These sites are Orestimba Creek at River Road near Crows Landing, Salt Slough at Highway 165 near Stevinson, and the Merced River at River Road near Newman. These sites were selected to evaluate the influence of major basin characteristics such as hydrology, land use, and pesticide application. These sites are termed “indicator” sites (Gilliom and others, 1995) because each is indicative of a certain set of local conditions.

The three subbasins have contrasting hydrology because of differences in physiography and sources of surface water (fig. 3). Orestimba Creek is an ephemeral stream in a relatively small basin (6,904 acres) within the valley floor on the west side of the valley. Streamflow in Orestimba Creek results from storm runoff in the winter, and irrigation return flows in the spring and summer (fig. 3A). During the winter, the creek can receive flow from the Coast Ranges (105,313 acres contributing area), as well as from the area that drains into the main canal of the Central California Irrigation District (CCID; 12,885 acres), depending on the intensity and duration of storms, thus increasing the drainage area to 125,102 acres. Consequently, storms result in higher discharges during the winter compared with the rest of the year.

The Salt Slough Basin (302,536 acres) is on the south side of the San Joaquin River Basin. Drainage to the site is highly controlled and can include the areas drained by Mud Slough. This subbasin is predominantly on the valley floor. Salt Slough streamflow is mainly agricultural drainage, which includes both sub-surface drainage and surface irrigation return flows (fig. 3B). Wetlands drainage in the late winter and early spring, and winter storm runoff, also contribute to create a fairly even distribution of streamflows throughout the year in Salt Slough.

The Merced River site is on the east side of the San Joaquin River Basin. The Merced River Basin is large (894,313 acres), and more than 80 percent of the subbasin lies in the foothills and Sierra Nevada. Reservoir releases are the main determinant of the Merced

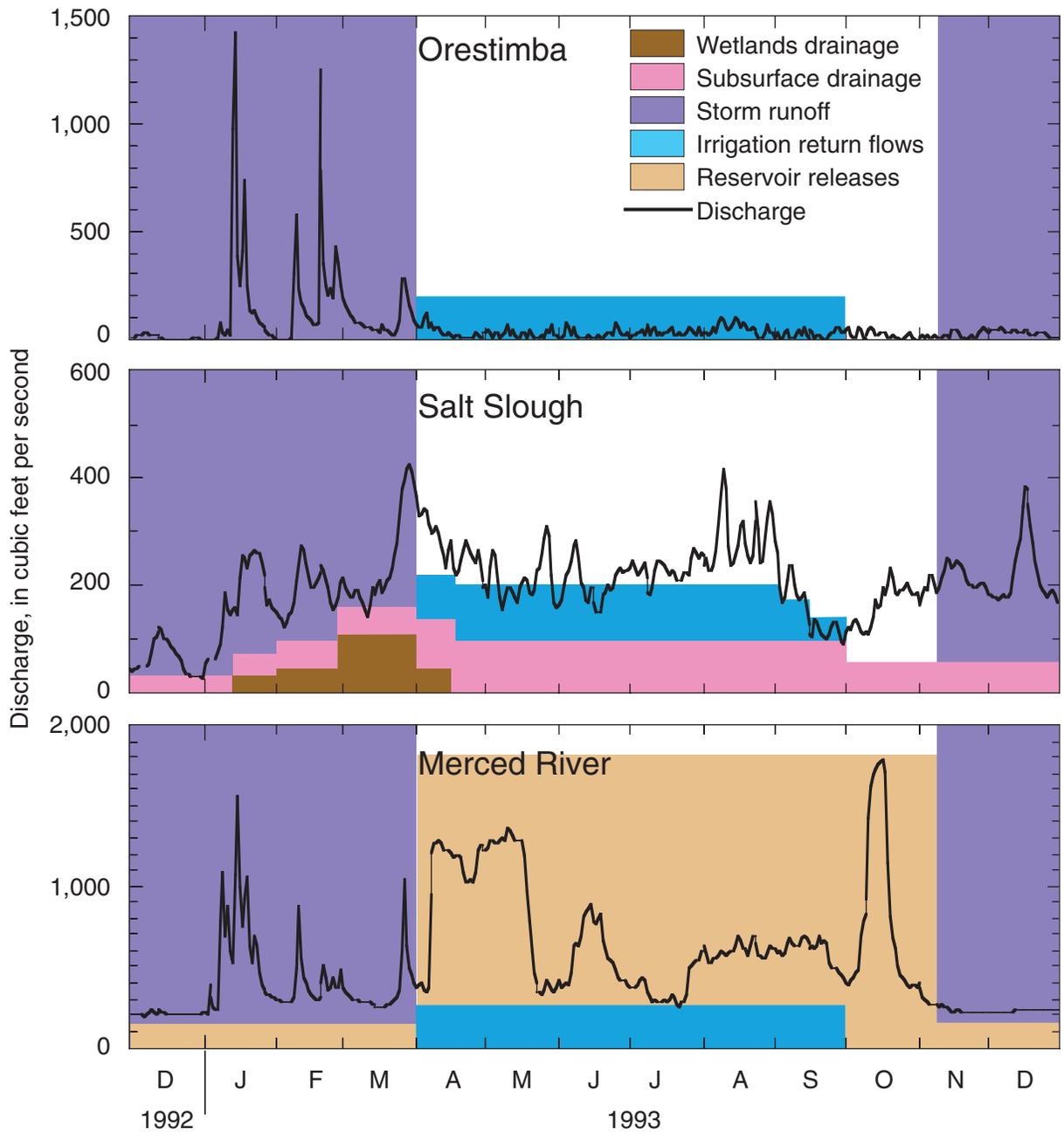


Figure 3. Hydrographs of three subbasins in the San Joaquin River Basin for December 1992 through December 1993 with a graphic representation of the seasonal variations in sources of water.

River streamflow (fig. 3C). Large reservoir releases are made during spring to assist out-migration of salmon and steelhead fingerlings, and during autumn to stimulate the upstream migration of adult fish. Streamflow is supplemented by storm runoff in the winter and irrigation return flow during spring and summer.

Field-scale land-use data obtained from the California Department of Water Resources (1985, 1988a,b, 1989a,b) indicate large contrasts in land use in the sub-basins (table 1). About 90 percent of the Orestimba Creek Basin is agricultural, and almost half of the agricultural land is planted in beans. About 75 percent of the Salt Slough Basin is agricultural, of which about 30 percent is planted in cotton. Overall, the Salt Slough

Basin has a greater variety of crops than the other sub-basins. About 13 percent of the Merced River Basin is agricultural, about 60 percent of which is orchards and vineyards. Most of this subbasin lies outside the valley floor and is dominated by forested land. The wide variety of crops grown in these subbasins is reflected in the wide variety of pesticides used in the study area, as discussed below.

A cursory look at the water quality of these three subbasins reveals differences that can be explained by the aforementioned characteristics. Because of the low solubility of the quartz and feldspars that make up the bulk of the Sierra Nevada, the Merced River characteristically has low concentrations of dissolved solids

Table 1. Distribution of major agricultural land use in the study area, San Joaquin River Basin, California

[All values are in acres unless otherwise noted; —, not applicable]

Land-use categories	Orestimba Creek Basin	Central California Irrigation District	Salt Slough Basin	Merced River Basin	San Joaquin River Basin
Basin area	6,904	12,885	302,536	894,313	4,700,707
Agricultural area	6,159	12,687	226,683	117,325	1,032,972
Orchard crops					
Almonds	208	2,129	941	48,158	166,588
Apricots	2	113	1,165	20	9,685
Walnuts	1,476	2,093	906	1,582	38,240
Peaches	—	17	—	3,763	17,417
Others	70	29	665	3,214	13,932
Vineyards	—	—	804	14,309	36,105
Citrus	—	—	361	31	1,225
Field crops					
Corn	—	402	6,429	7,595	79,664
Cotton	—	71	68,751	—	79,022
Beans	2,929	2,025	2,661	2,035	40,853
Others ¹	38	1,105	30,863	2,060	66,268
Rice	—	—	9,770	—	17,474
Grain		1,072	17,631	6,779	67,948
Truck crops ²	671	1,260	24,353	1,235	63,645
Semiagricultural	34	235	18,069	3,948	49,671
Pasture					
Alfalfa	727	2,002	29,383	4,654	103,901
Mixed pasture	—	55	5,597	15,198	141,655
Other	—	—	335	169	2,721
Agricultural land use accounted for by above crops, in percent	100	99	96	98	97

¹Other field crops: fallow, safflower, sudan, and sugar beets.

²Truck crops: broccoli, flowers and nurseries, melons, squash and cucumbers, onions and garlic, peppers, sweet potatoes, and tomatoes.

(42–120 mg/L in 1993). These low values reflect the large component of high quality water from the Sierra Nevada that is released from reservoirs throughout the year and the relatively small amount of irrigation return owing to the effective infiltration of irrigation water into the coarse, permeable soils. Conversely, because of the highly soluble minerals in the sediments of the Coast Ranges, runoff from western tributaries can contain high concentrations of dissolved solids. The higher dissolved solids values at Orestimba Creek (247–585 mg/L in 1993) also reflect this increased mineral solubility, greater proportions of irrigation return to the creek, and an absence of the diluting effect of reservoir releases present in the Merced River. Salt Slough has the highest dissolved-solids values (681–2,228 mg/L in 1993) as a result of a combination of surface irrigation returns and saline subsurface agricultural drainage. Values of dissolved solids for the San Joaquin River represent a composite of input from these subbasins, as well as from other sources; values were similar to those observed at the Orestimba Creek site. The contrasts in the values of dissolved solids among the subbasins show that the contrasts in the geology of the eastern and western parts of the San Joaquin Valley, as well as the effects of irrigation drainage, are clearly discernible in the most general water-quality characteristics of the subbasins. These clear contrasts in overall water quality, in turn, indicate that the three subbasins also can show contrasts in the occurrence of dissolved pesticides.

Temporal Strategy

The premise of the intensive fixed site sampling strategy is that relatively high frequency sampling at a few carefully chosen sites during key seasonal periods yields superior information about the occurrence and seasonal patterns compared with other design alternatives. The four intensive fixed sites (at Orestimba Creek, Salt Slough, the Merced River, and the San Joaquin River) were sampled throughout the year at varying frequency to target different types of pesticides during different seasons. Factors that influence the sampling frequency include seasonal hydrologic conditions, pesticide application patterns, and irrigation practices. Some pesticides are applied during the winter. Of particular concern, from the perspective of causing toxicity in surface waters, is the application of insecticides on fruit and nut orchards while dormant.

Because the growing season for most crops extends from March to October, the largest diversity of pesticides are applied during the spring and summer. Relatively little pesticide application occurs during October through December.

Sample collection was most frequent during the winter and spring rainy season when it was hypothesized that off-site movement of pesticides would be facilitated by rainfall. Sample collection was least frequent during the autumn when there is neither rainfall nor irrigation. Samples were collected once or twice a week at each site during the winter (January through March) largely because of the application of insecticides on dormant orchards. Samples were collected weekly during April, every 2 to 3 weeks from May through September, and about once a month from October through December. In addition to this periodic sampling, multiple samples were collected at the Orestimba Creek, the Merced River, and the San Joaquin River sites during two winter storms (February 8–10 and February 18–19, 1993) to study the transport of insecticides applied to dormant orchards (Domagalski and others, 1997). Collecting samples prior to, during, and after the storm, allowed an examination of the variation in pesticide concentrations relative to the storm hydrograph.

Pesticide Application Database

One goal of this project is to examine correlations between pesticide application and pesticide occurrence in surface water. Information on pesticide application in the study area was obtained from the database maintained by the California Department of Pesticide Regulation (1993, 1994). California state law requires that all agricultural, and most industrial and commercial, pesticide applications be reported to state officials and recorded in the database. The information available includes the name and amount of each pesticide that was applied, the commodity to which it was applied, the application date, and the application location. Pesticide data are divided into two categories: agricultural use and nonagricultural use. The latter classification includes pesticide applications for rights-of-way, structural pest control, landscape maintenance, commodity fumigation, and vertebrate pest control, among others. Data from the agricultural and the nonagricultural databases are available for 1992 and 1993, the period before and during this study. The

agricultural database includes the location of the application site to within a square mile, but the nonagricultural data are not as precise, specifying only the county in which the pesticide was applied. Because of this, the application data provided in this report include only agricultural use for the three subbasins of Orestimba Creek, Salt Slough, and the Merced River, but will include agricultural and nonagricultural use for the San Joaquin Basin as a whole. The nonagricultural data are from four counties: Mariposa, Merced, Stanislaus, and Tuolumne. In general, nonagricultural applications of pesticides are much lower in quantity than agricultural applications. For all sites, some pesticide applications (for example, those by an individual homeowner) are not reported to the state. Additionally, only data for the 83 pesticides selected by the NAWQA Program will be analyzed and discussed.

Reported pesticide applications in the San Joaquin River Basin for 1993 are summarized for major crops in table 2. The targeted pesticides included 5 of the 21 most heavily applied pesticides in the basin: propargite (overall rank of 11), chlorpyrifos (12), diazinon (15), trifluralin (19), and EPTC (21). The large variety of crops accounts for the large number of pesticides applied. Pesticide applications on major crops in the subbasins are presented in appendixes A, B, and C.

Table 3 shows the total amount of reported pesticide application in each subbasin, the San Joaquin River Basin, and the CCID. For each subbasin, the first column lists the total 1993 agricultural application, and the second column lists the rate of agricultural application, which is the total agricultural application divided by the agricultural area of the basin. Application rate is expressed as pounds of active ingredient applied per 1,000 acres of agricultural land. One subbasin, consisting of lands that likely drain to the main canal of the CCID, is not explicitly studied in this report, but the CCID drainage area can contribute substantial runoff to Orestimba Creek during the winter and only minimal amounts during the summer. For this reason, the CCID application data are considered only for the months of January through March 1993 when storms were likely to induce runoff from this area to Orestimba Creek. The last three columns of table 3 show data for the San Joaquin River, the site representative of the basin as a whole. The agricultural and agricultural-rate columns are as described above. The last column presents the nonagricultural application for the entire study area.

Among the subbasins, the Salt Slough Basin has the greatest variety of crops grown (table 1) and the largest number (42) of target pesticides applied to crops; the Merced River Basin has 34 target pesticides applied; and Orestimba Creek Basin has 28 target pesticides applied. Orestimba Creek Basin has the least variety in crops grown, but generally has the highest pesticide application rates.

METHODS

Field Methods

Discrete water samples were collected for analysis of concentrations of pesticides and for other chemical and physical properties. All samples were flow-weighted and cross-sectionally integrated by standard USGS methods (Ward and Harr, 1990). This protocol provides a sample representative of a particular site at the time of sampling.

Complete descriptions of sample collection and processing methods are provided in Shelton (1994). Each sample was split into two aliquots. About 1 L of sample was filtered; then the pesticides were extracted by passing the water through a 500-mg C-18 solid-phase extraction cartridge. The cartridge was dried with carbon dioxide or nitrogen gas. An additional 1-L aliquot was filtered; then the pesticides were removed from the water by passing the sample through a 500-mg graphitized carbon solid-phase extraction cartridge. The cartridge was then dried by pulling air through it with a vacuum pump. Samples usually were extracted in the field immediately following collection and always within 24 hours of collection. The cartridges were then shipped to the USGS National Water Quality Laboratory in Arvada, Colorado, for analysis.

Analytical Methods

The pesticides studied were chosen because they are applied heavily throughout the Nation and because they are amenable to analysis by the two methods developed for the NAWQA Program. Most of these pesticides are or were applied in the San Joaquin River Basin. Pesticides measured by the gas chromatography/mass spectrometry (GC/MS) method were analyzed throughout 1993; pesticides measured by the

Table 2. Pesticide application by commodity in 1993, San Joaquin River Basin, California

[All values are in pounds, active ingredient. —, none applied; in each pesticide, bold, for crop with highest application]

Pesticide	Almonds	Apricots	Walnuts	Peaches	Fruits and nuts	Vineyards	Corn	Cotton
2,4-D	41,724	790	4,600	3,380	340	576	1,605	—
2,4-DB	—	—	—	—	—	—	—	—
Alachlor	—	—	—	—	—	—	861	—
Aldicarb	—	—	—	—	—	—	—	6,930
Azinphos-methyl	42,760	—	14,362	8,275	10,423	—	—	—
Benfluralin	—	—	—	—	—	—	—	—
Bromacil	—	—	—	—	49	—	—	—
Bromoxynil	—	—	—	—	—	—	153	—
Butylate	—	—	—	—	—	—	47,647	—
Carbaryl	2,103	699	159	15,736	808	9,707	2,351	105
Carbofuran	—	—	—	—	—	219	—	—
Chlorothalonil	—	11,652	—	18,300	3,302	—	—	—
Chlorpyrifos	94,425	—	46,125	4,064	9,503	5	8,506	8,370
Cyanazine	—	—	—	—	—	—	10,590	35,520
Dacthal	—	—	—	—	—	—	—	—
Diazinon	83,056	15,719	4,994	10,094	5,924	117	465	489
Dicamba	—	—	—	—	—	—	60	—
Dichlobenil	—	—	—	—	—	—	—	—
Dinoseb	67	—	—	152	—	13	—	—
Disulfoton	—	—	—	—	—	—	—	—
Diuron	—	—	5,254	113	1,301	5,657	—	—
EPTC	21,239	—	1,855	—	—	—	52,049	—
Ethalfuralin	—	—	—	—	—	—	—	—
Ethoprop	—	—	—	—	—	—	—	—
Fonofos	—	—	—	—	—	—	—	—
HCH, gamma-	—	—	—	—	10	—	26	—
Linuron	—	—	—	—	—	—	—	—
MCPA	—	—	—	—	—	—	—	—
Malathion	40	—	6,521	79	530	40,615	—	655
Methomyl	—	—	4	50	31	1,488	1,836	57
Methyl parathion	—	—	—	1,844	44	17	—	—
Metolachlor	51	—	13	—	—	—	21,744	87
Metribuzin	—	—	—	—	—	—	—	—
Molinate	—	—	—	—	—	—	—	—
Napropamide	11,157	—	456	1,073	614	570	—	—
Norflurazon	23,949	767	1,284	2,408	2,022	1,230	—	—
Oryzalin	50,428	3,685	3,889	5,118	3,828	4,876	—	—
Oxamyl	—	—	—	—	411	—	—	—
Parathion	—	—	—	—	—	—	—	—
Pebulate	—	—	—	—	—	—	—	—
Pendimethalin	4,862	—	179	312	97	533	—	2,147
Permethrin, <i>cis</i> -	4,294	—	588	2,770	446	—	1,229	40
Phorate	—	—	—	—	—	—	139	1,054
Pronamide	—	—	—	—	—	3	—	—
Propanil	—	—	—	—	—	—	—	—
Propargite	61,430	1,356	16,073	1,976	1,300	6,548	93,690	52,982
Propoxur	—	—	—	—	—	—	—	—
Simazine	36,866	—	7,641	2,836	3,008	10,032	—	—
Tebuthiuron	—	—	—	—	—	—	—	—
Thiobencarb	—	—	—	—	—	—	—	—
Triclopyr	—	—	—	—	—	—	—	—
Trifluralin	820	410	26	1	57	787	—	25,294

Table 2. Pesticide application by commodity in 1993, San Joaquin River Basin, California—Continued

Pesticide	Beans	Field crops	Rice	Grain	Truck crops	Alfalfa	Other	Nonagricultural, 1993
2,4-D	—	—	68	7,176	—	—	3,933	8,216
2,4-DB	—	—	—	—	—	5,272	—	—
Alachlor	2,637	—	—	—	—	—	—	—
Aldicarb	—	—	—	—	—	—	10	—
Azinphos-methyl	—	—	—	—	—	—	20	—
Benfluralin	—	—	—	—	3	6,076	—	43
Bromacil	—	—	—	—	—	—	—	7,793
Bromoxynil	—	—	—	11,166	649	1,820	413	202
Butylate	—	—	—	—	—	—	—	—
Carbaryl	123	3,674	—	—	10,356	30	812	14,360
Carbofuran	—	—	190	—	—	4,298	—	—
Chlorothalonil	229	—	—	—	24,877	—	665	127
Chlorpyrifos	—	2,284	—	—	2,718	30,510	181	19,072
Cyanazine	—	—	—	—	—	—	124	—
Dacthal	—	—	—	—	3,130	—	—	27
Diazinon	291	1,236	—	—	12,397	5,721	88	7,087
Dicamba	—	6	—	925	—	—	26	104
Dichlobenil	—	—	—	—	—	—	8	190
Dinoseb	—	—	—	—	5	—	—	—
Disulfoton	—	—	—	129	2,281	—	24	15
Diuron	—	—	—	—	—	42,379	282	35,049
EPTC	441	6,324	—	—	4,788	10,156	209	37
Ethalfuralin	8,591	—	—	—	88	—	—	—
Ethoprop	—	—	—	—	6,772	—	—	123
Fonofos	637	—	—	—	1,438	—	—	—
HCH, gamma-	38	—	—	—	4	—	—	560
Linuron	—	—	—	—	1,300	—	—	—
MCPA	2,470	—	2,108	16,926	587	—	11	7
Malathion	645	289	—	762	7,815	13,880	11	15,204
Methomyl	2,981	5,231	—	38	36,193	8,198	1,733	15
Methyl parathion	—	—	—	—	79	314	—	—
Metolachlor	16,731	—	—	—	123	—	26	801
Metribuzin	—	—	—	—	1,282	—	60	—
Molinate	—	—	19,129	—	—	—	—	—
Napropamide	196	—	—	11	9,033	—	142	6
Norflurazon	—	—	—	—	1,143	—	1	275
Oryzalin	—	—	—	—	185	—	383	6,826
Oxamyl	—	—	—	—	8,284	—	0	—
Parathion	—	—	—	—	4	—	—	10
Pebulate	—	180	—	—	21,543	—	—	—
Pendimethalin	231	—	—	—	316	—	224	345
Permethin, <i>cis</i>	—	—	—	—	1,680	240	14	424
Phorate	—	5,714	—	—	—	—	—	—
Pronamide	—	—	—	—	25	33	35	88
Propanil	—	—	1,018	—	—	—	—	—
Propargite	11,198	—	—	—	—	728	391	—
Propoxur	—	—	—	—	—	—	—	19
Simazine	—	—	—	—	—	—	101	17,265
Tebuthiuron	—	—	—	—	—	—	—	14
Thiobencarb	—	—	5,608	—	—	—	—	—
Triclopyr	—	—	—	—	—	—	2	897
Trifluralin	6,181	1,316	—	26	18,066	62,472	293	562

Table 3. Total agricultural application and rate of application of each pesticide in 1993 in each subbasin and the San Joaquin River Basin, California [CCID, Central California Irrigation District; lb a. i., pound(s) active ingredient; —, no application]

Pesticide	Orestimba Creek Basin		CCID		Salt Slough Basin		Merced River Basin		San Joaquin River Basin		
	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Nonagricultural amount (lb a. i.)
2,4-D	317	51.47	156	12.30	5,489	24.21	18,280	155.81	64,195	62.15	8,216
2,4-DB	—	—	64	5.04	2,885	12.73	619	5.28	5,272	5.10	—
Alachlor	882	143.21	—	—	861	3.80	—	—	3,499	3.39	—
Aldicarb	—	—	—	—	3,632	16.02	—	—	6,941	6.72	—
Azinphos-methyl	2,340	379.93	—	—	793	3.50	26,469	225.60	75,842	73.42	0
Benfluralin	—	—	—	—	1,886	8.32	909	7.75	6,080	5.89	43
Bromacil	14	2.27	—	—	34	0.15	—	—	49	0.05	7,793
Bromoxynil	211	34.26	184	14.50	2,553	11.26	1,702	14.51	14,203	13.75	202
Butylate	—	—	—	—	—	—	5,311	45.27	47,647	46.13	—
Carbaryl	440	71.44	—	—	8,330	36.75	15,198	129.54	46,670	45.18	14,360
Carbofuran	111	18.02	194	15.29	182	0.80	790	6.73	4,708	4.56	—
Chlorothalonil	349	56.67	47	3.70	11,983	52.86	4,719	40.22	59,027	57.14	127
Chlorpyrifos	3,757	610.00	1,856	146.29	15,103	66.63	43,138	367.68	206,698	200.10	19,072
Cyanazine	—	—	—	—	34,736	153.24	1,445	12.32	46,235	44.76	—
Dacthal	171	27.76	54	4.26	2,106	9.29	—	—	3,130	3.03	27
Diazinon	2,300	373.44	201	15.84	13,828	61.00	17,693	150.80	140,599	136.11	7,087
Dicamba	—	—	—	—	44	0.19	458	3.90	1,018	0.99	104
Dichlobenil	—	—	—	—	—	—	—	—	8	0.01	190
Dinoseb	—	—	—	—	5	0.02	—	—	240	0.23	—
Disulfoton	—	—	—	—	1,581	6.97	24	0.20	2,435	2.36	15
Diuron	1,057	171.62	727	57.30	12,760	56.29	6,276	53.49	54,989	53.23	35,049
EPTC	250	40.59	—	—	7,224	31.87	22,410	191.01	97,064	93.97	37

Table 3. Total agricultural application and rate of application of each pesticide in 1993 in each subbasin and the San Joaquin River Basin, California (Continued)

Pesticide	Orestimba Creek Basin		CCID		Salt Slough Basin		Merced River Basin		San Joaquin River Basin		
	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Total amount (lb a. i.)	Amount per 1,000 acres (lb a. i.)	Nonagricultural amount (lb a. i.)
Ethalfuralin	1,170	189.97	—	—	1,861	8.21	726	6.19	8,679	8.40	—
Ethoprop	—	—	—	—	—	—	1,422	12.12	6,772	6.56	123
Fonofos	720	116.90	—	—	—	—	—	—	2,075	2.01	—
HCH, gamma-	—	—	—	—	—	—	—	—	79	0.08	560
Linuron	—	—	—	—	1,296	5.72	—	—	1,300	1.26	—
MCPA	191	31.01	55	4.34	3,275	14.45	4,294	36.60	22,105	21.40	7
Malathion	623	101.15	217	17.10	12,756	56.27	42,355	361.01	71,849	69.56	15,204
Methomyl	1,708	277.32	—	—	23,469	103.53	1,013	8.63	57,847	56.00	15
Methyl Parathion	—	—	—	—	44	0.19	47	0.40	2,300	2.23	—
Metolachlor	3,337	541.81	—	—	87	0.38	5,708	48.65	38,808	37.57	801
Metribuzin	—	—	—	—	—	—	—	—	1,343	1.30	—
Molinate	—	—	—	—	6,889	30.39	—	—	19,129	18.52	—
Napropamide	444	72.09	—	—	3,282	14.48	1,472	12.55	23,256	22.51	6
Norflurazon	192	31.17	209	16.47	1,381	6.09	7,452	63.52	32,808	31.76	275
Oryzalin	440	71.44	123	9.69	1,007	4.44	26,816	228.56	72,396	70.09	6,826
Oxamyl	—	—	—	—	6,450	28.45	9	0.08	8,696	8.42	0
Parathion	—	—	—	—	4	0.02	—	—	4	—	10
Pebulate	3,088	501.38	—	—	7,470	32.95	—	—	21,723	21.03	—
Pendimethalin	—	—	—	—	2,363	10.42	4,571	38.96	8,904	8.62	345
Permethrin, <i>cis</i> -	341	55.37	—	—	369	1.63	3,047	25.97	11,305	10.94	424
Phorate	—	—	—	—	2,097	9.25	139	1.18	6,908	6.69	—
Pronamide	—	—	—	—	33	0.15	35	0.30	98	0.09	88
Propanil	—	—	—	—	—	—	—	—	1,018	0.99	—
Propargite	8,640	1,402.83	—	—	59,673	263.24	31,884	271.76	247,676	239.77	—
Propoxur	—	—	—	—	—	—	—	—	—	—	19
Simazine	828	134.44	347	27.35	70	0.31	24,990	213.00	60,486	58.56	17,265
Tebuthiuron	—	—	—	—	—	—	—	—	—	—	14
Thiobencarb	—	—	—	—	3,050	13.45	—	—	5,608	5.43	—
Triclopyr	—	—	—	—	—	—	—	—	2	—	897
Trifluralin	1,541	250.20	820	64.63	72,105	318.09	5,094	43.42	115,755	112.06	562

high-performance liquid chromatography (HPLC) method were analyzed from March 1993 onward.

As previously noted, samples were split into two aliquots using a Teflon splitting device. The first aliquot was used for the analysis of 47 pesticides and pesticide metabolites by GC/MS (table 4). After extraction on a C-18 column as described above, the pesticides were eluted in the laboratory with hexane-isopropanol (3:1). The eluate was analyzed by GC/MS in the selected ion-monitoring mode using three characteristic ions for each pesticide. Complete details of this method are given in Zaugg and others (1995).

The other aliquot was used for analysis of 36 pesticides and pesticide metabolites by HPLC (table 4); these compounds are not amenable to analysis by gas chromatography or other high-temperature analytical techniques. After extraction on a graphitized carbon solid-phase extraction cartridge, the pesticides were eluted in the laboratory into two fractions: the first using methylene chloride-methanol (80:20), and the second using methylene chloride-methanol (80:20) acidified with 0.2 percent trifluoroacetic acid. Each fraction was analyzed separately using HPLC with a photodiode array, ultraviolet absorption detector. More details of this method are given in Werner and others (1996).

The name of each pesticide analyzed is listed in table 4. The analytical method, chemical family, pesticide type, and method detection limit (MDL) are also given. The MDL is the lowest concentration of pesticide that the analytical methods are capable of reliably detecting.

Quality Assurance Procedures

Quality assurance samples were collected and analyzed to determine the possible contamination, recovery, and reproducibility of the pesticides during the sampling, transport, and analysis procedures. Three types of quality assurance samples were evaluated: blanks, spiked samples, and replicates.

Field blanks were collected to estimate bias from contamination of the samples. Field blank water samples were collected in the field after an environmental sample was collected to determine whether the cleaning procedure following each sample collection was adequate to prevent cross-contamination and to

determine whether the sample was exposed to atmospheric contamination during sampling. Blanks consisted of organic-free water that was poured through the sample splitting device into a 1-L glass sample bottle, then extracted and analyzed in the same manner as a regular sample. A total of 22 blanks were collected from 1992 to 1995 during the surface-water phase of the San Joaquin–Tulare Basins NAWQA Program; 11 were analyzed by the GC/MS method, and 11 were analyzed by the HPLC method. Out of a possible 913 analyses, there were five detections in four field blanks; most blanks had no detectable pesticides. Those blanks with detectable pesticides contained only one or two compounds, which were present at low levels. The pesticides detected in the blanks (and their concentrations) were methomyl (0.067 µg/L), propargite (0.016 µg/L), simazine (0.002 µg/L, estimated), EPTC (0.001 µg/L, estimated), and carbaryl (0.012 µg/L, estimated). Except for methomyl, all of these compounds are GC/MS compounds that have low MDLs (table 4). The extremely low rate of detection in the data from the 22 blanks indicates that no systematic contamination was caused by the sampling or cleaning procedures.

Spiked samples, or spikes, were used to assess the recovery of the method and consisted of an environmental sample to which a known amount of certain analytes had been added. Each spike had a corresponding environmental sample, collected at the same time, to which nothing was added. The percent recovery of each compound in the spiked sample was determined by calculating the concentration of that compound in the spiked sample, subtracting the amount in the environmental sample, and dividing by the expected concentration in the spiked sample. The expected concentration was what would be detected if the compound were not present in the environmental sample, assuming 100 percent recovery from the spiked sample.

Thirteen spikes were analyzed using the GC/MS method. With the exceptions of butylate, carbaryl, carbofuran, and terbacyl, which had higher recovery (and high standard deviation), and DDE and desethylatrazine, which had lower recovery, the mean percent recovery ranged from 86 to 144 percent (table 5). Standard deviations of the mean percent recovery of these compounds ranged from 9 to 73 percent. Thus, for most compounds, the GC/MS method generally yields consistently reliable results for spiked samples.

Table 4. Pesticides, detection method, family, type of pesticide, and method detection limit

[Method: HPLC, high-performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry. Family: AM, amide; CA, carbamate; CH, chlorophenoxy; DI, dinitroaniline; MI, miscellaneous; OC, organochlorine; OP, organophosphate; PY, pyrethroid; TR, triazine; UL, uracil; UR, urea. Type: F, fungicide; H, herbicide; I, insecticide; M, metabolite. MDL, method detection limit]

Pesticide	Method	Family	Type	MDL (micrograms per liter)
2,4,5-T	HPLC	CH	H	0.035
2,4-D	HPLC	CH	H	0.150
2,4-DB	HPLC	CH	H	0.240
2,6-Diethylaniline	GC/MS	AM	M	0.003
Acetochlor	GC/MS	AM	H	0.002
Acifluorfen	HPLC	MI	H	0.035
Alachlor	GC/MS	AM	H	0.002
Aldicarb	HPLC	CA	I	0.550
Aldicarb sulfone	HPLC	CA	M	0.100
Aldicarb sulfoxide	HPLC	CA	M	0.021
Atrazine	GC/MS	TR	H	0.001
Atrazine, desethyl	GC/MS	TR	M	0.002
Azinphos-methyl	GC/MS	OP	I	0.001
Benfluralin	GC/MS	DI	H	0.002
Bentazon	HPLC	MI	H	0.014
Bromacil	HPLC	UL	H	0.035
Bromoxynil	HPLC	MI	H	0.035
Butylate	GC/MS	CA	H	0.002
Carbaryl	GC/MS	CA	I	0.003
Carbofuran	GC/MS	CA	I	0.003
Carbofuran, 3-hydroxy	HPLC	CA	I	0.014
Chloramben	HPLC	MI	H	0.420
Chlorothalonil	HPLC	OC	F	0.480
Chlorpyrifos	GC/MS	OP	I	0.004
Clopyralid	HPLC	MI	H	0.230
Cyanazine	GC/MS	TR	H	0.004
DDE, <i>p, p'</i> -	GC/MS	OC	I	0.006
DNOC	HPLC	MI	H,I	0.420
Dacthal	GC/MS	OC	H	0.002
Dacthal, mono-acid	HPLC	OC	M	0.017
Desethylatrazine (see Atrazine, desethyl)				
Diazinon	GC/MS	OP	I	0.002
Dicamba	HPLC	MI	H	0.035
Dichlobenil	HPLC	OC	H	1.200
Dichlorprop	HPLC	CH	H	0.032
Dieldrin	GC/MS	OC	I	0.001
Dinoseb	HPLC	MI	H	0.035
Disulfoton	GC/MS	OP	I	0.017
Diuron	HPLC	UR	H	0.020
EPTC	GC/MS	CA	H	0.002
Ethalfuralin	GC/MS	DI	H	0.004

Table 4. Pesticides, detection method, family, type of pesticide, and method detection limit—Continued

Pesticide	Method	Family	Type	MDL (micrograms per liter)
Ethoprop	GC/MS	OP	I	0.003
Fenuron	HPLC	UR	H	0.013
Fluometuron	HPLC	UR	H	0.035
Fonofos	GC/MS	OP	I	0.003
HCH, alpha-	GC/MS	OC	I	0.002
HCH, gamma-	GC/MS	OC	I	0.004
Linuron	GC/MS	UR	H	0.002
MCPA	HPLC	CH	H	0.170
MCPB	HPLC	CH	H	0.140
Malathion	GC/MS	OP	I	0.005
Methiocarb	HPLC	CA	I	0.026
Methomyl	HPLC	CA	I	0.017
Methyl parathion	GC/MS	OP	I	0.006
Metolachlor	GC/MS	AM	H	0.002
Metribuzin	GC/MS	TR	H	0.004
Molinate	GC/MS	CA	H	0.004
Napropamide	GC/MS	AM	H	0.003
Neburon	HPLC	UR	H	0.015
Norflurazon	HPLC	MI	H	0.024
Oryzalin	HPLC	DI	H	0.310
Oxamyl	HPLC	CA	I	0.018
Parathion	GC/MS	OP	I	0.004
Pebulate	GC/MS	CA	H	0.004
Pendimethalin	GC/MS	DI	H	0.004
Permethrin, <i>cis</i> -	GC/MS	PY	I	0.005
Phorate	GC/MS	OP	I	0.002
Picloram	HPLC	MI	H	0.050
Prometon	GC/MS	TR	H	0.018
Pronamide	GC/MS	AM	H	0.003
Propachlor	GC/MS	AM	H	0.007
Propanil	GC/MS	AM	H	0.004
Propargite	GC/MS	MI	I	0.013
Propham	HPLC	CA	H	0.035
Propoxur	HPLC	CA	I	0.035
Silvex	HPLC	CH	H	0.021
Simazine	GC/MS	TR	H	0.005
Tebuthiuron	GC/MS	UR	H	0.010
Terbacil	GC/MS	UL	H	0.007
Terbufos	GC/MS	OP	I	0.013
Thiobencarb	GC/MS	CA	H	0.002
Triallate	GC/MS	CA	H	0.001
Triclopyr	HPLC	CH	H	0.250
Trifluralin	GC/MS	DI	H	0.002

Table 5. Mean percent recoveries and standard deviation of percent recoveries for quality assurance spikes for gas chromatography/mass spectrometry and high-performance liquid chromatography pesticides

[All values are in percent. GS/MS, gas chromatography/mass spectrometry; HPLC, high-performance liquid chromatography. n, number of samples]

GS/MS pesticide			HPLC pesticide		
Pesticide	Mean (n=13)	Standard deviation	Pesticide	Mean (n=5)	Standard deviation
2,6-Diethylaniline	87.32	9.36	2,4,5-T	91.22	24.43
Alachlor	115.90	8.81	2,4-D	42.80	21.22
Atrazine	103.18	11.48	2,4-DB	36.61	7.21
Atrazine, desethyl	43.68	26.05	Aldicarb sulfone	24.82	13.72
Azinphos-methyl	99.60	38.41	Aldicarb sulfoxide	64.33	22.88
Benfluralin	101.04	15.05	Bentazon	30.94	30.19
Butylate	159.41	104.69	Bromacil	70.82	26.48
Carbaryl	156.31	39.02	Bromoxynil	71.78	2.34
Carbofuran	170.55	53.02	Carbaryl	33.61	12.34
Chlorpyrifos	126.17	24.87	Carbofuran	52.75	19.31
Cyanazine	113.51	28.16	DNOC (4,6-Dinitro- <i>o</i> -cresol)	66.79	0.61
DDE, <i>p,p'</i>	66.76	12.20	Dicamba	21.15	20.91
Dacthal	143.71	26.00	Dichlorprop	60.31	6.59
Desethylatrazine (see Atrazine, desethyl)			Dinoseb	53.40	8.51
Diazinon	101.84	14.64	Diuron	17.31	20.78
Dieldrin	96.43	19.53	Fenuron	84.08	56.38
Disulfoton	113.48	28.55	Fluometuron	58.42	20.82
EPTC	88.25	17.53	Linuron	80.98	11.92
Ethalfuralin	127.00	19.59	MCPA	34.23	17.12
Ethoprop	115.47	14.55	Methiocarb	37.47	10.49
Fonofos	103.52	10.33	Methomyl	50.54	19.41
HCH, alpha-	106.78	12.27	Neburon	40.73	6.88
Lindane	115.31	20.65	Oxamyl	13.68	9.56
Linuron	99.77	25.59	Picloram	31.21	28.08
Malathion	117.13	11.62	Propham	111.93	31.09
Methyl Parathion	130.21	34.95	Propoxur	46.00	17.52
Metolachlor	122.04	16.45	Silvex	64.14	7.21
Metribuzin	92.07	22.06			
Molinate	97.10	16.76			
Napromide	105.92	17.17			
Parathion	132.77	21.80			
Pebulate	90.41	17.17			
Pendimethalin	101.27	26.38			
Permethrin, <i>cis</i> -	98.66	72.94			
Phorate	94.27	12.32			
Prometon	101.24	18.10			
Pronamide	115.61	17.86			
Propachlor	106.13	14.20			
Propanil	106.12	16.78			
Propargite	114.40	28.64			
Simazine	109.28	34.95			
Tebuthiuron	85.83	14.51			
Terbacil	171.89	78.51			
Terbufos	100.21	12.49			
Thiobencarb	108.95	13.19			
Triallate	97.21	17.84			
Trifluralin	101.62	16.67			
Trifluralin	101.62	16.67			

Five spikes were analyzed using the HPLC method. The mean percent recoveries for most of these compounds were highly variable and ranged from 31 to 112 percent; standard deviation of the mean percent recovery ranged from 2 to 56 percent (table 5). Four compounds—aldicarb sulfone, dicamba, diuron, and oxamyl—had even lower recoveries. Low spike recoveries indicate that the compound has an increased chance of not being detected in environmental samples when it is present at low, but initially detectable concentrations. The HPLC method does not give results as reliable as those from the GC/MS method, but the results are reasonable given the difficulties of detecting low levels of compounds using the HPLC method.

Replicate samples were collected to assess the reproducibility of the method. These data allowed an examination of the variability owing to sample collection, field processing, and laboratory analysis procedures. The replicates were sequential, duplicate samples; that is, one sample (the environmental sample) was collected, then a second sample (the replicate) was collected while the first sample was being processed. The replicate was processed in a manner identical to the environmental sample. Thirteen pairs of replicates were analyzed to assess the reproducibility of the GC/MS method, and seven pairs were analyzed to assess the reproducibility of the HPLC method.

The simplest level of analysis of these replicates addresses the issue of detection or nondetection of a specific pesticide in the environmental sample and its corresponding replicate. Ideally, if a pesticide is not detected in the environmental sample, it should not be detected in the paired replicate. This pairing of nondetections occurred in 97 percent of the analyses. Conversely, if the pesticide is detected in the environmental sample, it should also be detected in the paired replicate. This pairing of detections occurred in 89 percent of the analyses. Thus, in 11 percent (14 samples) of the analyses, a pesticide was detected in the environmental sample, but not in the replicate. In half of these 14 samples, the detected value was very low, within a factor of two of the MDL.

For cases where the pesticide is detected in both the sample and the paired replicate, assessment of the difference in concentration between the environmental sample and the paired replicate is important. This assessment can be done by calculating the percent difference between the two values. The percent difference is defined as:

$$D = \left(\frac{|C_{Env} - C_{Rep}|}{(C_{Env} + C_{Rep})/2} \right) \times 100$$

where

- D = percent difference
- C_{Env} = concentration of pesticide in environmental sample
- C_{Rep} = concentration of pesticide in replicate sample.

When the pesticide was detected in both the replicate and the environmental sample, the GC/MS pesticides exhibited a mean percent difference of 22 percent ($n=109$), and the HPLC pesticides exhibited a mean percent difference of 46 percent ($n=7$). Although these values are high, they put limits on the data and indicate that concentrations of the pesticide both in the environmental and the replicate sample are within a factor of 1.6 of each other.

The mean percent difference between the environmental sample and the replicate can be estimated when the pesticide is detected in one but not the other. In this case, the samples that had nondetections were assigned a value equal to the MDL for that pesticide, and the percent difference was calculated using this value and the detected value. Calculation of the mean percent difference for these data yields values of 99 percent ($n=33$) for the GC/MS method and 154 percent ($n=2$) for the HPLC method. The data indicate that the detected concentrations were usually very close to the MDL. For all of the replicate data, it is important to remember that most of these concentrations are very low; therefore, a small absolute difference in the concentrations of the environmental sample and the replicate sample can lead to a large percent difference between the two values.

OCCURRENCE AND DISTRIBUTION OF PESTICIDES

Overall Occurrence of Pesticides at All Sites

In this study, many pesticides were detected in surface water. Several factors, including application, hydrology, and chemical and physical properties, influence the occurrence and distribution of these

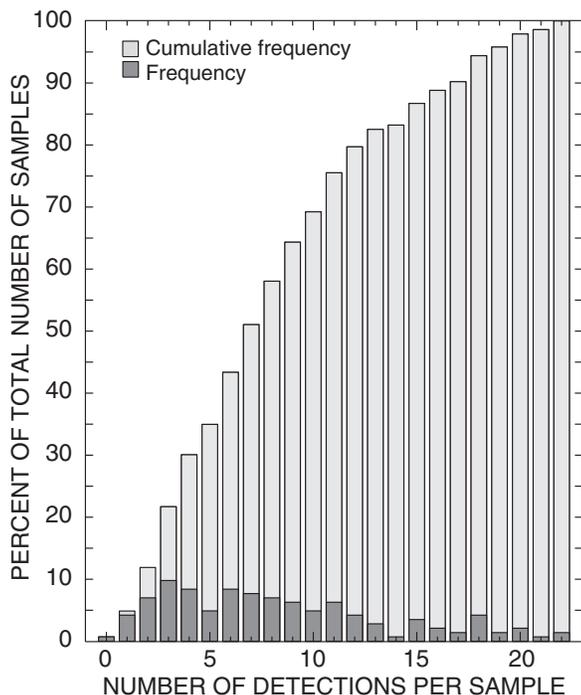


Figure 4. Percent of all samples with a specified number of detections, San Joaquin River Basin, California.

pesticides. Application, as the source of the pesticide, is only the beginning of the process that leads to an occurrence in surface water. Application could be local, or distant if the pesticide is subject to atmospheric transport. The location and timing of the application can affect the location and timing of pesticide detections within the basin. Pesticide occurrence also is influenced by hydrologic conditions. Pesticides applied to local fields must have a mode of transport, that is, water must travel from the field to the stream to reach the sampling site. This mode of transport can be accomplished either by overland flow caused by precipitation or drainage of irrigation water, or by subsurface flow such as agricultural drainage or ground-water inflow to the stream. Finally, the pesticide must have chemical and physical properties that make it amenable to transport. In general terms, the pesticide must be resistant to degradation for some nominal period of time, must be soluble enough to dissolve into detectable concentrations in the transport water, and must not be too tightly bound to the soil. These factors (application, hydrology, and chemical and physical properties) are discussed subsequently.

A total of 143 samples were collected at the four sites during 1993. All but one of these samples con-

tained at least one pesticide. The number of pesticides detected in all samples is shown in figure 4. More than 95 percent of the samples contained at least two pesticides, and more than 50 percent of the samples contained seven or more pesticides. One reason why this study detected so many pesticides is that the MDLs for the chemical methods used here are much lower than the MDLs of standard methods for these pesticides. The effect of low MDLs is reflected in the high detection frequencies of very low concentrations of pesticides: approximately 28 percent of all detections had concentrations less than three times the MDL. Fifteen pesticides had concentrations that were all very low, that is, less than three times the MDL; 8 of these had reported application (aldicarb; ethoprop; HCH, gamma-MCPA; permethrin, *cis*-; propanil; tebuthiuron; and triclopyr). The frequency of detection of the 49 pesticides detected is shown in figure 5. Thirty-three herbicides and 16 insecticides were detected; in general, herbicides were detected more frequently than insecticides. Six compounds were detected in more than 50 percent of the samples; four were herbicides (dacthal, EPTC, metolachlor, and simazine) and two were insecticides (chlorpyrifos and diazinon).

The concentrations for the detected compounds vary widely, ranging from less than detection to 20 $\mu\text{g/L}$. Figure 6 shows the 90th percentile concentration for all pesticides that occurred in at least 10 percent of the samples. Median concentrations are shown for the six compounds detected in at least 50 percent of the samples. Three compounds had 90th percentile concentrations greater than 0.2 $\mu\text{g/L}$: diuron (a herbicide applied to a wide variety of crops, including orchards, vineyards, alfalfa, truck crops, and rights-of-way), simazine (a herbicide applied primarily to orchards, vineyards, and rights-of-way), and diazinon (an insecticide applied to orchards, alfalfa, and truck crops). Simazine had the highest median concentration (0.050 $\mu\text{g/L}$).

Table 6 is a summary of pesticides detected at all sites and lists those pesticides with known application separately from those pesticides with no known application. Note that tebuthiuron is the only pesticide detected that has nonagricultural application, but no agricultural application. Most of this report will be devoted to pesticides that were known to be applied to agricultural land and were detected in surface water. Nine pesticides with known application were detected only once, but 19 were detected in at least 10 percent of

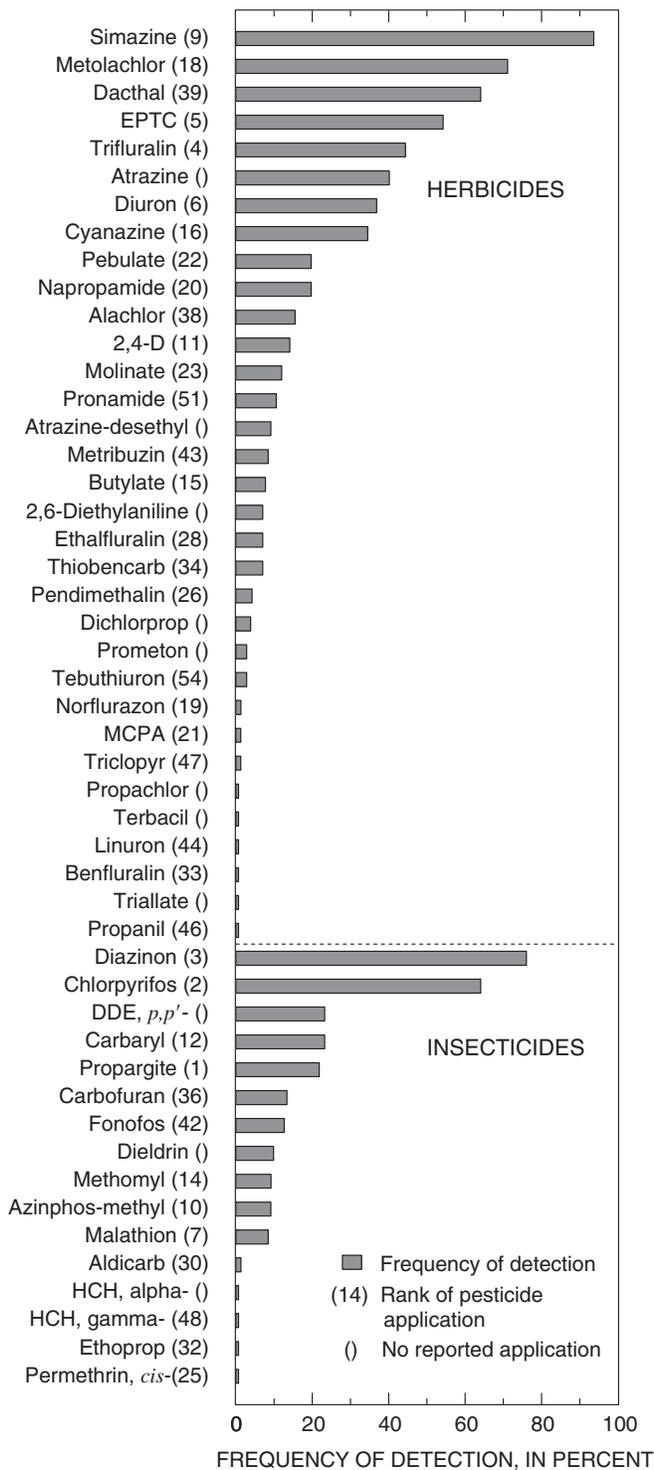


Figure 5. Frequency of detection for each pesticide in all samples, San Joaquin River Basin, California.

the samples. Of the 6 pesticides that occur in more than 50 percent of the samples (fig. 5), 4 compounds—chlorpyrifos, diazinon, EPTC, and simazine—are among the 10 most heavily applied

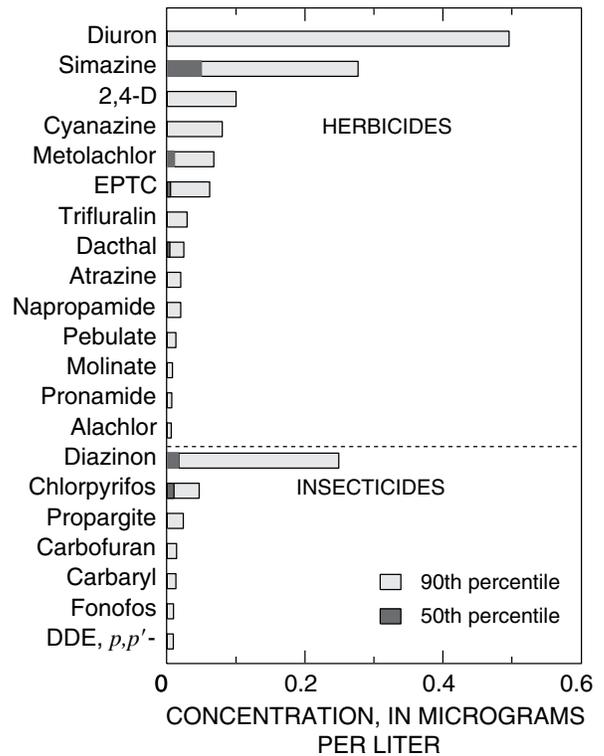


Figure 6. Median and 90th percentile concentrations for each pesticide detected in at least 10 percent of all samples, San Joaquin River Basin, California.

target pesticides in the San Joaquin River Basin. More than 75,000 lb a. i. of each of these pesticides was applied in the basin in 1993. Conversely, 3 of the 10 most heavily applied target pesticides—azinphos-methyl, malathion, and oryzalin (table 7)—were detected in 10 percent or less of the samples. Overall, 38 of the 54 pesticides with known application (70 percent) were detected during this study. This observation indicates that, in most cases, application of a pesticide resulted in its detection in the basin.

None of the measured concentrations exceeded USEPA MCL for drinking water criteria (table 6). The concentrations of seven pesticides exceeded the criteria for the protection of freshwater aquatic life: azinphos-methyl, carbaryl, chlorpyrifos, diazinon, diuron, malathion, and trifluralin. The 90th percentile concentration of diazinon also exceeded the criterion for the protection of freshwater aquatic life. Overall, some criteria for protection of aquatic life were exceeded in a total of 53 (37 percent) samples. Exceedance in 21 (15 percent) of these samples is solely due to the concentration of diazinon in the sample. Diazinon has a low suggested criterion for the protection of aquatic life

Table 6. Summary of pesticides detected in the occurrence assessment, San Joaquin River Basin, California

[MDL, method detection limit; USEPA, U.S. Environmental Protection Agency; HPLC, high-performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry; ld, less than the MDL; lb a.i., pound(s) active ingredient (a.i.); —, no data; e, estimated; blank cells, no application]

Pesticide	Method	MDL	Criteria	Detected and applied						Pesticide application (lb a.i.)		
				¹ USEPA Maximum Contaminant Level	Number of samples	Median	90th percentile	Maximum value	Frequency (%)	Agricultural	Non- agricultural	Total
				micrograms per liter								
2,4-D	HPLC	0.15	² 3.0	70	78	ld	0.10	1.2	14	64,196	8,216	72,411
Alachlor	GC/MS	0.002		2.0	142	ld	0.006	0.31	15	3,499		3,499
Aldicarb	HPLC	0.55	³ 1.0	7.0	76	ld	ld	e0.46	1.3	6,942		6,942
Azinphos-methyl	GC/MS	0.001	² 0.001	—	142	ld	ld	e0.39	9.2	75,842		75,842
Benfluralin	GC/MS	0.002	—	—	142	ld	ld	0.007	0.70	6,081	43	6,124
Butylate	GC/MS	0.002	—	—	142	ld	ld	0.010	7.8	47,647		47,647
Carbaryl	GC/MS	0.003	² 0.020	—	142	ld	0.013	e5.2	23	46,671	14,360	61,030
Carbofuran	GC/MS	0.003	⁴ 1.8	40	142	ld	0.014	e0.097	13	4,709		4,709
Chlorpyrifos	GC/MS	0.004	⁵ 0.083	—	142	0.010	0.046	0.26	64	206,698	19,072	225,771
Cyanazine	GC/MS	0.004	³ 2.0	—	142	ld	0.080	1.3	35	46,235		46,235
Dacthal	GC/MS	0.002	—	—	142	0.004	0.024	0.22	64	3,130	27	3,158
Diazinon	GC/MS	0.002	⁶ 0.080	—	142	0.017	0.25	3.8	76	140,599	7,087	147,687
Diuron	HPLC	0.020	² 1.6	—	76	ld	0.50	1.9	37	54,990	35,049	90,039
EPTC	GC/MS	0.002	—	—	142	0.005	0.062	2.2	54	97,064	37	97,102
Ethalfuralin	GC/MS	0.004	—	—	142	ld	ld	0.13	7.0	8,679		8,679
Ethoprop	GC/MS	0.003	—	—	142	ld	ld	0.003	0.70	6,773	123	6,895
Fonofos	GC/MS	0.003	—	—	142	ld	0.009	0.26	13	2,075		2,075
HCH, gamma-	GC/MS	0.004	⁷ 1.0	0.20	142	ld	ld	0.005	0.70	80	560	640
Linuron	GC/MS	0.002	³ 7.0	—	142	ld	ld	0.29	0.70	1,300		1,300
MCPA	HPLC	0.17	³ 2.6	—	78	ld	ld	e0.12	1.3	22,105	7	22,113
Malathion	GC/MS	0.005	² 0.008	—	142	ld	ld	0.39	8.5	71,849	15,204	87,054
Methomyl	HPLC	0.017	—	—	76	ld	ld	0.67	9.2	57,847	15	57,862
Metolachlor	GC/MS	0.002	³ 8.0	—	142	0.011	0.068	1.6	71	38,809	801	39,610
Metribuzin	GC/MS	0.004	³ 1.0	—	142	ld	ld	0.047	8.5	1,343		1,343
Molinate	GC/MS	0.004	—	—	142	ld	0.008	4.0	12	19,129		19,129
Napropamide	GC/MS	0.003	—	—	142	ld	0.020	0.14	20	23,257	6	23,262
Norflurazon	HPLC	0.024	—	—	76	ld	ld	0.44	1.3	32,809	275	33,083
Pebulate	GC/MS	0.004	—	—	142	ld	0.013	0.24	20	21,724		21,724
Pendimethalin	GC/MS	0.004	—	—	142	ld	ld	0.054	4.2	8,905	345	9,249
Permethrin, <i>cis</i> -	GC/MS	0.005	—	—	142	ld	ld	0.013	0.70	11,305	424	11,729
Pronamide	GC/MS	0.003	—	—	142	ld	0.007	0.022	11	98	88	186
Propanil	GC/MS	0.004	—	—	142	ld	ld	0.004	0.70	1,018		1,018
Propargite	GC/MS	0.013	—	—	142	ld	0.023	e20	22	247,677		247,677
Simazine	GC/MS	0.005	² 10	4.0	142	0.050	0.28	1.4	94	60,487	17,265	77,751
Tebuthiuron	GC/MS	0.010	³ 1.6	—	142	ld	ld	e0.008	2.8		14	14
Thiobencarb	GC/MS	0.002	—	—	142	ld	ld	0.51	7.0	5,609		5,609
Triclopyr	HPLC	0.25	—	—	78	ld	ld	e0.010	1.3	2	897	899
Trifluralin	GC/MS	0.002	⁴ 0.10	—	142	ld	0.029	0.11	44.4	115,755	562	116,318

Table 6. Summary of pesticides detected in the occurrence assessment, San Joaquin River Basin, California—Continued

Detected and not applied									
Pesticide	Method	MDL	Criteria	USEPA Maximum Contaminant Level	Number of samples	Median	90th percentile	Maximum value	Frequency (%)
micrograms per liter									
2,6-Diethylaniline	GC/MS	0.003	—	—	142	ld	ld	0.007	7.0
Atrazine	GC/MS	0.001	⁴ 2.0	3.0	142	ld	0.020	0.13	40
Atrazine, desethyl	GC/MS	0.002	—	—	142	ld	ld	e0.005	9.2
DDE, <i>p,p'</i> -	GC/MS	0.006	^{8,9} 1,050	—	142	ld	0.009	0.062	23
Desethylatrazine (see Atrazine, desethyl)									
Dichlorprop	HPLC	0.032	—	—	78	ld	ld	0.11	3.9
Dieldrin	GC/MS	0.001	^{2,10} 1.3	—	142	ld	ld	0.021	9.9
HCH, alpha-	GC/MS	0.002	^{7,8} 100	—	142	ld	ld	0.002	0.70
Prometon	GC/MS	0.018	—	—	142	ld	ld	0.021	2.8
Propachlor	GC/MS	0.007	—	—	142	ld	ld	e0.002	0.70
Terbacil	GC/MS	0.007	—	—	142	ld	ld	e0.008	0.70
Triallate	GC/MS	0.001	³ 0.24	—	142	ld	ld	0.003	0.70

¹U.S. Environmental Protection Agency (1996)

²Criteria for the protection of freshwater aquatic life are recommended maximum concentrations in water by the National Academy of Sciences and National Academy of Engineering (1973)

³Interim guidelines for the protection of freshwater aquatic life are Canadian water quality guidelines (Canadian Council of Ministers of the Environment, 1993)

⁴Guidelines for the protection of freshwater aquatic life are Canadian water quality guidelines (Canadian Council of Ministers of the Environment, 1993)

⁵U.S. Environmental Protection Agency (1986)

⁶International Joint Commission (1977)

⁷U.S. Environmental Protection Agency (1980c)

⁸Value shown is not a criterion, but rather the lowest observed adverse effect level (LOAEL). There were insufficient data to establish a criterion.

⁹U.S. Environmental Protection Agency (1980b)

¹⁰U.S. Environmental Protection Agency (1980a)

(0.080 µg/L), leading to the frequent exceedance of the criteria (International Joint Commission, 1977). However, 32 samples (22 percent) had concentrations exceeding an aquatic life criteria for at least one pesticide other than diazinon.

Lethal concentrations of a particular pesticide on a certain species almost always are determined by exposing the test organism to water containing only the single pesticide under study. As mentioned earlier, almost all samples in this study contained more than one pesticide. The number of pesticides present may be important from a toxicological standpoint. Although the effects of combinations of pesticides are largely unknown, some pesticides could be more toxic when combined with other toxic compounds than when present individually. It is important to note that most of the pesticides in this study do not have any official criteria; therefore, some of these pesticides could be present at toxic levels, but are not reported as such here.

Twelve pesticides that were detected in surface-water samples had no known agricultural application in 1993, one of which (tebuthiuron) had only a very small amount (14 lb a.i.) of nonagricultural use (table 6). Most of these compounds had a low frequency of detection and were present in low concentrations. Only 5 of the 12 pesticides were detected in more than 5 percent of the samples: atrazine, DDE, desethylatrazine, dieldrin, and 2,6-diethylaniline. Concentrations of the 12 pesticides did not exceed any criteria for the protection of aquatic life. All but one of the detected, but not applied, compounds were analyzed using the GC/MS method, which can detect very low concentrations.

Possible causes of the occurrence of these compounds, in spite of their lack of (or very small) application in 1993, include historical use, environmental persistence (the capability of the compound to exist in the environment for an extended period of time), and mobility (the capability of the compound to be readily removed from the point of application and transported to surface water). An extreme example of this is DDE, a degradation product of DDT. Use of DDT as an insecticide in the United States was banned in the early 1970s, but because of the persistence of DDT and its degradation products, DDE was detected in 23 percent of the samples. The presence of 2,6-diethylaniline likely is a result of the degradation of alachlor. Also, detection of some of these pesticides may be due to unreported applications.

Pesticides also may reach agricultural land by less conventional and, therefore, unreported methods. For example, atmospheric transport and deposition could be responsible for transporting pesticides to this area that were applied elsewhere (see Majewski and Capel [1995] for a summary of the literature on this topic). As another mode of application, some compounds are manufacturing by-products of other pesticides. During the production of gamma-HCH, some alpha-HCH is inadvertently created. Therefore, during the reported application of gamma-HCH to the field, alpha-HCH is also applied, but not reported.

As a complement to table 6, table 7 lists the pesticides that were not detected in any samples. Again, pesticides with known usage are listed separately from those with no known applications. Many of these were not applied in the San Joaquin River Basin in 1993, so their lack of occurrence in surface water is expected. Conversely, many other nondetected pesticides were applied in the San Joaquin River Basin in 1993. There are several possible reasons why these compounds were not detected. One reason is low application. Of the 14 compounds applied but not detected, 4 (dichlobenil, dinoseb, parathion, and propoxur) had applications of less than 250 lb a. i. in the entire San Joaquin Basin. Another reason could be the high MDLs and low recoveries of the HPLC method; 10 of the 14 pesticides applied but not detected were HPLC compounds. A third reason why compounds may be applied but not detected is based on their chemical and physical properties. Pesticides that degrade rapidly, are insoluble, are volatile, or are tightly bound to the soil are not likely to be transported to streams and, hence, will not be detected. Finally, samples were not analyzed by the HPLC method during January and February 1993, which is particularly important because some compounds exhibit a concentration maximum during winter storms.

As discussed earlier, whether a pesticide is detected or not depends in part on the characteristics of the chemical methods. The GC/MS method has lower detection limits and generally better extraction recoveries than the HPLC method. For those pesticides with known application, 89 percent of the GC/MS pesticides were detected in at least one sample, and 41 percent of the HPLC pesticides were detected in at least one sample. The effect of the level of the MDL on the number of pesticides detected can be illustrated by censoring the GC/MS data at two concentrations typical of the

MDLs for the HPLC method. Censoring the GC/MS data at a concentration of 0.02 µg/L results in the detection of 69 percent of the GC/MS compounds. Similarly, a censoring level of 0.05 µg/L results in the detection of 63 percent of the GC/MS compounds. Although the censoring lowers the percentage of pesticides detected by about 20 percent, the GC/MS method still detects a higher proportion of its target compounds than the HPLC method. The fact that a higher proportion of target compounds are detected in the censored GC/MS data than in the HPLC data indicates that differences in percentage of pesticides detected are not just an artifact of the contrast in the MDLs of the two methods, but reflect differences because of other factors.

Spatial Variation in Pesticide Occurrence and Concentrations

As discussed earlier, the three subbasins in the San Joaquin River Basin were selected to examine the influence of contrasts in hydrology, land use, and pesticide application on the occurrence of dissolved pesticides in surface water. Differences in the total number of pesticides detected in samples at the different sites are the most general measure of the contrasts in pesticide occurrence in the three subbasins. For each pesticide in each subbasin, table 8 lists the detection frequency, the maximum concentration, the 90th percentile and median concentrations, and the criteria for the protection of freshwater aquatic life. For all the

Table 7. Summary of pesticides not detected in the occurrence assessment, San Joaquin River Basin, California

[lb a. i., pound(s) active ingredient; HPLC, high-performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry]

Not detected and applied		Pesticide application (lb a. i.)			Not detected and not applied	
Pesticide	Method	Pesticide application (lb a. i.)			Pesticide	Method
		Agricultural	Non-agricultural	Total		
2,4-DB	HPLC	5,272	0	5,272	2,4,5-T	HPLC
Bromacil	HPLC	49	7,793	7,842	Acetochlor	GC/MS
Bromoxynil	HPLC	14,203	202	14,406	Acifluorfen	HPLC
Chlorothalonil	HPLC	59,028	127	59,155	Aldicarb sulfone	HPLC
Dicamba	HPLC	1,018	104	1,123	Aldicarb sulfoxide	HPLC
Dichlobenil	HPLC	8	190	198	Bentazon	HPLC
Dinoseb	HPLC	240	0	240	Carbofuran, 3-hydroxy	HPLC
Disulfoton	GC/MS	2,435	15	2,541	Chloramben	HPLC
Methyl Parathion	GC/MS	2,301	0	2,301	Clopyralid	HPLC
Oryzalin	HPLC	72,397	6,826	79,223	DNOC	HPLC
Oxamyl	HPLC	8,696	0	8,696	Dacthal, mono-acid	HPLC
Parathion	GC/MS	4	10	15	Fenuron	HPLC
Phorate	GC/MS	6,909	0	6,909	Fluometuron	HPLC
Propoxur	HPLC	0	19	19	MCPB	HPLC
					Methiocarb	HPLC
					Neburon	HPLC
					Picloram	HPLC
					Propham	HPLC
					Silvex	HPLC
					Terbufos	GC/MS

Table 8. Frequency of detection, and maximum, 90th percentile, and median concentrations for each pesticide for each subbasin site and the San Joaquin River near Vernalis, California

[MDL, method detection limit; HPLC, high-performance liquid chromatography; GC/MS, gas chromatography/mass spectrometry; —, no data. USEPA, U.S. Environmental Protection Agency, ld, less than the MDL; e, estimated]

Pesticide	Method	MDL	Criteria	¹ USEPA Maximum contaminant level	Number of samples	Orestimba Creek at River Road				Salt Slough at Highway 165				Overall frequency (%)	
						Median	90th percentile	Maximum value	Frequency (%)	Number of samples	Median	90th percentile	Maximum value		Frequency (%)
micrograms per liter															
2,4-D	HPLC	0.15	² 3.0	70	20	ld	0.16	0.26	20	18	ld	0.69	1.2	17	14
2,6-Diethylaniline	GC/MS	0.003	—	—	48	ld	ld	0.005	8.3	26	ld	ld	0.003	3.9	7.0
Alachlor	GC/MS	0.002	—	2.0	48	ld	0.014	0.31	23	26	ld	0.021	0.030	15	15
Aldicarb	HPLC	0.55	³ 1.0	7.0	20	ld	ld	ld	0.0	18	ld	ld	ld	0.0	1.3
Atrazine	GC/MS	0.001	⁴ 2.0	—	48	ld	0.020	0.13	38	26	0.018	0.028	0.036	88	40
Atrazine, desethyl	GC/MS	0.002	—	—	48	ld	0.002	e0.005	13	26	ld	0.004	e0.005	15	9.2
Azinphos-methyl	GC/MS	0.001	² 0.001	—	48	ld	0.11	e0.39	19	26	ld	ld	ld	0.0	9.2
Benfluralin	GC/MS	0.002	—	—	48	ld	ld	0.007	2.1	26	ld	ld	ld	0.0	0.70
Butylate	GC/MS	0.002	—	—	48	ld	ld	0.007	2.1	26	ld	ld	0.005	7.7	7.8
Carbaryl	GC/MS	0.003	² 0.020	—	48	ld	0.009	e0.033	23	26	ld	0.017	e0.078	19	23
Carbofuran	GC/MS	0.003	⁴ 1.8	40	48	ld	0.014	e0.045	13	26	ld	0.023	e0.097	15	13
Chlorpyrifos	GC/MS	0.004	⁵ 0.083	—	48	0.008	0.064	0.14	54	26	0.009	0.030	0.052	65	64
Cyanazine	GC/MS	0.004	³ 2.0	—	48	ld	0.010	1.0	15	26	0.057	0.46	1.3	92	35
DDE, <i>p,p'</i> -	GC/MS	0.006	^{6,7} 1,050	—	48	ld	0.014	0.062	40	26	ld	0.001	e0.005	12	23
Dacthal	GC/MS	0.002	—	—	48	0.009	0.097	0.22	77	26	0.004	0.017	0.045	69	64
Desethylatrazine (see Atrazine, desethyl)															
Diazinon	GC/MS	0.002	⁸ 0.080	—	48	0.013	0.56	3.8	71	26	0.03	0.16	0.28	88	76
Dichlorprop	HPLC	0.032	—	—	20	ld	ld	0.040	5.0	18	ld	ld	0.11	5.6	3.9
Dieldrin	GC/MS	0.001	^{2,9} 1.3	—	48	ld	0.014	0.021	27	26	ld	ld	ld	0.0	9.9
Diuron	HPLC	0.020	² 1.6	—	20	ld	0.46	0.51	35	18	0.14	1.27	1.900	56	37
EPTC	GC/MS	0.002	—	—	48	ld	0.035	0.061	35	26	0.037	0.65	2.200	96	54
Ethalfuralin	GC/MS	0.004	—	—	48	ld	0.051	0.13	19	26	ld	ld	ld	0.0	7.0
Ethoprop	GC/MS	0.003	—	—	48	ld	ld	0.003	2.1	26	ld	ld	ld	0.0	0.70
Fonofos	GC/MS	0.003	—	—	48	ld	0.062	0.26	29	26	ld	ld	ld	0.0	13

Table 8. Frequency of detection, and maximum, 90th percentile, and median concentrations for each pesticide for each subbasin site and the San Joaquin River near Vernalis, California—Continued

Pesticide	Method	MDL	Criteria	¹ USEPA Maximum contaminant level	Number of samples	Orestimba Creek at River Road				Salt Slough at Highway 165				Overall frequency (%)	
						Median	90th percentile	Maximum value	Frequency (%)	Number of samples	Median	90th percentile	Maximum value		Frequency (%)
micrograms per liter															
HCH, alpha-	GC/MS	0.002	^{6,10} 100	—	48	ld	ld	ld	0.0	26	ld	ld	ld	0.0	0.70
HCH, gamma-	GC/MS	0.004	^{5,10} 1.0	0.20	48	ld	ld	ld	0.0	26	ld	ld	ld	0.0	0.70
Linuron	GC/MS	0.002	³ 7.0	—	48	ld	ld	ld	0.0	26	ld	ld	0.29	3.9	0.70
MCPA	HPLC	0.17	³ 2.6	—	20	ld	ld	ld	0.0	18	ld	ld	e0.12	5.6	1.3
Malathion	GC/MS	0.005	² 0.008	—	48	ld	ld	0.006	2.1	26	ld	0.044	0.39	23	8.5
Methomyl	HPLC	0.017	—	—	20	ld	0.15	0.33	10	18	ld	0.27	0.67	22	9.2
Metolachlor	GC/MS	0.002	³ 8.0	—	48	0.018	0.31	1.6	85	26	0.011	0.029	0.053	77	71
Metribuzin	GC/MS	0.004	³ 1.0	—	48	ld	0.009	0.016	17	26	ld	ld	ld	0.0	8.5
Molinate	GC/MS	0.004	—	—	48	ld	0.007	0.045	10	26	ld	0.20	4.0	23	12
Napropamide	GC/MS	0.003	—	—	48	ld	0.039	0.14	38	26	ld	0.025	0.050	19	20
Norflurazon	HPLC	0.024	—	—	20	ld	ld	ld	0.0	18	ld	ld	0.44	5.6	1.3
Pebulate	GC/MS	0.004	—	—	48	ld	0.060	0.24	27	26	ld	0.014	0.043	27	20
Pendimethalin	GC/MS	0.004	—	—	48	ld	0.007	0.011	10	26	ld	ld	ld	0.0	4.2
Permethrin, <i>cis</i> -	GC/MS	0.005	—	—	48	ld	ld	ld	0.0	26	ld	ld	ld	0.0	0.70
Prometon	GC/MS	0.018	—	—	48	ld	ld	0.021	4.2	26	ld	ld	e0.006	3.9	2.8
Pronamide	GC/MS	0.003	—	—	48	ld	0.011	0.017	19	26	ld	0.019	0.022	23	11
Propachlor	GC/MS	0.007	—	—	48	ld	ld	ld	0.0	26	ld	ld	ld	0.0	0.70
Propanil	GC/MS	0.004	—	—	48	ld	ld	ld	0.0	26	ld	ld	0.004	3.9	0.70
Propargite	GC/MS	0.013	—	—	48	ld	0.070	e20	35	26	ld	0.015	0.095	15	22
Simazine	GC/MS	0.005	² 10	4.0	48	0.037	0.30	0.51	92	26	0.029	0.080	0.085	96	94
Tebuthiuron	GC/MS	0.010	³ 1.6	—	48	ld	ld	e0.008	4.2	26	ld	ld	e0.004	3.9	2.8
Terbacil	GC/MS	0.007	—	—	48	ld	ld	e0.008	2.1	26	ld	ld	ld	0.0	0.70
Thiobencarb	GC/MS	0.002	—	—	48	ld	ld	0.030	4.2	26	ld	0.039	0.51	15	7.0
Triallate	GC/MS	0.001	³ 0.24	—	48	ld	ld	0.003	2.1	26	ld	ld	ld	0.0	0.70
Triclopyr	HPLC	0.25	—	—	20	ld	ld	e0.010	5.0	18	ld	ld	ld	0.0	1.3
Trifluralin	GC/MS	0.002	⁴ 0.10	—	48	0.006	0.039	0.076	54	26	0.010	0.060	0.11	65	44

Table 8. Frequency of detection, and maximum, 90th percentile, and median concentrations for each pesticide for each subbasin site and the San Joaquin River near Vernalis, California—Continued

Pesticide	Method	MDL	Criteria	¹ USEPA Maximum contaminant level	Number of samples	Merced River at River Road			Frequency (%)	Number of samples	San Joaquin River near Vernalis			Overall frequency (%)	
						Median	90th percentile	Maximum value			Median	90th percentile	Maximum value		Frequency (%)
micrograms per liter															
2,4-D	HPLC	0.15	² 3.0	70	21	ld	0.008	e0.030	9.5	19	ld	0.020	e0.10	11	14
2,6-Diethylaniline	GC/MS	0.003	—	—	40	ld	ld	0.007	5.0	28	ld	0.001	0.006	11	7.0
Alachlor	GC/MS	0.002	—	2.0	40	ld	ld	0.003	2.5	28	ld	0.006	0.034	21	15
Aldicarb	HPLC	0.55	³ 1.0	7.0	20	ld	ld	e0.46	5.0	18	ld	ld	ld	0.0	1.3
Atrazine	GC/MS	0.001	⁴ 2.0	—	40	ld	ld	0.007	7.5	28	ld	0.012	0.015	46	40
Atrazine, desethyl	GC/MS	0.002	—	—	40	ld	ld	ld	0.0	28	ld	0.002	e0.004	11	9.2
Azinphos-methyl	GC/MS	0.001	² 0.001	—	40	ld	ld	e0.056	2.5	28	ld	0.028	e0.079	11	9.2
Benfluralin	GC/MS	0.002	—	—	40	ld	ld	ld	0.0	28	ld	ld	ld	0.0	0.70
Butylate	GC/MS	0.002	—	—	40	ld	0.003	0.010	10	28	ld	0.005	0.009	14	7.8
Carbaryl	GC/MS	0.003	² 0.020	—	40	ld	0.012	e5.2	18	28	ld	0.038	e0.14	36	23
Carbofuran	GC/MS	0.003	⁴ 1.8	40	40	ld	0.010	e0.024	10	28	ld	0.032	e0.052	18	13
Chlorpyrifos	GC/MS	0.004	⁵ 0.083	—	40	0.018	0.048	0.26	75	28	0.009	0.030	0.033	64	64
Cyanazine	GC/MS	0.004	³ 2.0	—	40	ld	ld	ld	0.0	28	0.017	0.066	0.12	64	35
DDE, <i>p,p'</i> -	GC/MS	0.006	^{6,7} 1,050	—	40	ld	ld	e0.004	5.0	28	ld	0.005	0.020	32	23
Dacthal	GC/MS	0.002	—	—	40	ld	0.007	0.011	40	28	0.004	0.028	0.10	71	64
Desethylatrazine (see Atrazine, desethyl)															
Diazinon	GC/MS	0.002	⁸ 0.80	—	40	0.012	0.15	2.5	65	28	0.021	0.27	0.62	89	76
Dichlorprop	HPLC	0.032	—	—	21	ld	ld	ld	0.0	19	ld	ld	0.040	5.3	3.9
Dieldrin	GC/MS	0.001	^{2,9} 1.3	—	40	ld	ld	ld	0.0	28	ld	ld	0.009	3.6	9.9
Diuron	HPLC	0.020	² 1.6	—	20	ld	0.46	0.63	20	18	ld	0.32	0.36	39	37
EPTC	GC/MS	0.002	—	—	40	ld	0.021	1.4	25	28	0.012	0.10	0.12	89	54
Ethalfuralin	GC/MS	0.004	—	—	40	ld	ld	ld	0.0	28	ld	ld	0.017	3.6	7.0
Ethoprop	GC/MS	0.003	—	—	40	ld	ld	ld	0.0	28	ld	ld	ld	0.0	0.70
Fonofos	GC/MS	0.003	—	—	40	ld	ld	ld	0.0	28	ld	0.003	0.005	14	13
HCH, alpha-	GC/MS	0.002	^{6,10} 100	—	40	ld	ld	ld	0.0	28	ld	ld	0.002	3.6	0.70
HCH, gamma-	GC/MS	0.004	^{5,10} 1.0	0.20	40	ld	ld	ld	0.0	28	ld	ld	0.005	3.6	0.70
Linuron	GC/MS	0.002	³ 7.0	—	40	ld	ld	ld	0.0	28	ld	ld	ld	0.0	0.70
MCPA	HPLC	0.17	³ 2.6	—	21	ld	ld	ld	0.0	19	ld	ld	ld	0.0	1.3
Malathion	GC/MS	0.005	² 0.008	—	40	ld	ld	0.009	2.5	28	ld	0.006	0.025	14	8.5
Methomyl	HPLC	0.017	—	—	20	ld	ld	e0.010	5.0	18	ld	ld	ld	0.0	9.2
Metolachlor	GC/MS	0.002	³ 8.0	—	40	0.001	0.021	0.051	50	28	0.013	0.069	0.17	71	71
Metribuzin	GC/MS	0.004	³ 1.0	—	40	ld	ld	ld	0.0	28	ld	0.011	0.047	14	8.5

Table 8. Frequency of detection, and maximum, 90th percentile, and median concentrations for each pesticide for each subbasin site and the San Joaquin River near Vernalis, California—Continued

Pesticide	Method	MDL	Criteria	¹ USEPA Maximum contaminant level	Number of samples	Merced River at River Road				San Joaquin River near Vernalis				Overall frequency (%)	
						Median	90th percentile	Maximum value	Frequency (%)	Number of samples	Median	90th percentile	Maximum value		Frequency (%)
micrograms per liter															
Molinate	GC/MS	0.004	—	—	40	ld	ld	0.011	2.5	28	ld	0.012	0.16	18	12
Napropamide	GC/MS	0.003	—	—	40	ld	ld	0.009	2.5	28	ld	0.013	0.072	14	20
Norflurazon	HPLC	0.024	—	—	20	ld	ld	ld	0.0	18	ld	ld	ld	0.0	1.3
Pebulate	GC/MS	0.004	—	—	40	ld	ld	ld	0.0	28	ld	0.017	0.021	29	20
Pendimethalin	GC/MS	0.004	—	—	40	ld	ld	0.054	2.5	28	ld	ld	ld	0.0	4.2
Permethrin, <i>cis</i> -	GC/MS	0.005	—	—	40	ld	ld	ld	0.0	28	ld	ld	0.013	3.6	0.70
Prometon	GC/MS	0.018	—	—	40	ld	ld	e0.004	2.5	28	ld	ld	ld	0.0	2.8
Pronamide	GC/MS	0.003	—	—	40	ld	ld	ld	0.0	28	ld	ld	ld	0.0	11
Propachlor	GC/MS	0.007	—	—	40	ld	ld	ld	0.0	28	ld	ld	e0.002	3.6	0.70
Propanil	GC/MS	0.004	—	—	40	ld	ld	ld	0.0	28	ld	ld	ld	0.0	0.70
Propargite	GC/MS	0.013	—	—	40	ld	0.008	0.038	10	28	ld	0.030	2.0	21	22
Simazine	GC/MS	0.005	² 10	4.0	40	0.070	0.41	1.4	95	28	0.058	0.23	0.57	93	94
Tebuthiuron	GC/MS	0.010	³ 1.6	—	40	ld	ld	ld	0.0	28	ld	ld	e0.004	3.6	2.8
Terbacil	GC/MS	0.007	—	—	40	ld	ld	ld	0.0	28	ld	ld	ld	0.0	0.70
Thiobencarb	GC/MS	0.002	—	—	40	ld	ld	0.004	2.5	28	ld	0.002	0.026	11	7.0
Triallate	GC/MS	0.001	³ 0.24	—	40	ld	ld	ld	0.0	28	ld	ld	ld	0.0	0.70
Triclopyr	HPLC	0.25	—	—	21	ld	ld	ld	0.0	19	ld	ld	ld	0.0	1.3
Trifluralin	GC/MS	0.002	⁴ 0.10	—	40	ld	0.010	0.057	25	28	ld	0.011	0.014	36	44

¹U.S. Environmental Protection Agency (1996)²Criteria for the protection of freshwater aquatic life are recommended maximum concentrations in water by the National Academy of Sciences and National Academy of Engineering (1973)³Interim guidelines for the protection of freshwater aquatic life are Canadian water quality guidelines (Canadian Council of Ministers of the Environment, 1993)⁴Guidelines for the protection of freshwater aquatic life are Canadian water quality guidelines (Canadian Council of Ministers of the Environment, 1993)⁵U.S. Environmental Protection Agency (1986)⁶Value shown is not a criterion, but rather the lowest observed adverse effect level (LOAEL). There were insufficient data to establish a criterion.⁷U.S. Environmental Protection Agency (1980b)⁸International Joint Commission (1977)⁹U.S. Environmental Protection Agency (1980a)¹⁰U.S. Environmental Protection Agency (1980c)

subbasins, a total of 49 compounds was detected. The individual sites had the following numbers of compounds detected: Orestimba Creek, 40 (28 herbicides, 12 insecticides); Salt Slough, 33 (25 herbicides, 8 insecticides); the Merced River, 26 (16 herbicides, 10 insecticides); and the San Joaquin River, 35 (22 herbicides, 13 insecticides). In the following section, data for the San Joaquin River Basin is presented along with data for the three subbasins to provide context on how pesticide occurrence in the subbasins affects the San Joaquin River Basin as a whole.

The number of compounds detected per sample in each subbasin, and the variability in this number over the course of a year, are a measure of how consistently pesticides are detected at each site. Figure 7 shows four boxplots representing the number of compounds detected per sample for each subbasin site and for the San Joaquin River Basin. The median number of pesticides detected in each sample is 8 at the Orestimba Creek site, 10 at the Salt Slough site, 4 at the Merced River site, and 8 at the San Joaquin River site. The only significant difference in the number of pesticides detected among the sites is between the Merced River and Salt Slough ($p=0.05$, Kruskal-Wallis test). Although Salt Slough has a higher median number of pesticides per sample than Orestimba Creek, the number of pesticides per sample at Orestimba Creek is much more variable.

The variability in the number of pesticides detected per sample during the year (fig. 8) is partly due to hydrologic factors. During the winter precipitation season, the high variability in samples from Orestimba Creek is attributed to rapid changes in the source of streamflow during a storm. Samples with many compounds are attributed to the first flush of pesticides off the fields, and samples with few compounds are believed to be representative of streamflow derived primarily from the substantial nonagricultural areas in the upper part of the Orestimba Creek Basin (Domagalski and others, 1997). The low number and high variability in the number of pesticides detected in samples from the Merced River during the winter also likely are due, in part, to a large amount of streamflow originating from nonagricultural land in the upper part of the Merced River Basin. The number of pesticides in samples from Orestimba Creek and the Merced River are less variable during the April through September irrigation season when many compounds are applied and the primary mechanism of transport of pesticides to the streams is likely via irrigation return flows. Samples from Salt Slough, in contrast, have a consistently high number of pesticides detected throughout the year—a result of the high proportion of irrigation drainage and the lack of significant runoff from nonagricultural land in this subbasin.

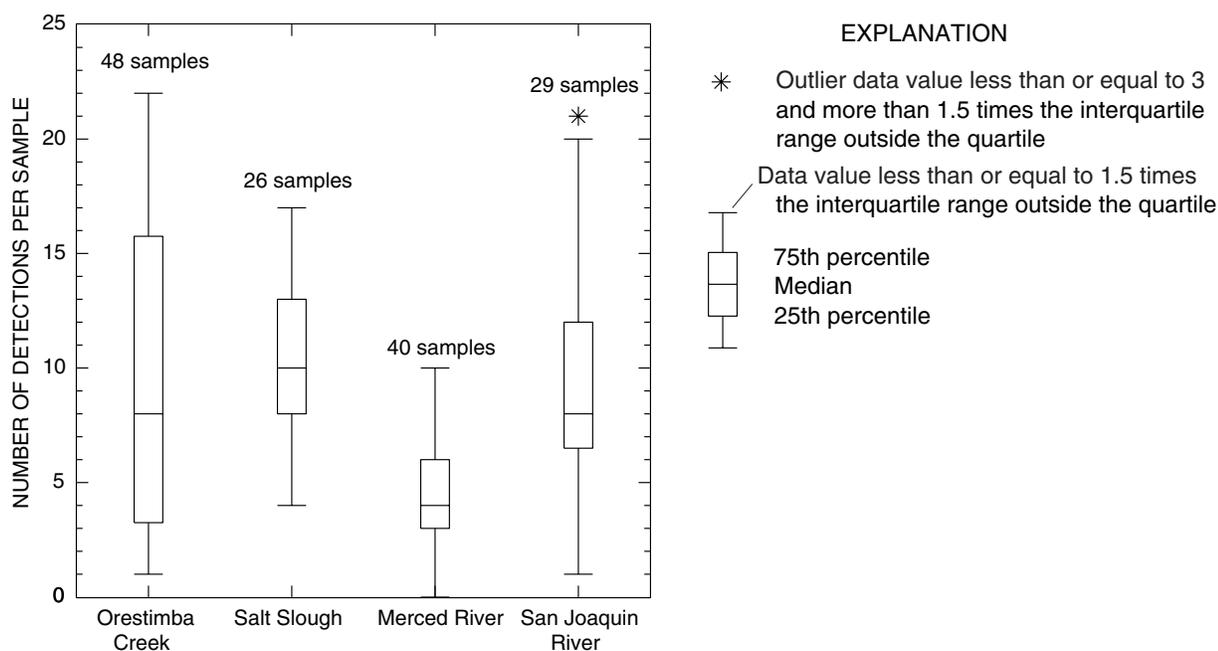


Figure 7. Number of detections per sample for each subbasin site and the San Joaquin River site, California.

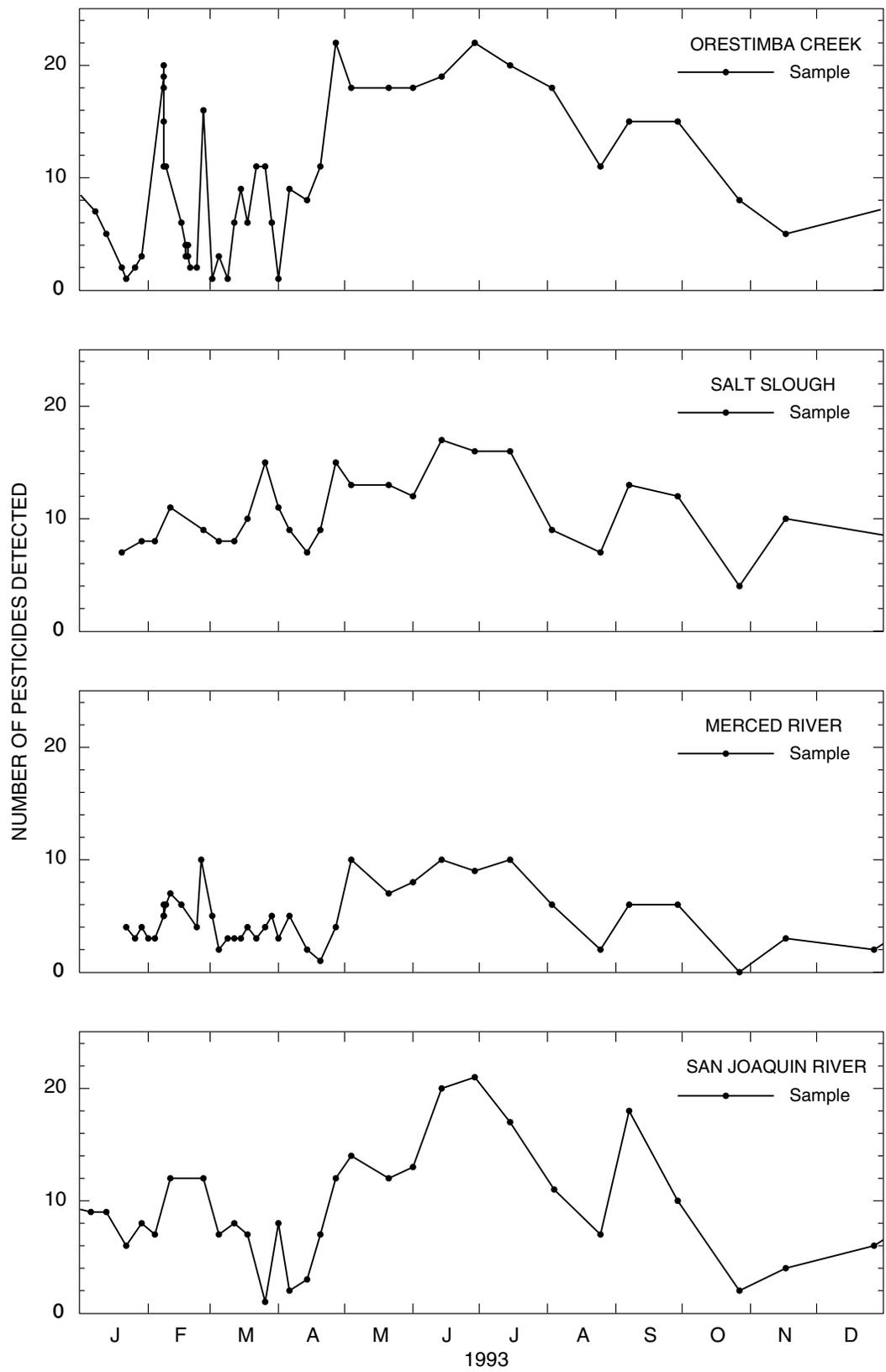


Figure 8. Number of pesticides detected per sample at each subbasin site and the San Joaquin River site, California.

Samples from the Merced River consistently had the lowest number of pesticides detected per sample despite the fact that a higher number of pesticides (34 different pesticides) were applied in this basin during 1993 than were applied in the Orestimba Creek Basin (27 different pesticides) during the same period (table 3). This discrepancy between the number of applied and detected pesticides in the Merced River is especially evident for the April through September irrigation season when an average of 22 pesticides were applied each month, but the average number of pesticide detections in the samples was only six. This inconsistency between application and detection is likely the result of a combination of two hydrologic differences between the Merced River Basin and the Orestimba Creek and Salt Slough basins. First, because the soils are highly permeable in the eastern San Joaquin Valley, irrigation return flow generated per unit of irrigated land generally is less in the Merced River Basin than in the other two subbasins. Second, the contribution of pesticide-free streamflow from reservoir releases during the summer dilutes the concentration of pesticides that may be present at low concentrations in irrigation

return flow to below the MDL, resulting in the non-detection of those pesticides at the Merced River site.

The 22 compounds that have a frequency of detection of at least 20 percent in any of the subbasins or the San Joaquin River Basin are shown in figure 9. Several of the pesticides are frequently detected in samples from each of the subbasins and are also frequently detected at the San Joaquin River site. These compounds include simazine, diazinon, metolachlor, chlorpyrifos, and carbaryl. Dacthal and trifluralin were most frequently detected in samples collected from the Orestimba Creek, Salt Slough, and San Joaquin River sites. Other pesticides are frequently detected at only one of the subbasin sites and in the San Joaquin River, indicating that the physiographic area represented by that subbasin likely is a major source of that pesticide. DDE, propargite, fonofos, and napropamide frequently occur in samples from the Orestimba Creek and San Joaquin River sites. EPTC, cyanazine, atrazine, diuron, molinate, and malathion frequently occur in samples from the Salt Slough and San Joaquin River sites. Chlorpyrifos is the only pesticide that has a higher frequency of detection in samples from the Merced River site than at any other site. With the exception of

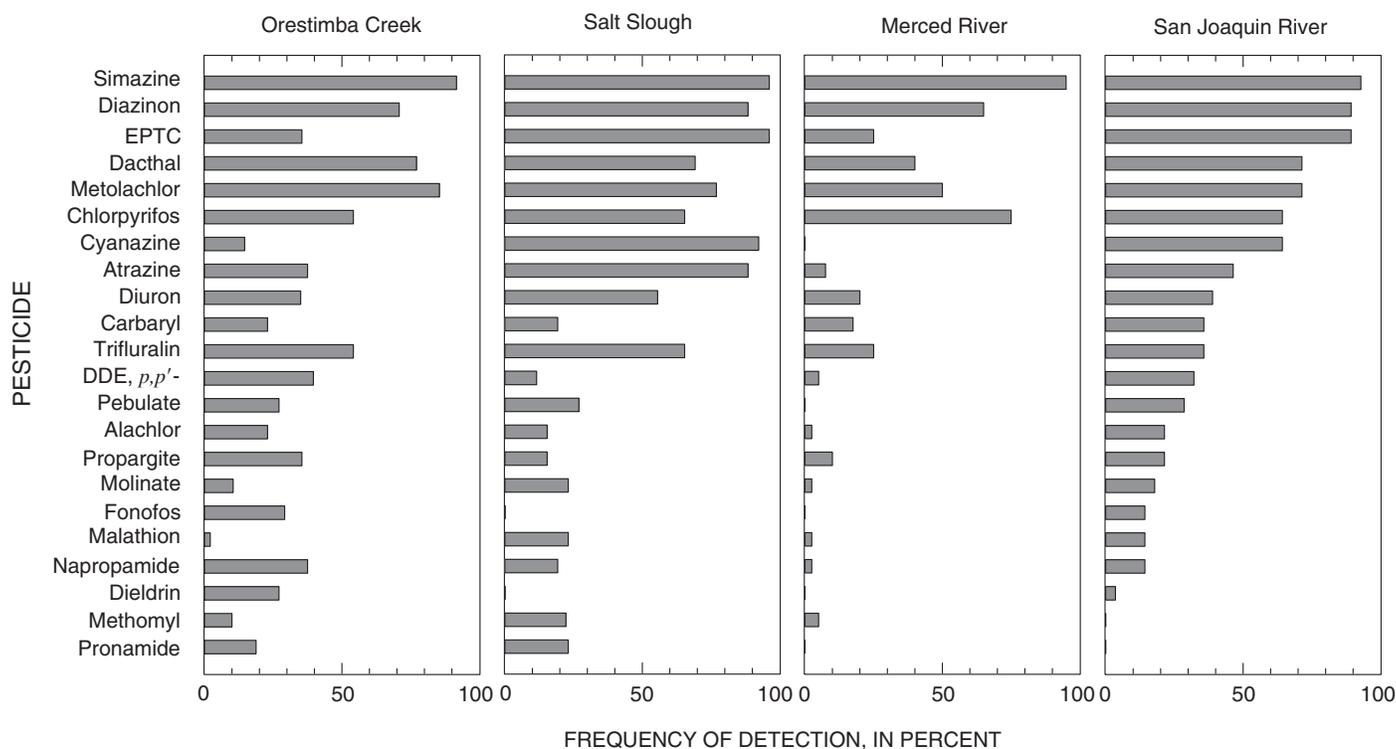


Figure 9. Frequency of detection for each subbasin site and the San Joaquin River site for each pesticide with a frequency of detection of at least 20 percent at any of the sites.

simazine, fonofos, malathion, dieldrin, methomyl, and pronamide, all the remaining pesticides were detected less frequently at the Merced River site than at any of the other sites.

The median and 90th percentile concentrations for the same 22 pesticides shown in figure 9 are shown in figure 10. The 90th percentile values range from less than detection for one or more pesticides in each subbasin, up to 1.3 $\mu\text{g/L}$ for diuron in Salt Slough. Median values are shown for pesticides that occur in more than 50 percent of the samples from a particular subbasin; these medians range from 0.004 $\mu\text{g/L}$ for dacthal at the San Joaquin River site to 0.14 $\mu\text{g/L}$ for diuron at the Salt Slough site. In general, the compounds that occur most frequently also have the highest 90th percentile and median concentrations. Conversely, some of the frequently detected pesticides are present only in low concentrations (for example, atrazine), and some of the less frequently detected pesticides have relatively high 90th percentile concentrations (for example, diuron).

Different pesticides were detected in high concentrations in different subbasins. Four pesticides had relatively high concentrations at all of the sites: simazine, diazinon, chlorpyrifos, and diuron (fig. 10). The highest concentrations of EPTC, cyanazine, malathion, and molinate occurred in samples from the Salt Slough site, and the highest concentrations of fonofos and metolachlor occurred in samples from the Orestimba Creek site. Overall, 14 compounds attained their highest 90th percentile concentration in samples from the Orestimba Creek site, 13 attained their highest 90th percentile concentration in samples from the Salt Slough site, 7 attained their highest 90th percentile concentration in samples from the San Joaquin River site, and only 1 attained its highest 90th percentile concentration in samples from the Merced River site.

Data for each subbasin were examined to determine how well differences in pesticide occurrence reflect differences in pesticide application. Table 9 lists the seven pesticides that satisfy the following criteria: (1) the frequency of detection of the pesticide differs by at least 20 percent between at least two subbasins; (2) the differences between the frequency of detection in the subbasins are significant (Chi-square test, $\alpha=0.05$); and (3) the difference in detection frequency is consistent with contrasts in the amount of agricultural application of the pesticide in the different subbasins. For each pesticide listed, the subbasin with the highest application rate is the subbasin with the highest

frequency of detection, and, except for cyanazine, the subbasin with the lowest application rate is the one with the lowest frequency of detection.

Alachlor, dacthal, fonofos, and napropamide were detected most frequently in samples from the Orestimba Creek site (table 9). Beans and truck crops account for the dominance of these pesticides in the Orestimba Creek subbasin. Although the detection frequency (19 percent) of azinphos-methyl (walnuts and almonds) and ethalfluralin (beans) does not meet the above criteria, the almost exclusive occurrence of these pesticides in samples from the Orestimba Creek site is consistent with the large relative application rate of these pesticides in this subbasin. Propargite also came close to meeting the above criteria; it is detected most frequently in samples from the Orestimba Creek site (35 percent) and has a higher application rate in this subbasin than in the Salt Slough and Merced subbasins. Cyanazine, molinate, and trifluralin (table 9) were detected most frequently in samples from the Salt Slough site. Molinate and a similar herbicide, thiobencarb, are applied only to rice (table 2), which is grown in the Salt Slough subbasin (9,770 acres cultivated in rice), but not in the Orestimba Creek or Merced River subbasins. Application of cyanazine to cotton and trifluralin to alfalfa, cotton, and truck crops accounts for the frequent occurrence of these pesticides in the Salt Slough subbasin. Cotton is grown almost exclusively in this subbasin. In general, pesticides that are applied exclusively or dominantly to one crop in one subbasin are the pesticides most likely to show differences in the frequency of detection among the subbasins.

Six additional pesticides satisfy the first two criteria (the frequency of detection of the pesticide differs by at least 20 percent between subbasins, and the differences between the frequency of detection in the subbasins are significant at $\alpha=0.05$), but the differences in occurrence are not consistent with the differences in agricultural application. Two of the six pesticides were detected most frequently in samples from Orestimba Creek: metolachlor, and pebulate. The remaining four were detected most frequently in samples from Salt Slough: atrazine, EPTC, malathion, and pronamide. The reason for the lack of correspondence between spatial contrasts in application and occurrence for these compounds is not known; however, in all cases, the link between application and frequency of detection is complicated by the contrasts between the physiography, hydrology, and farming practices of the

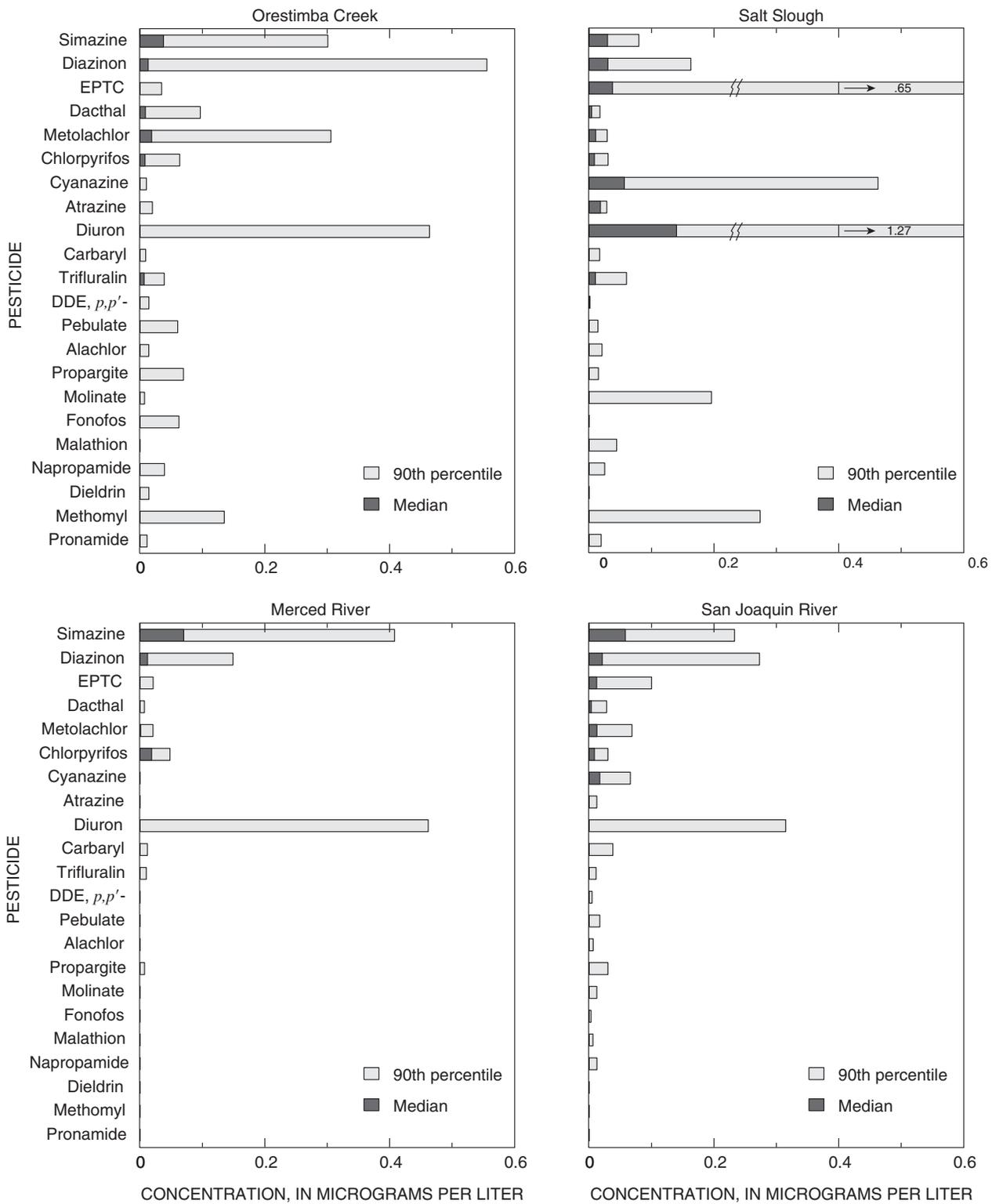


Figure 10. Median and 90th percentile concentrations for each subbasin site and the San Joaquin River site for each pesticide with a frequency of detection of at least 20 percent at any of the sites.

Table 9. Pesticides with frequencies of detection that differ by at least 20 percent between subbasins and are consistent with spatial differences in rate of application, San Joaquin River Basin, California

[A. Frequency of detection, B. rate of pesticide application in pounds active ingredient, C. total pesticide application, and D. major crops are listed for each subbasin. Dacthal and trifluralin include contributions from Central California Irrigation District to Orestimba]

Pesticide	Orestimba Creek Basin	Salt Slough Basin	Merced River Basin
Alachlor	A: 23 percent B: 143 pounds per 1,000 acres C: 882 pounds D: beans	15 percent 4 pounds per 1,000 acres 861 pounds corn	3 percent 0 pounds per 1,000 acres 0 pounds none
Cyanazine	A: 15 percent B: 0 pounds per 1,000 acres C: 0 pounds D: none	92 percent 153 pounds per 1,000 acres 34,736 pounds cotton	0 percent 12 pounds per 1,000 acres 1,445 pounds corn
Dacthal	A: 77 percent B: 12 pounds per 1,000 acres C: 225 pounds D: truck crops	69 percent 9 pounds per 1,000 acres 2,106 pounds truck crops	40 percent 0 pounds per 1,000 acres 0 pounds none
Fonofos	A: 29 percent B: 117 pounds per 1,000 acres C: 720 pounds D: truck crops and beans	0 percent 0 pounds per 1,000 acres 0 pounds none	0 percent 0 pounds per 1,000 acres 0 pounds none
Molinate	A: 10 percent B: 0 pounds per 1,000 acres C: 0 pounds D: none	23 percent 30 pounds per 1,000 acres 6,889 pounds rice	3 percent 0 pounds per 1,000 acres 0 pounds none
Napropamide	A: 38 percent B: 72 pounds per 1,000 acres C: 444 pounds D: truck crops	19 percent 14 pounds per 1,000 acres 3,282 pounds truck crops	3 percent 13 pounds per 1,000 acres 1,472 pounds almonds
Trifluralin	A: 54 percent B: 120 pounds per 1,000 acres C: 2,361 pounds D: beans and alfalfa	65 percent 318 pounds per 1,000 acres 72,105 pounds alfalfa, cotton, and truck crops	25 percent 43 pounds per 1,000 acres 5,094 pounds alfalfa and vineyards

subbasins. Finally, the almost exclusive occurrence of the banned organochlorine insecticides DDE and dieldrin in samples from Orestimba Creek likely reflects an historical application pattern.

Temporal Variation in Pesticide Occurrence and Concentrations

The spatial distribution of pesticides in surface waters can be explained in part by the spatial distribution of pesticide application. Similarly, there should be a direct relation between the time of application and the time of detection of a pesticide in a surface-water sample. Temporal relations between pesticide application and occurrence have been documented in a variety of

surface-water systems that range from very large river systems (Larson and others, 1995) to small agricultural basins (Richards and Baker, 1993). In the San Joaquin River Basin, this relation is dependent on other factors that vary in time, the most important of which are those that directly influence the transport of pesticides from the site of application to the river or stream. These factors include seasonal patterns in precipitation and the hydrology and sources of water in a particular stream. In the following section, data on pesticide occurrence, concentrations, and application will be evaluated in the context of streamflow data to determine to what degree temporal variation in pesticide occurrence and concentration is a function of temporal variation in pesticide application. Assessment of the influence of specific

on-farm water and pesticide management practices are beyond the scope of this study.

The relation between pesticide occurrence, pesticide application, and hydrology of each of the three subbasins and the San Joaquin River Basin can be examined by overlaying plots of the pesticide concentration in each sample on a hydrograph of stream discharge and juxtaposing a histogram of the monthly pesticide application. This has been done for each of the 33 compounds with two or more detections in any of the four basins (appendix D). Twenty-seven of these pesticides also had reported agricultural application. A plot of precipitation data (fig. 2) shows that most of the precipitation occurs during November through March. For the plots in appendix D, the periods of the most intense precipitation can be inferred from the hydrograph of Orestimba Creek: periods of intense precipitation preceded peaks on the hydrograph in mid-January, early and mid-February, and late March.

The data in appendix D indicate that, although there is a large amount of variability in the relation between pesticide concentrations in samples and applications, there is a reasonable correspondence that follows general seasonal patterns. These patterns, the result of a combination of application and hydrologic factors, can be characterized by grouping pesticides into categories on the basis of seasonal patterns of application and occurrence. These broad patterns of application, occurrence, and concentrations are graphically summarized in figures 11 through 14. These figures show months classified into one of four ranges of relative application and relative concentration, along with the temporal location of the maximum application and the maximum concentration. Although these figures display the general relations between occurrence and application, not all the details described below are reflected in the general categories shown. Appendix D should be consulted for data on any specific site.

Four seasonal patterns of application and occurrence were observed in the data: (1) pesticides applied primarily during the late autumn through spring and detected during the winter precipitation season (December through March); (2) pesticides applied and detected during the summer irrigation season (April through September); (3) pesticides applied and detected throughout the year, but whose concentrations usually peak during the winter precipitation season; and (4) other complex patterns of application and occurrence. For reference during the following discussion, time series plots of the application and

concentration of selected pesticides are shown in figure 15 as examples of the correspondence between application and occurrence for the four categories.

Five compounds are applied predominantly during late autumn through early spring. The occurrence or

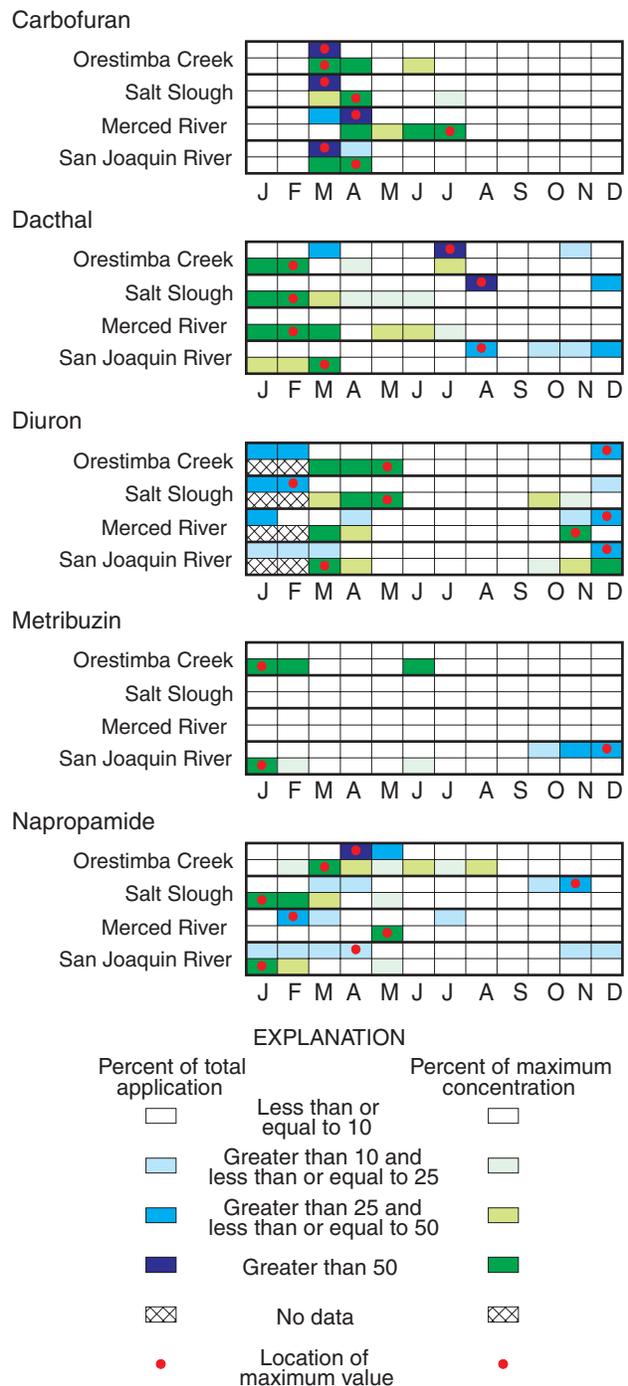


Figure 11. Relative application and relative concentration of pesticides applied primarily from autumn through spring for each subbasin site and the San Joaquin River site, San Joaquin River Basin, California.

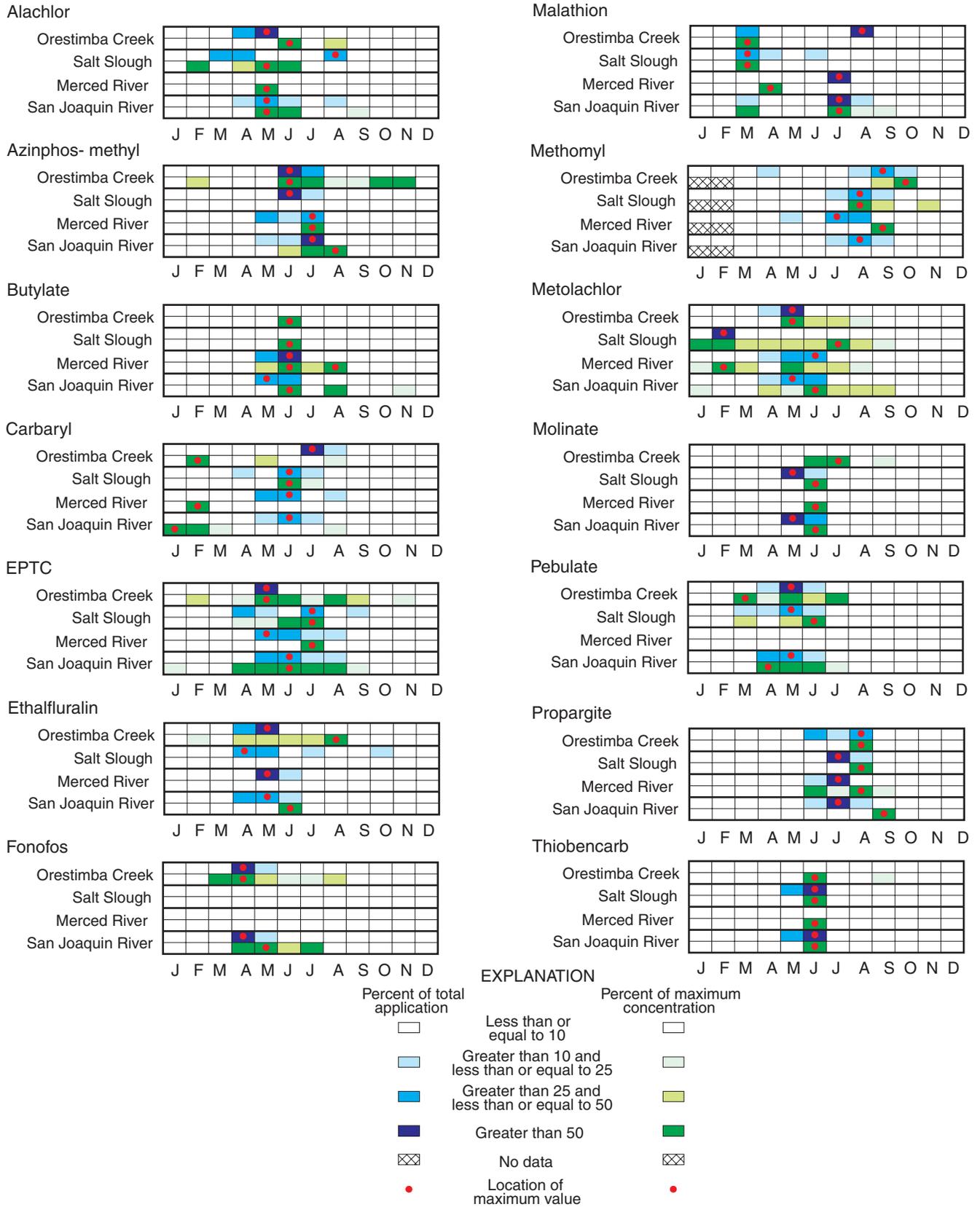


Figure 12. Relative application and relative concentration of pesticides applied primarily during the irrigation season for each subbasin site and the San Joaquin River site, San Joaquin River Basin, California.

highest concentrations of these compounds generally matches the period of application (fig. 11). Included in this category are dacthal, metribuzin (both primarily applied on truck crops), and diuron (alfalfa). As seen for the San Joaquin River in figure 15, diuron was detected at elevated concentrations in the early spring and autumn, during and after the period of maximum application. Dacthal is applied primarily in the late summer and autumn, and the greatest concentrations occur during the winter, after the application period

(fig. 15). The occurrence of napropamide in the winter in samples from the San Joaquin River and Salt Slough sites (fig. 11) generally corresponds to the period of application on almonds and truck crops; most of the high concentrations in Orestimba Creek follow the spring application on truck crops. Most of the carbofuran detections (fig. 11) occur during a narrow window of time from March through May, which corresponds to the period of carbofuran application on alfalfa.

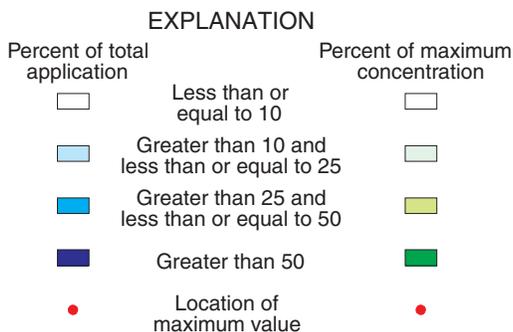
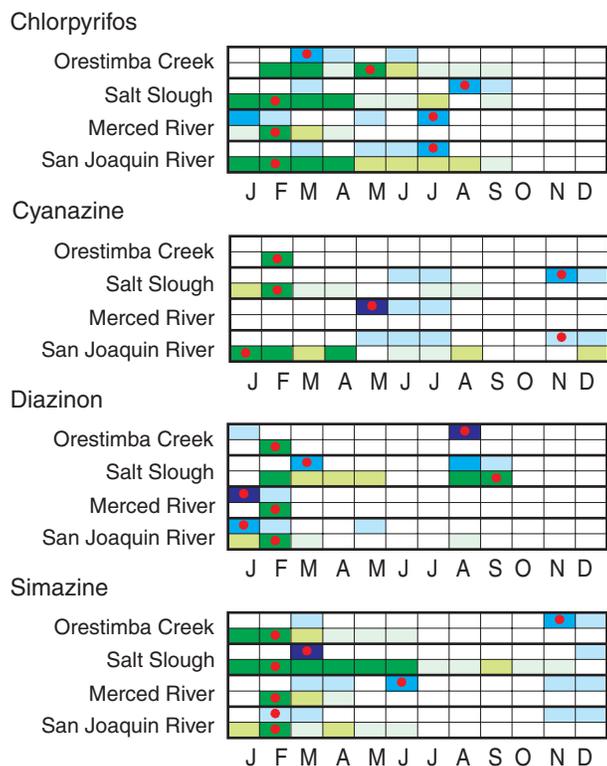


Figure 13. Relative application and relative concentration of pesticides applied for most of the year for each subbasin site and the San Joaquin River site, San Joaquin River Basin, California.

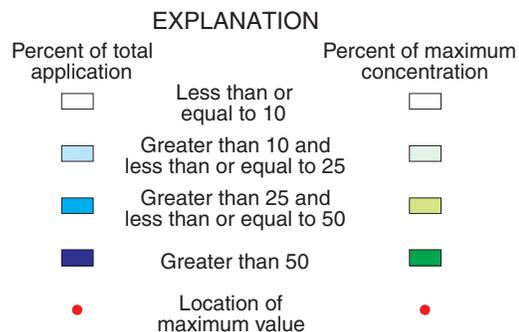
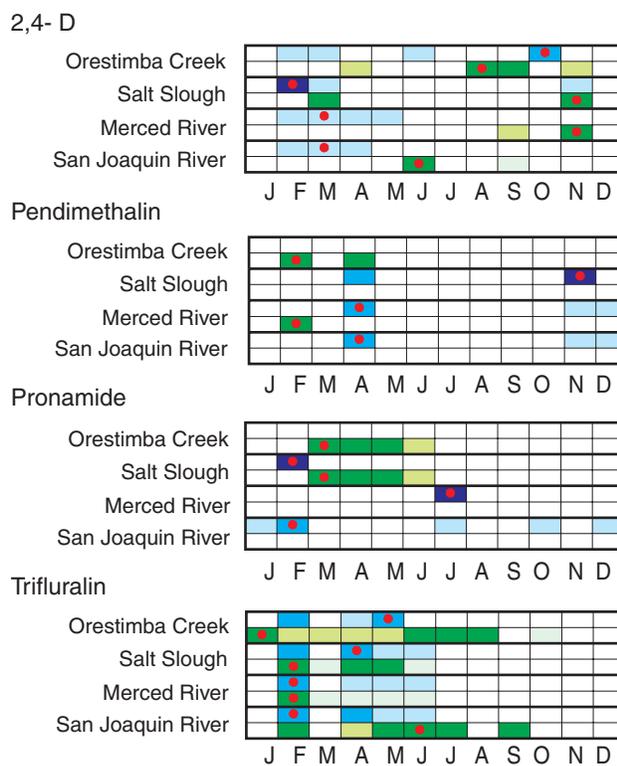


Figure 14. Relative application and relative concentration of pesticides with complex application patterns for each subbasin site and the San Joaquin River site, San Joaquin River Basin, California.

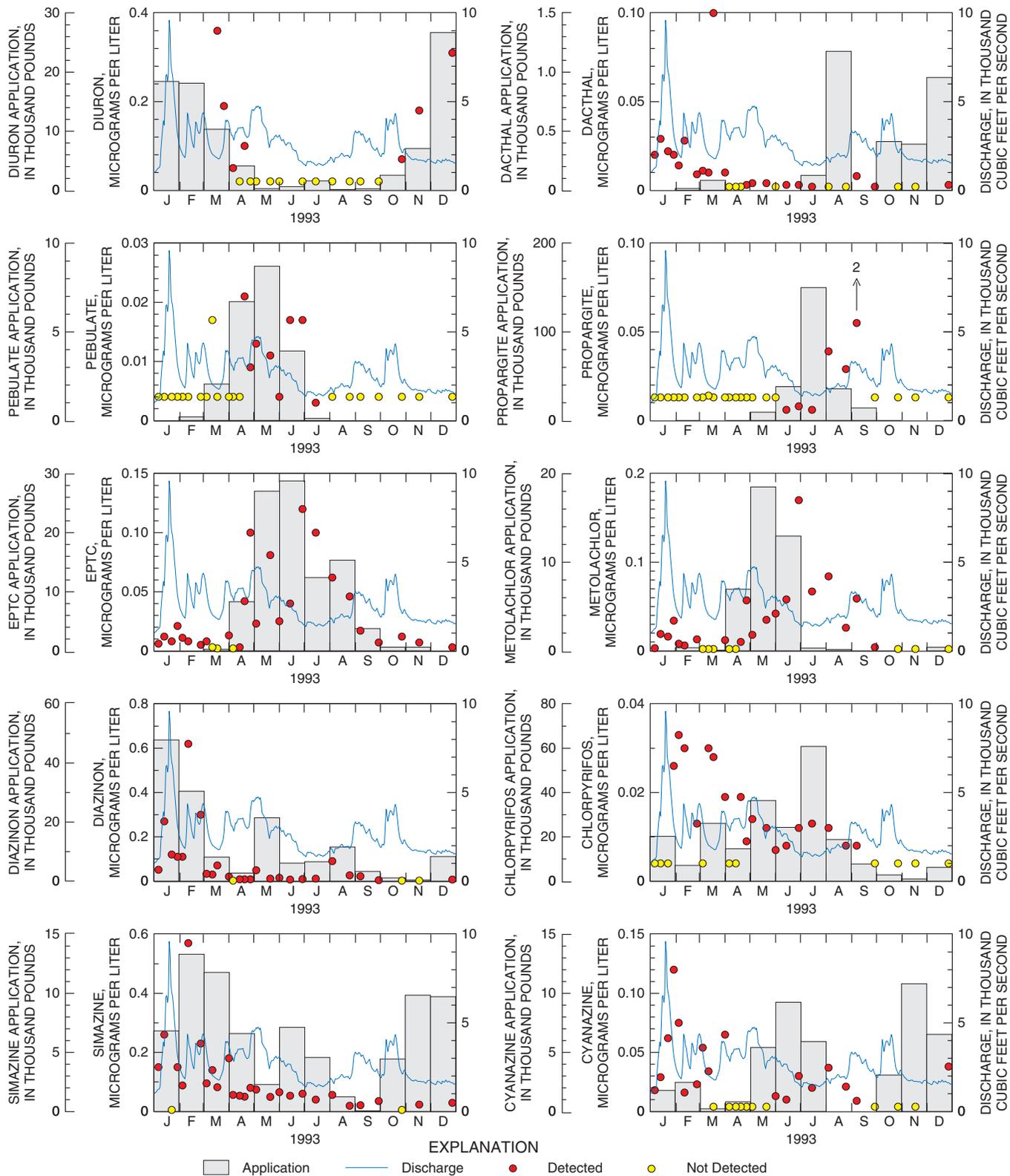


Figure 15. Monthly pesticide application, pesticide concentration in samples, and discharge for the San Joaquin River site, California.

Correspondence between application and occurrence for the 14 pesticides applied during the irrigation season is good (fig. 12). Compounds in this category include alachlor and metolachlor (predominantly applied on corn and beans), azinphos-methyl (on almonds and walnuts), butylate (on corn), ethalfluralin and fonofos (on dry beans), thiobencarb and molinate (on rice), malathion (on vineyards and alfalfa), methomyl (on alfalfa and truck crops), pebulate (on truck crops), EPTC (on corn and almonds), propargite (on corn, almonds, and cotton), and carbaryl (on a variety of crops). Pebulate and propargite are detected only during and immediately following the period of application (fig. 15). EPTC and metolachlor are detected throughout most of the year, but are present at their highest concentrations during and immediately following application (fig. 15). The maximum carbaryl concentrations usually occur during the winter precipitation season (January through March) rather than during the period of maximum application (April through August).

Four pesticides applied almost every month are detected in samples during much of the year (fig. 13). Compounds in this category include chlorpyrifos (predominantly applied on almonds, walnuts, and alfalfa), cyanazine (on cotton and corn), diazinon (on almonds, truck crops, and apricots), and simazine (on almonds and vineyards). Chlorpyrifos, simazine, and diazinon have maximum winter concentrations that clearly are related to the coincidence of high stream discharges generated by precipitation following the application of these pesticides on dormant orchards (fig. 15) (Kuivila and Foe, 1995; Ross and others, 1996; Domagalski and others, 1997; Kratzer, 1997). Conversely, although the maximum monthly application of chlorpyrifos is during July, and cyanazine is heavily applied during May through July, concentrations during these periods are lower than during winter (fig. 15). Similarly, the maximum concentrations of diazinon in samples collected from the Orestimba Creek site and of simazine in samples collected from the Merced River site are associated with winter high flows rather than the period of maximum application (appendix D). These data indicate that winter application may dominate the occurrence and generate concentration maximums, even if application is higher during the summer. In some cases, therefore, precipitation is more efficient than irrigation

at transporting a specific pesticide from the site of application to the receiving stream or river.

The last 4 of the 27 pesticides with reported agricultural application and detections in two or more samples from at least one of the sites are 2,4-D, pendimethalin, pronamide, and trifluralin (fig. 14). Pendimethalin and 2,4-D were detected too infrequently to relate occurrence to application. Pronamide occurrence appeared to be unrelated to reported agricultural applications. Although pronamide was detected in samples collected from the Orestimba Creek and Salt Slough sites during 4 months, it had no reported agricultural application in the Orestimba Creek subbasin; only 33 lb a. i. of agricultural application, which occurred during February, was reported for Salt Slough. Trifluralin concentrations were high during both winter high flows and the irrigation season. This pattern is due to application on different crops at different times in different subbasins, but within each subbasin the concentration and frequency of detection are generally highest during and immediately following the period of application (see appendix D).

Although the data indicate a general correspondence between the time of pesticide application and its occurrence, there is a large variability in occurrence and concentration that clearly is not a simple function of application. Factors that may modify a simple temporal relation between application and occurrence are the same as those that may complicate the pattern of the spatial distribution of pesticides—chemical and physical properties of the pesticide that affect environmental persistence and mobility, contrasts in the physical and hydrologic characteristics of the basins, unreported application (agricultural, nonagricultural, nonpoint source, or point source), irrigation and tailwater management, and mode of application.

The data also indicate that, in some cases, transport during the irrigation season and autumn is not as efficient as transport during storms. This difference in transport efficiency is partially attributed to the different sources of water to the streams at different times of the year, as shown graphically in figure 3. As mentioned earlier, the largest amount of precipitation in the San Joaquin River Basin occurs from January to March (fig. 2). During winter, precipitation and the resulting overland flow account for a large amount of the stream discharge at certain times. The overland flow can effectively transport pesticides into the stream. During the

irrigation season, sources of water to the streams include ground-water inflow, operational spills of water from irrigation canals, reservoir releases to tributaries on the east side of the basin, and tailwater and subsurface drainage from agricultural fields. The latter can transport pesticides to the stream, but these pesticides may be diluted to a concentration below the MDL by the other sources of water. During autumn, sources of water to the streams are ground-water inflow, reservoir releases to tributaries on the east side of the basin, and minor amounts of precipitation. In general, none of these water sources are effective at carrying pesticides to surface water. The exception is the transport of diuron, a pesticide used on rights-of-way along the banks of irrigation canals. This pesticide is transported to streams during autumn, perhaps because small amounts of precipitation are capable of mobilizing the diuron along canal banks and because of drift during application.

The potential effect of the physical and chemical properties on the temporal distribution of a pesticide is discussed in more detail in the following section, but the significance of these factors can be illustrated by examining the temporal distribution of one very persistent group of pesticides. Although the organochlorine insecticide DDT has not been used in the study area since the late 1970s, DDT and one of its degradation products (DDE) persist in soils in the western San Joaquin Valley. DDE is strongly sorbed to the soils, but does slightly partition into each new parcel of water that comes in contact with the soil, resulting in its frequent detection in samples from the Orestimba Creek and the San Joaquin River sites. Similarly, the broad temporal distribution and disproportionately high frequency of detection of another organochlorine insecticide, dacthal, relative to the small amount of reported agricultural application, also may be due to its environmental persistence. In cases where a pesticide may persist in soils and be released to runoff long after application, the temporal distribution of the occurrence and concentration of the pesticide may be more a function of physical factors that control transport to the stream than of the time of application. EPTC and metolachlor also are applied during a narrow window of time, but consistently occur in surface water beyond the period of application.

Influence of Chemical and Physical Properties on Pesticide Occurrence and Concentrations

Chemical and physical properties are important factors affecting the environmental behavior of chemical families and individual compounds. The influence of physical and chemical properties in the most general sense can be illustrated by examining the relation between pesticide occurrence and runoff potential of each pesticide. Runoff potential is a categorical aggregate of the influence of water solubility, soil half-life, and the organic-carbon-normalized adsorption coefficient (K_{oc}) on the likelihood of pesticide transport to surface water (Goss, 1992). Figure 16A shows the frequency of detection for each compound plotted against the total application in the San Joaquin River Basin, with each pesticide coded according to runoff potential. Even though there is some scatter in the data, some trends are evident. Most pesticides fall within the "medium" runoff potential category. All but two pesticides with medium runoff potential follow a distinct trend that indicates a systematic increase in occurrence with increasing application for this group. Consistent with their classification, the three compounds with "small" runoff potential occur less frequently relative to application than the pesticides with "medium" runoff potential. Similarly, most of the 11 pesticides with "large" runoff potential occur more frequently relative to application than the pesticides with "medium" runoff potential. In general, classification by runoff potential is consistent with the frequency of detection relative to application for the most commonly detected pesticides.

The relation between application and overall occurrence can be examined more specifically for differences between chemical families. This method of grouping was chosen because individual members of chemical families often have similar chemical structures and similar chemical and physical properties.

The frequency of detection as a function of application is shown in figure 16B for four different chemical families: amides, carbamates, organophosphates, and triazines. In general, amides exhibit a higher response (higher frequency of detection relative to application) compared with the other families. Of the four amides shown, three have a large runoff potential, and one has a medium runoff potential. Similar to the amides, but exhibiting a slightly lower frequency of detection relative to application, are the triazines. Two triazines have a large runoff potential, and one has a

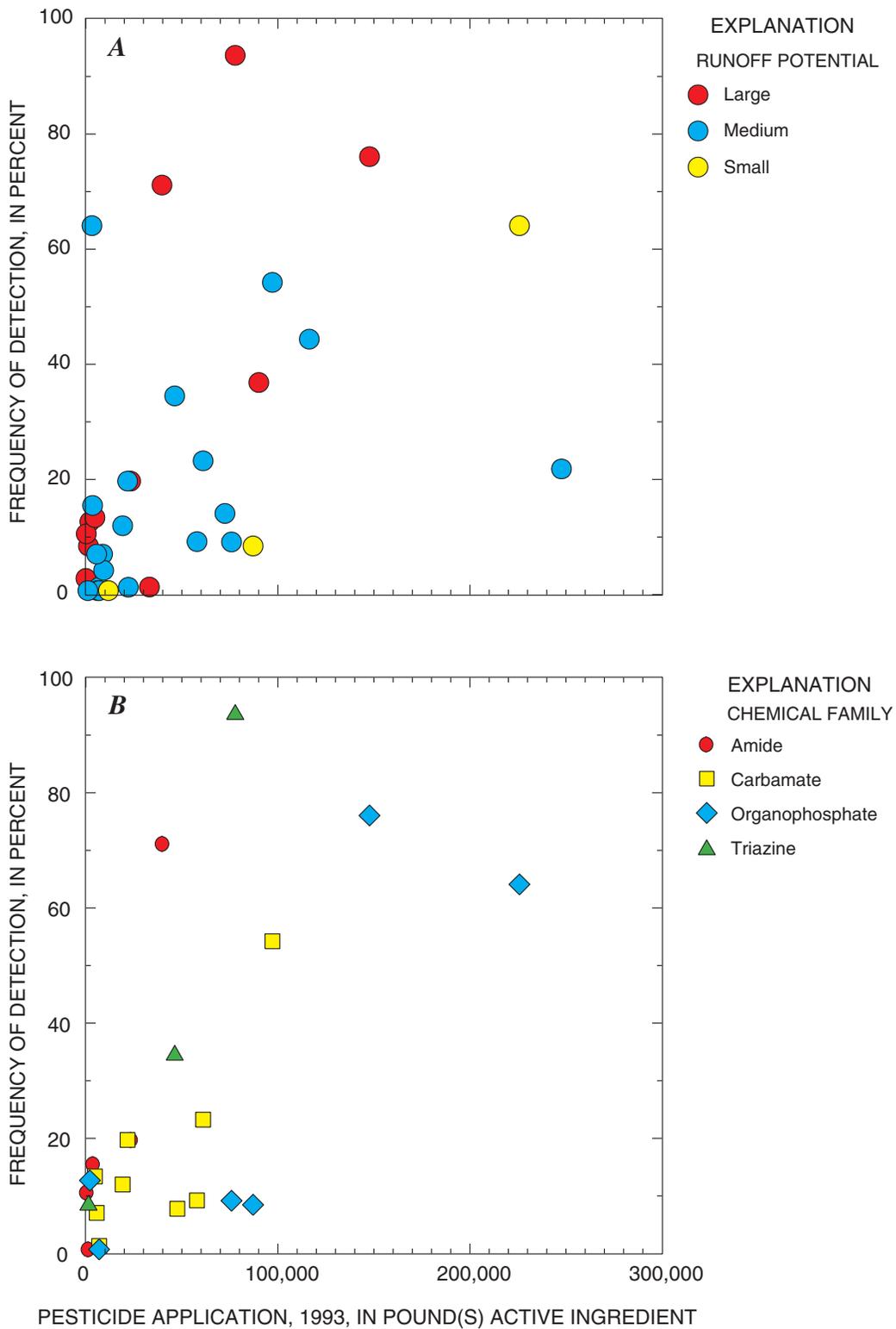


Figure 16. Pesticide detection frequency at all sites plotted against total pesticide application in the San Joaquin River Basin; *A.* for all compounds with runoff potential shown by color; *B.* for amides, carbamates, organophosphates, and triazines.

medium runoff potential. Carbamates have a lower and more variable response than the other two families, and all nine of the compounds have a medium runoff potential. The organophosphates have more scatter in their response than the carbamates, but overall, the organophosphates have a lower response than any of the other families. The variability in the response of organophosphates reflects the differences in runoff potential in this group—two compounds have a small runoff potential, two have a medium runoff potential, and two have a large runoff potential. These data indicate that some consistency exists in the behavior of pesticides within chemical families (that is, compounds with similar chemical structures), suggesting a specific chemical property or suite of chemical properties that influences the transport of like compounds.

Five of the chemical and physical properties believed to influence transport are solubility, K_{oc} , vapor pressure, Henry's law constant, and hydrolysis half-life. Values of these properties for the target pesticides are listed in table 10. The effect of these properties on pesticide transport to surface water was evaluated by plotting the relative load of the compound as a function of each property. Relative load is defined as the total load of pesticide coming off the field during the irrigation season (April through September) divided by the total amount applied during the irrigation season, expressed as a percent. The total load is calculated by measuring the pesticide concentration in each sample and by assuming that the concentration remains constant until the midpoint between samples. The concentration then changes in a step-wise manner to the concentration measured in the next sample. Pesticides not detected during an interval were assigned a concentration of zero for that interval. These concentrations are multiplied by the instantaneous stream discharge during the appropriate interval to calculate the load during that interval; these loads are summed to obtain the total load during the irrigation season. Loads were calculated only for the San Joaquin River site.

Five different chemical and physical properties were plotted as a function of the relative load (fig. 17). Regression of the relative load on the five properties was significant for K_{oc} ($p=0.002$) and solubility ($p=0.008$), and was nearly significant for hydrolysis half-life ($p=0.094$) and for Henry's law constant ($p=0.096$). There was no correlation between vapor pressure and relative load; thus the relation between Henry's law

constant and relative load is likely due to the dependence of Henry's law constant on solubility (Henry's law constant is a function of solubility and vapor pressure.). Figure 17A is a plot of relative load as a function of $\log K_{oc}$ and shows a negative correlation between relative load and $\log K_{oc}$. This behavior is expected because compounds with high $\log K_{oc}$ will sorb to the soil, making it less likely that they will be transported to the surface water. Examples of pesticides that have a relatively high $\log K_{oc}$ (greater than 3.5), and for which sorption may limit transport, are chlorpyrifos, trifluralin, ethalfluralin, and *cis*-permethrin. Figure 17B is a plot of relative load as a function of solubility and shows that pesticides with higher solubility have a larger relative load than those with lower solubilities. Compounds that are more soluble are more likely to be dissolved in water that runs off the field and, therefore, more likely to be transported to a stream. Pesticides for which a high relative load may be attributed in part to high solubility (greater than 500 mg/L) include metolachlor, carbofuran, metribuzin, and molinate.

A plot of the relative load of pesticides as a function of hydrolysis half-life of the compounds is shown in figure 17C. Pesticides with longer half-lives have a larger relative load than those with shorter half-lives. This relation between relative load and half-life is consistent with the anticipated effects because compounds that remain unchanged in the environment for an extended period have a greater chance of being transported to the stream; compounds with short half-lives may degrade before transport can occur. Carbofuran, gamma-HCH, fonofos, and diazinon all have relatively long half-lives (57 to 207 days) and higher relative loads than the other pesticides. As mentioned earlier, the correlation between Henry's law constant and relative load is not significant and is indicative of the correlation between relative load and solubility (fig. 17D). Although vapor pressure did not correlate with relative load, this property may be responsible for the behavior of individual pesticides. For example, the high vapor pressure of propargite may contribute to its low detection frequency and low concentrations in surface water. Propargite is the most heavily applied compound in the San Joaquin River Basin, yet it is detected in only 22 percent of the samples. The high vapor pressure may cause it to volatilize from the field before it can be effectively transported to surface water.

Table 10. Chemical and physical properties of analyzed pesticides

[>, greater than; <, less than]

Pesticide	Solubility (milligrams per liter)	Log K _{oc}	Vapor Pressure (Pascals)	Henry's law constant: (Pascals per cubic meter per mole)	Hydrolysis half-life pH 7	Runoff potential	Relative load (percent)
2,4,5-T	¹ 2.20E+2	² 1.72	¹ 5.00E-3	¹ 5.8E-3			
2,4- D	¹ 4.00E+2	² 1.68-2.73	¹ 1.00E0	¹ 5.50E-1		Medium	0.081
2,4-DB	³ 4.60E+1	⁴ 2.83			⁵ stable for 40 days	Medium	
2,6-Diethylaniline							
Acetochlor							
Acifluorfen	⁴ 2.50E+5	⁴ 2.05	⁴ 0	⁶ 1.54E-8	⁶ >56 days		
Alachlor	¹ 1.30E+2	⁴ 2.23	¹ 3.00E-3	¹ 6.20E-3	⁶ none at 30 days	Medium	0.46
Aldicarb	¹ 6.00E+3	⁴ 1.48	¹ 1.00E-2	¹ 3.20E-4	⁷ 245 days	Medium	
Aldicarb sulfone	⁴ 1.00E+4	² 0.85-1.67	² 1.20E-2				
Aldicarb sulfoxide		⁶ 1.00					
Atrazine	¹ 3.00E+1	⁴ 2.00	¹ 4.00E-5	¹ 2.9E-4	² 1,771 years	Large	
Atrazine, desethyl							
Azinphos-methyl	¹ 3.00E+1	⁴ 3.00	¹ 3.00E-5	¹ 3.2E-3	⁶ 23 hours	Medium	0.033
Benfluralin	⁴ 1.00E-1	⁸ 4.03	⁴ 8.80E-3	¹ 1.34E0	⁶ stable	Medium	
Bentazon	⁴ 2.30E+6	⁶ 1.32	⁴ 0	⁶ 6.38E-7		Medium	
Bromacil	¹ 6.70E+2	⁶ 1.86	¹ 5.00E-3	¹ 1.90E-3		Large	
Bromoxynil	³ 1.30E+2	² 2.48	² 6.40E-4	² 1.40E-1			
Butylate	¹ 4.00E+1	⁴ 2.60	¹ 1.00E-1	¹ 5.60E-1	⁶ stable		0.0080
Carbaryl	¹ 3.20E+1	⁴ 2.48	¹ 2.00E-4	¹ 1.30E-3	² 15 days	Medium	0.030
Carbofuran	¹ 6.50E+2	⁶ 1.46	¹ 1.50E-3	¹ 5.10E-4	² 8.2 weeks	Large	0.69
Carbofuran, 3-hydroxy							
Chloramben	² 7.00E+2	⁴ 1.18	² 9.33E-1	⁶ 2.70E-1	⁶ stable		
Chlorothalonil	⁴ 6.00E-1	⁴ 3.14	⁴ 1.33E-1	² 1.99E-2	⁶ stable	Medium	
Chlorpyrifos	¹ 3.00E-1	⁴ 3.78	¹ 1.50E-3	¹ 1.75E0	² 35.3 days	Small	0.015
Clorpyralid	⁴ 3.00E+5	⁴ 0.78	⁴ 0			Medium	
Cyanazine	⁴ 1.70E+2	⁴ 2.28	⁴ 2.13E-7	⁷ 2.82E-7	⁶ stable	Medium	0.13
DDE, <i>p,p'</i> -	¹ 4.00E-2	² 5.29	¹ 1.00E-3	¹ 7.95E0	⁴ stable		
DNOC	¹ 1.50E+2	² 2.64	¹ 1.10E-2	¹ 1.10E-2			
Dacthal	⁴ 5.00E-1	⁴ 3.70	⁴ 3.33E-4	² 2.20E-1		Medium	0.53
Dacthal, mono-acid-						Medium	
Desethylatrazine (see Atrazine, desethyl)							
Diazinon	¹ 3.80E+1	⁷ 1.60-2.63	¹ 8.00E-3	¹ 6.7E-2	² 184 days	Large	0.11
Dicamba	¹ 5.60E+3	⁴ 0.3	¹ 3.00E-3	¹ 1.20E-4		Medium	
Dichlobenil	¹ 1.80E+1	⁴ 2.60	¹ 7.00E-2	¹ 6.70E-1	⁶ >150 days	Large	
Dichlorprop	⁴ 5.00E+1	⁸ 2.23					
Dieldrin	¹ 1.70E-1	² 4.08-4.55	¹ 5.00E-4	¹ 1.12E0	² 10.5 years		
Dinoseb	¹ 4.70E+1	² 2.09	¹ 1.00E+1	¹ 5.11E+1	⁶ stable		
Disulfoton	¹ 2.50E+1	⁴ 2.78	¹ 2.00E-2	¹ 2.20E-1	² 1.2-103 days	Large	
Diuron	¹ 4.00E+1	⁴ 2.68	¹ 2.00E-4	¹ 1.20E-3	² stable after 30 days	Large	0.29
EPTC	¹ 3.70E+2	² 2.38	¹ 2.00E0	¹ 1.02E0	⁶ stable	Medium	0.12
Ethalfuralin	⁴ 3.00E-1	⁴ 3.60	⁴ 1.17E-2	⁷ 1.83E-1	⁶ stable after 31 days	Medium	0.027
Ethoprop	⁴ 7.50E+2	⁴ 1.85	⁴ 5.07E-2	² 1.61E-2	⁶ stable	Medium	
Fenuron	¹ 3.00E+3	⁸ 1.43	¹ 5.00E-3	¹ 2.70E-4			
Fluometuron	⁴ 1.10E+2	⁴ 2.00	⁴ 1.25E-4	² 1.72E-4	⁶ stable	Large	
Fonofos	⁴ 1.69E+1	⁴ 2.94	⁴ 4.53E-2	² 5.27E-1	² 74-127 days	Large	0.12
HCH, alpha-	¹ 1.00E0	² 3.28	¹ 3.00E-3	¹ 8.70E-1	⁵ 207 days		

Table 10. Chemical and physical properties of analyzed pesticides—Continued

Pesticide	Solubility (milligrams per liter)	Log K_{oc}	Vapor Pressure (Pascals)	Henry's law constant: (Pascals per cubic meter per mole)	Hydrolysis half-life pH 7	Runoff potential	Relative load (percent)
HCH, gamma-	¹ 8.00E0	⁴ 3.04	¹ 2.00E-3	¹ 7.30E-2	⁵ 207 days		0.24
Linuron	¹ 6.50E+1	⁴ 2.60	¹ 1.40E-3	¹ 5.40E-3		Large	
MCPA	⁴ 5.00E0	² 2.03-2.07	² 2.00E-4			Medium	
MCPB	⁴ 2.00E+5					Medium	
Malathion	¹ 1.45E+2	⁴ 3.26	¹ 1.00E-3	¹ 2.30E-3	² 9 days (pH 6)	Small	0.0076
Methiocarb	⁴ 2.40E+1	⁴ 2.48	⁴ 1.60E-2		² <35 days	Large	
Methomyl	¹ 1.00E+4	⁸ 2.20	⁴ 4.00E-3	¹ 6.50E-5	² 262 days	Medium	
Methyl parathion	¹ 2.50E+1	⁴ 3.71	⁴ 2.00E-3	¹ 2.10E-2	⁵ 72 days	Medium	
Metolachlor	⁴ 5.30E+2	⁴ 2.30	⁴ 4.18E-3	² 9.32E-4	² >200 days	Large	0.29
Metribuzin	⁴ 1.22E+3	⁴ 1.78	⁴ <1.33E-3	² 1.20E-5		Large	7.7
Molinate	⁴ 9.70E+2	⁴ 2.28	⁴ 7.47E-1	² 1.62E-1		Medium	0.20
Napropamide	⁴ 7.40E+1	² 2.83	⁴ 2.27E-5	⁷ 1.97E-3		Large	0.051
Neburon	³ 5.00E0	² 3.49	² 0				
Norflurazon	⁴ 2.80E+1	⁴ 2.85	⁴ 2.67E-6			Large	
Oryzalin	⁴ 2.50E0	⁴ 2.78	⁴ <1.3E-6			Medium	
Oxamyl	² 5.00E+4	⁴ 1.40	¹ 3.00E-2	¹ 2.60E-4		Medium	
Parathion	¹ 1.50E+1	⁴ 3.70	¹ 6.00E-4	¹ 1.20E-2	² 3.5 weeks (pH 6)		
Pebulate	¹ 6.00E+1	² 2.80	¹ 3.50E0	¹ 1.17E+1		Medium	0.086
Pendimethalin	⁴ 2.75E-1	⁴ 3.70	³ 1.25E-3	² 8.67E-2		Medium	
Permethrin, <i>cis</i> -	⁴ 6.00E-3	⁴ 5.00	⁴ 1.73E-6	⁴ 1.57E-1		Small	0.018
Phorate	¹ 4.00E+1	⁴ 3.00	¹ 1.00E-1	¹ 6.50E-1	² 96 hours	Large	
Picloram	¹ 4.30E+2	⁴ 1.20	¹ 6.00E-5	¹ 3.40E-5		Large	
Prometon	¹ 7.50E+2	⁴ 2.18	¹ 3.00E-4	¹ 9.00E-5		Large	
Pronamide	⁴ 1.50E+1	⁴ 2.90	⁴ 1.13E-2	⁷ 1.93E-1		Large	
Propachlor	¹ 6.00E+2	⁴ 1.90	¹ 3.00E-2	¹ 1.10E-2		Medium	
Propanil	¹ 3.00E+2	⁴ 2.17	¹ 5.00E-3	¹ 3.60E-3		Medium	
Propargite	⁴ 5.00E-1	⁴ 3.60	⁴ 4.00E-1	⁴ 2.80E+2		Medium	0.23
Propham	⁴ 2.50E+2	⁴ 2.30	⁴ sublimes				
Propoxur	¹ 1.60E+3	⁴ 1.48	¹ 1.00E0	¹ 1.30E-1	² 290 days		
Silvex	⁷ 1.40E+2	⁷ 3.41	⁷ 6.93E-4	⁷ 1.33E-3			
Simazine	¹ 5.00E0	² 2.14	¹ 8.50E-6	¹ 3.40E-4		Large	0.62
Tebuthiuron	⁴ 2.50E+3	² 2.79	⁴ 2.67E-4	² 2.50E-5	² >64 days	Large	113
Terbacil	¹ 6.00E+2	⁴ 1.74	¹ 5.00E-5	¹ 1.80E-5		Large	
Terbufos	⁴ 5.00E0	⁴ 2.70	⁴ 4.27E-2	² 2.20E0		Medium	
Thiobencarb	⁴ 2.80E+1	⁴ 2.95	⁴ 2.93E-3			Medium	0.076
Triallate	¹ 3.00E0	⁴ 3.38	¹ 1.00E-2	¹ 1.02E0		Large	
Triclopyr	⁴ 2.30E+1	⁸ 1.43	³ 2.00E-4				
Trifluralin	¹ 5.00E-1	² 2.94-4.49	¹ 6.00E-3	¹ 4.02E0		Medium	0.019

¹Suntio and others (1988)

²Montgomery (1993)

³Tomlin (1994)

⁴Wauchope and others (1992)

⁵Howard and others (1991)

⁶U.S. Environmental Protection Agency (1997)

⁷Howard (1991)

⁸Kenega (1980)

Variations in the chemical and physical properties of the pesticides are consistent with the amount of transport out of the basin on the whole. This relation is shown both by the general analysis of runoff potentials and the specific analyses of the properties used to calculate runoff potential. This information could be helpful for formulating a strategy to reduce off-site movement of pesticides.

Efficacy of the Integrator Site for Representing Pesticide Occurrence

Monitoring surface water to describe complex patterns of pesticide occurrence is an expensive undertaking. Because of the high expense, it is important to design a network that allows for the minimum amount of data collection while providing the information necessary to address the questions posed. As discussed in

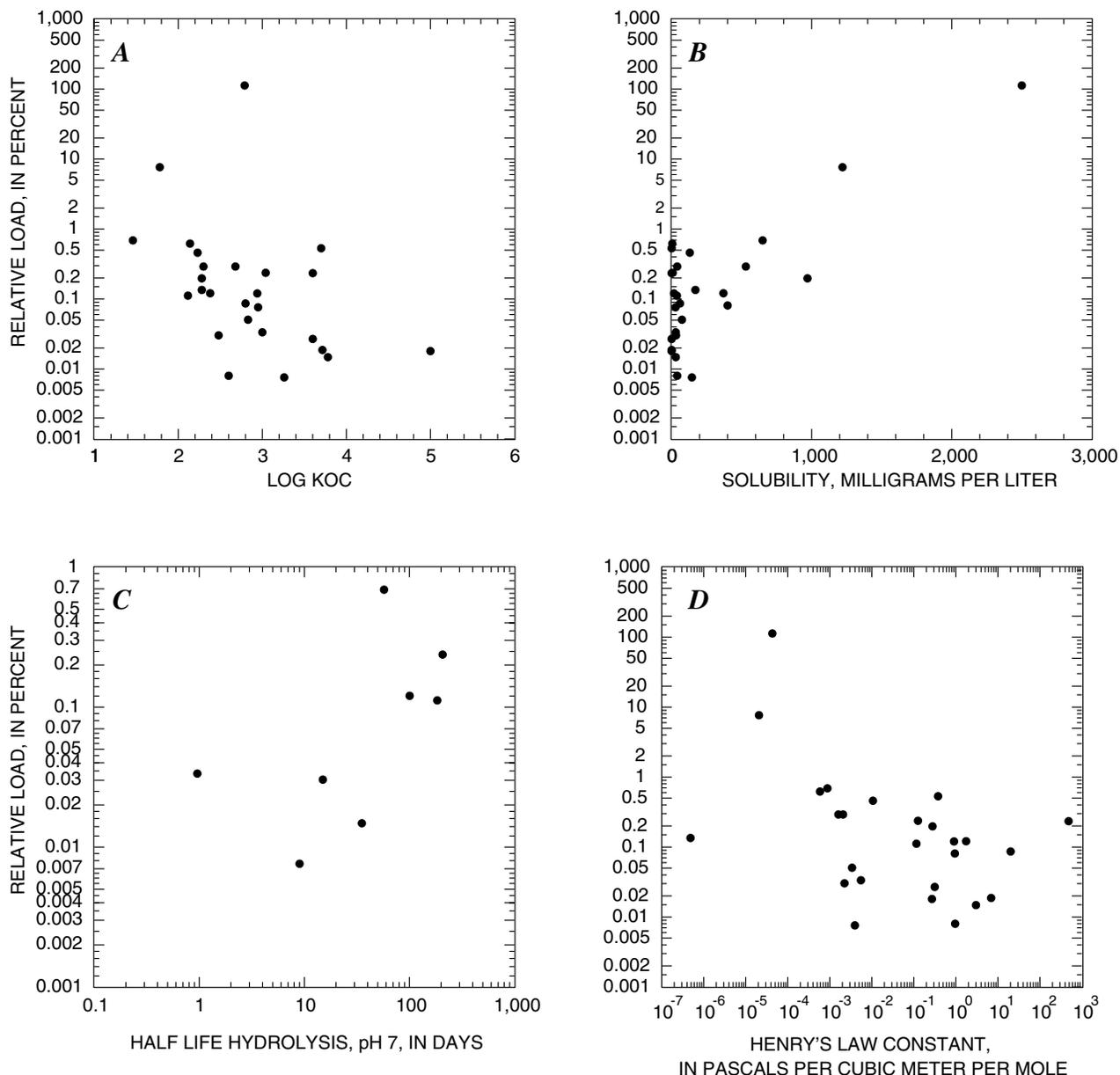


Figure 17. Relative load of pesticides for the 1993 irrigation season (total load divided by total application for April through September) plotted against physical and chemical properties for the San Joaquin River Basin, California. **A.** relative load versus log K_{OC}; **B.** relative load versus solubility; **C.** relative load versus hydrolysis half-life; and **D.** relative load versus Henry's law constant.

the description of the study design, it was hypothesized that the sampling at the mouth of the basin would integrate the effects of the major land uses, and, hence, pesticide applications within the basin. In view of the need to minimize the sampling cost of any future monitoring, it is important to evaluate this hypothesis. As will be seen, the hypothesis may or may not be valid depending on the question posed.

First, let us consider How do data from the integrator site on the San Joaquin River reflect the overall occurrence of pesticides in the three diverse subbasins? A total of 45 pesticides were detected in samples from the three subbasins. Thirty-one of these 45 pesticides (69 percent) also were detected in samples from the San Joaquin River site. Of the 14 pesticides detected in a subbasin site, but not in the San Joaquin River site, 10 were detected in only one sample; therefore, 89 percent of the 35 pesticides detected in two or more samples from the subbasins also were detected in samples from the San Joaquin River site. In addition, figure 9 shows that the pesticides that occur most frequently in samples from the subbasin sites also occur most frequently in samples from the San Joaquin River site, with 15 of the 22 pesticides that were detected in more than 20 percent of the samples from any one subbasin site also detected in more than 20 percent of the samples from the San Joaquin River site. These data show that anal-

ysis of samples from the San Joaquin River site provides a good indication of what pesticides occur in the subbasins, as well as the frequency of detection of the most commonly occurring pesticides.

The second basic question is How do data on the range of pesticide concentrations in samples from the integrator represent the range in concentrations in samples from the subbasins? This question was addressed by comparing three specific concentration levels—the maximum, 90th percentile, and median—for each pesticide in data for the integrator site and the subbasins, and expressing the comparison as a ratio. The contrasts were illustrated by dividing the maximum, 90th percentile, and median concentrations for each pesticide in samples collected from the San Joaquin River site by the highest corresponding value for the three subbasin sites. In cases where a pesticide had a value at one of the subbasin sites, but was below the detection limit in all samples from the integrator site (that is, the San Joaquin River site), the integrator site was assigned a value equal to the detection limit so that these cases could be included in the analysis.

The resulting ratios for the comparison of the maximum values for 45 pesticides, the 90th percentile concentrations for 35 pesticides, and the median concentrations for 10 pesticides are summarized in figure 18. The data show a lot of scatter in the ratios of the

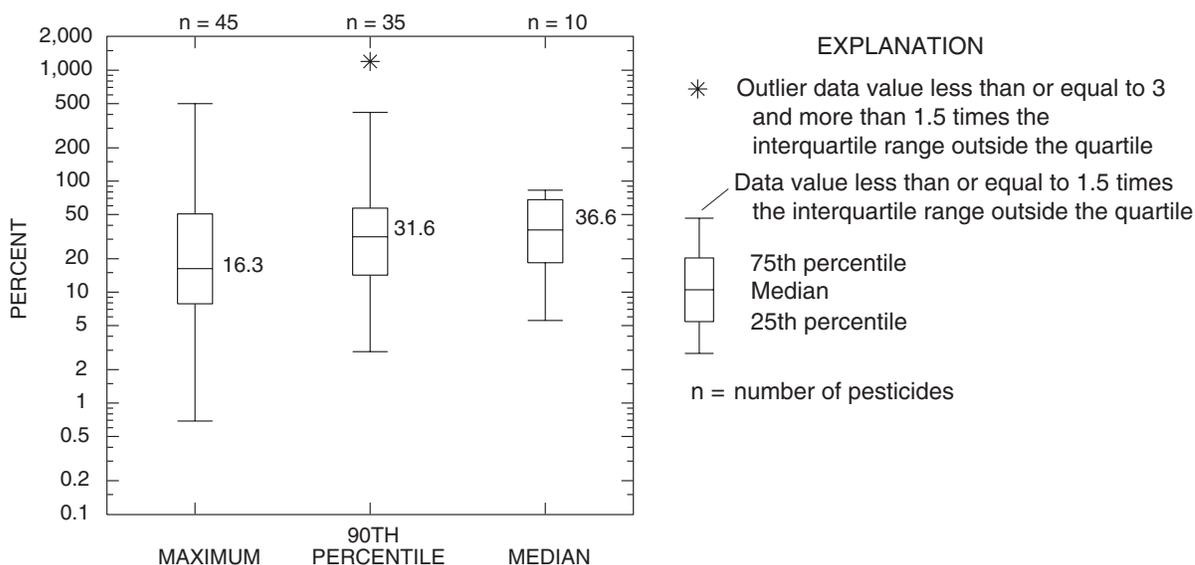


Figure 18. Ratios for each pesticide for the maximum, 90th percentile, and median concentrations of the San Joaquin River site, to the highest corresponding value for the subbasin sites (if San Joaquin River site concentration is below the detection limit, then the value is set to Method Detection Limit).

maximum concentrations. The data have a median of about 16 percent; for half of the pesticides, the maximum concentration at the integrator was between only 8 and 50 percent of the highest maximum for the subbasins. Thus, the concentrations measured in samples from the San Joaquin River site are poor indicators of the maximum values observed at the subbasin sites. The plot of the ratios of the 90th percentile values have a median value of 32 percent. These data indicate that, compared to maximum values, 90th percentile values for the San Joaquin River site provide a better representation of the concentration of pesticides. Comparison of the median values show only a slight improvement in this value, with a median ratio of 37 percent. These data show that concentrations at the integrator site are generally lower than at the subbasin sites. As would be anticipated, the data on pesticide concentrations at the integrator site are not representative of the maximum concentrations measured in samples from the subbasin sites; however, data for the integrator site are a fair representation of more frequently occurring (90th percentile and median) concentrations.

These evaluations show that, if the objective of the monitoring is to describe the maximum concentrations of pesticides in the basin, sampling at the integrator site at the mouth of the basin is insufficient, and sampling at small indicator subbasins is required. If the objectives of the monitoring are to identify what pesticides occur in surface water in the basin and to provide a gross indication of the concentration levels of the most commonly occurring pesticides, then sampling at the basin mouth integrator site may be sufficient.

SUMMARY AND CONCLUSIONS

Several factors that affect the spatial and temporal occurrence of pesticides in surface water were examined during this study. These factors include the location and timing of pesticide application in the different basins, the hydrology of these basins, and the chemical and physical properties of the individual pesticides. All but one of the 143 samples collected throughout 1993 contained at least one pesticide, and most contained more than seven. Overall, 49 pesticides were detected, 6 of which were in more than 50 percent of the samples: 4 herbicides (dacthal, EPTC, metolachlor, and simazine) and 2 insecticides (chlorpyrifos and diazinon). Concentrations varied widely, and none of the measured concentrations exceeded drinking

water criteria. The concentrations of seven pesticides exceeded the criteria for protection of freshwater aquatic life in one or more samples: azinphos-methyl, carbaryl, chlorpyrifos, diazinon, diuron, malathion, and trifluralin. Overall, 38 of the 54 pesticides with known application (70 percent) were detected during this study.

Several differences were noted in the occurrence of pesticides at the four sites. The Merced River site had the fewest pesticides detected and the lowest median number of pesticides per sample. The Orestimba Creek site had the most pesticides detected, and the Salt Slough site had the highest median number of pesticides per sample detected. Pesticides that were detected frequently at all of the sites were simazine, diazinon, metolachlor, chlorpyrifos, and carbaryl. The pesticides DDE, propargite, fonofos, and napropamide, were detected most frequently at the Orestimba Creek and San Joaquin River sites. EPTC, cyanazine, atrazine, diuron, molinate, and malathion were detected most frequently at the Salt Slough and San Joaquin River sites. In many cases, the frequency of detection was related directly to the rate of pesticide application in the subbasins. Thirteen pesticides exhibited a statistically significant difference in detection frequency of 20 percent or more between subbasins. These differences in occurrence were consistent with the differences in the rates of application in the subbasins for seven pesticides—alachlor, cyanazine, dacthal, fonofos, molinate, napropamide, and trifluralin. Four additional pesticides—azinphos-methyl, ethalfluralin, propargite, and thiobencarb—came close to meeting these criteria. In general, pesticides applied exclusively or dominantly to one crop in one basin are the most likely to show basin differences in frequency of detection reflective of application rates.

A spatial component to the concentrations of detected pesticides also was observed. The highest 90th percentile concentrations for 14 pesticides occurred at the Orestimba Creek site, for 13 pesticides at the Salt Slough site, for 7 pesticides at the San Joaquin River site, and for 1 pesticide at the Merced River site. In general, the compounds that occur most frequently have the highest median and 90th percentile concentrations.

The occurrence of pesticides in surface water also has a temporal component. The number of pesticides present in each sample can vary widely during the year and is dependent on the source of water to the stream. Runoff from precipitation on nonagricultural land, which occurs in the upper part of the Orestimba

Creek and Merced River subbasins during winter storms, results in a more variable number of pesticide detections during the winter than during the summer. The number of pesticide detections is consistently high in Orestimba Creek and Salt Slough during the summer when these streams receive irrigation return flow.

Most pesticides show a clear correspondence between the time of application and occurrence. For example, 14 pesticides, including pebulate, propargite, and fonofos, had corresponding high application rates and concentrations during the summer irrigation season. Similarly, the occurrence, or highest concentrations, of compounds applied before or during the winter precipitation season generally matches the period of application. Conversely, several pesticides exhibited maximum concentrations during winter storms, even though maximum application occurred at some other time of year. These pesticides include chlorpyrifos, cyanazine, diazinon, and simazine. The data indicate that precipitation is more efficient than irrigation tailwater at transporting some pesticides from the site of application to the receiving river or stream.

Chemical and physical properties of pesticides also play a role in their occurrence in surface water. Transport of a pesticide from a field is influenced by how soluble the compound is, how strongly it is sorbed to the soil, and how long it exists in the soil system. These factors can be combined to determine the runoff potential of each pesticide; the runoff potential generally was consistent with the frequency of pesticide detection in surface water relative to the amount of pesticide applied to agricultural land. The relative load of each pesticide in surface water was used to determine the strength of several individual chemical and physical properties as predictors of transport. Three properties—solubility, half-life, and K_{oc} —are generally, but weakly, correlated with load.

Pesticide occurrence and concentration at the San Joaquin River near Vernalis and pesticide occurrence and concentration in the three subbasins were compared to evaluate how well sampling at the mouth of the basin reflects conditions in the subbasins. Results showed that data from samples collected at the mouth of the basin provide a good indication of pesticide occurrence, as well as the frequency of detection of the most commonly occurring pesticides. These data are poor indicators of the maximum pesticide concentrations measured in samples from the subbasins, but provide a gross indication of the concentration levels of the most commonly occurring pesticides.

Pesticide application generally is a reliable predictor of occurrence. Many pesticides that are the most heavily applied are the ones most frequently detected overall. Spatial contrasts in occurrence can be attributed partly to differences in application patterns. A few pesticides were applied and detected in only one subbasin. Other compounds were applied in all three subbasins and their frequency of detection followed the rate of application. In addition, the temporal distribution of frequency of detection and the concentration for many pesticides coincided to a great extent with the application of those pesticides.

Hydrology also influences the spatial and temporal occurrence of pesticides. The distribution, concentration range, and maximum concentration of some compounds differ as a function of seasonal hydrology and the hydrologic differences among basins. A major seasonal hydrologic difference is the presence of winter storms during October through March and the lack of precipitation during the irrigation season of April through September. In some basins, winter storms are more effective than irrigation return flows at transporting certain pesticides from the fields to surface water. Large, rapid fluctuations in concentration are common during the winter in Orestimba Creek and the Merced River. At Salt Slough, however, precipitation does not have a great effect on stream discharge. In this subbasin, agricultural return flows and wetlands drainage are the two most important sources of water, and discharge is fairly constant throughout the year.

Finally, the chemical and physical properties of the pesticides affect their occurrence in surface water. Pesticides that exist in the environment for a short period, or that have properties limiting their movement off the field, are less likely to be detected in streams. Although three of the specific properties explored explain some of the transport of pesticides from the site of application to surface water, more investigation is needed to understand the relation between these properties and transport before they can be used to predict transport of pesticides accurately.

Although this study examined many of the links between pesticide occurrence and some causative factors, other potentially important factors were not examined. These factors include the method of pesticide application and the method of crop irrigation. Both of these factors could be important influences on the occurrence of pesticides in surface water. The San Joaquin River Basin is a complicated hydrologic system with extremely heterogeneous agricultural land

uses, and as many causative factors as possible need to be examined to understand the transport processes of pesticides to streams and to achieve the ultimate goal of minimal transport from the fields to surface water.

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Appendix A. Pesticide application by commodity, Orestimba Creek Basin, California, 1993 (including Central California Irrigation District Basin for January through March) (California Department of Pesticide Regulation, 1994)

[All values are in pounds, active ingredient; —, no application]

Pesticide	Almonds	Apricots	Walnuts	Peaches	Fruits and nuts	Corn	Beans	Grain	Truck crops ¹	Alfalfa	Other
2,4-D	178	8	152		18						116
2,4-DB										64	
Alachlor							882				
Azinphos-methyl	347		1,992								
Bromacil					14						
Bromoxynil								222	36	137	
Carbaryl					307				133		
Carbofuran										306	
Chlorothalonil		68		65					262		
Chlorpyrifos	92		2,035		330					3,156	
Dacthal									225		
Diazinon	173	118	1,585	75	163		68		298	17	
Diuron			172		168					1,444	
EPTC						250					
Ethalfuralin							1,170				
Fonofos					v		338		382		
MCPA							24	94	128		
Malathion			539						84	217	
Methomyl					10		193		1,330	173	
Metolachlor						79	3,258				
Napropamide					21				422		
Norflurazon	330	11	31		28						
Oryzalin	227		233		103						
Pebulate											
Permethin, <i>cis</i> -	66					24			3,088		
Propargite	362	57	3,672		142	205	4,200		239	11	
Simazine	226		731		217						
Trifluralin							1,148		392	820	

¹Truck crops: melons; squash and cucumbers; onions and garlic; peppers; and tomatoes.

Appendix B. Pesticide application by commodity, Salt Slough Basin, California, 1993. (California Department of Pesticide Regulation, 1994)

[All values are in pounds, active ingredient; —, no application]

Pesticide	Almonds	Apricots	Walnuts	Peaches	Fruits and nuts	Vineyards	Corn	Cotton	Beans	Field ¹ crops	Rice	Grain	Truck ² crops	Alfalfa	Other
2,4-D	151	—	9	—	20	—	17	—	—	—	—	3,252	—	—	2,038
2,4-DB	—	—	—	—	—	—	—	—	—	—	—	—	—	2,885	—
Alachlor	—	—	—	—	—	—	861	—	—	—	—	—	—	—	—
Aldicarb	—	—	—	—	—	—	—	3,632	—	—	—	—	—	—	—
Azinphos-methyl	—	—	443	—	350	—	—	—	—	—	—	—	—	—	—
Benfluralin	—	—	—	—	—	—	—	—	—	—	—	—	—	1,886	—
Bromacil	—	—	—	—	34	—	—	—	—	—	—	—	—	—	—
Bromoxynil	—	—	—	—	—	—	—	—	—	—	—	2,024	306	222	—
Carbaryl	—	24	—	24	118	1	168	70	—	3,286	—	—	4,623	15	—
Carbofuran	—	—	—	—	—	—	—	—	—	—	—	—	—	182	—
Chlorothalonil	—	751	—	—	290	—	—	—	—	—	—	—	10,942	—	—
Chlorpyrifos	190	—	1,335	—	189	—	157	7,654	—	305	—	—	528	4,742	—
Cyanazine	—	—	—	—	—	—	64	34,546	—	—	—	—	—	—	124
Dacthal	—	—	—	—	—	—	—	—	—	—	—	—	2,106	—	—
Diazinon	1,040	301	29	—	277	—	465	444	—	426	—	—	5,885	4,957	—
Dicamba	—	—	—	—	—	—	—	—	—	—	—	44	—	—	—
Dinoseb	—	—	—	—	—	—	—	—	—	—	—	—	5	—	—
Disulfoton	—	—	—	—	—	—	—	—	—	—	—	68	1,513	—	—
Diuron	—	—	—	—	58	620	—	—	—	—	—	—	—	12,081	—
EPTC	—	—	—	—	—	—	—	—	—	2,166	—	—	1,174	3,882	—

Appendix B. Pesticide application by commodity, Salt Slough Basin, California, 1993. (California Department of Pesticide Regulation, 1994)—Continued

Pesticide	Almonds	Apricots	Walnuts	Peaches	Fruits and nuts	Vineyards	Corn	Cotton	Beans	Field ¹ crops	Rice	Grain	Truck ² crops	Alfalfa	Other
Ethalfuralin	—	—	—	—	—	—	—	—	1,773	—	—	—	88	—	—
Linuron	—	—	—	—	—	—	—	—	—	—	—	—	1,296	—	—
MCPA	—	—	—	—	—	—	—	—	—	—	—	3,275	—	—	—
Malathion	—	—	—	—	413	—	—	375	—	236	—	—	3,111	8,620	—
Methomyl	—	—	—	—	—	762	1,381	23	346	3,142	—	—	12,787	5,024	—
Methyl Parathion	—	—	—	—	44	—	—	87	—	—	—	—	—	—	—
Metolachlor	—	—	—	—	—	—	—	—	—	—	6,889	—	—	—	—
Molinate	—	—	—	—	—	—	—	—	—	—	—	—	—	—	—
Napropamide	—	—	—	—	—	—	—	—	—	—	—	—	3,282	—	—
Norflurazon	171	—	—	—	66	—	—	—	—	—	—	—	1,143	—	—
Oryzalin	586	—	—	—	227	193	—	—	—	—	—	—	—	—	—
Oxamyl	—	—	—	—	—	—	—	—	—	—	—	—	6,450	—	—
Parathion	—	—	—	—	—	—	—	—	—	—	—	—	4	—	—
Pebulate	—	—	—	—	—	—	—	—	—	180	—	—	7,290	—	—
Pendimethalin	—	—	—	—	—	—	—	2,047	—	—	—	—	316	—	—
Permethin, <i>cis</i> -	35	—	—	—	58	—	36	1	—	—	—	—	149	86	—
Phorate	—	—	—	—	—	—	—	279	—	1,818	—	—	—	—	—
Pronamide	—	—	—	—	—	—	—	—	—	—	—	—	—	33	—
Propargite	684	236	138	11	390	1,381	5,657	48,435	2,008	—	—	—	—	728	—
Simazine	54	—	16	—	—	—	—	—	—	—	—	—	—	—	—
Thiobencarb	—	—	—	—	—	—	—	—	—	—	3,050	—	—	—	—
Trifluralin	—	—	—	—	57	109	—	21,130	92	402	—	26	10,233	39,904	147

¹Field crops: fallow; grain sorghums; safflower; and sugar beets.

²Truck crops: asparagus; cole crops; flowers and nurseries; melons, squash, and cucumbers; onions and garlic; and tomatoes.

Appendix C. Pesticide application by commodity, Merced River Basin, California, 1993. (California Department of Pesticide Regulation, 1994)

[All values are in pounds, active ingredient; —, no application]

Pesticide	Almonds	Apricots	Walnuts	Peaches	Fruits and nuts	Vineyards	Corn	Beans	Field ¹ crops	Grain	Truck ² crops	Alfalfa	Other
2,4-D	15,285	196	118	938	11	319	272	—	—	1,136	—	—	—
2,4-DB	—	—	—	—	—	—	—	—	—	—	—	619	—
Azinphos-methyl	16,805	—	286	2,560	6,816	—	—	—	—	—	—	—	—
Benfluralin	—	—	—	—	—	—	—	—	—	—	—	909	—
Bromoxynil	—	—	—	—	—	—	19	—	—	1,407	—	275	—
Butylate	—	—	—	—	—	—	5,311	—	—	—	—	—	—
Carbaryl	15	437	—	7,571	90	6,475	344	—	—	—	135	—	127
Carbofuran	—	—	—	—	—	—	—	—	—	—	—	790	—
Chlorothalonil	—	592	—	3,627	1	—	—	—	—	—	4	—	493
Chlorpyrifos	29,220	—	2,210	1,157	6,725	—	1,289	—	—	—	406	2,086	42
Cyanazine	—	—	—	—	—	—	1,445	—	—	—	—	—	—
Diazinon	15,830	—	—	1,245	561	—	—	—	12	—	15	27	0
Dicamba	—	—	—	—	—	—	36	—	—	421	—	—	24
Disulfoton	—	—	—	—	—	—	—	—	—	—	—	—	—
Diuron	—	—	115	—	804	2,026	—	—	—	—	—	3,330	—
EPTC	3,144	—	—	—	—	—	18,202	—	—	—	—	1,064	—
Ethalfuralin	—	—	—	—	—	—	—	726	—	—	—	—	—
Ethoprop	—	—	—	—	—	—	—	—	—	—	1,422	—	—
MCPA	—	—	—	—	—	—	—	2,335	—	1,909	550	—	—
Malathion	—	—	859	38	—	40,195	—	—	—	—	707	554	—
Methomyl	—	—	—	29	—	433	—	154	—	—	421	—	3
Methyl Parathion	—	—	—	—	—	17	—	—	—	—	—	—	—
Metolachlor	—	—	—	—	—	—	4,098	1,610	—	—	—	—	—
Napropamide	1,364	—	3	60	—	45	—	—	—	—	—	—	—
Norflurazon	5,987	91	—	258	629	485	—	—	—	—	—	—	—
Oryzalin	20,252	119	112	1,877	1,256	3,166	—	—	—	—	29	—	—
Oxamyl	—	—	—	—	9	—	—	—	—	—	—	—	—
Pendimethalin	4,070	—	—	19	2	478	—	—	—	—	—	—	—
Permethin, <i>cis</i> -	1,628	—	—	1,152	1	—	231	—	—	—	—	33	—
Phorate	—	—	—	—	—	—	139	—	—	—	—	—	—
Pronamide	—	—	—	—	—	—	—	—	—	—	—	—	35
Propargite	14,766	—	25	544	—	—	12,471	—	—	—	—	—	0
Simazine	17,317	—	305	304	2,129	4,933	—	—	—	—	—	—	—
Trifluralin	498	—	—	—	—	657	—	239	—	—	—	3,699	—

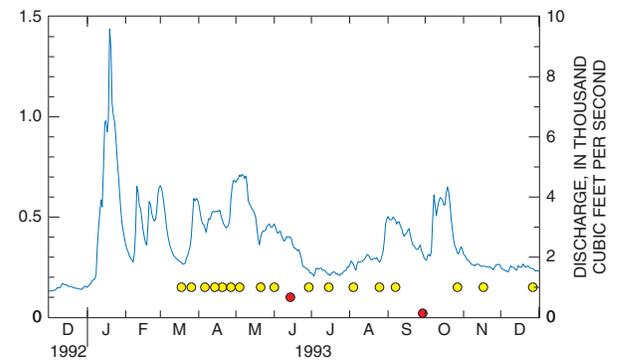
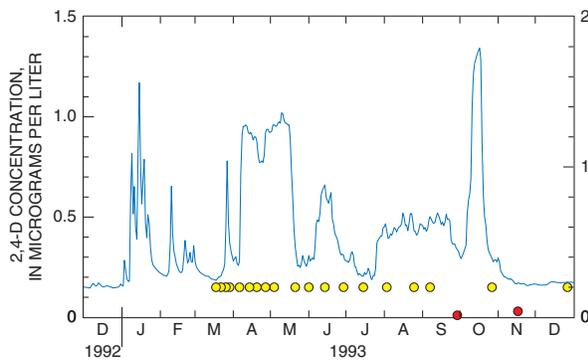
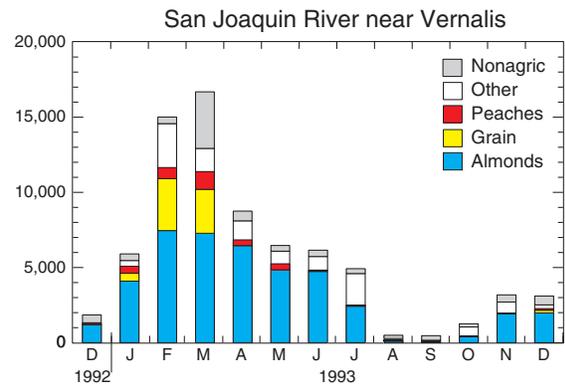
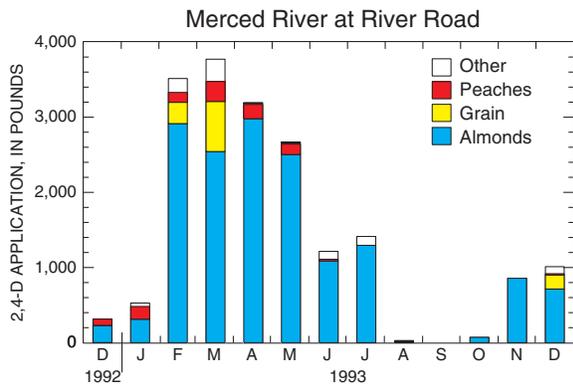
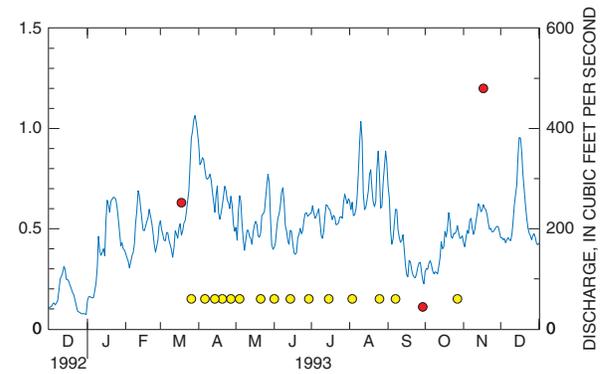
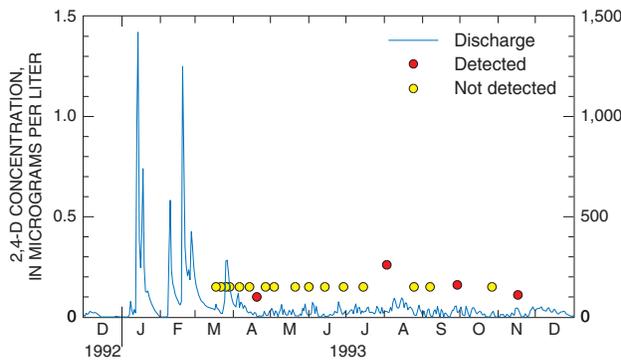
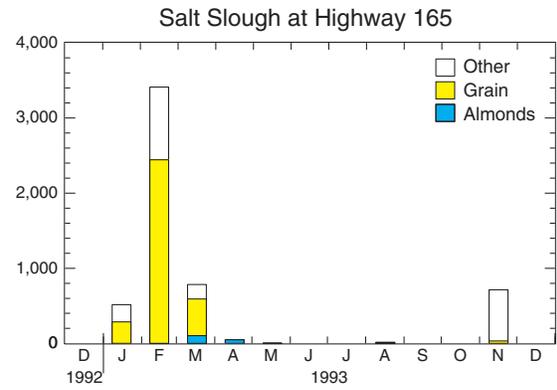
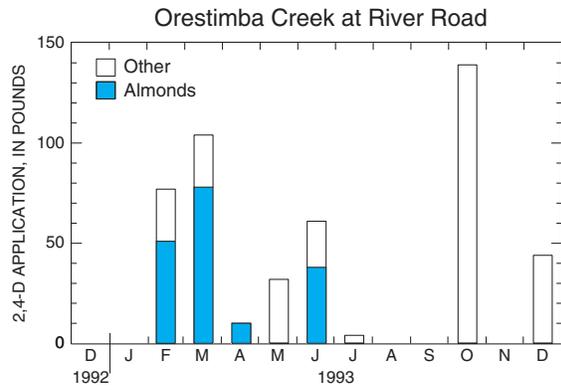
¹Field crops: fallow and sudan.

²Truck crops: flowers and nurseries; melons, squash, and cucumbers; potatoes; and sweet potatoes.

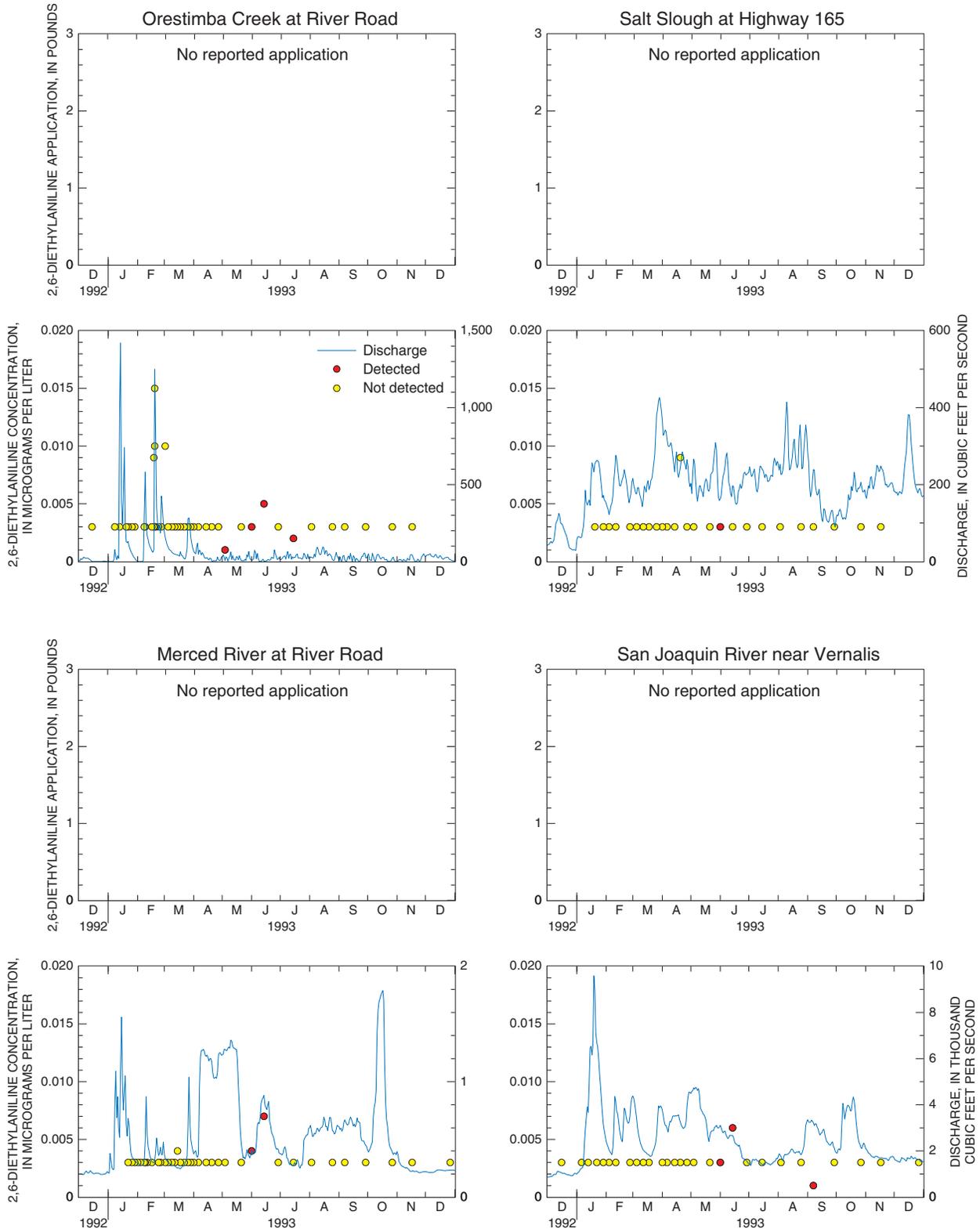
APPENDIX D

Time Series Plots of
Pesticide Application, Pesticide
Concentration, and Discharge at
Subbasins and the San Joaquin
River Basin, California

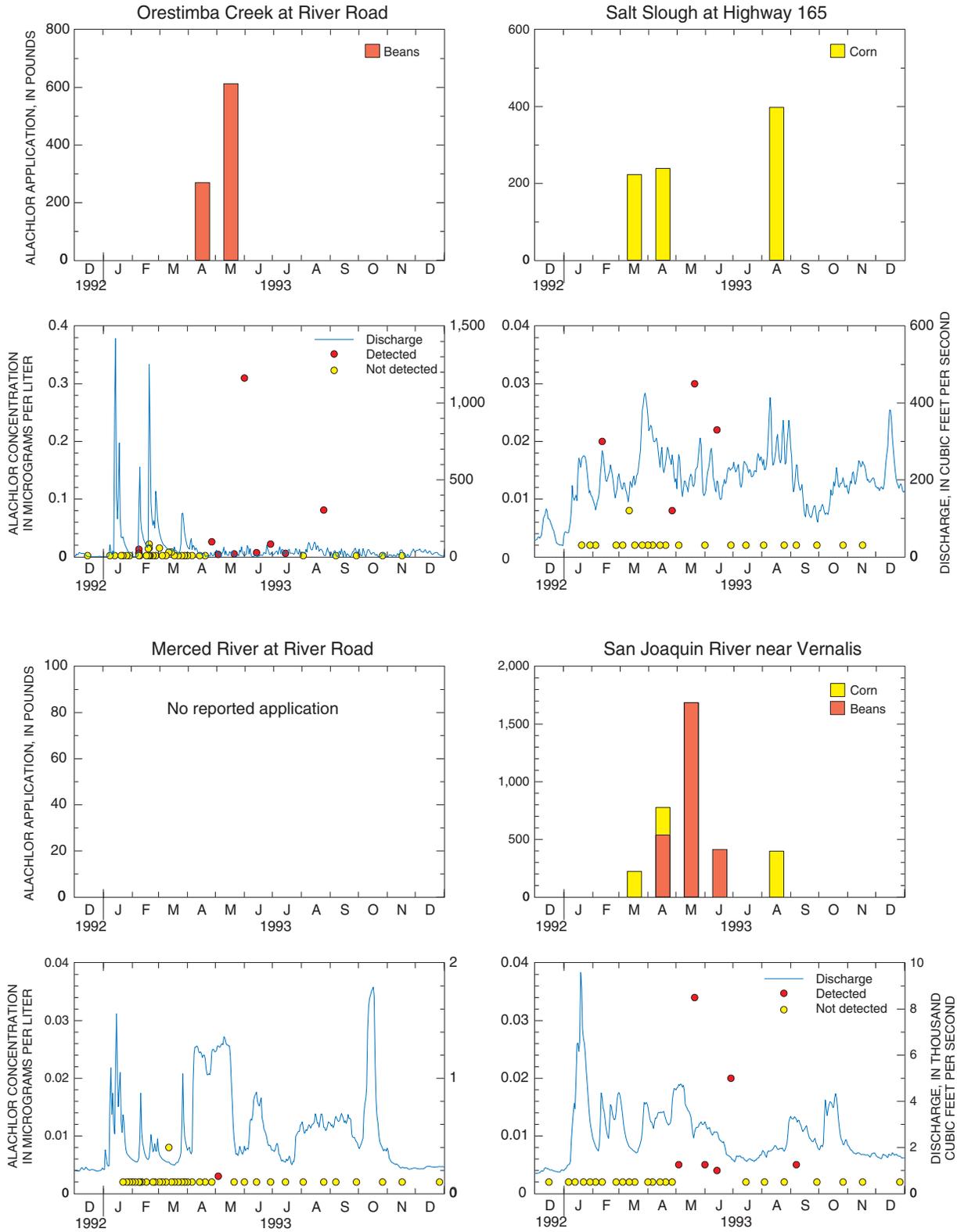
2,4-D



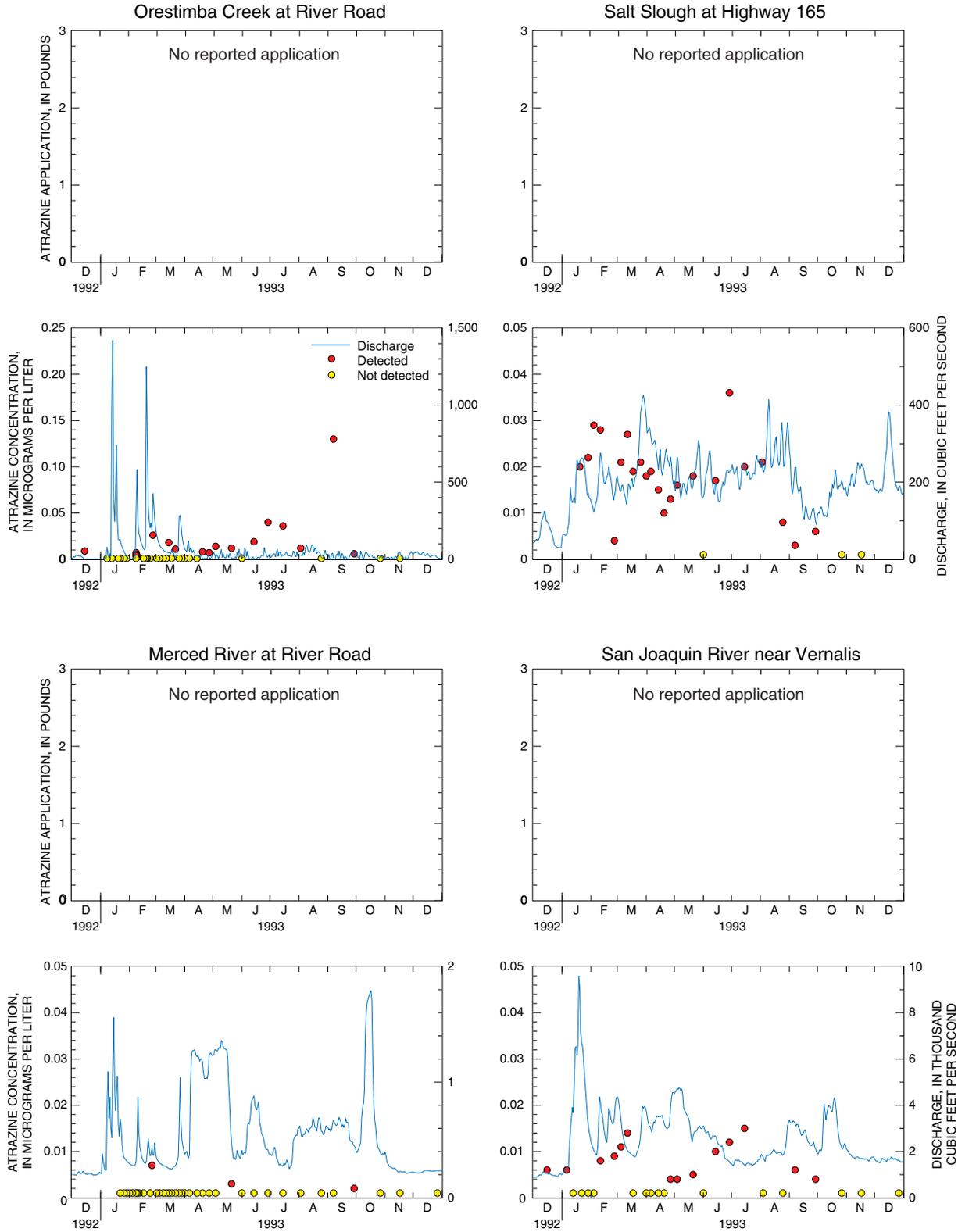
2,6-Diethylaniline



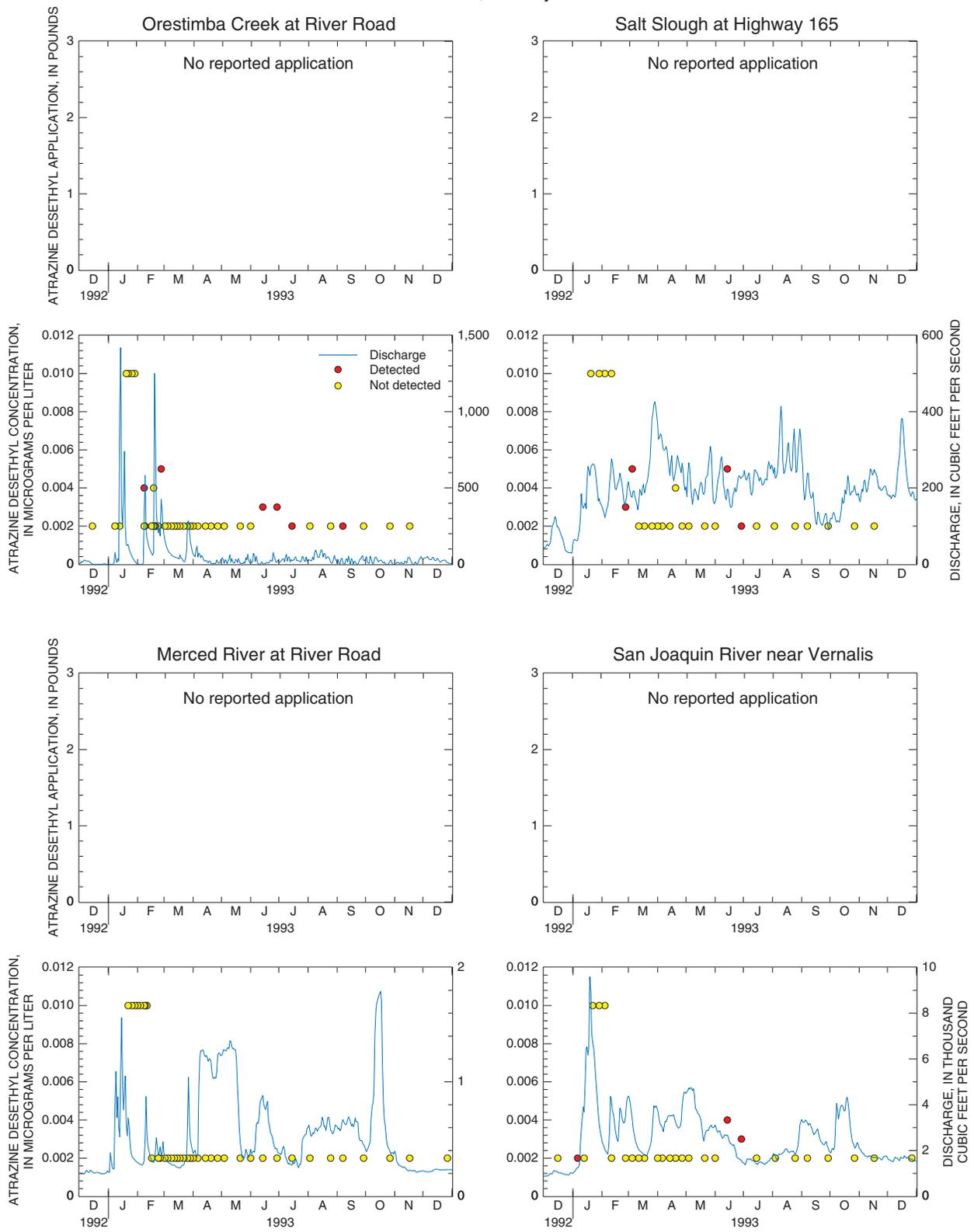
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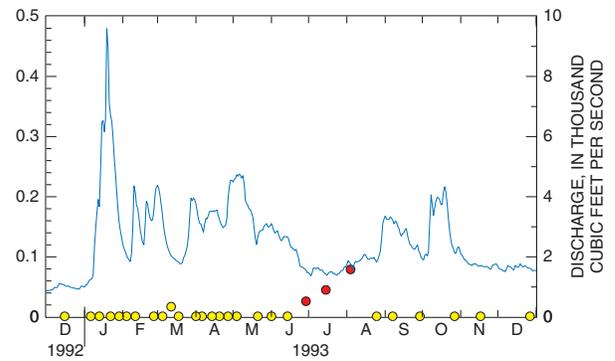
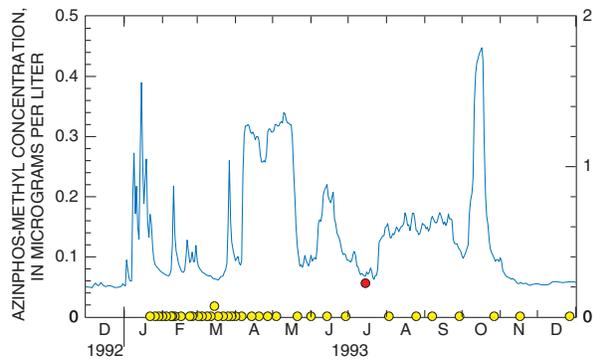
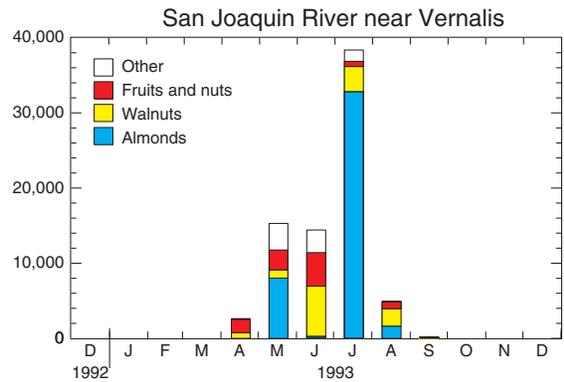
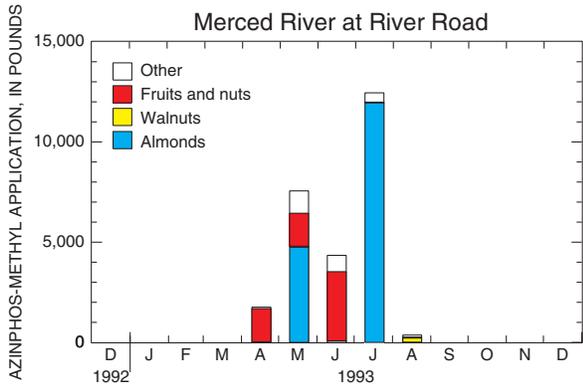
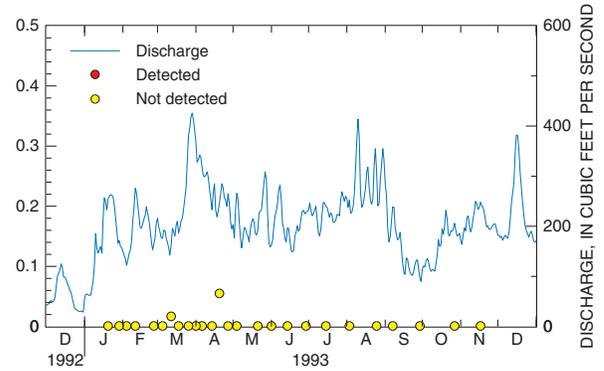
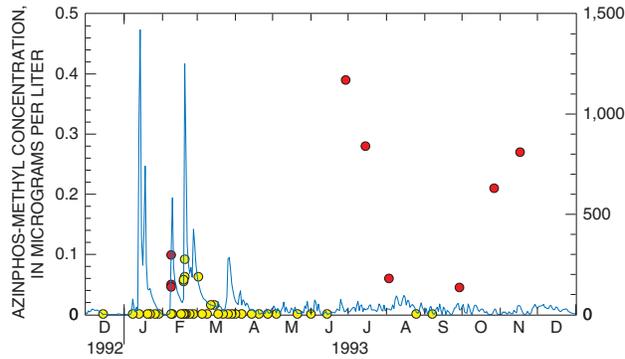
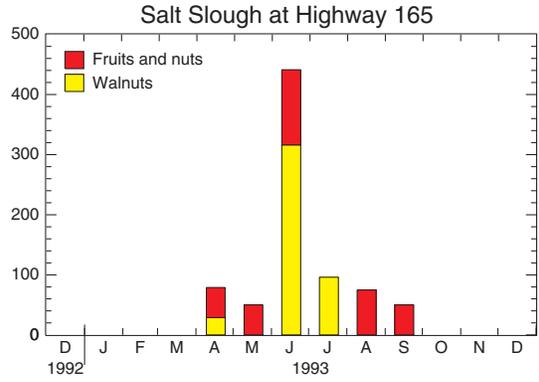
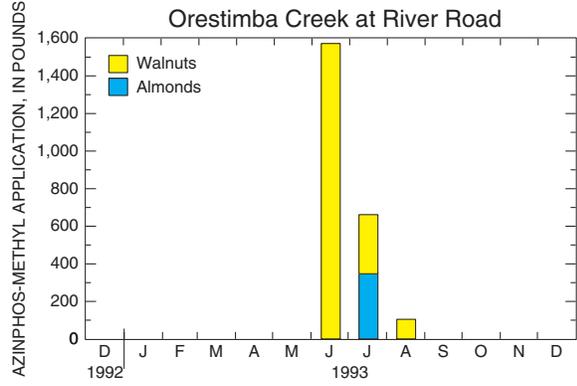
Atrazine



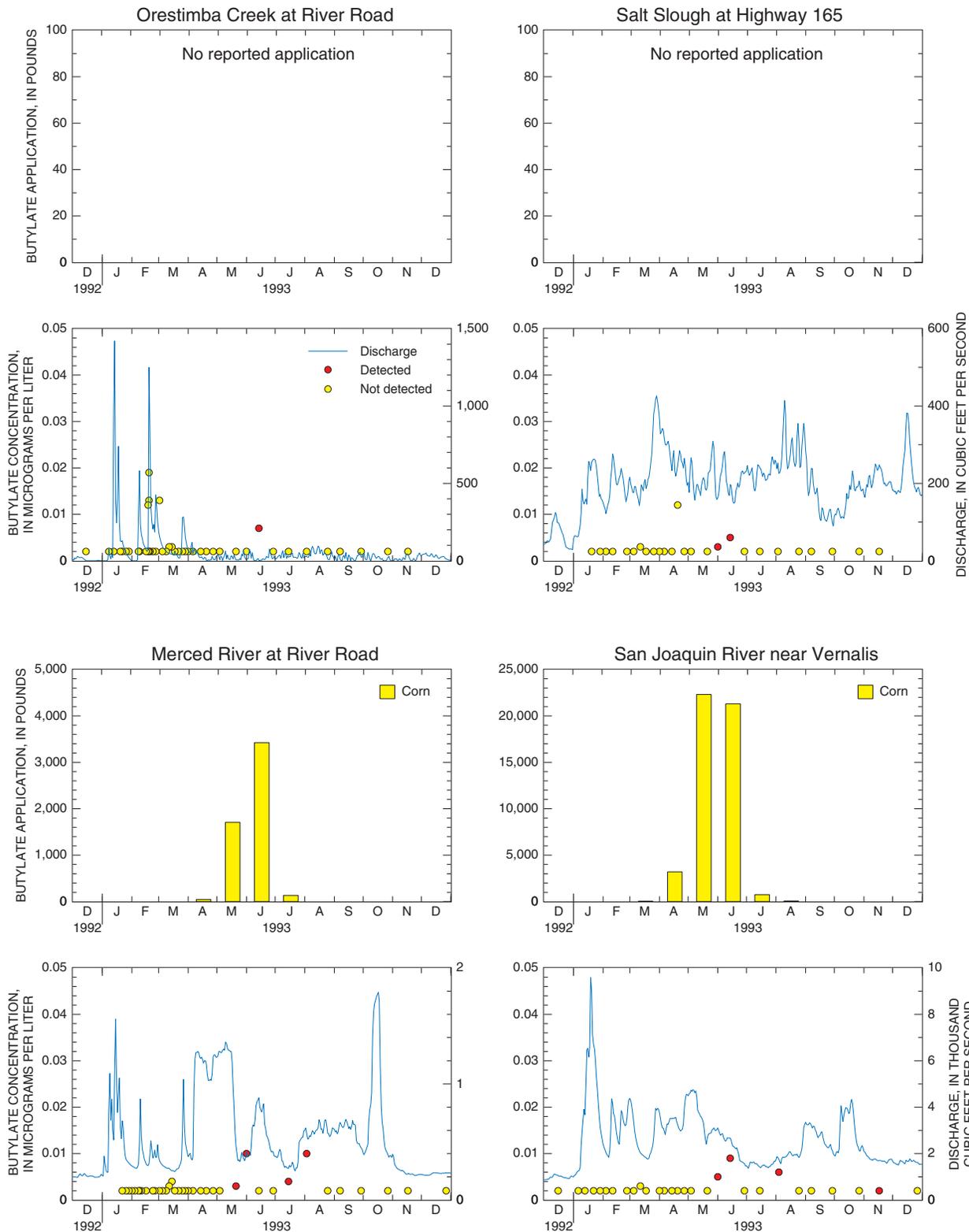
Atrazine, desethyl-



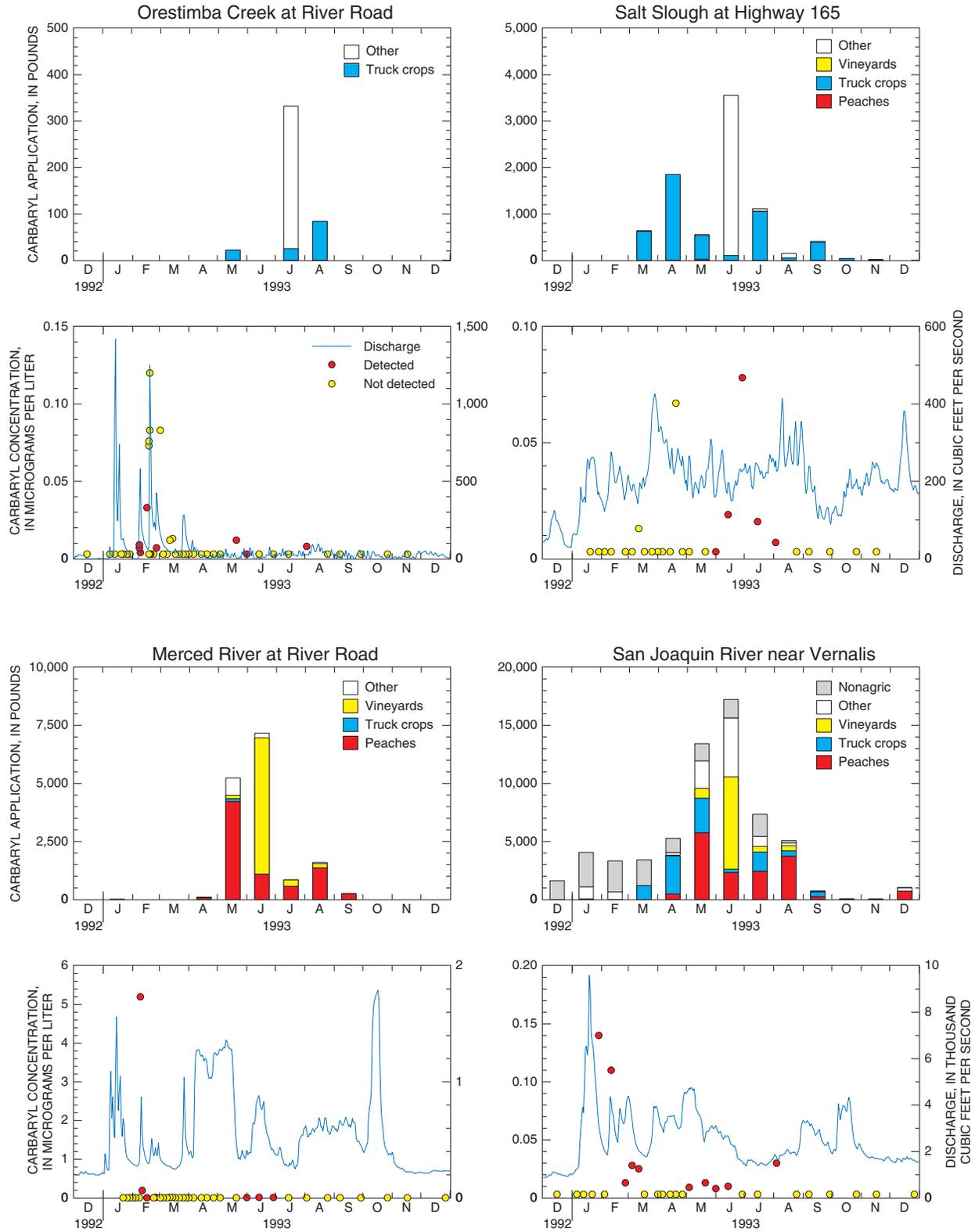
Azinphos-Methyl



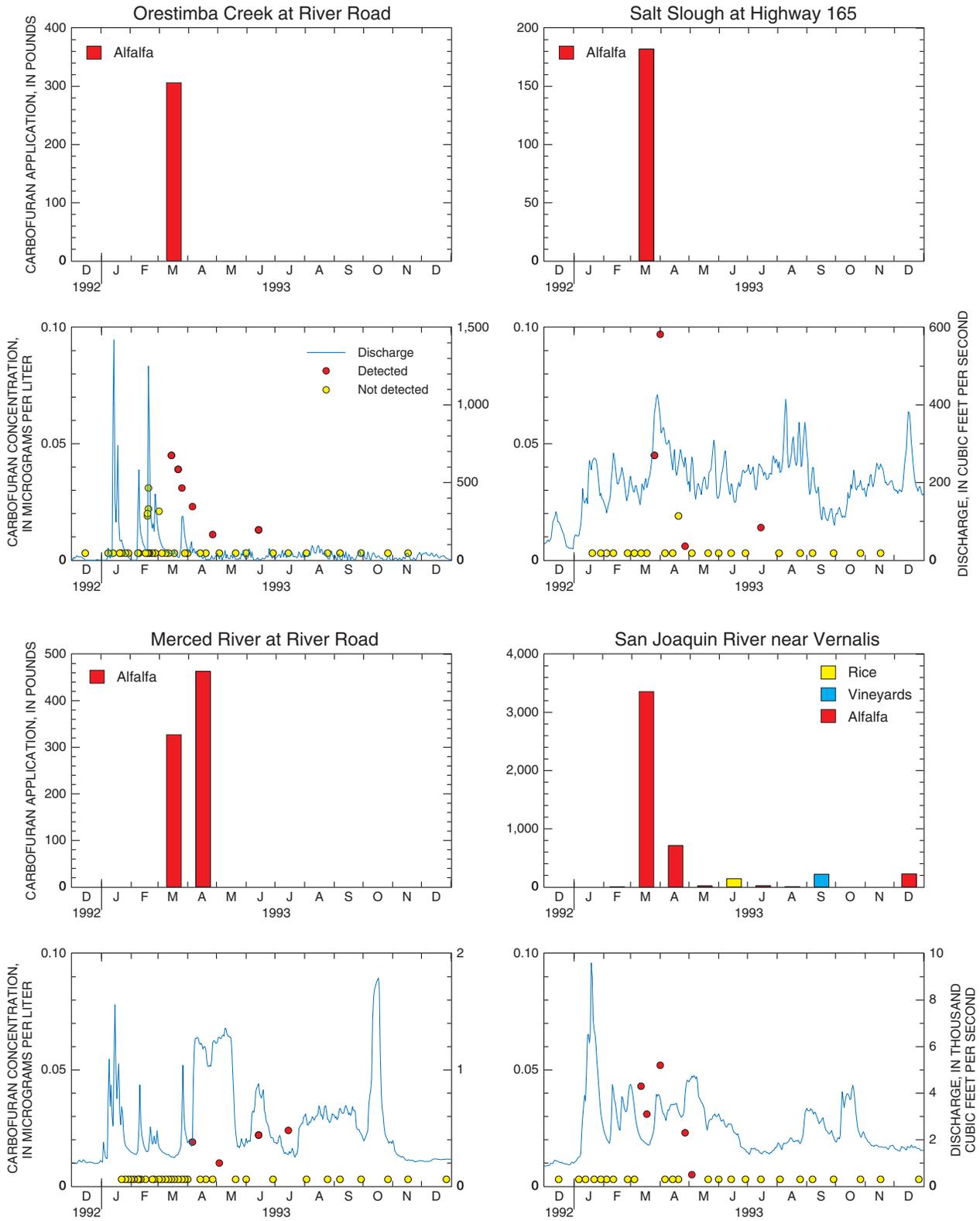
Butylate



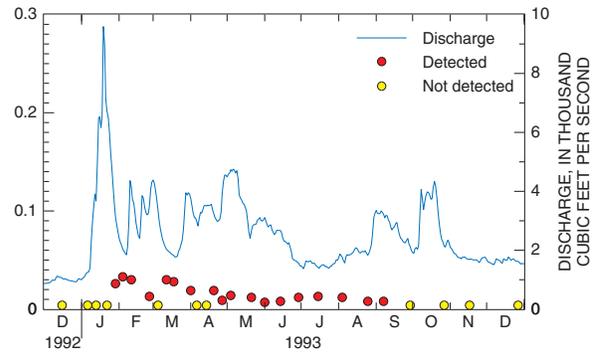
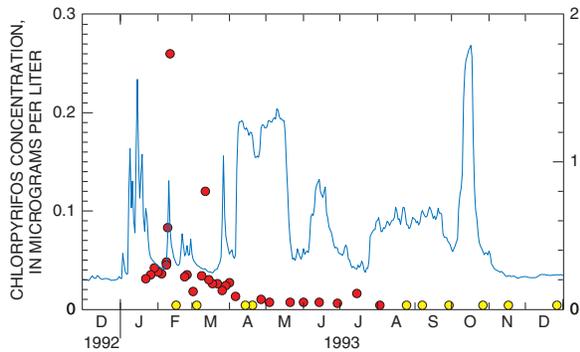
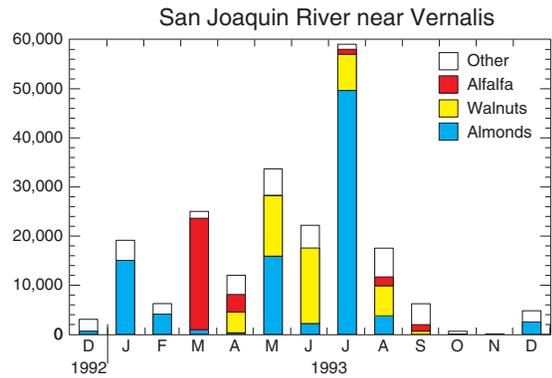
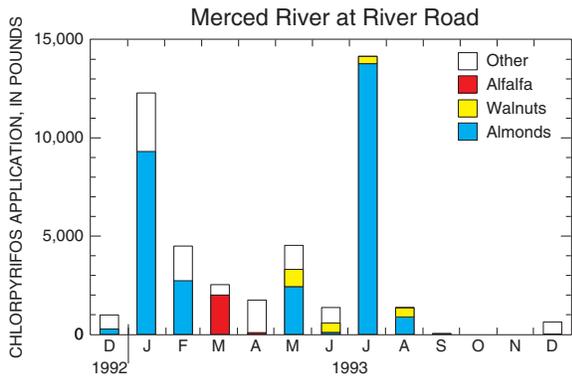
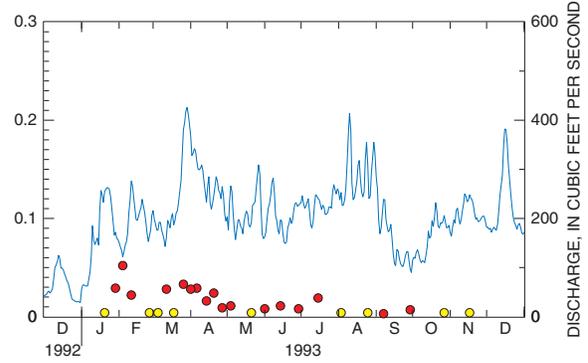
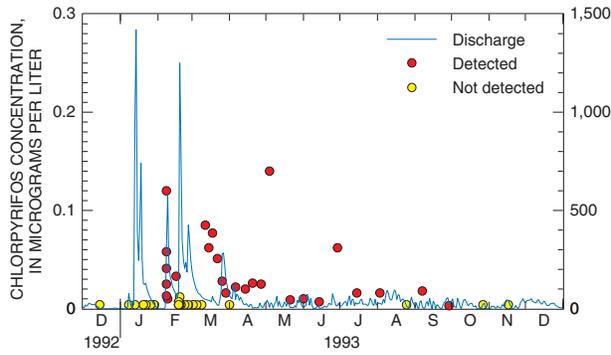
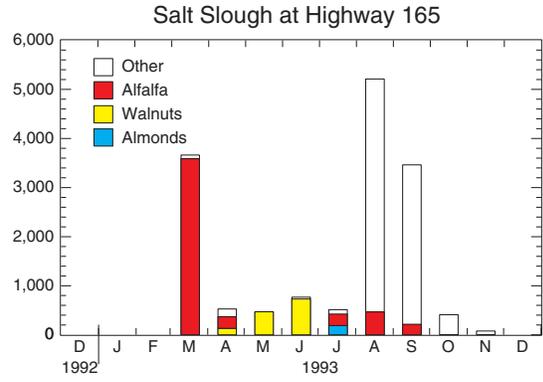
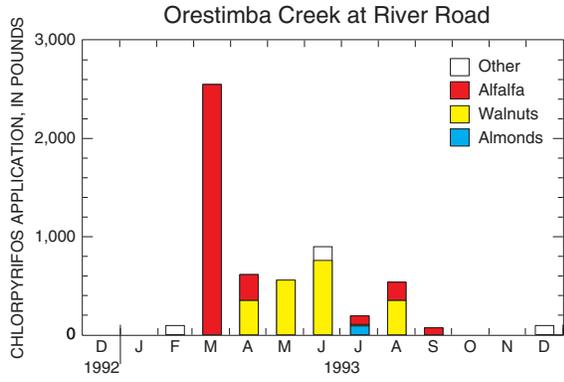
Carbaryl



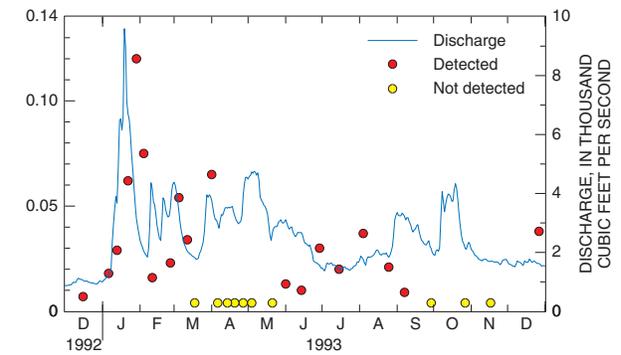
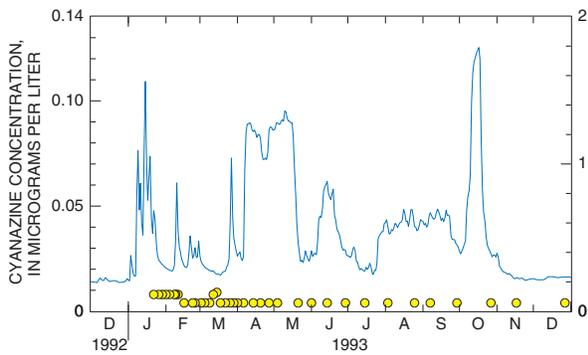
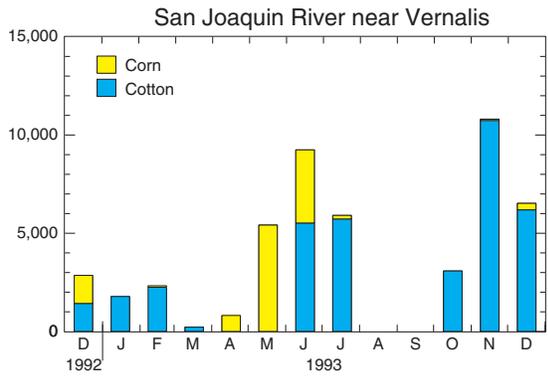
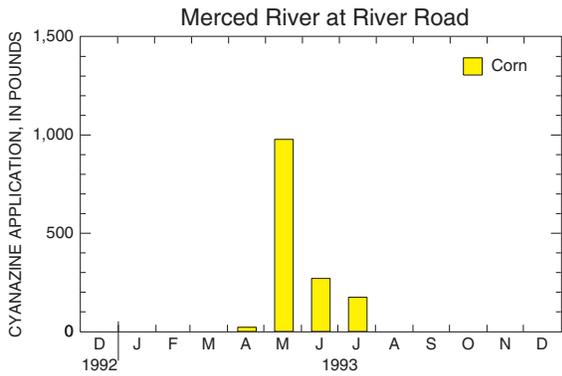
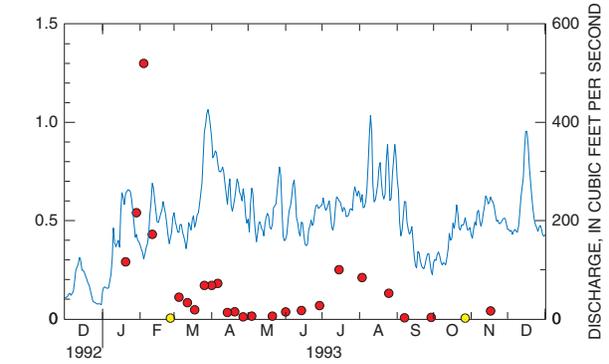
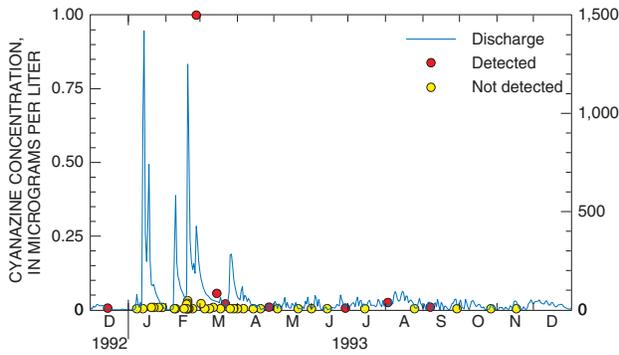
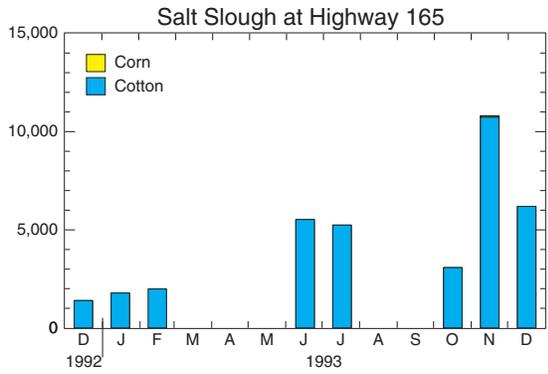
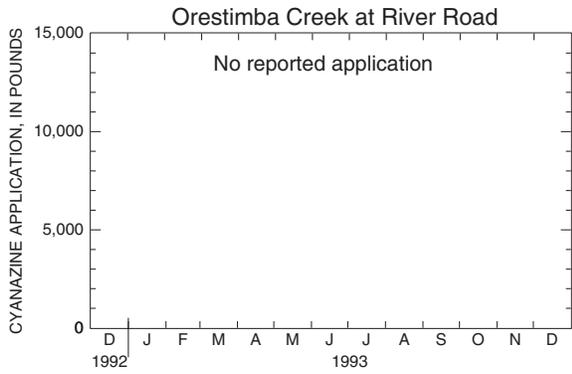
Carbofuran



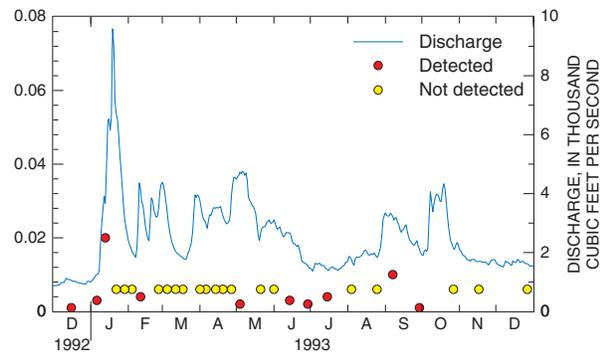
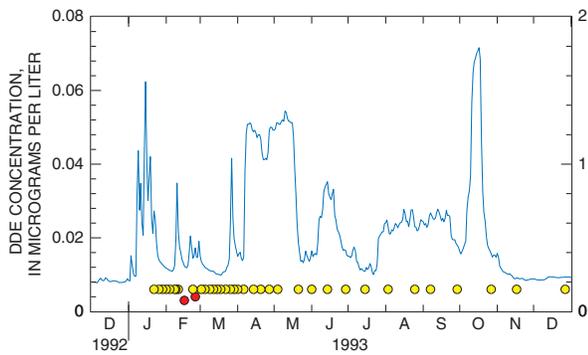
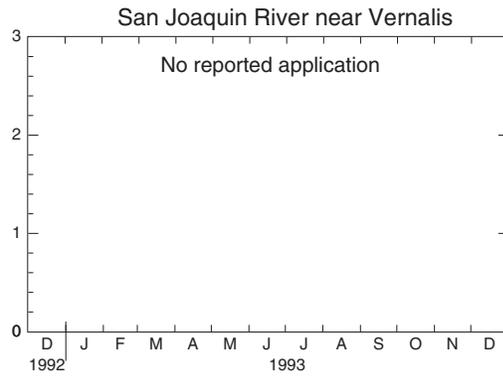
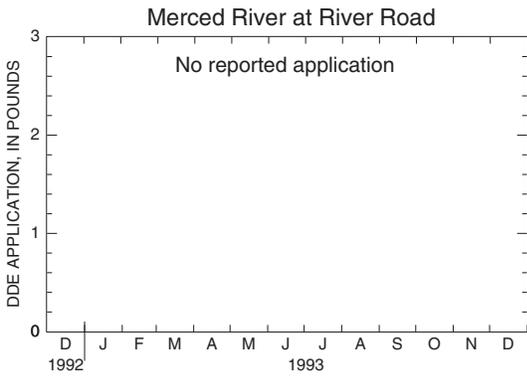
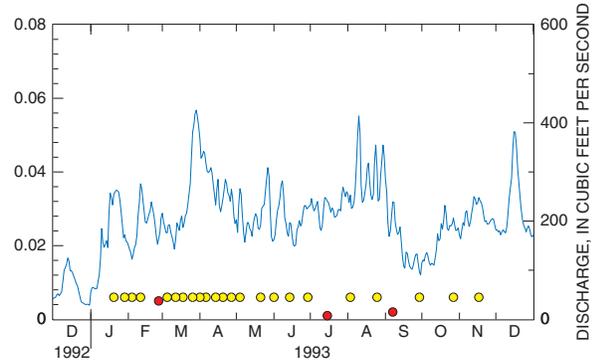
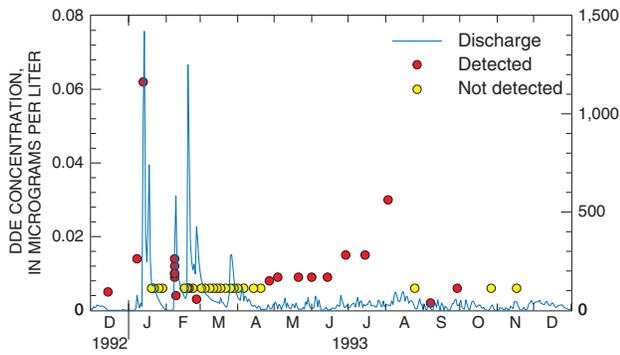
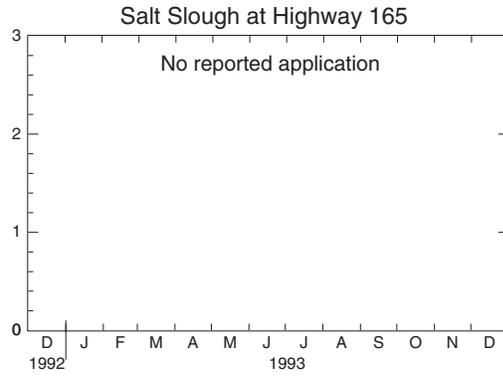
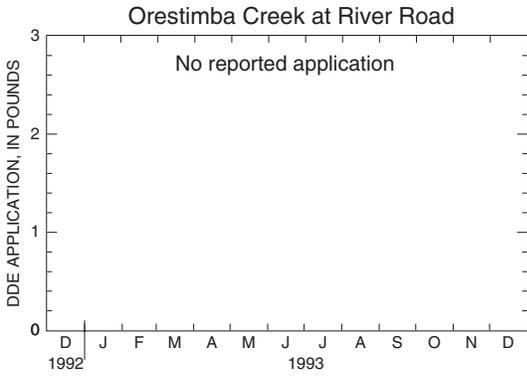
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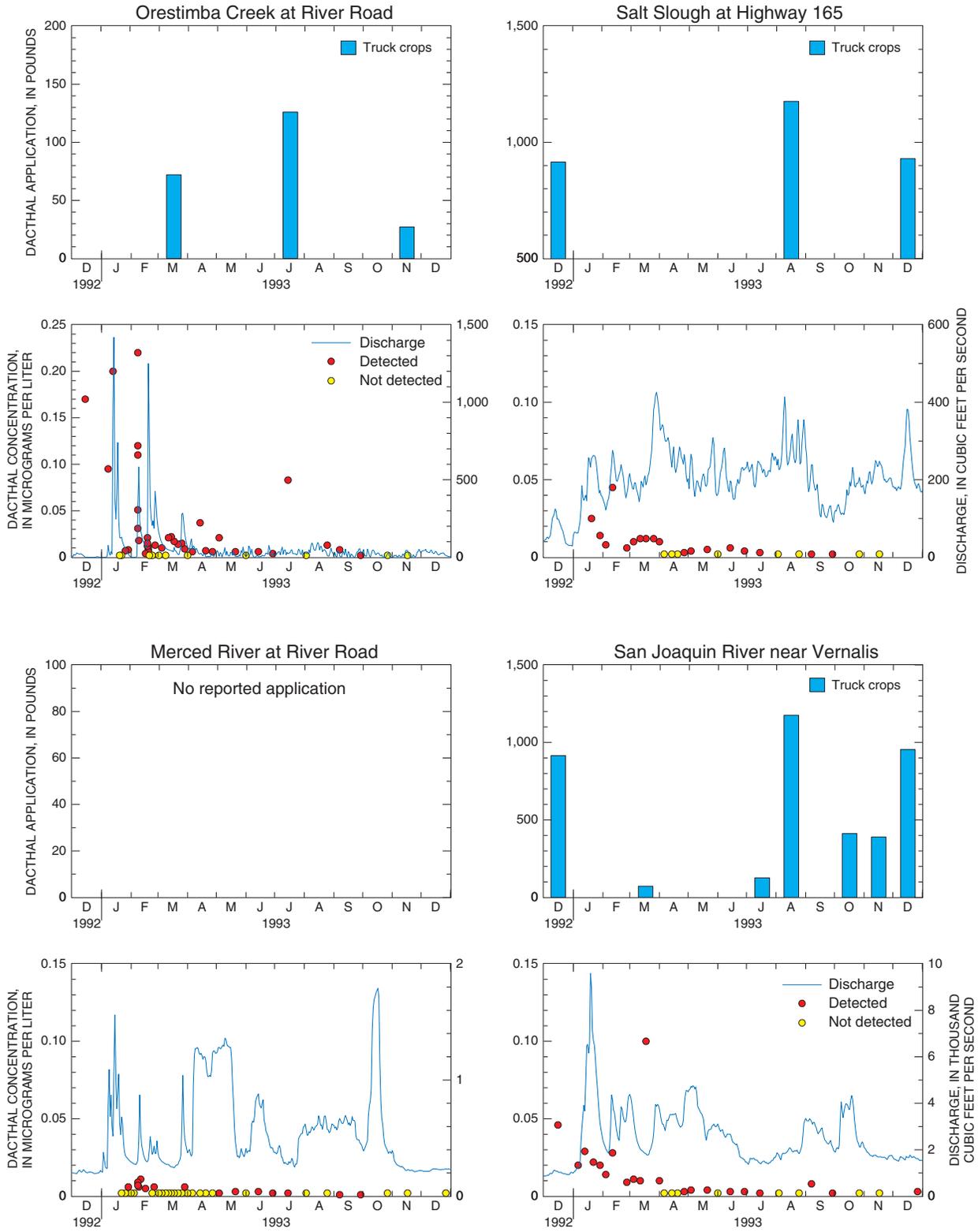
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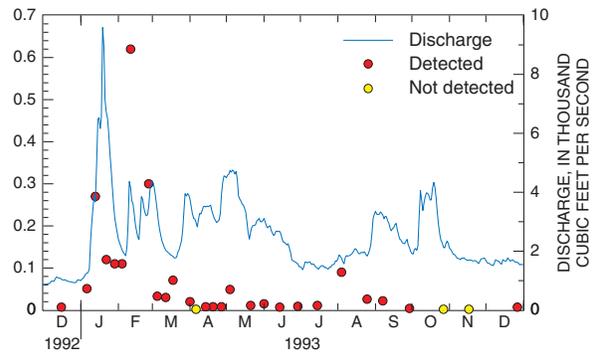
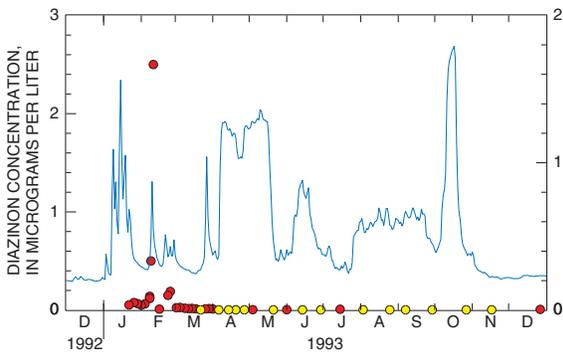
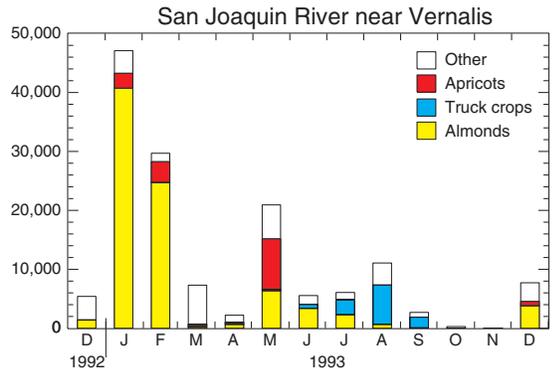
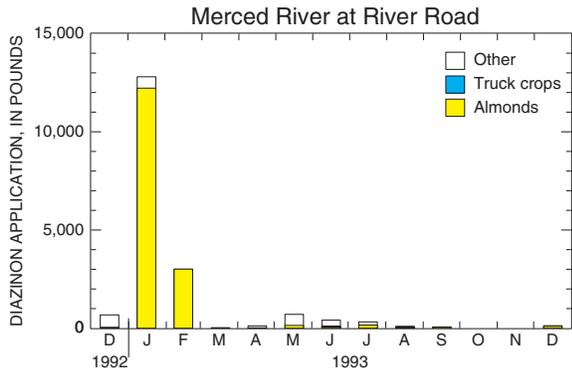
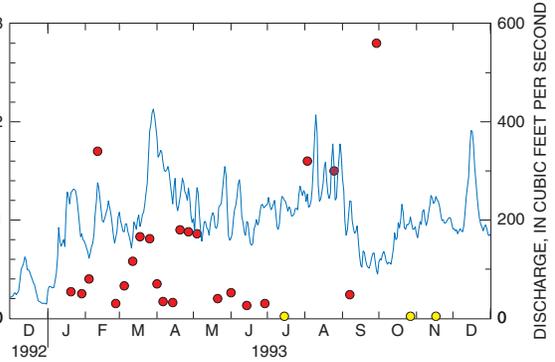
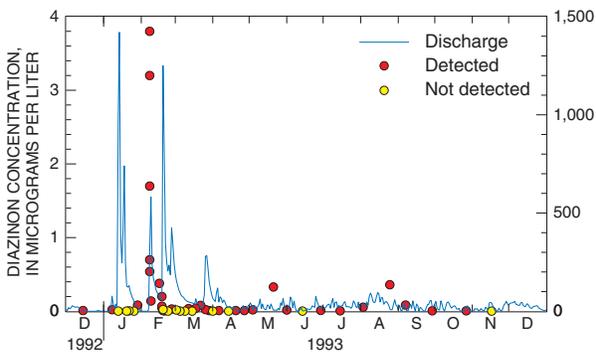
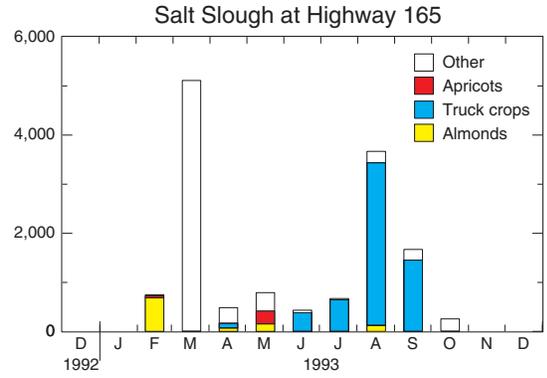
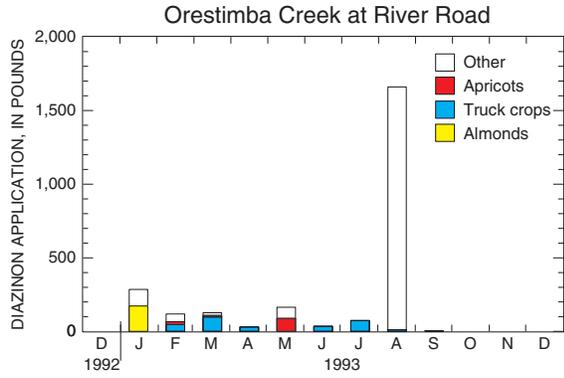
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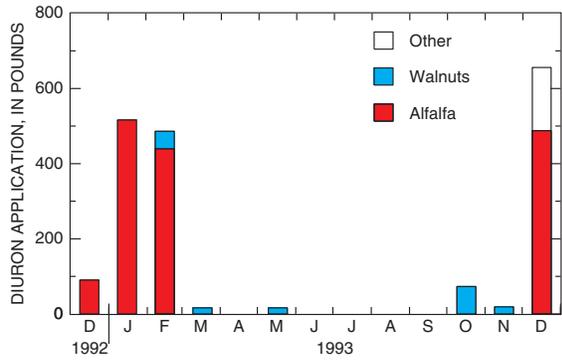


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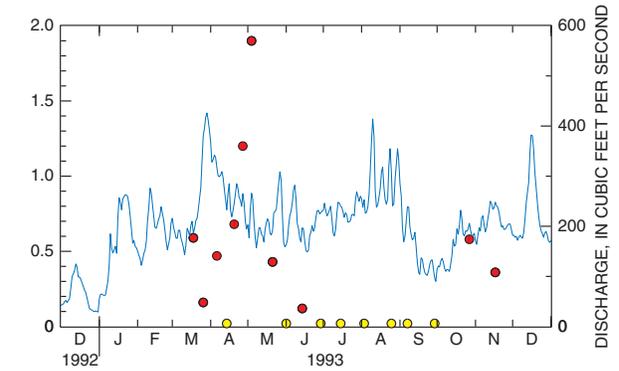
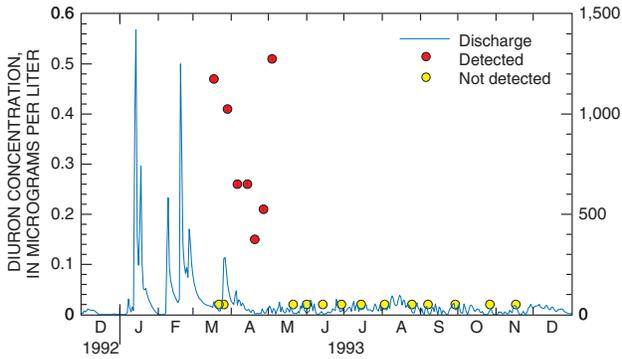
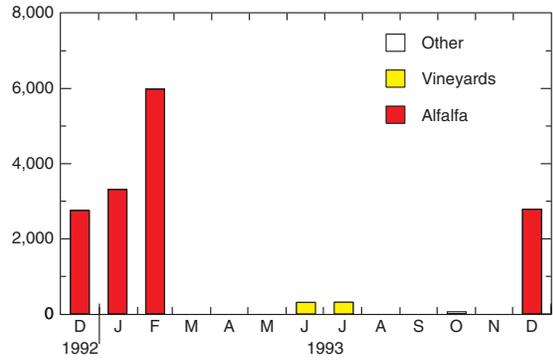


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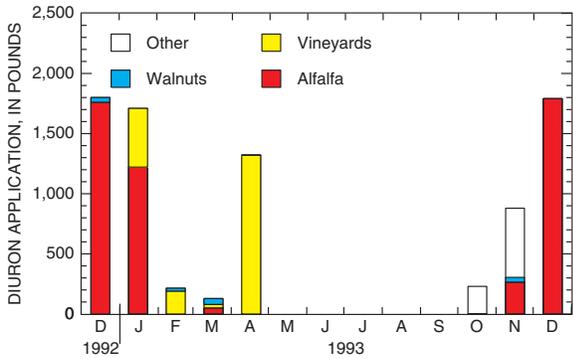
Orestimba Creek at River Road



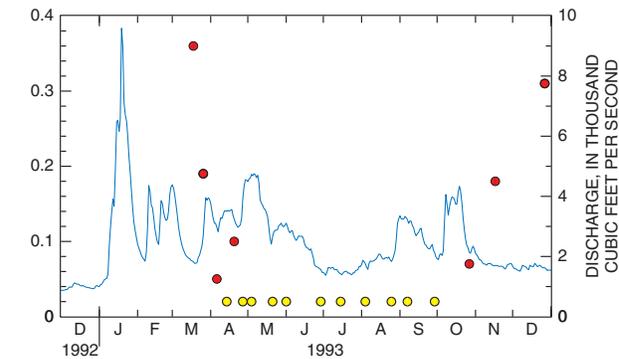
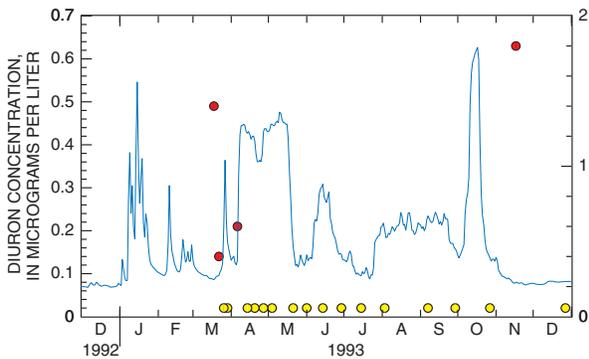
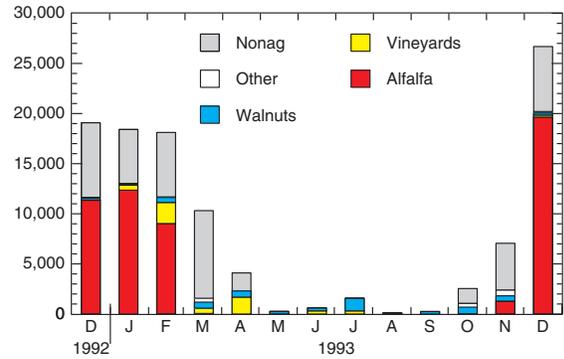
Salt Slough at Highway 165



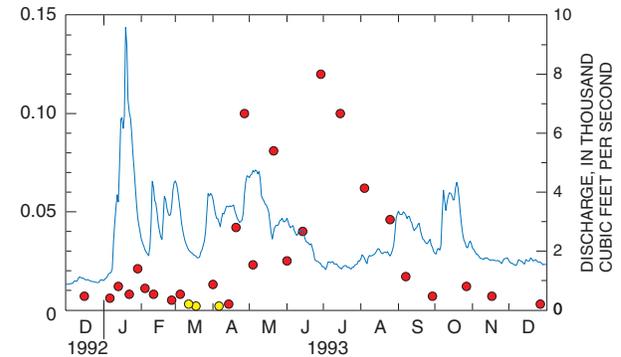
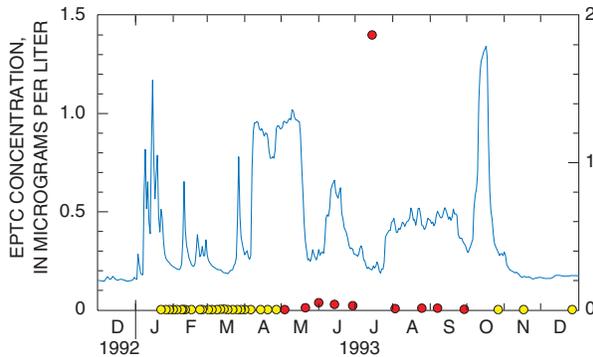
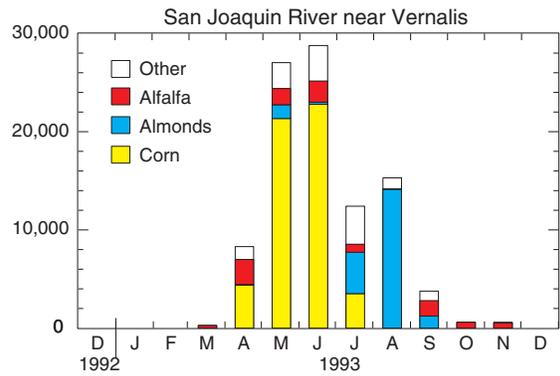
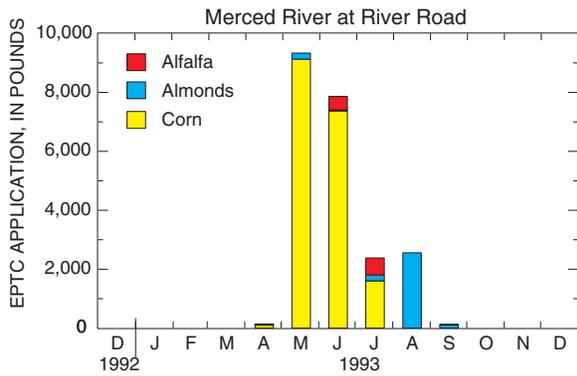
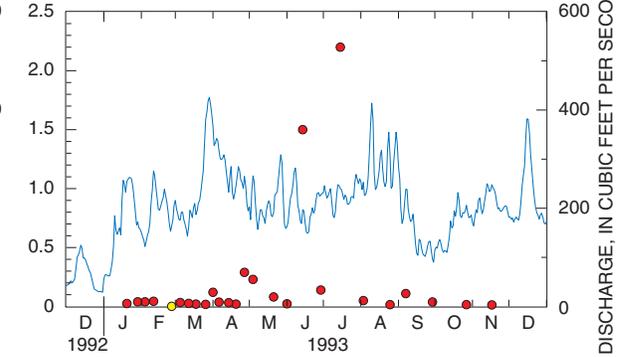
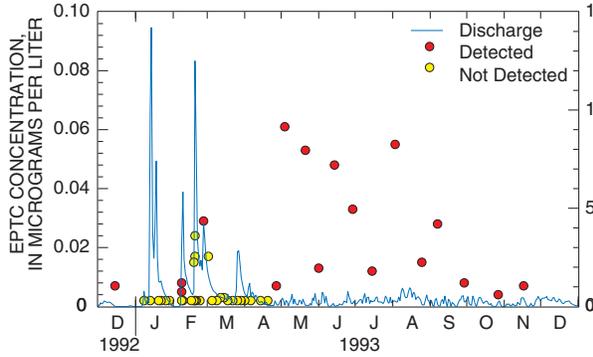
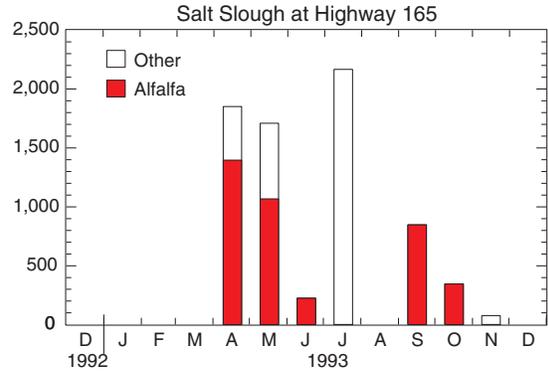
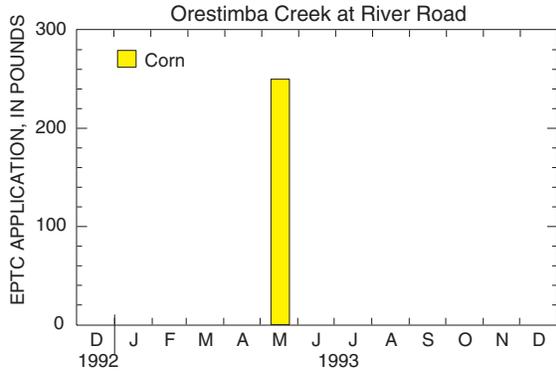
Merced River at River Road



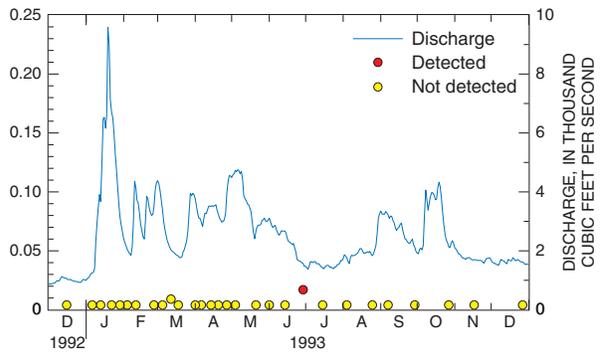
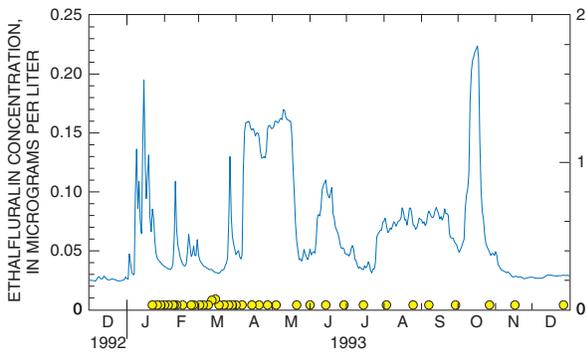
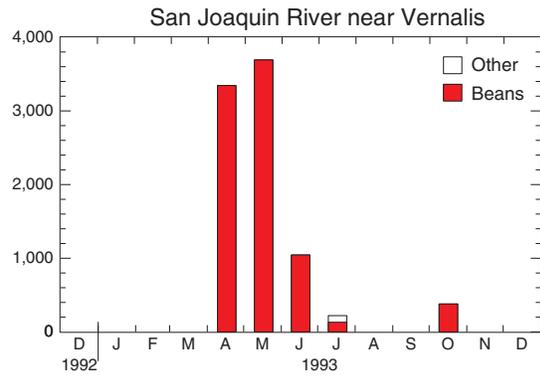
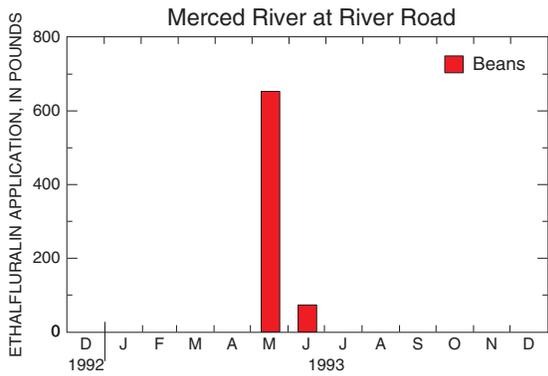
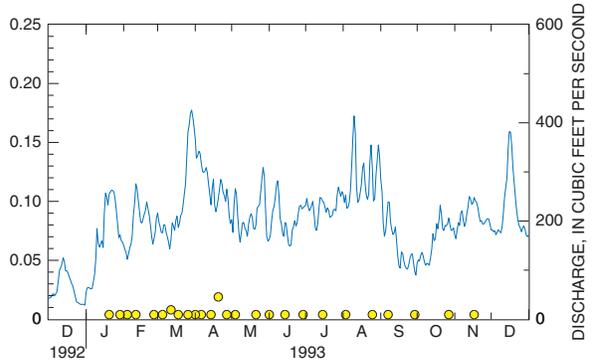
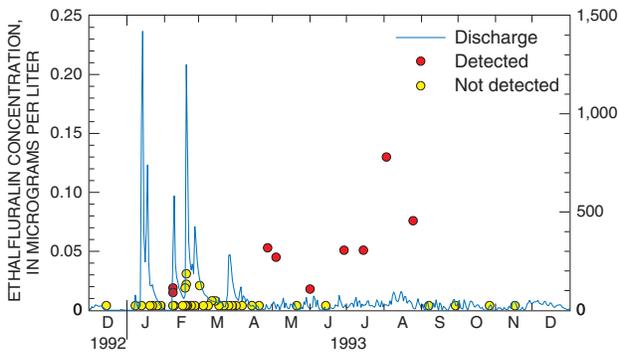
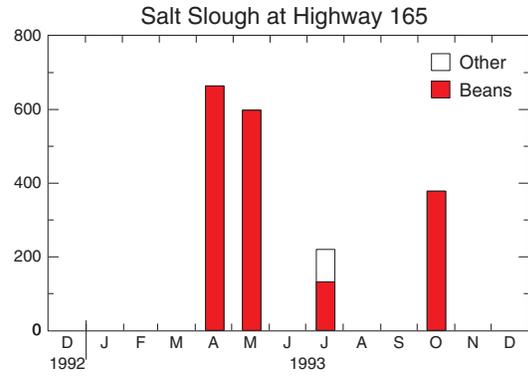
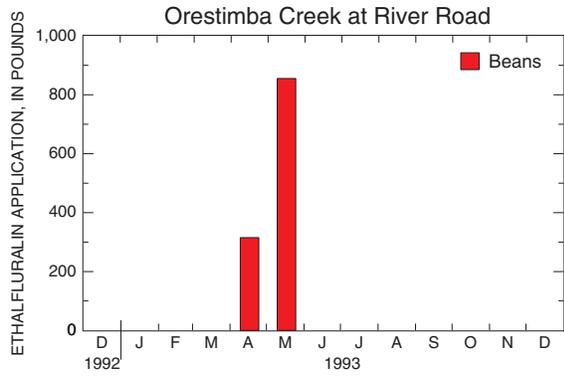
San Joaquin River near Vernalis



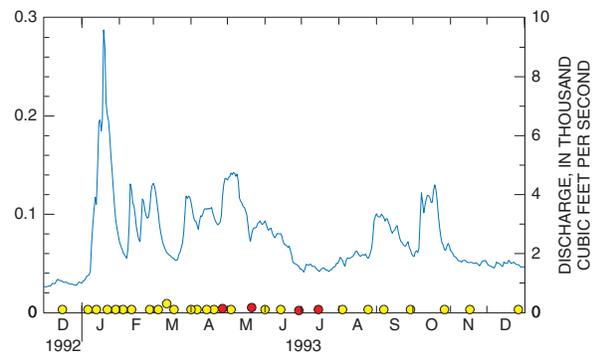
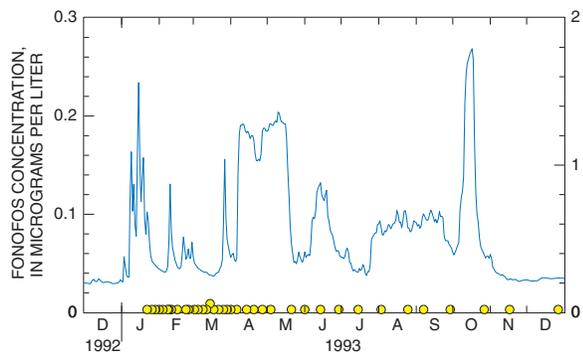
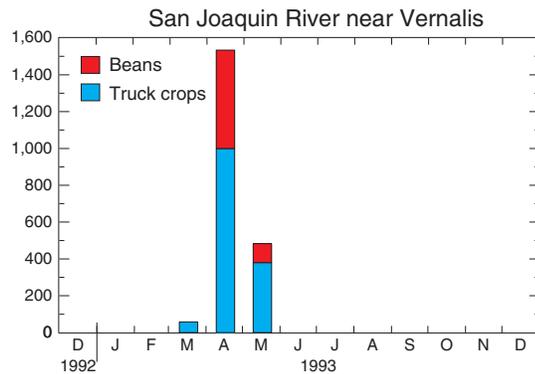
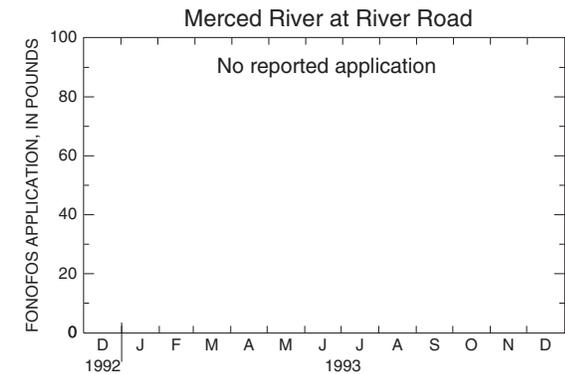
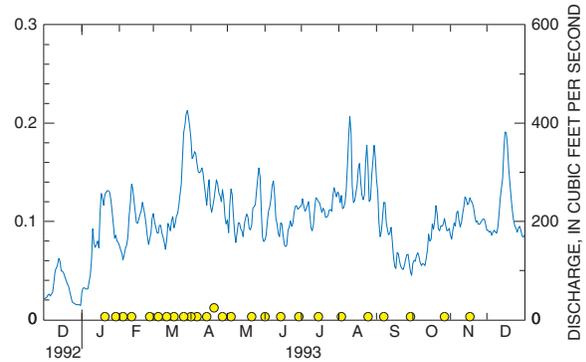
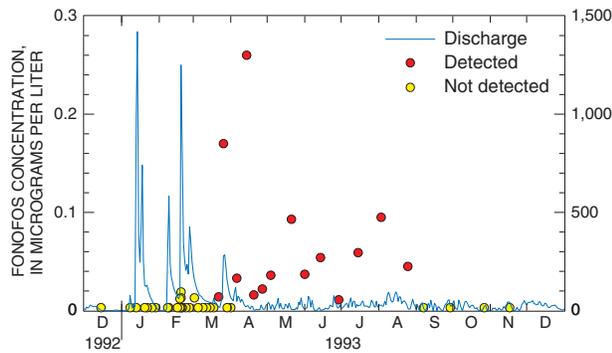
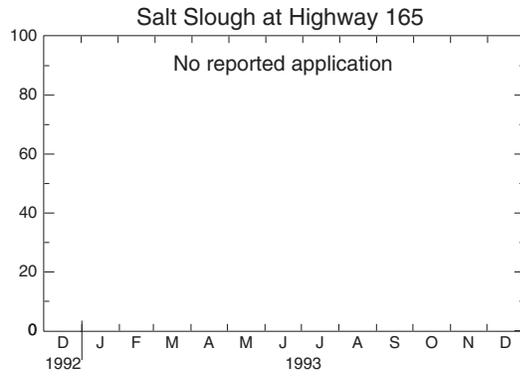
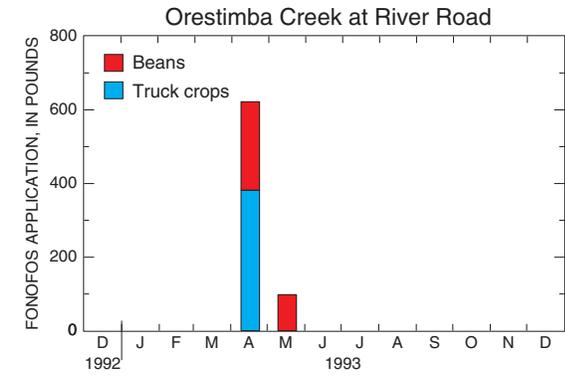
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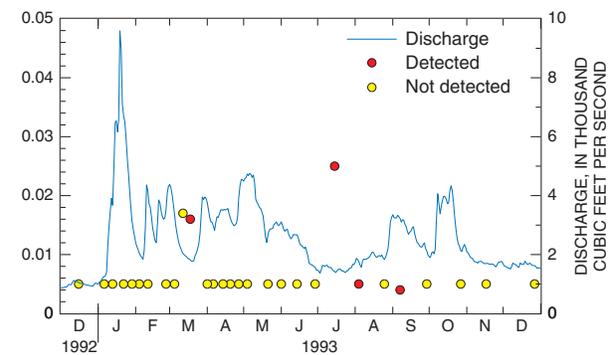
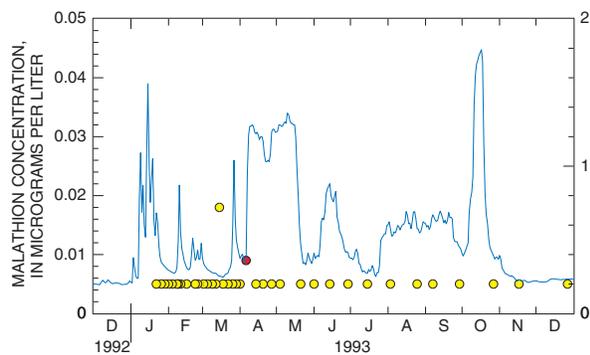
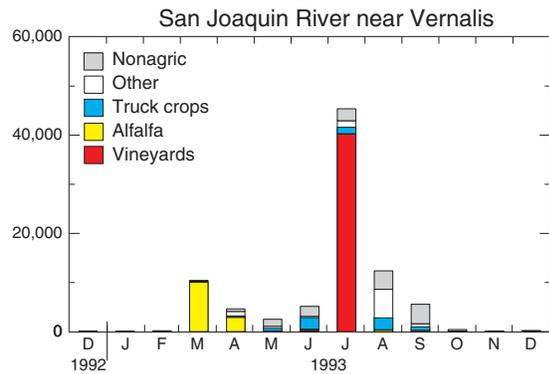
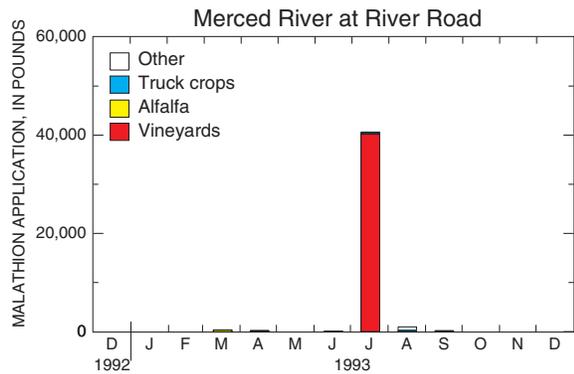
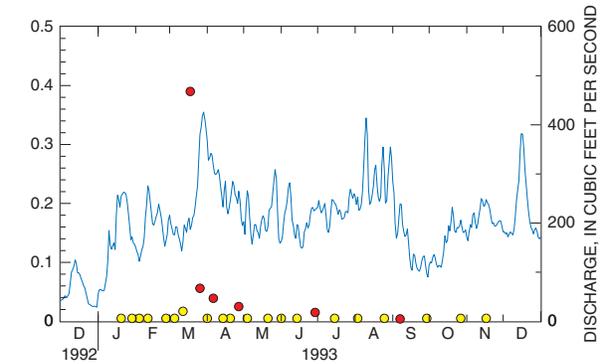
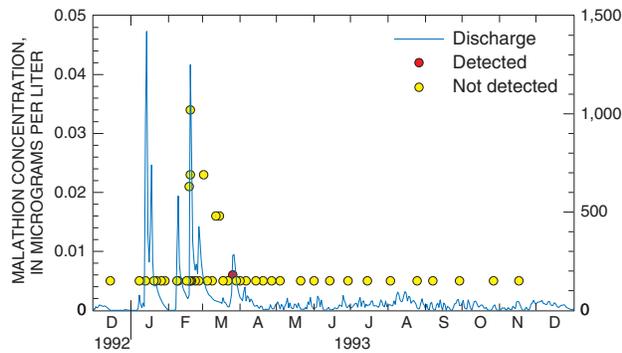
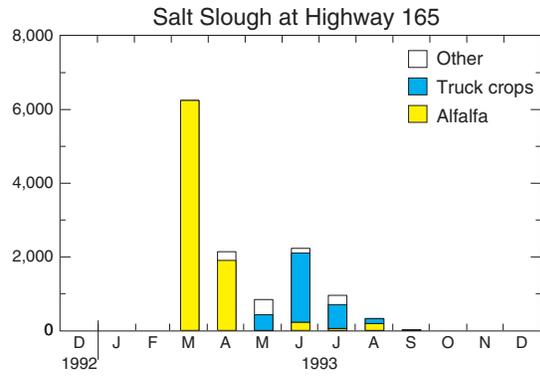
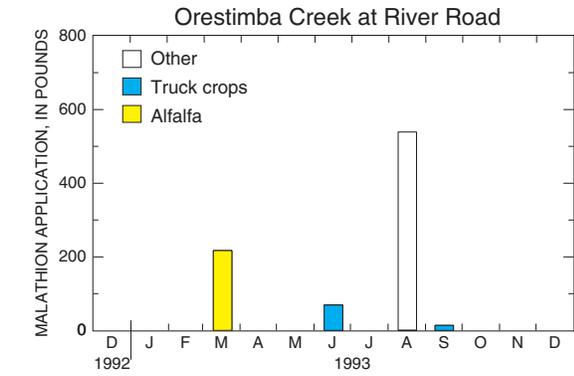
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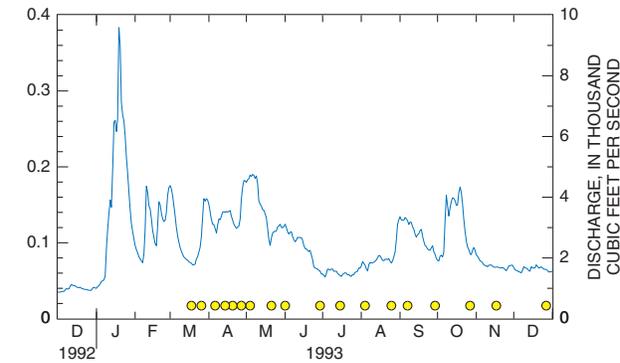
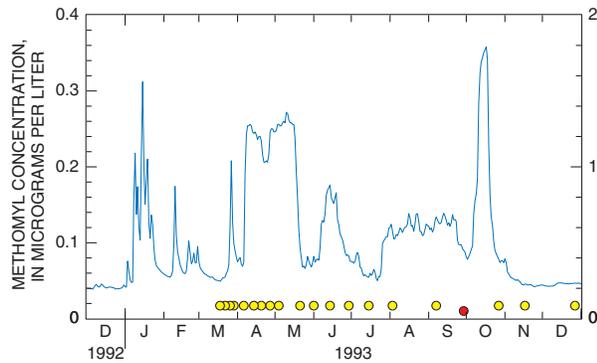
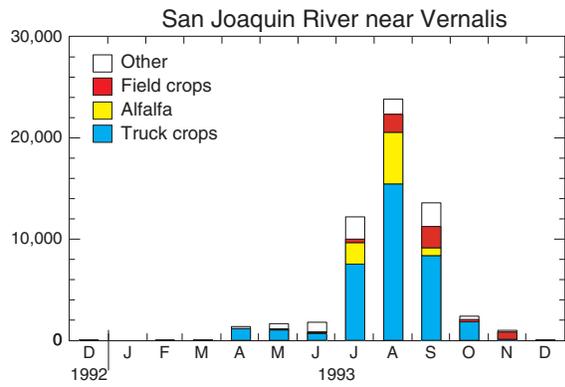
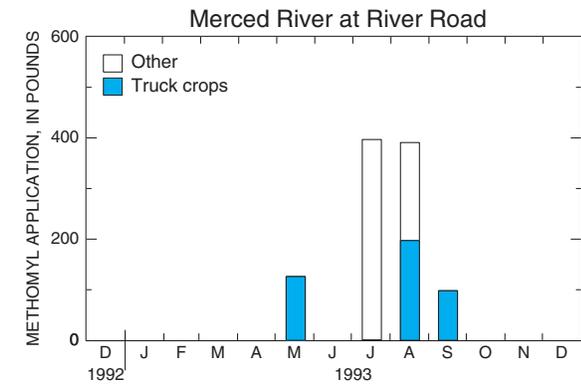
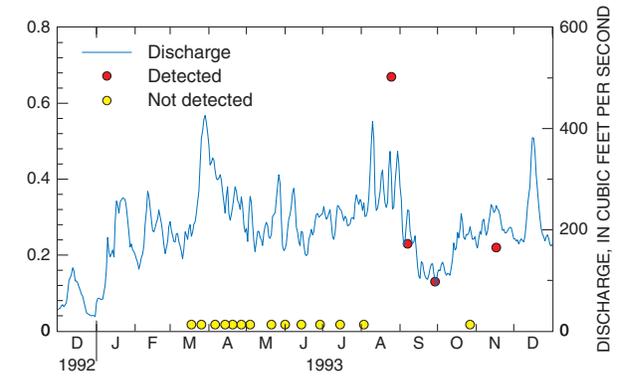
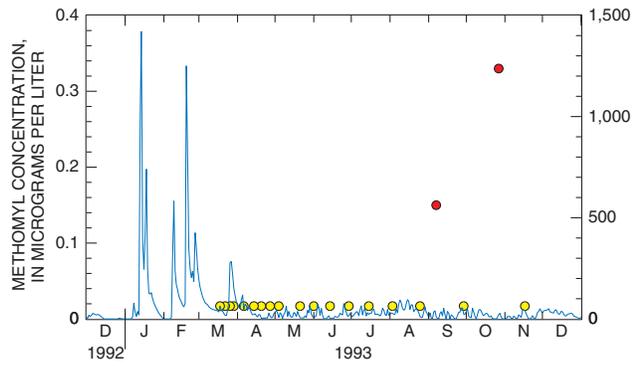
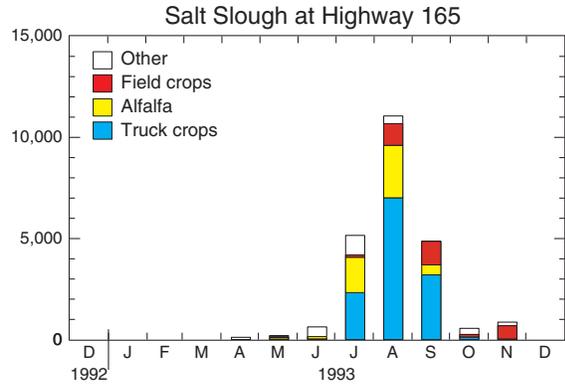
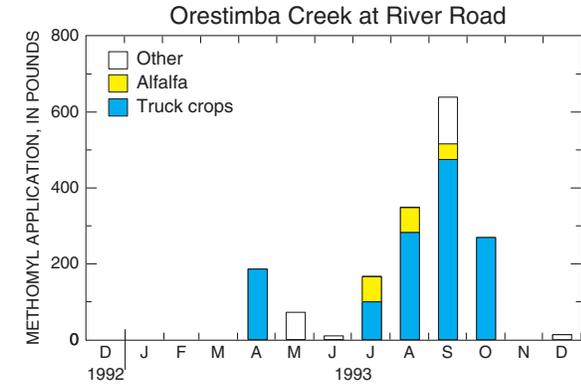
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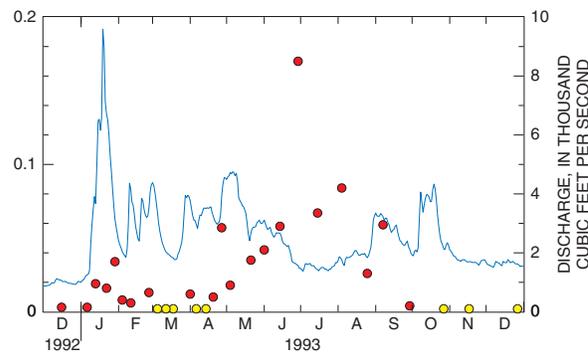
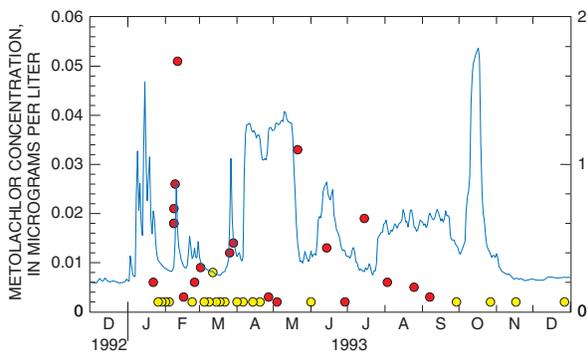
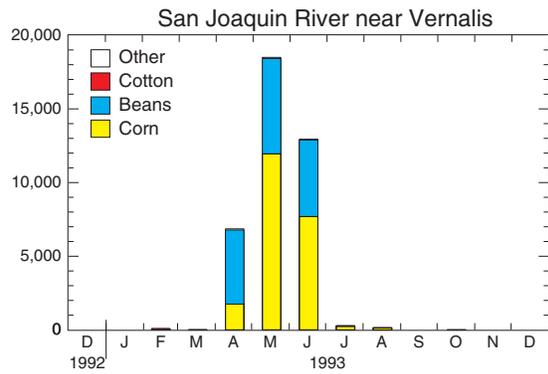
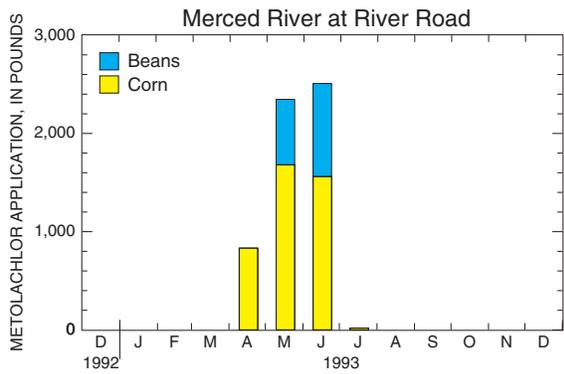
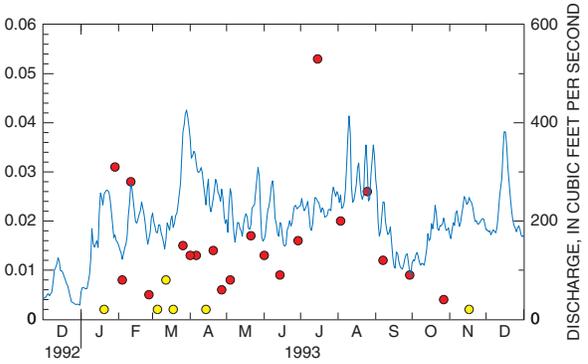
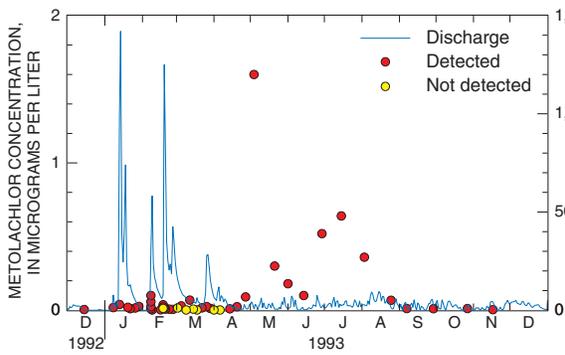
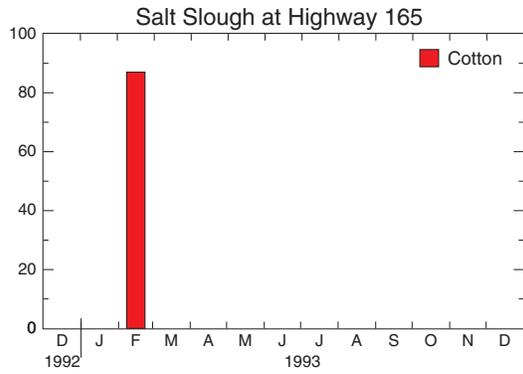
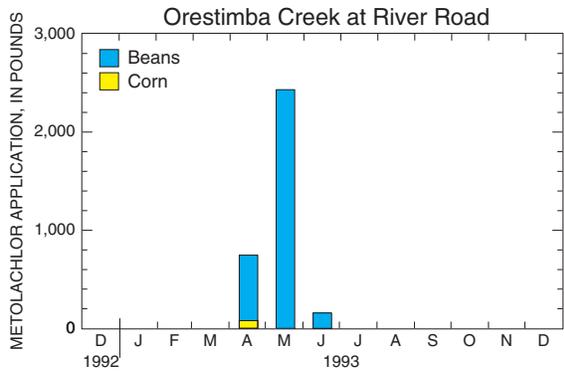
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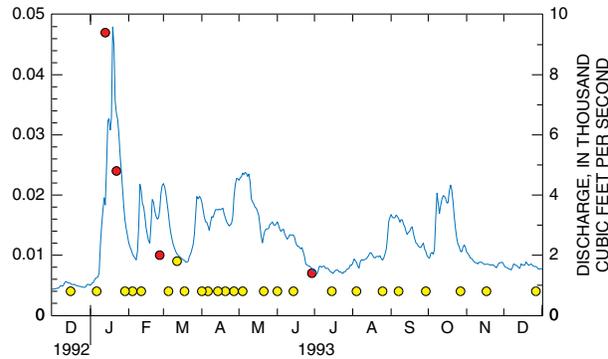
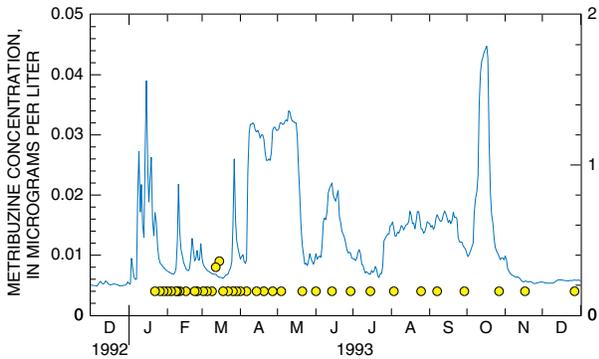
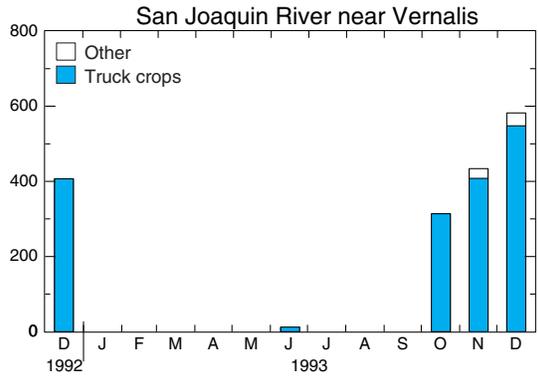
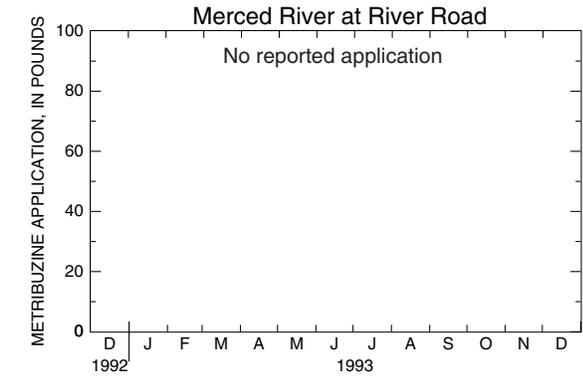
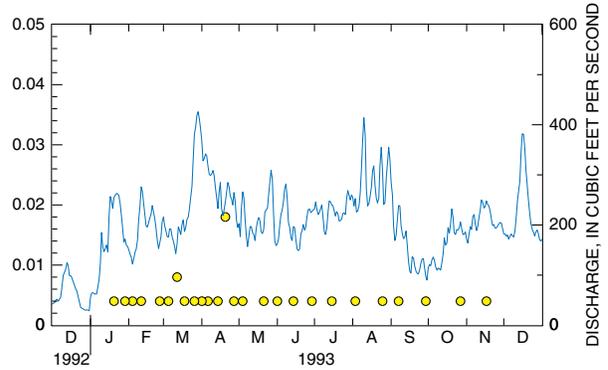
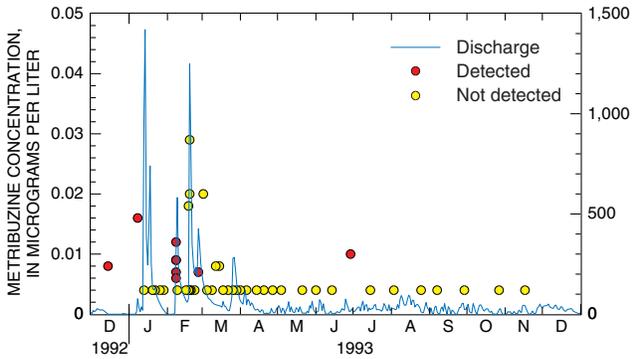
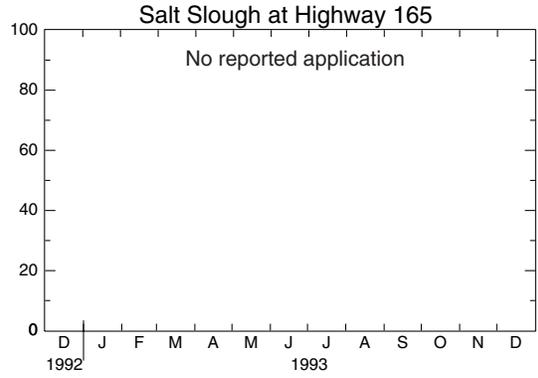
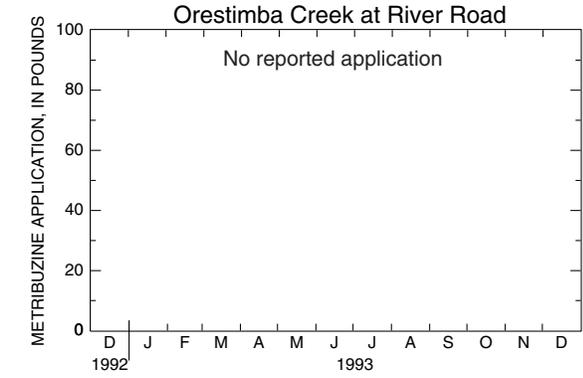
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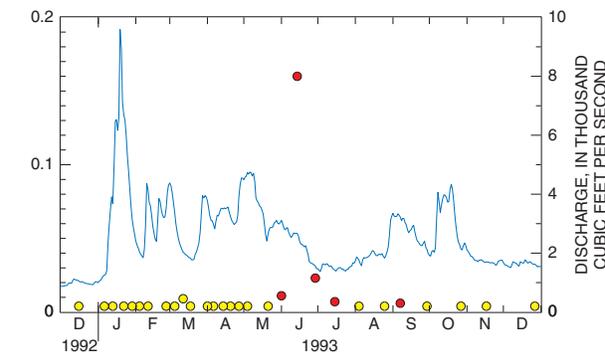
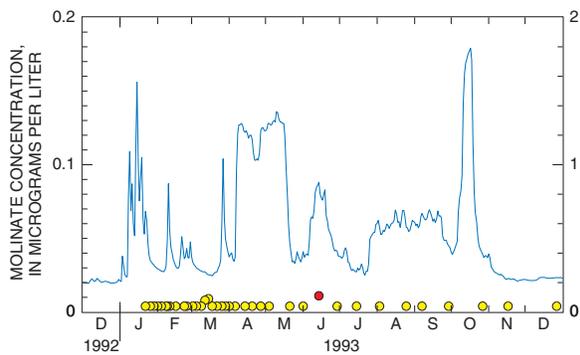
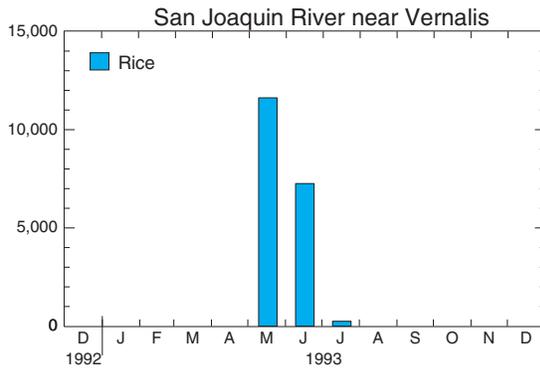
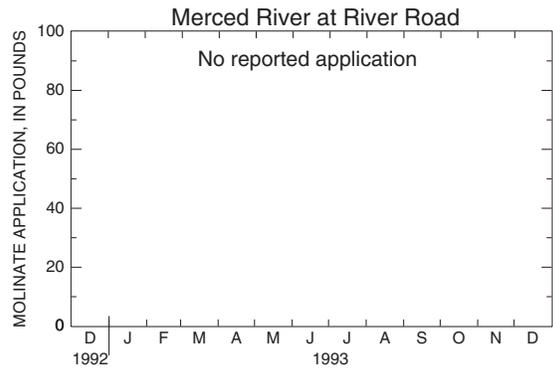
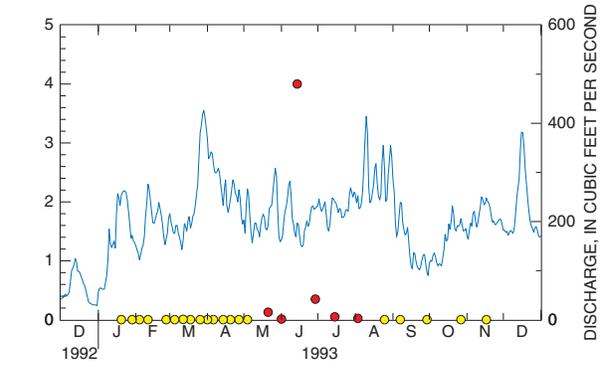
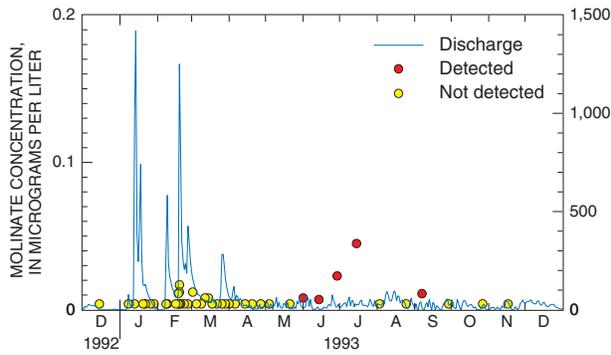
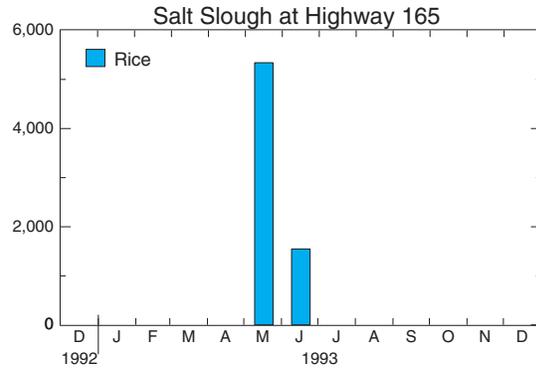
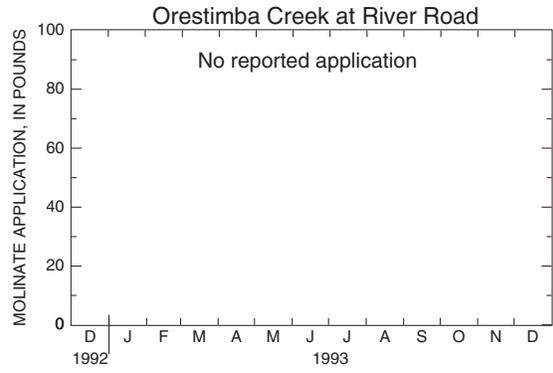
Metolachlor



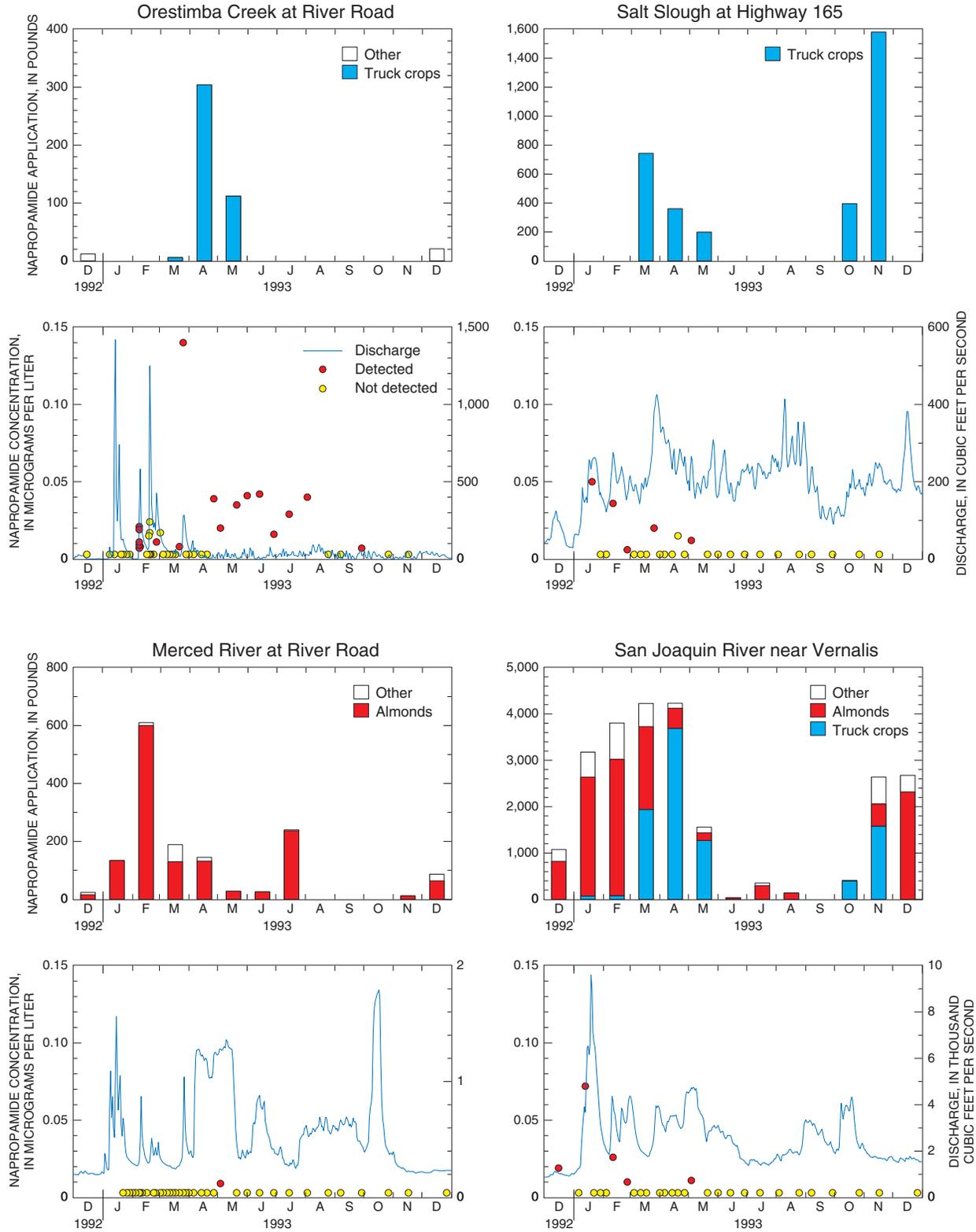
Metribuzin



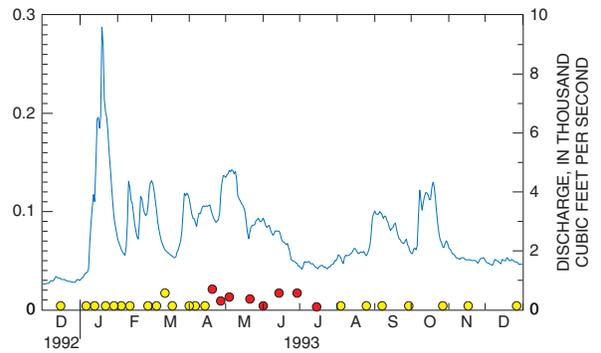
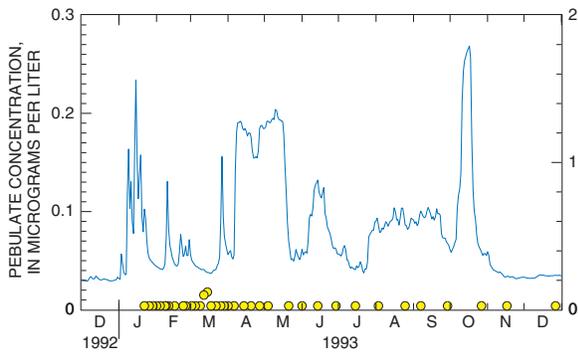
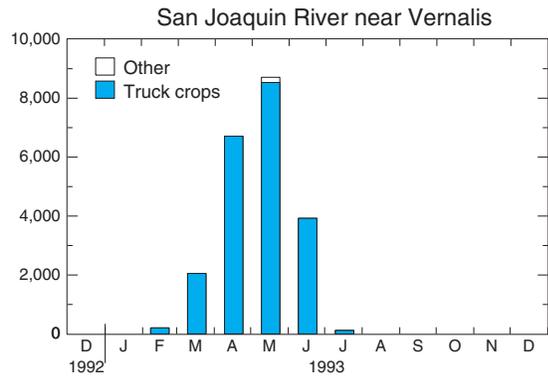
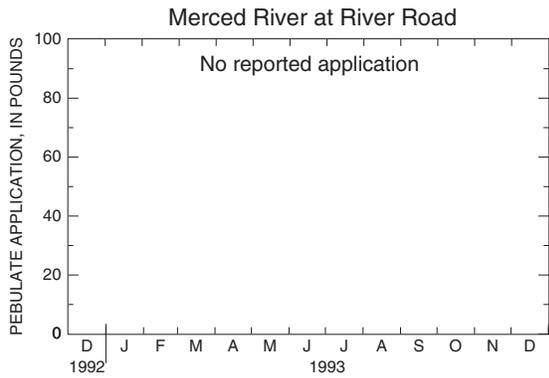
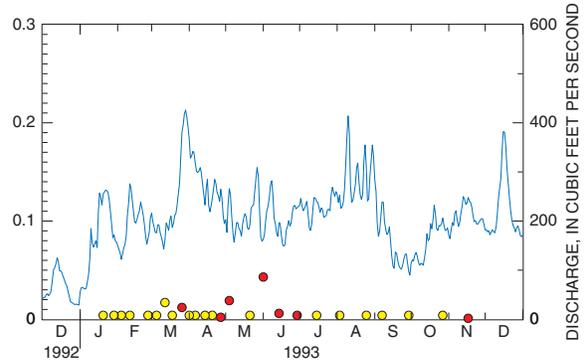
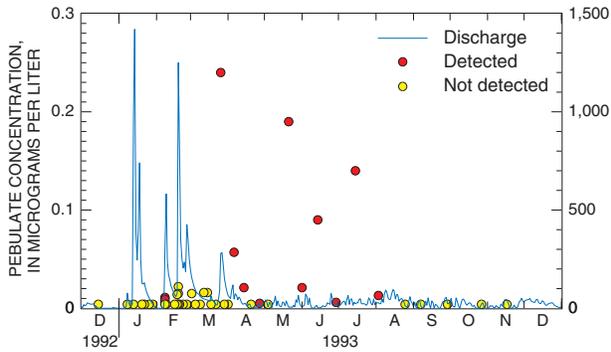
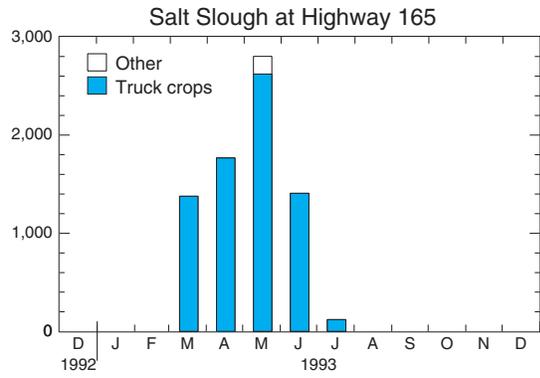
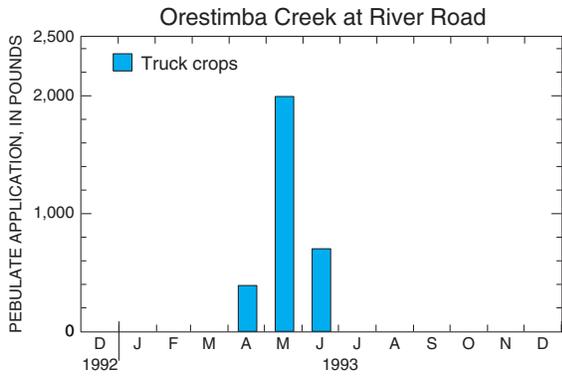
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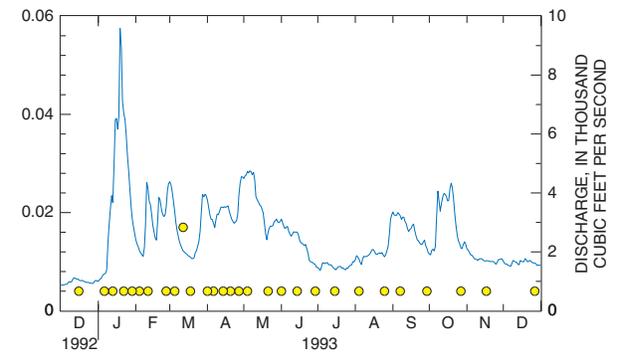
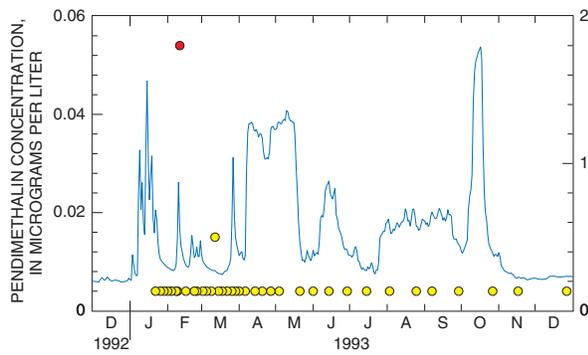
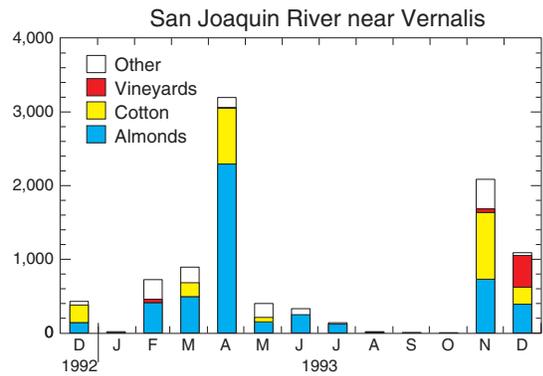
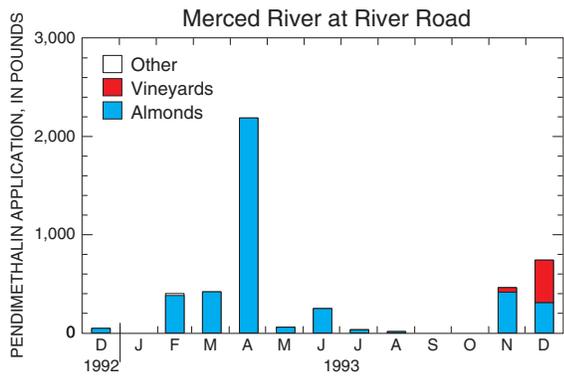
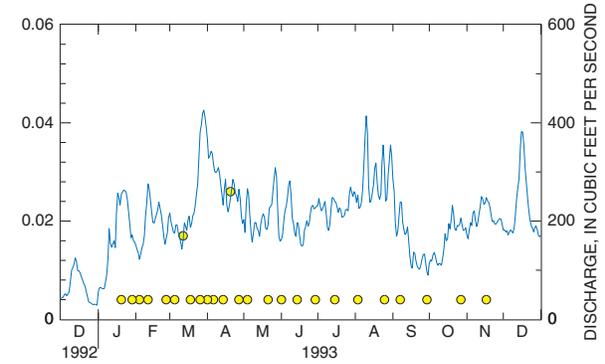
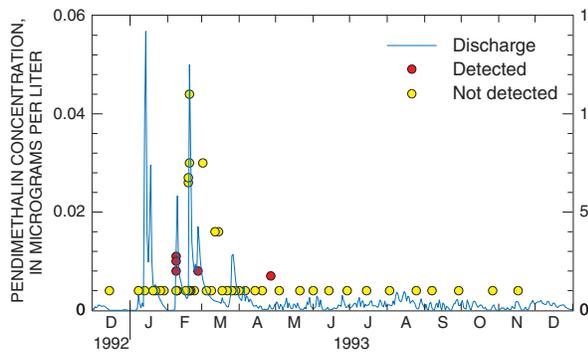
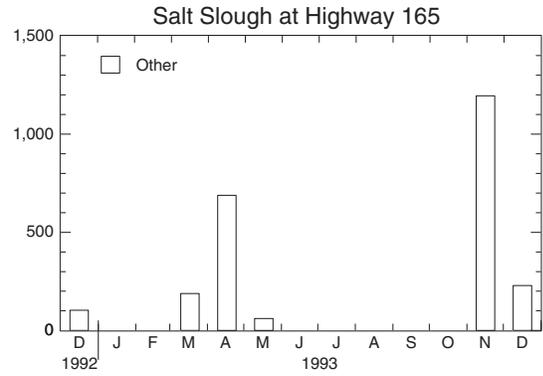
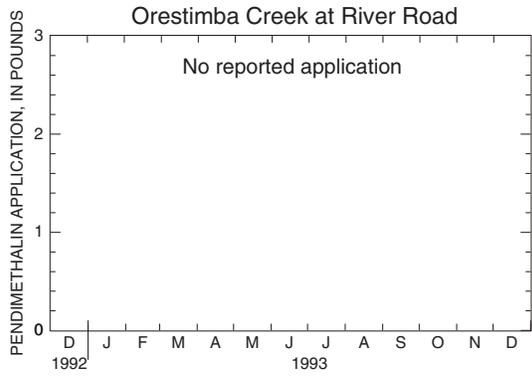
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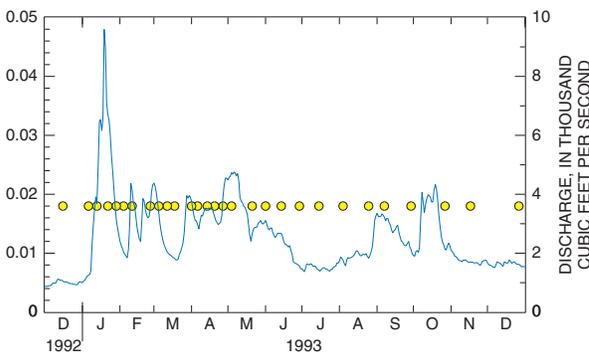
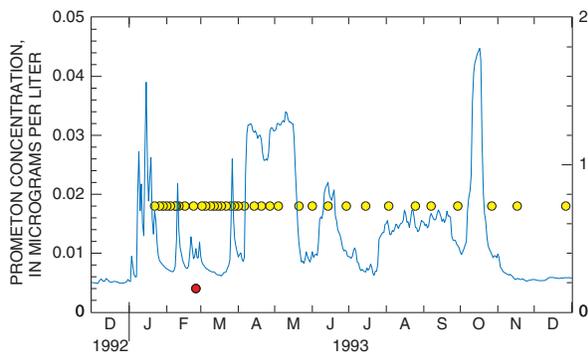
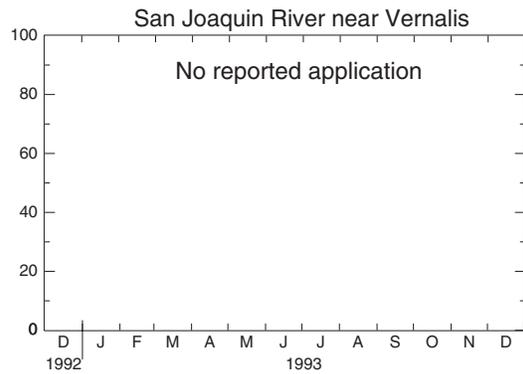
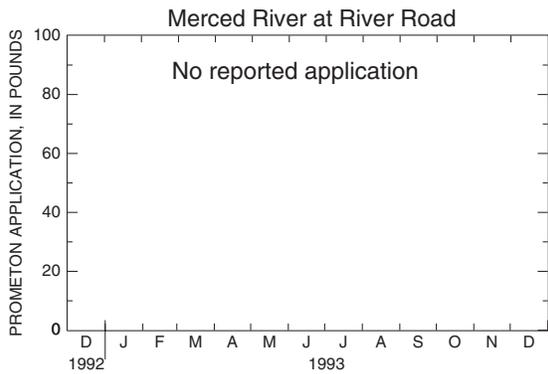
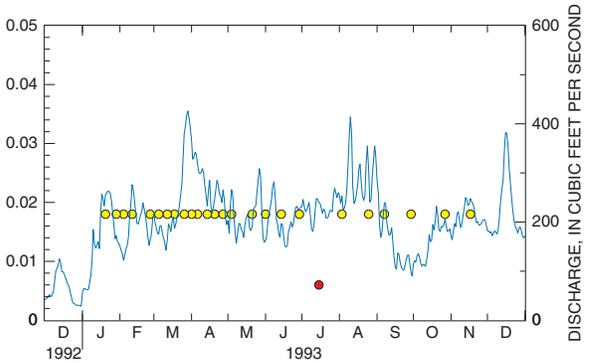
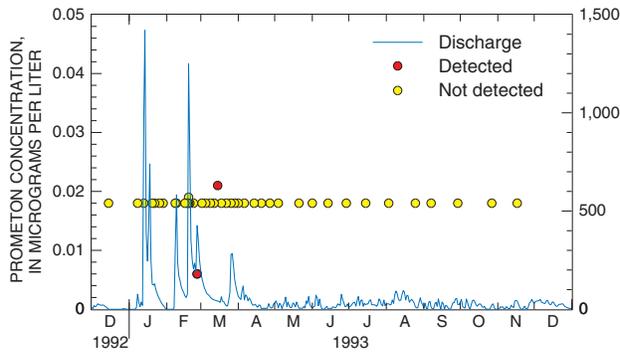
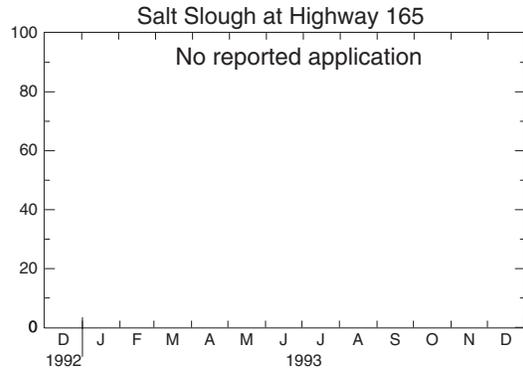
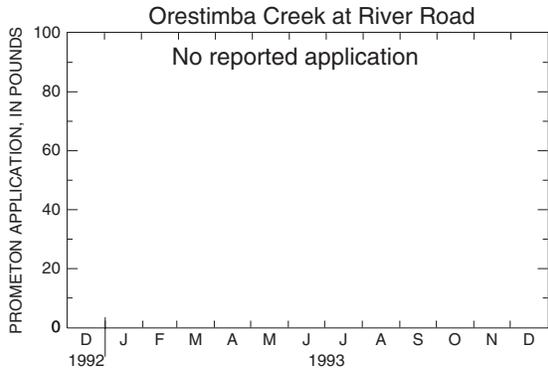
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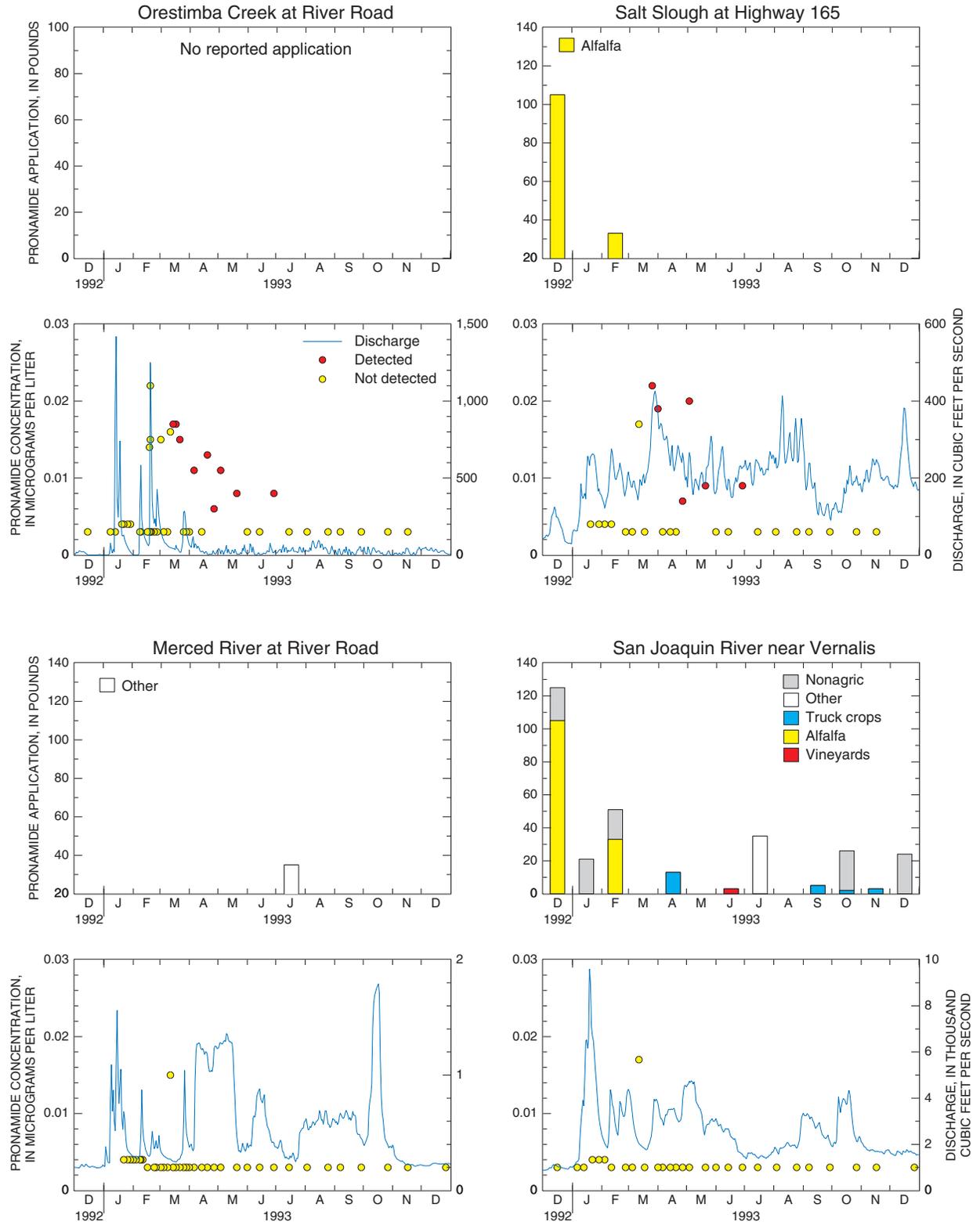
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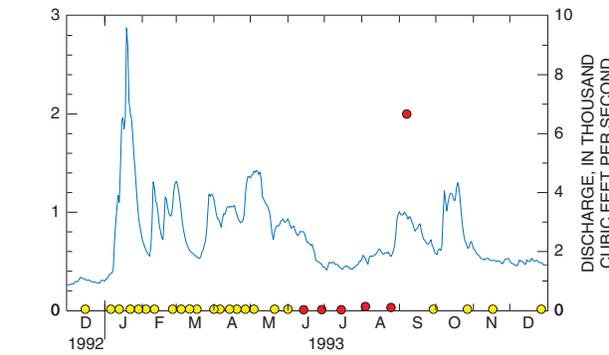
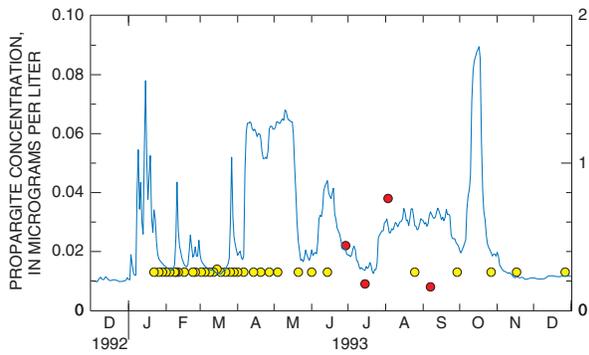
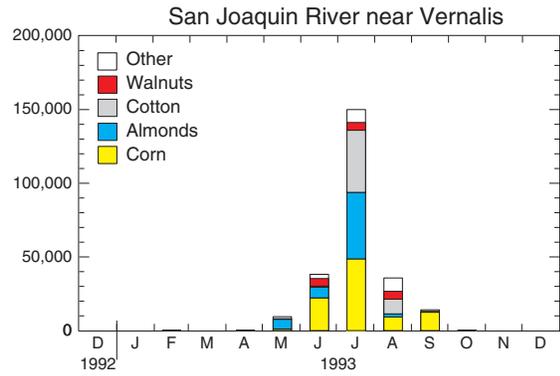
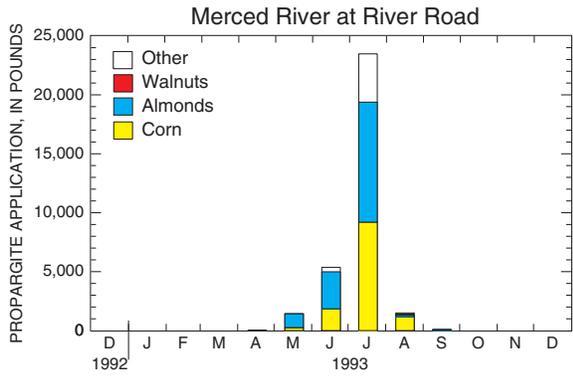
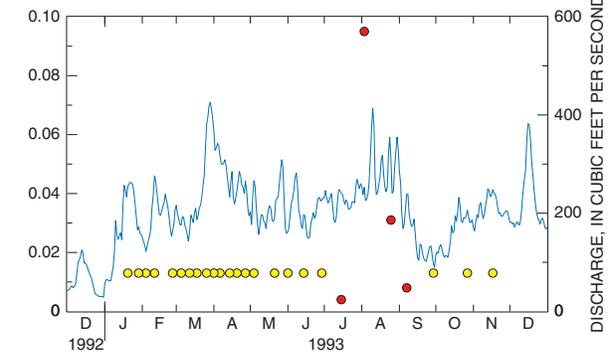
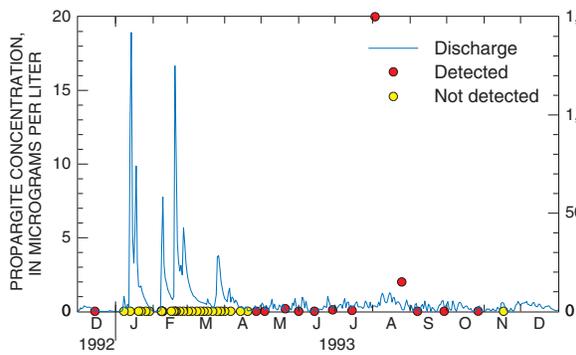
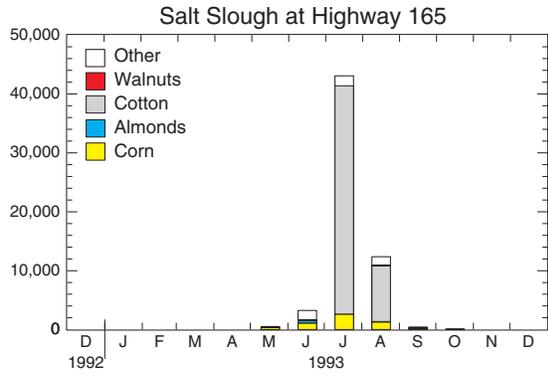
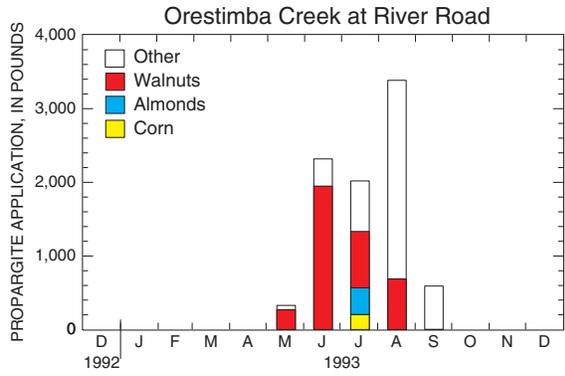
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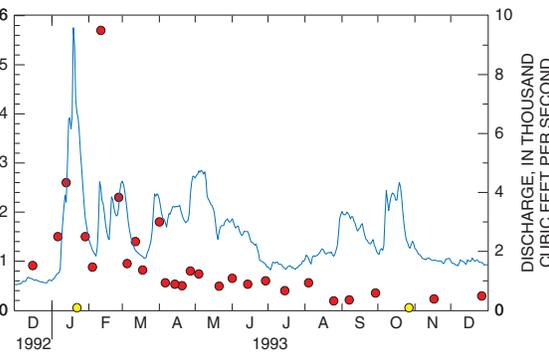
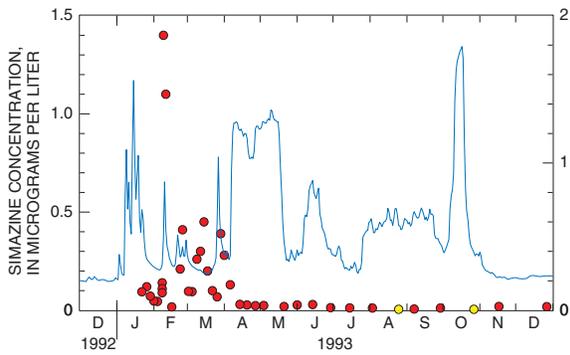
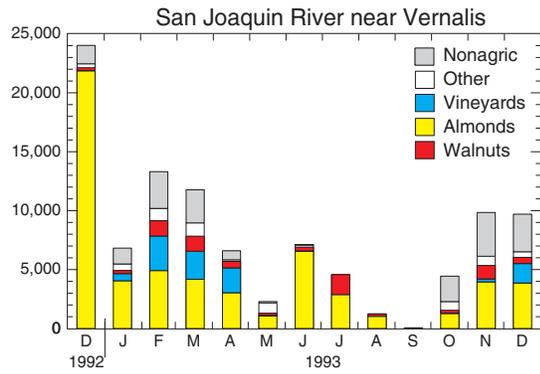
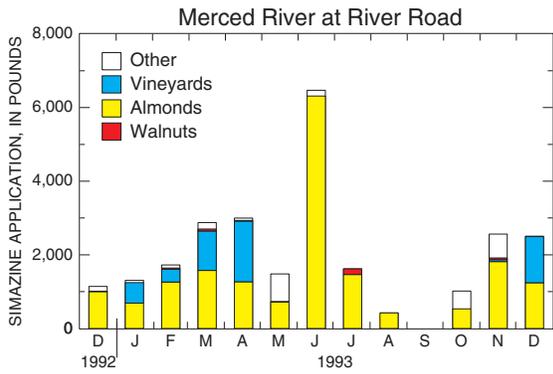
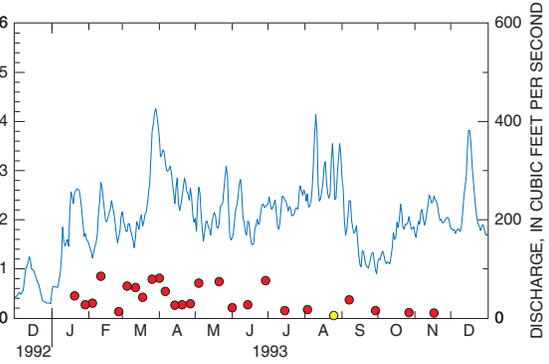
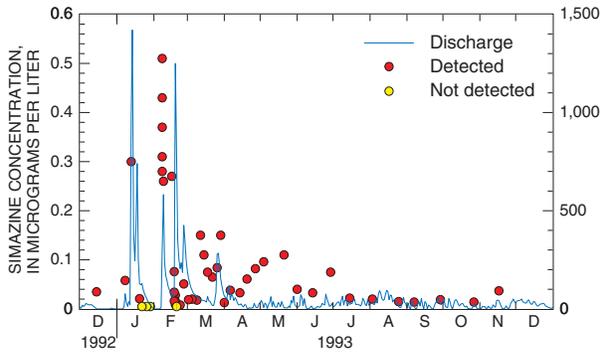
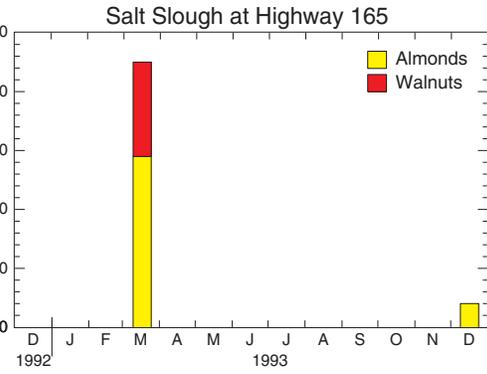
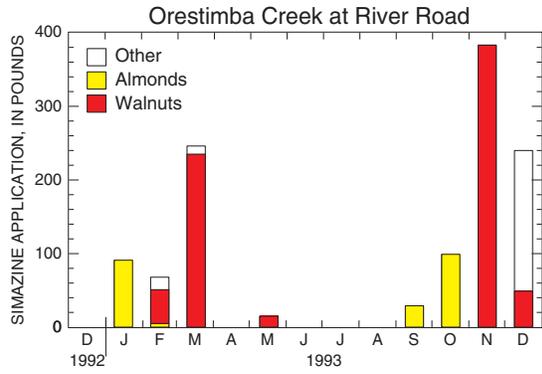
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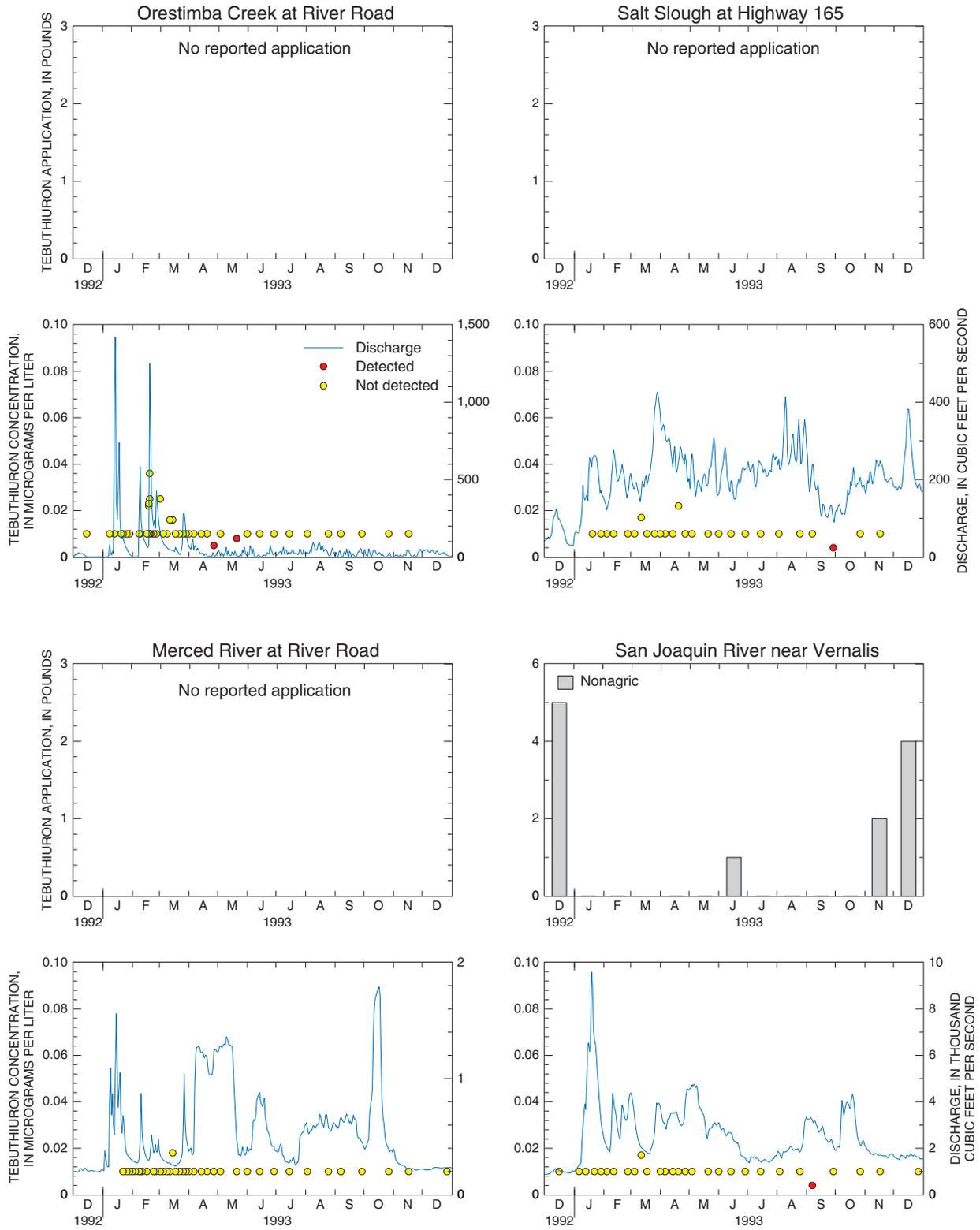
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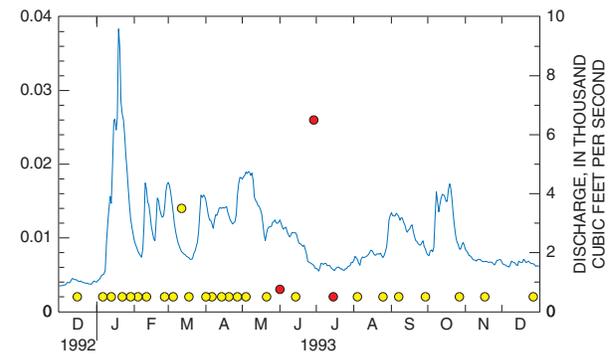
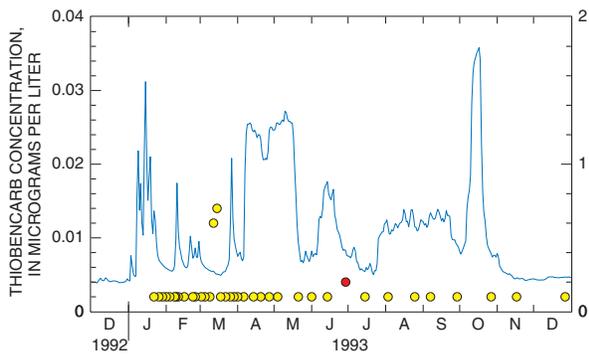
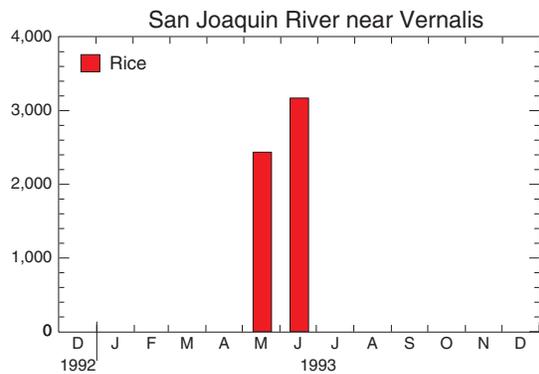
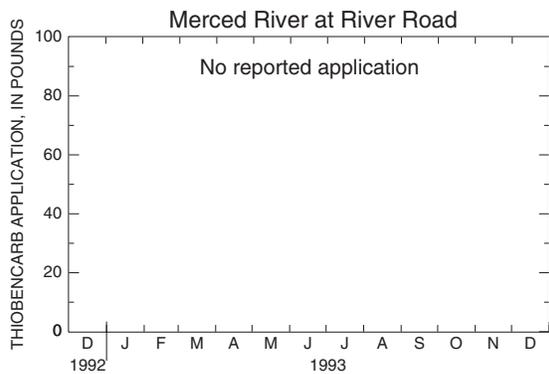
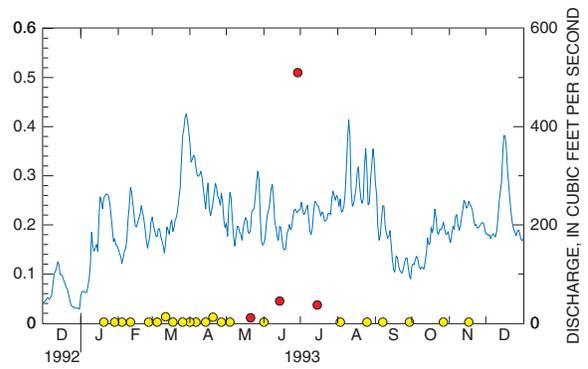
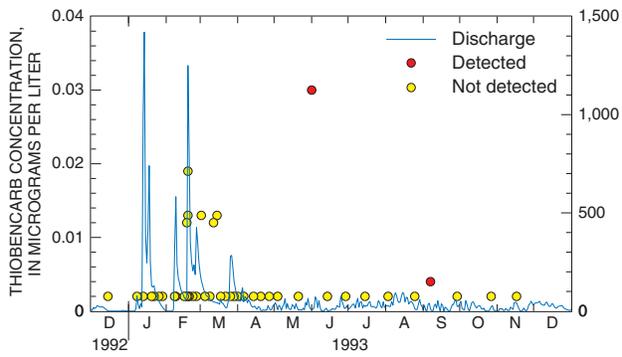
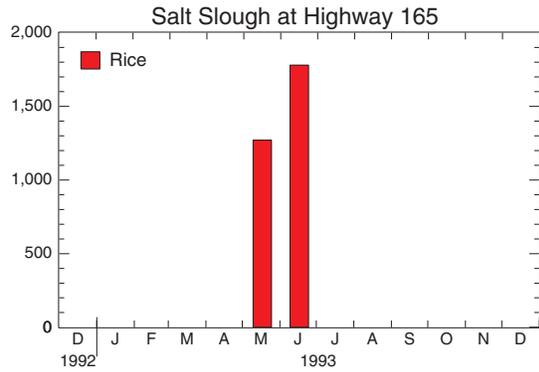
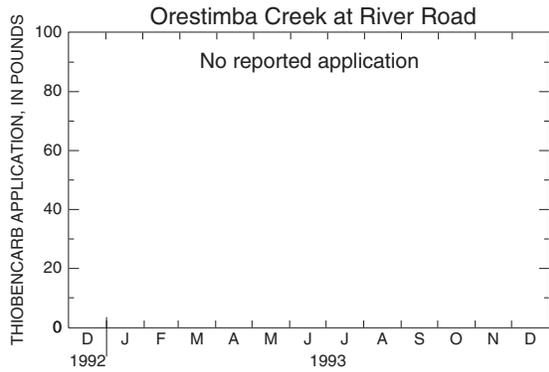
Simazine



Tebuthiuron



Thiobencarb



Trifluralin

