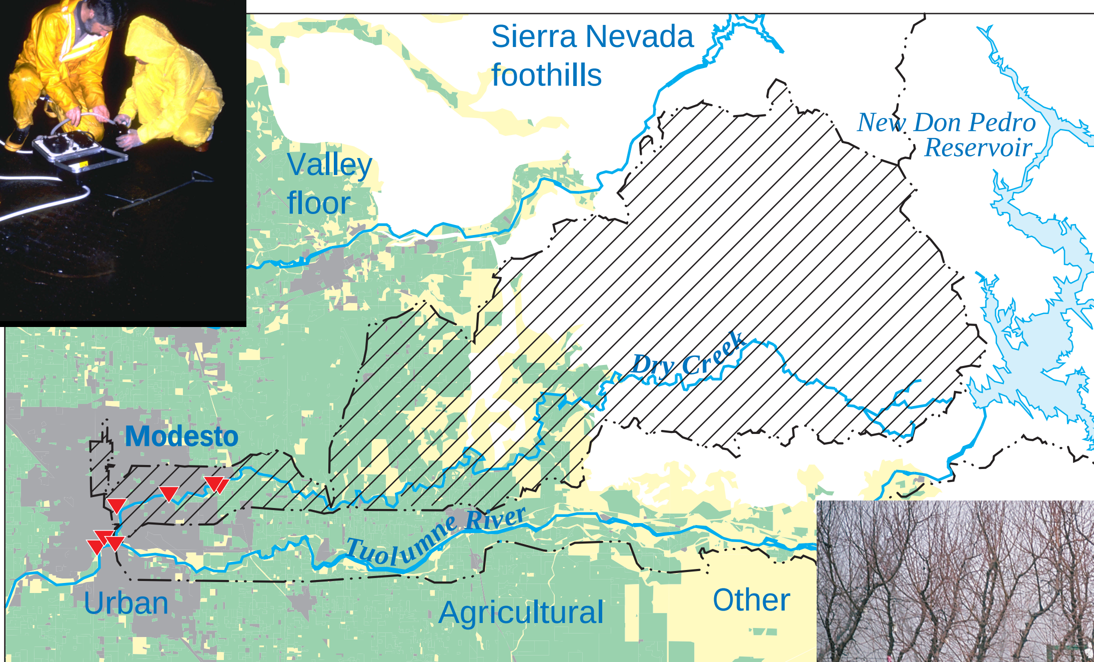
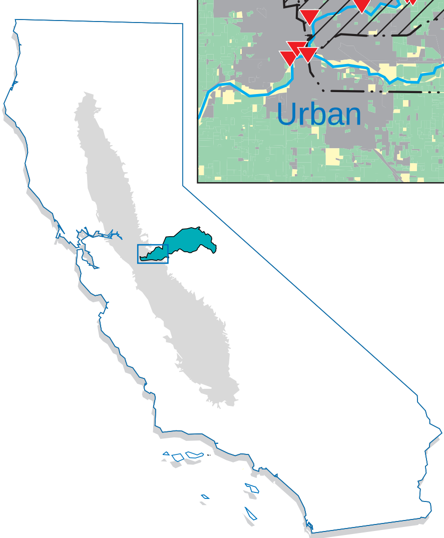
Pesticides in Storm Runoff from Agricultural and Urban Areas in the Tuolumne River Basin in the Vicinity of Modesto, California

Water-Resources Investigations Report 98-4017





U.S. Department of the Interior
U.S. Geological Survey

NATIONAL WATER-QUALITY ASSESSMENT PROGRAM

Pesticides in Storm Runoff from Agricultural and Urban Areas in the Tuolumne River Basin in the Vicinity of Modesto, California

By Charles R. Kratzer

U.S. GEOLOGICAL SURVEY

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National Water-Quality Assessment Program

6440-51

Sacramento, California
1998

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

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

For additional information write to:

District Chief
U.S. Geological Survey
Water Resources Division
Placer Hall
6000 J Street
Sacramento, CA 95819-6129

Copies of this report can be purchased from:

U.S. Geological Survey
Information Services
Box 25286
Federal Center
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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

Robert M. Hirsch
Chief Hydrologist

CONTENTS

FIGURES

TABLES

CONVERSION FACTORS AND ACRONYMS

Multiply	By	To obtain
cubic foot per second (ft^3/s)	0.02832	cubic meter per second (m^3/s)
inch (in.)	2.54	centimeter (cm)
pound, avoirdupois (lb)	0.4536	kilogram (kg)
pound per day (lb/d)	0.4536	kilogram per day (kg/d)
square mile (mi^2)	2.590	square kilometer (km^2)

Temperature: Degrees Celsius (^oC) can be converted to degrees Fahrenheit (^oF) by using the formula $^oF = [1.8(^oC)]+32$. Degrees Fahrenheit can be converted to degrees Celsius by using the formula $^oC = 0.556(^oF-32)$.

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

L, liter
µg/L, microgram per liter
µm, micrometer

CDPR, California Department of Pesticide Regulation
DCPA, dacthal
MDL, method detection limit
NAS/NAE, National Academy of Sciences and National Academy of Engineering
PCO, pest control operators
USGS, U.S. Geological Survey

Pesticides in Storm Runoff from Agricultural and Urban Areas in the Tuolumne River Basin in the Vicinity of Modesto, California

By Charles R. Kratzer

ABSTRACT

The occurrence, concentrations, and loads of dissolved pesticides in storm runoff were compared for two contrasting land uses in the Tuolumne River Basin, California, during two different winter storms: agricultural areas (February 1994) and the Modesto urban area (February 1995). Both storms followed the main application period of pesticides on dormant almond orchards. Eight samples of runoff from agricultural areas were collected from a Tuolumne River site, and 10 samples of runoff from urban areas were collected from five storm drains. All samples were analyzed for 46 pesticides. Six pesticides were detected in runoff from agricultural areas, and 15 pesticides were detected in runoff from urban areas. Chlorpyrifos, diazinon, dacthal (DCPA), metolachlor, and simazine were detected in almost every sample. Median concentrations were higher in the runoff from urban areas for all pesticides except napropamide and simazine. The greater occurrence and concentrations in storm drains is partly attributed to dilution of agricultural runoff by nonstorm baseflow in the Tuolumne River and by storm runoff from nonagricultural and nonurban land. In most cases, the occurrence and relative concentrations of pesticides found in storm runoff from agricultural and urban areas were related to reported pesticide application.

Pesticide concentrations in runoff from agricultural areas were more variable during the storm hydrograph than were concentrations in runoff from urban areas. All peak pesticide concentrations in runoff from agricultural areas occurred during the rising limb of the storm hydrograph, whereas peak concentrations in the storm drains occurred at varying times during the storm hydrograph. Transport of pesticides from agricultural areas during the February 1994 storm exceeded transport from urban areas during the February 1995 storm for chlorpyrifos, diazinon, metolachlor, napropamide, and simazine. Transport of DCPA was about the same from agricultural and urban sources, and the main source of transport for the other pesticides could not be determined because of concentrations less than the method detection limit.

INTRODUCTION

The city of Modesto is located in the San Joaquin Valley at the confluence of Dry Creek and the Tuolumne River (fig. 1). The 1990 population of the Modesto urban area was 230,609 (California Department of Finance, 1991). Mean annual rainfall during 1971-92 was 12.2 in., with 11.4 in. falling during October through April (City of Modesto, 1993). Land use in the valley part of the Tuolumne River at Modesto drainage basin is about 53 percent agricultural, 13 percent urban, and 34 percent other (table 1). Almond orchards are the dominant agricultural land use and the other land-use category is mostly native vegetation. In the urban area, about one-third of the city discharges stormwater to surface water, and the other two-thirds discharges stormwater to ground water by way of dry wells (City of Modesto, 1993). The total area presently discharging to surface

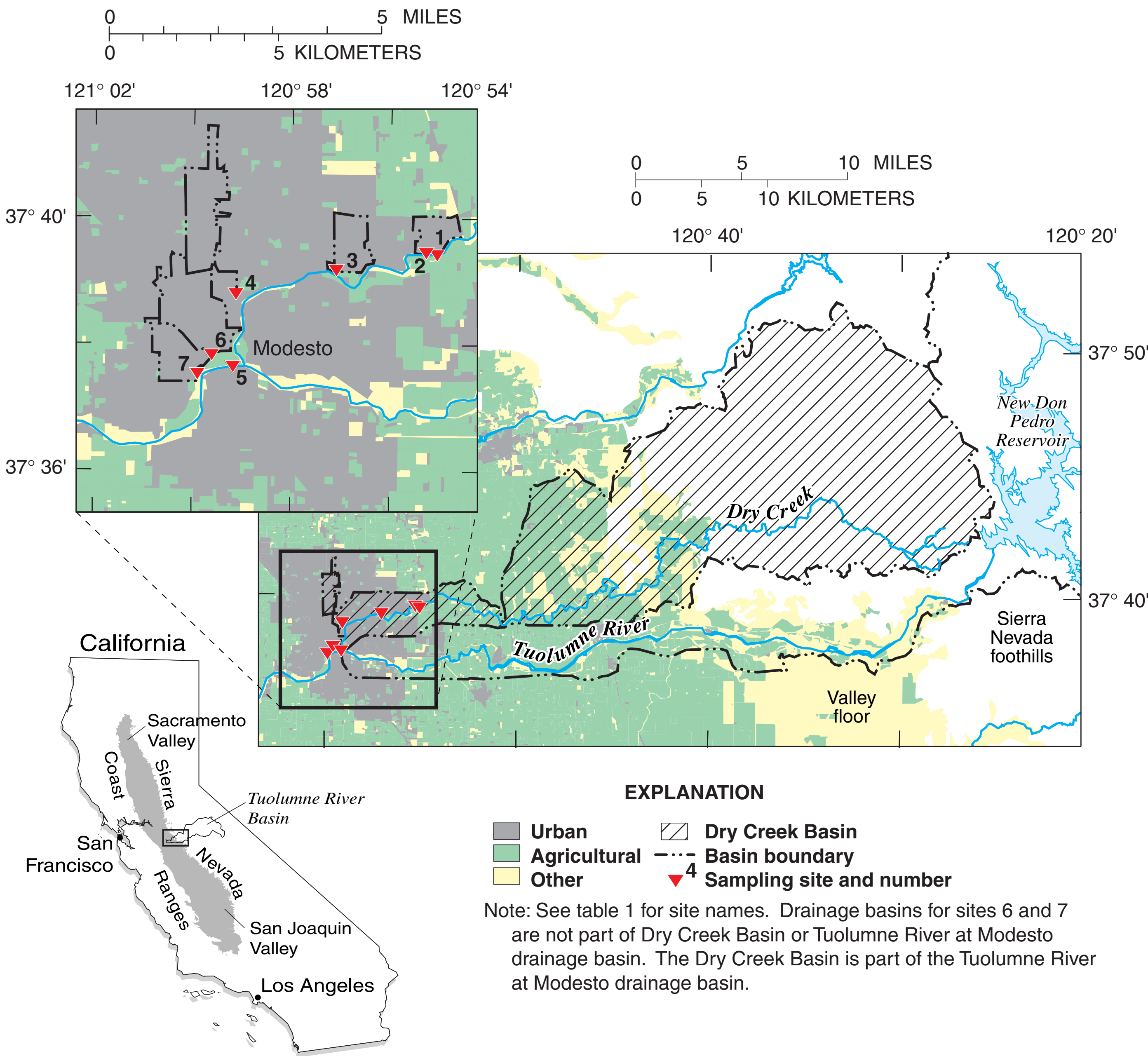

Figure 1. Sampling sites, drainage basins, and land use in the San Joaquin Valley part of basins in the Tuolumne River Basin, California.

Table 1. Site number, name, drainage basin area, and land use in the San Joaquin Valley part of basins in the Tuolumne River Basin, California

Site no. (see fig. 1)	Site name	Drainage basin area in San Joaquin Valley (square miles)	Land use in San Joaquin Valley part of drainage basin [1] (percent)		
			Agricultural	Urban	Other
—	Dry Creek Basin	66.7	56.3	13.7	30.0
1	Farabuindo Storm Drain	.50	0	100	0
2	Dry Creek at Claus Road	55.4	63.5	1.0	35.5
3	Sonoma Storm Drain	.65	0	100	0
4	McHenry Storm Drain	1.33	0	100	0
5	Tuolumne River at Modesto	130	52.8	12.8	34.4
6	Ninth Street Storm Drain	1.56	0	100	0
7	Westside Storm Drain	.80	0	100	0

[1] From 1988 land use coverage from California Department of Water Resources. Land use at sites 1, 3, 4, 6, and 7 was updated to reflect conversions to urban use in the Modesto area.

water is about 10.4 mi^2. The land use in the storm drain basins sampled in this study is 100 percent urban (table 1).

Previous studies that analyzed for the same 46 pesticides as in this study (table 2) compared pesticide occurrence and concentrations in paired basins with agricultural and urban land use in other parts of the United States (Hippe and others, 1994; Kimbrough and Litke, 1996). In Colorado, 30 pesticides were detected in an agricultural watershed north of Denver and 22 pesticides were detected in a Denver watershed (Kimbrough and Litke, 1996). Concentrations were generally higher in the agricultural samples, except for simazine, carbaryl, and diazinon. Atrazine, metolachlor, prometon, and EPTC were the most frequently detected pesticides in the agricultural samples; prometon, simazine, carbaryl, and diazinon were most frequently detected in the urban samples. In Georgia, 21 pesticides were detected in two agricultural watersheds south of Atlanta, and 25 pesticides were detected in an Atlanta watershed (Hippe and others, 1994). Concentrations were generally higher in the urban samples. Metolachlor, atrazine, simazine, and alachlor were the most frequently detected pesticides in the agricultural samples; simazine, atrazine, diazinon, chlorpyrifos, and carbaryl were most frequently detected in the urban samples.

Diazinon has been frequently detected in rivers and creeks throughout the San Joaquin River Basin following storms in January and February, sometimes in toxic concentrations (Kuivila and Foe, 1995; Domagalski and others, 1997; Kratzer, 1997). Diazinon is an insecticide that is heavily used on dormant orchards, especially almonds, in the San Joaquin Valley. It is also used by licensed pest control operators (PCO) for structural pest control, and has many outdoor household uses. Diazinon and chlorpyrifos (another insecticide with similar agricultural and urban uses as diazinon) have been detected frequently in rainfall, storm drains, and creeks in many northern California urban areas (Cooper, 1996; Valerie Connor, California Regional Water Quality Control Board, written commun., 1997).

The purpose of this report is to describe the occurrence of pesticides in storm runoff from agricultural and urban areas in the Tuolumne River Basin, and to relate occurrence, concentrations, and loads to application. Samples of storm runoff from agricultural areas were collected during February 8-10, 1994, and samples of storm runoff from urban areas were collected during February 13-14, 1995. This study was part of the National Water-Quality Assessment Program of the U.S. Geological Survey (USGS).

Table 2. Pesticides analyzed for in this study and their method detection limits

[Abbreviations: H, herbicide; I, insecticide; μg/L, microgram per liter]

Pesticide name	Pesticide type	Method detection limit, (mg/L)
Alachlor	H	0.002
Atrazine	H	.001
Atrazine, desethyl	H	.002
Azinphos-methyl	I	.001
Benfluralin	H	.002
Butylate	H	.002
Carbaryl	I	.003
Carbofuran	I	.003
Chlorpyrifos	I	.004
Cyanazine	H	.004
Dacthal (DCPA)	H	.002
DDE, *p,p′* -	I	.006
Diazinon	I	.002
Dieldrin	I	.001
Diethylanaline, 2,6-	H	.003
Disulfoton	I	.017
EPTC	H	.002
Ethalfluraline	H	.004
Ethoprop	I	.003
Fonofos	I	.003
HCH, *alpha*-	I	.002
HCH, *gamma*-	I	.004
Linuron	H	.002
Malathion	I	.005
Metolachlor	H	.002
Metribuzin	H	.004
Molinate	H	.004
Napropamide	H	.003
Parathion	I	.004
Parathion-methyl	I	.006
Pebulate	H	.004
Pendimethalin	H	.004
Permethrin, *cis*-	I	.005
Phorate	I	.002
Prometon	H	.018
Pronamide	H	.003
Propachlor	H	.007
Propanil	H	.004
Propargite	I	.013
Simazine	H	.005
Tebuthiuron	H	.010
Terbacil	H	.007
Terbufos	I	.013
Thiobencarb	H	.002
Triallate	H	.001
Trifluralin	H	.002

Several personnel from the city of Modesto, Modesto Irrigation District, and the USGS contributed to the completion of this study. The author would especially like to thank Phillip Tomlin and Garner Reynolds from the city of Modesto for their help in locating suitable sampling sites for the storm drains and for setting up an autosampler in the McHenry Storm Drain. Leo Havener and Bill Ketscher of Modesto Irrigation District provided real-time rainfall data and a better understanding of the hydrology of the Tuolumne River Basin upstream of Modesto. Rhodora Biagtan, formerly with the USGS, helped to select sampling sites and estimate discharge in the storm drains. Finally, Jo Ann Gronberg of the USGS provided the summaries of land use and pesticide application data presented in this report.

METHODS

Sample-Collection Strategy

Runoff in the Tuolumne River Basin was sampled for 46 pesticides following a February 6-8, 1994, storm that resulted in 0.77 in. of rain at Modesto in the valley and 3.56 in. of rain at New Don Pedro Reservoir in the foothills of the Sierra Nevada (fig. 1). All storm runoff was from Dry Creek Basin (fig. 1) and drainage to the Tuolumne River below New Don Pedro Reservoir; runoff in the Sierra Nevada was captured in the reservoir. The Dry Creek at Claus Road (site 2, fig. 1) drainage basin accounted for more than 76 percent of the runoff during the storm (Kratzer, 1997). Land use in this basin is 63.5 percent agricultural, 1.0 percent urban, and 35.5 percent other (table 1). The storm sampling was designed to determine the concentrations and loads of pesticides used on dormant almond orchards (Kratzer, 1997). Ten samples were collected from the Tuolumne River at Modesto (site 5, fig. 1) throughout the storm hydrograph (fig. 2*A*) to evaluate the temporal variability of pesticide occurrence and concentrations during the storm. All samples were analyzed for 46 pesticides (table 2). The first two samples were collected after most urban runoff from Modesto had ceased, based on the observation that most storm drains in Modesto stop flowing within 4 hours following significant rainfall (City of Modesto, 1993), and on estimated traveltimes in Dry Creek from the location of the storm drain outfalls to the Tuolumne River at Modesto (site 5) (Kratzer and Biagtan, 1997). However, on the basis of

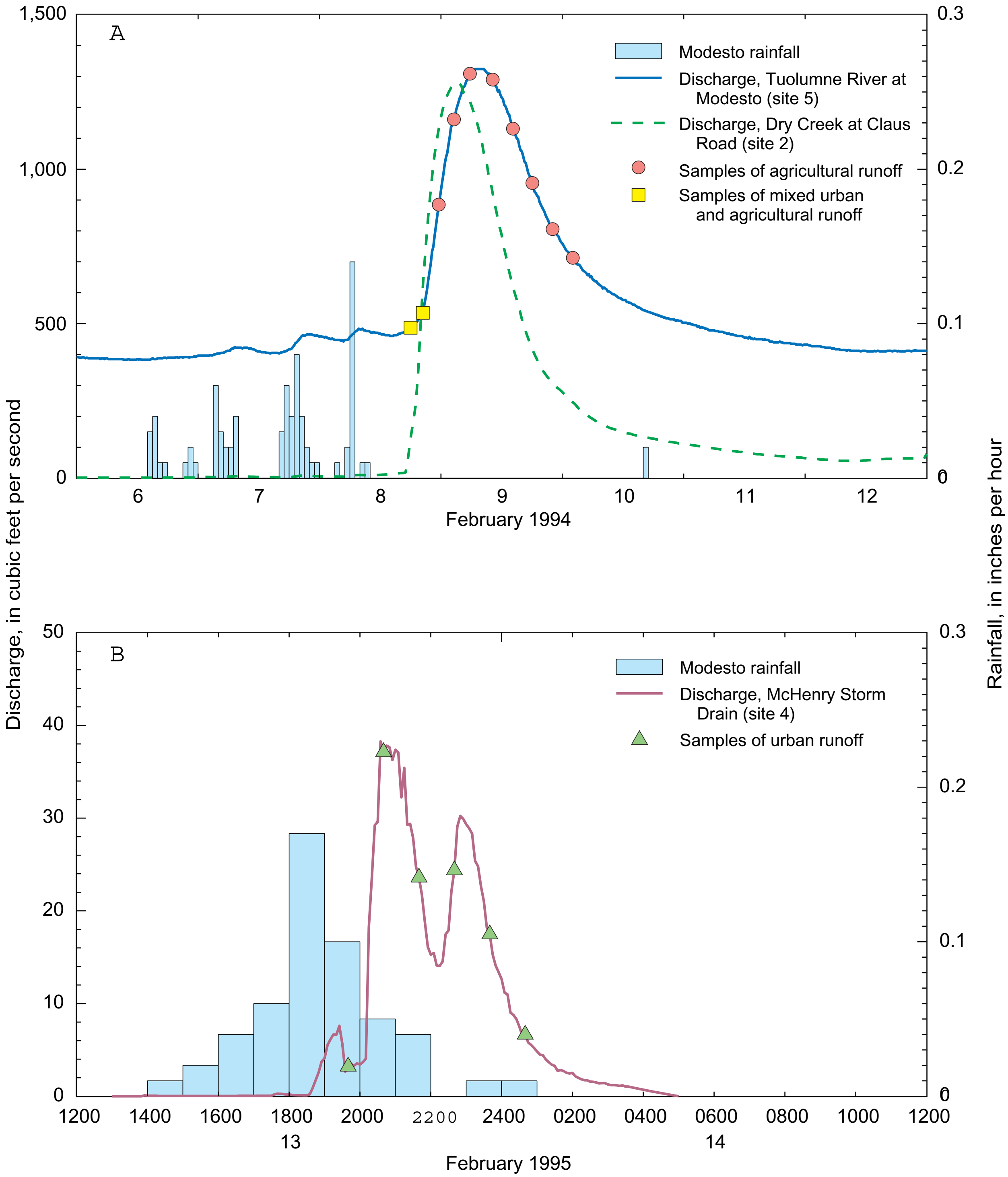

Figure 2. Rainfall, storm hydrographs, and sample-collection times for (A) agricultural runoff to the Tuolumne River at Modesto in February 1994 and (B) urban runoff to the McHenry Storm Drain in February 1995.

estimated traveltimes from Dry Creek at Claus Road (site 2) to the Tuolumne River at Modesto (site 5), the runoff from the Dry Creek at Claus Road drainage basin had not yet reached site 5 in the first two samples. Thus, the first two samples collected in the Tuolumne River at Modesto (site 5) were probably a mixture of residual urban runoff from Modesto and early agricultural runoff to the Tuolumne River below New Don Pedro Reservoir. Therefore, these two samples were not included in the analysis in this report.

The eight "agricultural runoff" samples (fig. 2*A*) collected from site 5 (after the urban runoff was no longer a factor at the site) represent a mixture of non-storm baseflow of about 400 ft^3/s (consisting mainly of releases from New Don Pedro Reservoir) and storm runoff from agricultural and nonagricultural land (primarily native vegetation). Since there is little reported pesticide use on the nonagricultural land, the occurrence of pesticides in these samples is determined by the runoff from the agricultural land. Thus, these samples are used to represent runoff from agricultural areas in this report.

Runoff from urban areas in Modesto was sampled in storm drains during a February 13-14, 1995, storm which resulted in 0.51 in. of rain at Modesto. The storm sampling was designed to determine the occurrence of pesticides in urban runoff during a storm following the main application of pesticides on dormant almond orchards outside of Modesto. Ten samples were collected from five storm drains (sites 1, 3, 4, 6, and 7 in fig. 1) and were analyzed for the same 46 pesticides as the Tuolumne River samples. These storm drains account for 47 percent of the urban area in Modesto with drainage to surface waters (City of Modesto, 1993). The McHenry Storm Drain (site 4) was sampled six times throughout the storm hydrograph (fig. 2*B*) to evaluate temporal variability. This storm drain accounts for 13 percent of the urban area in Modesto with drainage to surface waters.

The drainage basin for the McHenry Storm Drain (site 4, fig. 1) is about 70 percent residential and 30 percent commercial land use. This is fairly representative of the urban land use in Modesto, and this site is used by the city of Modesto to represent stormwater quality (City of Modesto, 1993). The six samples collected from McHenry Storm Drain in this study were used to define temporal variability and loads in runoff from the Modesto urban area. The four samples from the other storm drains together with the six samples from McHenry Storm Drain were used to define the spatial variability in pesticide occurrence and concentrations in runoff from urban areas.

Sample Collection, Processing, and Laboratory Methods

The Tuolumne River (site 5 in fig. 1, USGS gaging station 11290000) samples were collected as depth- and width-integrated samples using a D-77 isokinetic sampler with Teflon nozzle and 3-L Teflon bottle (Shelton, 1994). The samples were stored on ice and processed (that is, filtered and extracted) within 3 days. Discharge at the Tuolumne River at Modesto (site 5) was determined by the USGS.

The McHenry Storm Drain (site 4, fig.1) samples were collected by an autosampler equipped with Teflon tubing and a rack with 24 glass bottles. Discharge was determined from water depth data that was collected using a pressure transducer attached to the autosampler, and converted to discharge using a depth-discharge relation provided by city of Modesto staff. Samples at the other storm drains (sites 1, 3, 6, and 7 in fig. 1) were collected as grab samples using a 3-L Teflon bottle strapped into a metal cage suspended from a rope down the manhole. Discharge at Sonoma Storm Drain (site 3), Ninth Street Storm Drain (site 6), and Westside Storm Drain (site 7) were determined from water depth measurements converted to discharge using a depth-discharge relation specific to each storm drain provided by city of Modesto staff. Discharge at Farabuindo Storm Drain (site 1) was estimated on the basis of the changes in discharge at Dry Creek at Claus Road (site 2) (California Department of Water Resources gage B04130) immediately downstream of the storm drain outfall.

All samples were filtered through a baked 0.7-μm glass-fiber filter and the dissolved pesticides were extracted by solid-phase extraction cartridges containing porous silica coated with a C-18 phase and preconditioned with methanol. The samples were then sent to the USGS National Water Quality Laboratory in Arvada, Colo., for analysis. The adsorbed pesticides and metabolites were removed from the cartridges by elution with hexane-isopropanol (3:1). Extracts of the eluant were analyzed by a capillary-column gas chromatograph/mass spectrometer operated in the selected-ion monitoring mode (Zaugg and others, 1995). The method detection limit (MDL) is defined as the minimum concentration of a substance that can be identified, measured, and reported with 99-percent confidence that the concentration of the compound is greater than zero.

PESTICIDES IN STORM RUNOFF

Occurrence

Median concentrations of pesticides detected in the six samples collected from McHenry Storm Drain were comparable to the individual samples from the other four storm drains (table 3). This indicates that the assumption that McHenry Storm Drain is representative of urban runoff to surface waters in the Modesto area is valid for pesticides during the February 1995 storm.

Six pesticides were detected in samples of agricultural runoff and 15 pesticides were detected in samples of urban runoff (table 4). Dacthal (DCPA), diazinon, napropamide, and simazine were detected in all eight samples of agricultural runoff. Chlorpyrifos and metolachlor were detected in seven samples. Carbaryl, chlorpyrifos, DCPA, diazinon, malathion, simazine, and trifluralin were detected in all 10 samples of urban runoff. Benfluralin, EPTC, metolachlor, and pendimethalin were detected in seven to nine samples. Several pesticides were detected primarily in samples of agricultural or urban runoff (table 4). Napropamide was detected primarily in samples of agricultural runoff. Nine pesticides were detected only in samples of urban runoff—benfluralin, carbaryl, disulfoton, EPTC, malathion, pendimethalin, prometon, propanil, and trifluralin. Chlorpyrifos, DCPA, diazinon, metolachlor, and simazine were detected in almost every sample of agricultural and urban runoff. Concentrations of four of these pesticides were usually higher in the urban samples: chlorpyrifos, DCPA, and to a lesser degree diazinon and metolachlor. Simazine had higher concentrations in samples of agricultural runoff (table 4). Samples of urban runoff were collected directly from storm drains, whereas samples of agricultural runoff were collected from the receiving water (Tuolumne River) and not from agricultural drains. Thus, the samples of agricultural runoff also consist of nonstorm baseflow in the Tuolumne River and storm runoff from nonagricultural land. This dilution reduces the occurrence and concentrations of pesticides in samples of agricultural runoff relative to pesticides in samples of urban runoff in this study.

None of the samples of agricultural or urban runoff had pesticide concentrations that exceeded drinking water criteria (table 4). Chlorpyrifos

Table 3. Pesticide concentrations in storm runoff from five storm drains in Modesto, California

[Symbol: <, less than]

Pesticide name	Pesticide concentration, in micrograms per liter				
	Farabuindo Storm Drain	Sonoma Storm Drain	McHenry Storm Drain [1]	Ninth Street Storm Drain	Westside Storm Drain
Benfluralin	0.008	0.008	0.011	0.014	<0.002
Carbaryl	.32	.19	.093	.070	.048
Chlorpyrifos	.30	.25	.067	.050	.031
Dacthal (DCPA)	.29	.70	.12	.046	.55
Diazinon	.81	.83	.80	.66	.60
Disulfoton	.060	<.017	<.017	<.017	<.017
EPTC	.006	.013	.020	<.002	.019
Malathion	.068	.038	.065	.046	.066
Metolachlor	.005	.031	.010	.007	<.002
Napropamide	<.003	<.003	<.003	<.003	<.003
Pendimethalin	.057	.080	.030	.055	<.004
Prometon	.044	.052	<.018	<.018	<.018
Propanil	.011	<.004	<.004	<.004	<.004
Simazine	.073	.070	.13	.19	.13
Trifluralin	.024	.016	.013	.013	.013

[1] Median concentration of six samples collected from McHenry Storm Drain.

Table 4. Frequency of detections and concentrations, and water-quality criteria for detected pesticides in samples of agricultural runoff and samples of urban runoff

[Abbreviations: H, herbicide; I, insecticide, MDL, method detection limit; µg/L, microgram per liter; <, less than; —, no data]

Pesticide		MDL (mg/L)	Samples of agricultural runoff (n=8)			Samples of urban runoff (n=10)			Water-quality criteria (mg/L)	
			Fre-quency of detec-tions (percent)	Concentration (mg/L)		Fre-quency of detec-tions (percent)	Concentration (mg/L)		Drinking water	Protec-tion of fresh-water aquatic life
Name	Type			Median	Maximum		Median	Maximum		
Benfluralin	H	0.002	0	<0.002	<0.002	80	0.010	0.014	—	—
Carbaryl	I	.003	0	<.003	<.003	100	.093	.32	[1]60	[2]0.020
Chlorpyrifos	I	.004	88	.007	.013	100	.067	.30	—	[3].083/ [4].041/ [2].001
DCPA	H	.002	100	.004	.009	100	.13	.70	—	—
Diazinon	I	.002	100	.19	.92	100	.80	1.1	[1]14	[2].009
Disulfoton	I	.017	0	<.017	<.017	10	<.017	.060	—	[2].05
EPTC	H	.002	0	<.002	<.002	80	.017	.027	—	—
Malathion	I	.005	0	<.005	<.005	100	.061	.096	[1]160	[4].1/ [2].008
Metolachlor	H	.002	88	.004	.009	90	.009	.031	—	—
Napropamide	H	.003	100	.030	.059	10	<.003	.031	—	—
Pendimethalin	H	.004	0	<.004	<.004	70	.046	.080	—	—
Prometon	H	.018	0	<.018	<.018	30	<.018	.052	—	—
Propanil	H	.004	0	<.004	<.004	10	<.004	.011	—	—
Simazine	H	.005	100	.73	1.1	100	.13	.24	[5]4	[2]10
Trifluralin	H	.002	0	<.002	<.002	100	.014	.024	[6]5	—

[1] From California Department of Water Resources (1995). These are the State of California action level values. These values are health-based numbers that take into account analytical detection levels. They are interim guidance levels that may trigger mitigation action on the part of a water purveyor. These values are not enforceable.

[2] From National Academy of Sciences and National Academy of Engineering (1973). These values are recommended maximum concentrations in water, sampled at any time and any place. These guidelines were derived by multiplying acute toxicity values by an appropriate factor. These values are not enforceable.

[3] From Nowell and Resek (1994, table 3, section 5). This is the U.S. Environmental Protection Agency acute criterion for the protection of freshwater aquatic life. Concentrations at or below this value should not result in unacceptable effects on aquatic organisms and their uses during a short-term exposure. This criterion is presented as a 1-hour average concentration by dividing the instantaneous maximum criterion value by 2. This value is not enforceable.

[4] From Nowell and Resek (1994, table 3, section 5). These are the U.S. Environmental Protection Agency chronic criteria for the protection of freshwater aquatic life. Concentrations at or below these values should not result in unacceptable effects on aquatic organisms and their uses during chronic exposure. These criteria are for 4-day average concentrations. These values are not enforceable.

[5] From Nowell and Resek (1994, table 3, section 1). This is the U.S. Environmental Protection Agency maximum contaminant level. This value is the maximum permissible level of contaminant in water that is delivered to any user of a public water system. This value is enforceable.

[6] From Nowell and Resek (1994, table 3, section 2). This is the U.S. Environmental Protection Agency health advisory (risk specific dose) value. This value is the concentration of a potential carcinogen in drinking water that is estimated to result in an excess cancer risk of one in a million, assuming consumption of 2 liters per day of water contaminated at this concentration by a 70-kilogram body weight individual over a lifetime (70 years). This value is not enforceable.

concentrations in two samples of urban runoff exceeded the U.S. Environmental Protection Agency acute criteria of 0.083 μg/L for the protection of freshwater aquatic life. The chronic criteria of 0.041 μg/L were exceeded in nine samples of urban runoff (table 4). The National Academy of Sciences and National Academy of Engineering (1973) recommended guidelines for protection of freshwater aquatic life were exceeded frequently. All samples of urban runoff exceeded the National Academy of Sciences and National Academy of Engineering (NAS/NAE) guidelines for carbaryl, chlorpyrifos, diazinon, and malathion. One sample of urban runoff exceeded the NAS/NAE guidelines for disulfoton. All samples of agricultural runoff exceeded the NAS/NAE guidelines for diazinon. Seven of eight samples of agricultural runoff exceeded the NAS/NAE guidelines for chlorpyrifos, and the other sample could possibly also exceed the NAS/NAE guideline because the MDL (0.004 μg/L) exceeds the guideline (0.001 μg/L) (table 4).

Variation in Concentrations

The highest pesticide concentrations occurred in the first sample of agricultural runoff during the February 1994 storm (fig. 3). The concentrations generally decreased sharply in the second sample, followed by a more gradual decline, except for simazine and napropamide. This is a common pattern for pesticide concentrations during a storm hydrograph, with peak concentrations occurring on the rising limb (Richards and Baker, 1993). For simazine and napropamide, concentrations rose at the beginning of the falling limb before falling again at the end of the storm hydrograph.

For samples of urban runoff at McHenry Storm Drain (site 4), the peak concentrations of simazine, carbaryl, EPTC, and metolachlor occurred in the first sample (fig. 4). Pendimethalin concentrations were less than the MDL in the first two samples, then increased sharply almost halfway through the storm hydrograph. Diazinon and chlorpyrifos concentrations increased gradually throughout the storm hydrograph, with peak concentrations in the last sample. Overall, there was less variation in pesticide concentrations throughout the storm hydrograph for samples of urban runoff than for samples of agricultural runoff.

Loads

The instantaneous loads of the five pesticides detected frequently in samples of both agricultural and urban runoff are compared in figure 5. The eight samples from the Tuolumne River at Modesto (site 5) represent the instantaneous loads owing to agricultural runoff, and the six samples from the McHenry Storm Drain (site 4) represent the instantaneous loads from 13 percent of the urban area in Modesto with drainage to surface waters. The mean of the instantaneous loads in the Tuolumne River exceeded the mean of the instantaneous loads in McHenry Storm Drain for the five pesticides, primarily because of the much greater discharge in the Tuolumne River.

If McHenry Storm Drain is representative of Modesto storm drains with respect to pesticide loads, this load can be multiplied by 7.7 (100 percent divided by 13 percent) to estimate the instantaneous loads from the urban area in Modesto with drainage to surface waters. When this is done, the resulting mean of the instantaneous loads in urban runoff exceeded the mean of the instantaneous loads in agricultural runoff for carbaryl, chlorpyrifos, DCPA, EPTC, malathion, and pendimethalin (table 5). The mean of the instantaneous loads in agricultural runoff exceeded the mean of the instantaneous loads in urban runoff for diazinon, metolachlor, napropamide, and simazine (table 5).

The duration of storm runoff from the urban area was only about 7 hours, compared with more than 30 hours from the agricultural area (fig. 5). This greatly increased the total storm transport from the agricultural areas relative to transport from the urban areas. The storm loads in agricultural runoff exceeded the storm loads in urban runoff for chlorpyrifos, diazinon, metolachlor, napropamide, and simazine (table 5). The storm loads of DCPA was about the same from agricultural and urban sources. Because of the large volume of storm runoff in the Tuolumne River, even concentrations below the MDL could result in a larger pesticide load than that estimated for the urban runoff. Therefore, the main source of transport for the other pesticides was indeterminate. Even though runoff from urban areas contributed less loads of most pesticides than runoff from agricultural areas in the Tuolumne River Basin, the greater occurrence and relative concentrations of pesticides in the urban runoff make it important to evaluate urban pesticide sources.

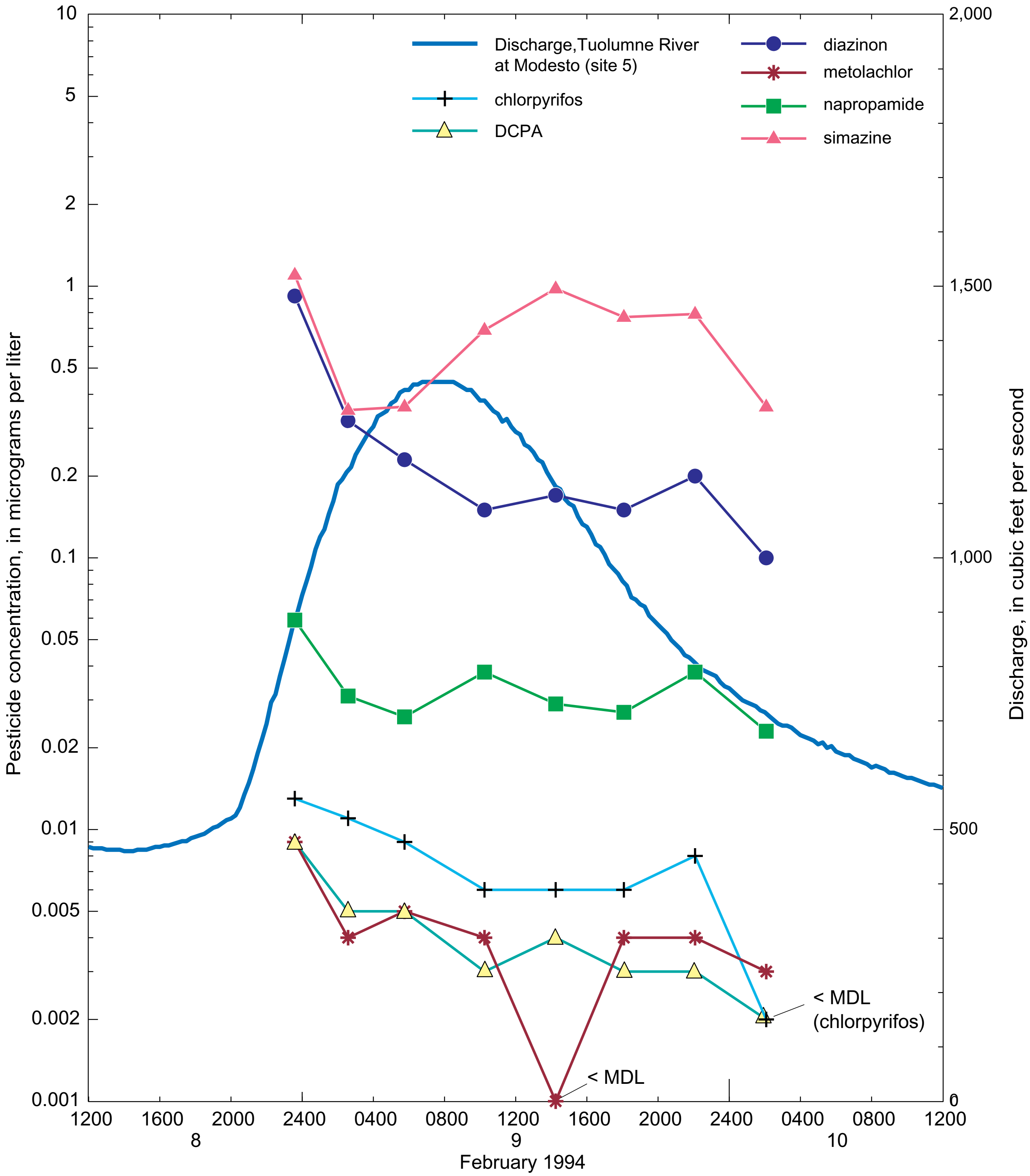

Figure 3. Concentrations of chlorpyrifos, DCPA, diazinon, metolachlor, napropamide, and simazine in samples of agricultural runoff in the Tuolumne River at Modesto during the February 1994 storm.

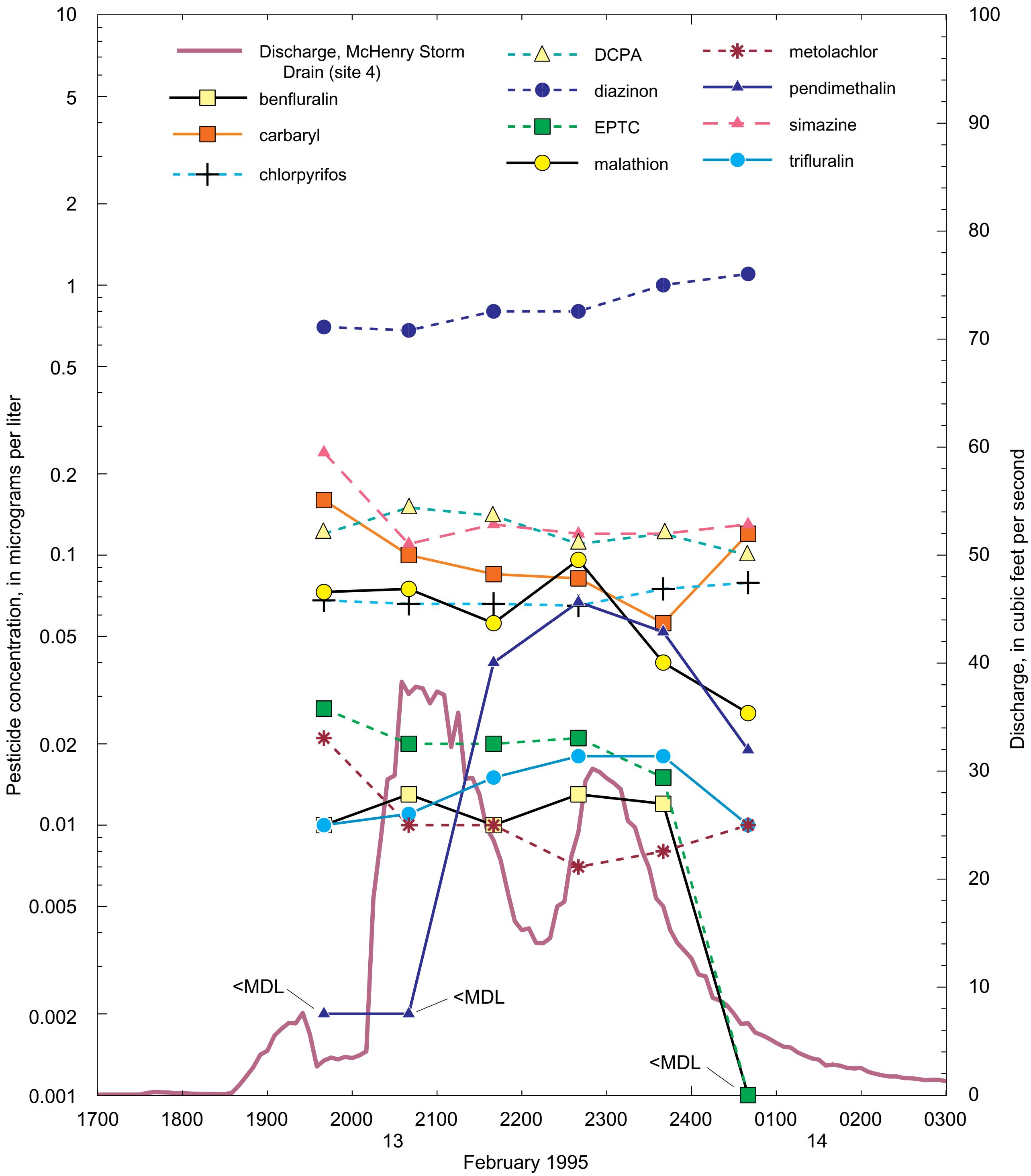

Figure 4. Concentrations of benfluralin, carbaryl, chlorpyrifos, DCPA, diazinon, EPTC, malathion, metolachlor, pendimethalin, simazine, and trifluralin in samples of urban runoff in the McHenry Storm Drain during the February 1995 storm.

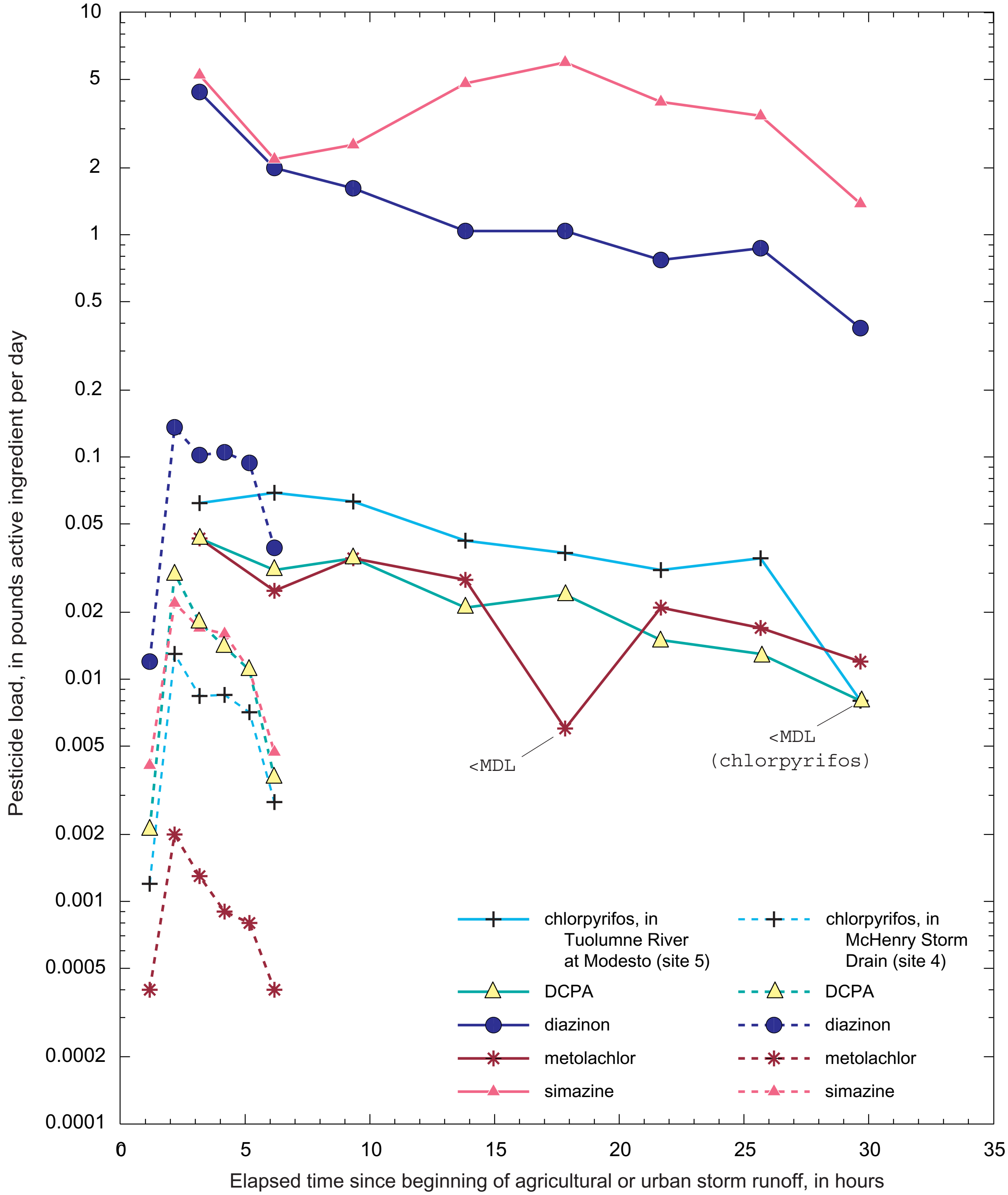

Figure 5. Instantaneous loads of chlorpyrifos, DCPA, diazinon, metolachlor, and simazine during agricultural storm runoff in the Tuolumne River at Modesto and during urban storm runoff in the McHenry Storm Drain.

Table 5. Loads of pesticides in runoff from agricultural areas in the Tuolumne River at Modesto drainage basin during the February 6–8, 1994, storm and in runoff from urban areas in Modesto during the February 13–14, 1995, storm

[Abbreviations: MDL, method detection limit; ft^3/s, cubic feet per second; h, hours; lb a.i., pound active ingredient; lb a.i./d, pound active ingredient per day; µg/L, microgram per liter; <, less than]

Pesticide name	Mean instantaneous load (lb a.i./d)		Storm load (lb a.i.)	
	Agricultural runoff [1]	Urban runoff [2]	Agricultural runoff [3]	Urban runoff [4]
Benfluralin	[5]<0.011	0.009	<0.014	0.003
Carbaryl	<.017	.069	<.021	.020
Chlorpyrifos	.043	.052	.054	.015
DCPA	.024	.10	.030	.029
Diazinon	1.5	.63	1.9	.18
Disulfoton	<.095	<.013	<.12	<.004
EPTC	<.011	.014	<.014	.004
Malathion	<.028	.052	<.035	.015
Metolachlor	.023	.008	.029	.002
Napropamide	.19	.001	.23	<.001
Pendimethalin	<.022	.026	<.028	.007
Prometon	<.10	<.014	<.13	<.004
Propanil	<.022	<.003	<.028	<.001
Simazine	3.7	.096	4.6	.028
Trifluralin	<.011	<.014	<.014	.003

[1] Mean of eight instantaneous loads for Tuolumne River at Modesto, where each instantaneous load is calculated as follows:

instantaneous load (lb a.i./d) = 0.00539 x concentration (µg/L) x discharge (ft^3/s)

[2] Mean of six instantaneous loads for McHenry Storm Drain multiplied by (100 percent/13 percent) to estimate mean of instantaneous loads from the Modesto urban area.

[3] Mean instantaneous load multiplied by (30h/24h) to estimate load for entire storm.

[4] Mean instantaneous load multiplied by (7h/24h) to estimate load for entire storm.

[5] For pesticides with no detections, loads are shown as less than the load on the basis of the MDL. For pesticides with at least one detection, loads are calculated with less-than detections set to half the MDL.

Occurrence of Pesticides in Relation to Application

Agricultural and urban use of the 15 pesticides detected in this study are shown in table 6 for the dry periods preceding the February 1994 storm (dry period 1) and preceding the February 1995 storm (dry period 2). Dry period 1, which is from January 26, 1994, to February 5, 1994, was preceded by a storm on January 23–25, 1994, that resulted in 1.31 in. of rain at Modesto. Dry period 2, which is from January 28, 1995, to February 12, 1995, was preceded by a series of storms during January 22–27, 1995, that resulted in a total of 2.27 in. of rain at Modesto. It is anticipated that these significant storms would have transported much of the prior pesticide application out of the basin. This was generally the case for diazinon transport from agricultural areas in the San Joaquin River Basin (which includes the Tuolumne River Basin) during two storms close in time during February 1993 (Domagalski and others, 1997). However, less mobile and(or) more persistent pesticides may remain in the basin following these significant storms.

Agricultural use of pesticides in California is reported to the California Department of Pesticide Regulation (CDPR) by time, location, amount, and crop. Four of the six pesticides that were detected in agricultural runoff were applied on crops during dry period 1 (California Department of Pesticide Regulation, 1995). These four pesticides were applied primarily to dormant almond orchards. The pesticides applied most for agricultural use during dry period 1 were diazinon, simazine, and napropamide (table 6). These three pesticides were also detected in all samples of agricultural runoff and had the highest median concentrations. The median concentration of

Table 6. Pesticide applications and main uses of detected pesticides for dry periods preceding sampled storms in Dry Creek Basin, Tuolumne River at Modesto drainage basin, and Stanislaus County

[Dry period 1, 1/26/94–2/5/94; dry period 2, 1/28/95–2/12/95; —, no reported use]

Pesticide name	Main uses during dry periods 1 and 2		Agricultural applications, in pounds active ingredient				Urban applications, in pounds active ingredient	
			Dry period 1		Dry period 2		Dry period 1	Dry period 2
	Agricultural uses	Urban uses	Dry Creek Basin	Tuolumne River at Modesto drainage basin	Dry Creek Basin	Tuolumne River at Modesto drainage basin	Stanislaus County	Stanislaus County
Benfluralin	—	Landscape maintenance	0	0	0	0	20	17
Carbaryl	—	Structural pest control	0	0	0	0	24	14
Chlorpyrifos	Almonds	Structural pest control	99	146	66	120	742	449
Dacthal (DCPA)	—	Landscape maintenance	0	0	0	0	2	0
Diazinon	Almonds	Structural pest control	569	1,697	131	491	167	159
Disulfoton	—	—	0	0	0	0	0	0
EPTC	—	—	0	0	0	0	0	0
Malathion	—	Structural pest control	0	0	0	0	128	3
Metolachlor	—	Landscape maintenance	0	0	0	0	0	4
Napropamide	Almonds, peaches	Rights-of-way	335	375	25	130	11	4
Pendimethalin	Nurseries, almonds, peaches	Landscape maintenance, rights-of-way	0	18	0	51	125	154
Prometon	—	—	0	0	0	0	0	0
Propanil	—	—	0	0	0	0	0	0
Simazine	Almonds, peaches, walnuts	Rights-of-way	239	512	380	651	771	2,048
Trifluralin	—	Rights-of-way	0	0	0	0	18	4

chlorpyrifos was lower and the amount applied in agricultural areas also was lower. Although pendimethalin was not detected in any samples, a small amount was applied in agricultural areas. Low concentrations of DCPA and metolachlor were detected with no reported use in agricultural areas.

Urban use of pesticides in California is only reported to CDPR by licensed pest control operators (PCOs) by time, county, amount, and type of use. No household use is reported. Ten of the 15 pesticides detected in urban runoff were applied by PCOs in Stanislaus County during dry period 2 (California Department of Pesticide Regulation, 1996). The urban uses reported were structural pest control, landscape maintenance, and rights-of-way. The Modesto urban area accounts for about 62 percent of the population in Stanislaus County (Gronberg and others, in press). Household use of pesticides could be significant during this dry period. A study of diazinon household use in Palo Alto, California, showed that household use was similar to use by PCOs on an annual basis (Cooper, 1996). Thus, the reported urban use of pesticides by PCOs during dry period 2 is an indication of what may have been applied in the drainage basins of the sampled Modesto storm drains.

The pesticides with the greatest reported urban applications during dry period 2 were simazine, chlorpyrifos, diazinon, and pendimethalin (table 6). These four pesticides were also detected frequently and at relatively high concentrations in the storm drains. However, DCPA, carbaryl, and malathion were also detected in all samples of urban runoff with relatively high concentrations despite little or no reported use. On the basis of a 1990 home use survey, these three pesticides are used in and around the home and garden in many products and for many applications (Whitmore and others, 1992). All three pesticides are applied to a wide range of ornamentals (Meister Publishing Company, 1994, 1995). DCPA and carbaryl are used to control broadleaf weeds and insects on lawns, respectively. Carbaryl and malathion are applied to many fruit trees commonly grown in residential areas of Modesto.

The discovery of high diazinon concentrations in rainfall in urban areas in the San Joaquin Valley during the dormant-orchard spray period has raised the question of whether the diazinon in the storm drains comes from urban applications or from drift or volatilization from applications on neighboring agricultural areas. For both dry periods, the agricultural application of diazinon was much greater than the reported urban application (table 6). The only other detected pesticides with agricultural applications were chlorpyrifos, napropamide, pendimethalin, and simazine (table 6). Except for napropamide, reported urban application of these pesticides were greater than agricultural applications.

On the basis of agricultural and reported urban applications during dry period 2 and pesticide occurrence in urban runoff, it appears unlikely that the occurrence and relative concentrations of pesticides other than diazinon were significantly affected in the urban areas by agricultural applications. Napropamide was applied in much greater quantities in agricultural areas, but also was detected in 100 percent of agricultural runoff samples versus only 10 percent of urban runoff samples. The other pesticides applied for agricultural uses during dry period 2—chlorpyrifos, simazine, and pendimethalin—also had at least three times more reported urban application than agricultural application. The other 10 pesticides detected in the storm drains had no agricultural applications since at least December 1, 1994 (California Department of Pesticide Regulation, 1995, 1996). During the period December 1, 1994, to February 12, 1995, the city of Modesto received 8.47 in. of rain. Four of these 10 pesticides—benfluralin, carbaryl, malathion, and trifluralin—had at least some reported urban use during dry period 2 and were subsequently detected only in samples of urban runoff. EPTC and prometon were detected in several samples of urban runoff and have several household uses (Whitmore and others, 1992). Propanil and disulfoton each were detected in only one sample of urban runoff. Metolachlor was detected in most agricultural and urban samples, although there was little or no reported use. Metolachlor was one of the few pesticides detected frequently (in relatively low concentrations) in the Merced River Basin (next basin south of the Tuolumne River Basin) that did not correlate with application (Panshin and others, in press). The question of drift or volatilization from application on neighboring agricultural areas needs additional study.

SUMMARY AND CONCLUSIONS

The occurrence, concentrations, and loads of dissolved pesticides in storm runoff were compared for two contrasting land uses in the Tuolumne River Basin, California. Runoff from agricultural areas upstream of Modesto was sampled in the Tuolumne River following a storm in February 1994 that resulted in 0.77 in. of rain at Modesto and 3.56 in. of rain at New Don Pedro Reservoir. Eight samples were collected after the passage of urban runoff to represent storm runoff from agricultural areas. Runoff from urban areas in Modesto was sampled in storm drains during a storm in February 1995 that resulted in 0.51 in. of rain at Modesto. Ten samples were collected—six from McHenry Storm Drain to evaluate temporal variability and four from other storm drains to evaluate spatial variability. Both storms followed the main application of pesticides on dormant almond orchards. All samples were analyzed for 46 pesticides.

Six pesticides were detected in runoff from agricultural areas, and 15 pesticides were detected in runoff from urban areas. Chlorpyrifos, diazinon, DCPA, metolachlor, and simazine were detected in almost every sample. Except for napropamide and simazine, median concentrations were higher in the runoff from urban areas. The greater occurrence and concentrations in storm drains is partly attributed to dilution of the samples of agricultural runoff by non-storm baseflow in the Tuolumne River and by storm runoff from nonagricultural land. None of the samples had pesticide concentrations that exceeded drinking water criteria. Some samples of urban runoff exceeded U.S. Environmental Protection Agency acute and chronic criteria and NAS/NAE recommended guidelines for the protection of freshwater aquatic life for chlorpyrifos; several samples exceeded NAS/NAE recommended guidelines for carbaryl, diazinon, disulfoton, and malathion. Samples of agricultural runoff frequently exceeded NAS/NAE guidelines for chlorpyrifos and diazinon.

Pesticide concentrations in runoff from agricultural areas were more variable than concentrations in runoff from urban areas during the storm hydrograph. All peak pesticide concentrations in runoff from agricultural areas occurred during the rising limb of the storm hydrograph, whereas peak concentrations in McHenry Storm Drain occurred at varying times during the storm hydrograph. Diazinon and chlorpyrifos concentrations in McHenry Storm Drain increased gradually throughout the storm hydrograph, with peak concentrations occurring in the last sample. Transport of pesticides from agricultural areas exceeded transport from urban areas for chlorpyrifos, diazinon, metolachlor, napropamide, and simazine. This greater transport from agricultural areas was due primarily to greater discharge and duration of storm runoff. Transport of DCPA was about the same from agricultural and urban sources. The main source of transport for the other pesticides could not be determined because of concentrations less than the method detection limit.

In most cases, the occurrence and relative concentrations of pesticides found in storm runoff from agricultural and urban areas was related to application. Diazinon, simazine, and napropamide had the greatest amount of agricultural application during dry period 1 and were detected in all samples of agricultural runoff and had the highest median concentrations. Simazine, chlorpyrifos, diazinon, and pendimethalin had the greatest reported amount of urban application during dry period 2 and were detected frequently and at relatively high concentrations in the storm drains. Carbaryl, DCPA, and malathion were detected frequently and at relatively high concentrations in the storm drains despite little or no reported urban use. However, reported pesticide use in urban areas is incomplete and only includes use by licensed pest control operators and not household use. On the basis of agricultural and reported urban applications during dry period 2 and pesticide occurrence in urban runoff, it appears unlikely that the occurrence and relative concentrations of pesticides other than diazinon were significantly affected in the urban areas by agricultural applications. The question of drift or volatilization from application on neighboring agricultural areas needs additional study.

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