

Changes in Rice Pesticide Use and Surface Water Concentrations in the Sacramento River Watershed, California

By James L. Orlando and Kathryn M. Kuivila

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Conversion Factors, Datum, and Abbreviations

CONVERSION FACTORS

Multiply	By	To obtain
feet (ft)	0.3048	meter
inch (in.)	2.54	centimeter
mile (mi)	1.609	kilometer
square mile (mi ²)	12.590	square kilometer
pound, avoirdupois (lb)	0.4536	kilogram

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

$$^{\circ}\text{F} = 1.8 ^{\circ}\text{C} + 32.$$

Specific conductance is given microsiemens per centimeter at 25 degrees Celsius ($\mu\text{S}/\text{cm}$ at 25°C).

Concentrations of chemical constituents in water are given either in milligrams per liter (mg/L) or micrograms per liter ($\mu\text{g}/\text{L}$).

DATUM

Vertical coordinate information is referenced to the *North American Vertical Datum of 1988 (NAVD 88)*.

Horizontal coordinate information is referenced to the *North American Datum of 1983 (NAD 83)*.

Altitude, as used in this report, refers to distance above the vertical datum.

ABBREVIATIONS

C	carbon
CBD	Colusa Basin Drain
cc	cubic centimeter
CO ₂	carbon dioxide
DOC	dissolved organic carbon
GC/MS	gas chromatography-mass spectrometry
GIS	geographic information system
GPC/HPLC	gel permeation chromatography/high pressure liquid chromatography
HCl	hydrochloric acid
in.	inch
km	kilometer
L	liter
μL	microliter
lb	pound
m	meter
μm	micrometer

MASE	microwave-assisted solvent extraction
MDL	method detection limit
mg	milligram
µg/L	microgram per liter
mi ²	square mile
mL	milliliter
N	nitrogen
N ₂	nitrogen gas
ng	nanogram
ng/g	nanogram per gram dry weight
NPOC	nonpurgeable organic carbon
Pt	platinum
RPD	relative percent difference
SPE	solid-phase extraction
SSC	suspended sediment concentration
µS/cm	microsiemens per centimeter
v/v	volume-to-volume ratio

Organizations

CDFG	California Department of Fish and Game
CDPR	California Department of Pesticide Regulation
CRWQCB	California Regional Water Quality Control Board
CVRWQCB	Central Valley Regional Water Quality Control Board
USGS	U.S. Geological Survey

Changes in Rice Pesticide Use and Surface Water Concentrations in the Sacramento River Watershed, California

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Abstract

Pesticides applied to rice fields in California are transported into the Sacramento River watershed by the release of rice field water. Despite monitoring and mitigation programs, concentrations of two rice pesticides, molinate and thiobencarb, continue to exceed the surface-water concentration performance goals established by the Central Valley Regional Water Quality Control Board. There have been major changes in pesticide use over the past decade, and the total amount of pesticides applied remains high. Molinate use has declined by nearly half, while thiobencarb use has more than doubled; carbofuran has been eliminated and partially replaced by the pyrethroid pesticide lambda-cyhalothrin.

A study was conducted in 2002 and 2003 by the U.S. Geological Survey to determine if the changes in pesticide use on rice resulted in corresponding changes in pesticide concentrations in surface waters. During the rice growing season (May–July), water samples, collected weekly at three sites in 2002 and two sites in 2003, were analyzed for pesticides using both solid-phase and liquid-liquid extraction in combination with gas chromatography/mass spectrometry. Analytes included lambda-cyhalothrin, molinate, thiobencarb, and two degradation products of molinate: 2-keto-molinate and 4-keto-molinate.

Molinate, thiobencarb, and 4-keto-molinate were detected in all samples, 2-keto-molinate was detected in less than half of the samples, and lambda-cyhalothrin was not detected in any samples. At two of the sites sampled in 2002 (Colusa Basin Drain 1 and Sacramento Slough), concentrations of molinate were similar, but thiobencarb concentrations differed by a factor of five. Although concentrations cannot be estimated directly from application amounts in different watersheds, the ratio of molinate to thiobencarb concentrations can be compared with the ratio of molinate to thiobencarb use in the basins. The higher concentration ratio in the Sacramento Slough Basin,

compared with the ratio in the basin area feeding the Colusa Basin Drain 1, is consistent with the higher use ratio, suggesting that differences in application amounts can explain the observed concentration differences. The samples from the downstream site (Tower) sampled in 2002 had the lowest concentrations of pesticides. Performance goals were exceeded for either molinate or thiobencarb in six samples from the upstream sites, but not in any samples from the downstream Tower site. In 2003, concentrations at upstream sites were much lower than the previous year with only one sample containing thiobencarb at a concentration above the performance goal. Lower concentrations could be partially due to delays in rice planting and pesticide application owing to spring rainstorms.

Historical data is available on peak concentrations of molinate and thiobencarb measured at Colusa Basin Drain 5 (one of our sites in 2003) since 1981. Implementing holding times for pesticide-treated rice field water in the early 1980s succeeded in decreasing concentrations in surface waters. Detailed pesticide use data is available since 1991 and changing use patterns for molinate and thiobencarb can explain some, but not all, of the trends in peak pesticide concentrations. A stronger relationship is seen between the lengths of time that performance goals were exceeded and the amount of a pesticide applied within a basin.

Different extraction and analytical techniques were used to improve the recovery and lower the method detection limit for lambda-cyhalothrin. Recoveries of lambda-cyhalothrin from solid-phase extraction cartridges typically vary, so subsamples were processed by liquid-liquid extraction. The advantage of using a larger sample volume (3 L instead of 1 L) to lower detection limits was offset by poor recovery during the cleanup step using an activated carbon column. Results suggest that as the concentrations of dissolved organic carbon in the sample increase, the recovery goes down. Limiting the sample size to 1 L and eliminating the activated carbon cleanup step improved the analysis for lambda-cyhalothrin.

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Suspended sediment samples were collected at two sites in July 2002 for analysis of molinate, thiobencarb, and lambda-cyhalothrin. Molinate was detected in both samples, thiobencarb was detected and quantified in one sample, but could not be quantified in the other, and lambda-cyhalothrin was not detected in either sample. Sediment concentrations of both molinate and thiobencarb were higher than predicted by calculated equilibrium partitioning using concentrations in the surrounding aqueous phase.

Introduction

Background

The Sacramento Valley of California is the nation's second largest producer of rice with nearly 2 million tons harvested from approximately 507,000 acres in 2003 (fig. 1) (U.S. Department of Agriculture, National Agricultural Statistics Service, 2004). Rice is a pesticide-intensive crop with over 5.9 million lb of pesticide active ingredients applied to rice in the Sacramento Valley in 2002 (California Department of Pesticide Regulation, 2002). Most of these pesticides are applied either directly to the soil prior to planting and flooding of the fields, or a few weeks after flooding, to control noxious weeds and pests. When the rice field water is released, it flows into local drains and creeks, and ultimately into the Sacramento River.

Rice pesticide contamination in surface waters of the Sacramento Valley was first studied in the early 1980s by the California Department of Fish and Game (CDFG) in response to reported fish kills in agricultural drains. The study concluded that the fish kills were caused by exposure to high concentrations of molinate, an herbicide used on rice (Finlayson and others, 1982). This study also implicated another rice herbicide, thiobencarb, as the cause of taste and smell problems in city of Sacramento drinking water in May and June of 1981 and 1982. Concentrations as high as 700 µg/L for molinate and 170 µg/L for thiobencarb were detected in 1982 in surface waters of the Sacramento Valley (California Department of Pesticide Regulation, 1992).

The high concentrations of rice pesticides and related deleterious effects prompted the Central Valley Regional Water Quality Control Board (CVRWQCB) to establish performance goals for molinate and thiobencarb in surface water. In 1990, these goals were established at 30 µg/L for molinate and 1.5 µg/L for thiobencarb. The performance goal for molinate was subsequently reduced to 20 µg/L in 1991 and 10 µg/L (the current goal) in 1992 (California Regional Water Quality Control Board, 1989). These performance goals are daily maximum concentrations and were established on the basis of the lowest observed effect concentrations for a number

of aquatic species divided by an uncertainty factor of 10. In addition, California state law established primary maximum contaminant levels (MCLs) in drinking water for molinate at 20 µg/L and thiobencarb at 70 µg/L, and a secondary MCL for thiobencarb at 1 µg/L (California Code of Regulations, 2003).

Management practices were modified to help meet the performance goals. Mandatory holding times for rice field water after pesticide application were established to allow for the natural degradation and dissipation of pesticides prior to release into local surface waters. Current rice water holding times vary with the type of pesticide and local hydrologic conditions, but are generally on the order of 28 to 30 days. This practice has significantly reduced the levels of rice pesticides in surface waters. Other changes in pesticide management practices include recirculating field water systems, seepage control programs, and drift-reducing pesticide formulations and application procedures.

In 1984, the California Department of Food and Agriculture established the Rice Herbicides Control Program to coordinate efforts among multiple state agencies working on this issue. Management of this program was later passed to the California Department of Pesticide Regulation (CDPR), which continues a yearly monitoring program for rice pesticides in cooperation with CDFG, CVRWQCB, the California Rice Commission, and others. This program produces annual reports describing its protocols and findings. In addition, the U.S. Geological Survey (USGS) has conducted studies of the occurrence and fate of rice pesticides in both surface waters and ground waters of the Sacramento Valley (Domagalski and Kuivila, 1991; Bergamaschi and others, 1997; Crepeau and Kuivila, 2000; Domagalski, 2000; Dawson, 2001).

Pesticide Use Patterns

Since 1990, the CDPR's full use reporting system has required pesticide applicators to provide detailed information on pesticide use. This data is extremely valuable in assessing trends in pesticide use, changes in application patterns, and potential for environmental contamination.

During the past decade, major changes have occurred in the types and amounts of pesticides applied to rice in the Sacramento Valley (fig. 2). Use of one herbicide, molinate, peaked in 1994 at nearly 1.5 million lb, but has declined significantly since then and is scheduled to be phased out by 2009. In contrast, another herbicide, thiobencarb, has gradually increased in use from less than 75,000 lb in 1991 to over 800,000 lb in 2002. The most dramatic change has been the increase in application of propanil, which increased from less than 10,000 lb applied in 1991 to nearly 1.4 million lb in 2002, becoming the most heavily used rice herbicide in 2002 (California Department of Pesticide Regulation, 1992–2002).



Figure 1. Locations of sampling sites and rice growing areas within the Sacramento Valley of California.

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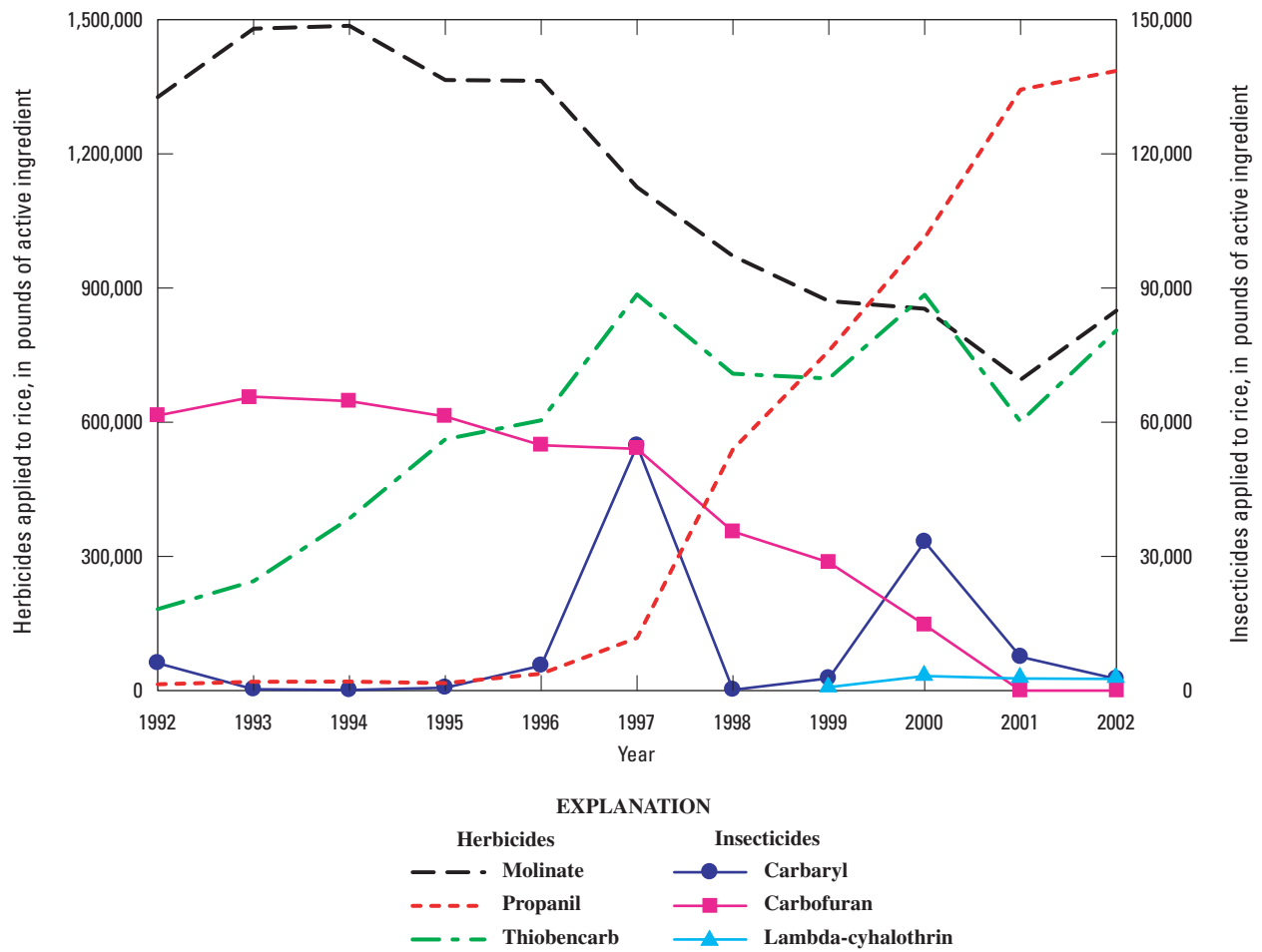


Figure 2. Amounts of pesticides (pounds active ingredient) applied to rice annually in the Sacramento River watershed.

There have been similar changes in the use of insecticides on rice. Carbofuran use has been phased out, declining from about 60,000 lb in 1992 to no use by 2001. The use of another insecticide, carbaryl, has varied considerably over the past decade. In contrast, lambda-cyhalothrin, a pyrethroid insecticide, was first used in 1999 and its use has since increased to nearly 2,400 lb in 2002 (California Department of Pesticide Regulation, 2002). The application amount of lambda-cyhalothrin is much lower than the other insecticides because of its higher toxicity to target organisms.

Current pesticide use data (2002) was incorporated into a geographic information system (GIS) coverage of the study area, which allowed for spatial and temporal mapping of pesticide use during the first year of the study. Through this process, it was also possible to determine the application amounts of various pesticides within selected subbasins of the Sacramento River watershed ([table 1](#)). This information was extremely useful during project planning and data interpretation. Pesticide use data covering the second year of the study (2003) was not yet available from C DPR.

Project Design

This project was designed to measure the concentrations of three rice pesticides and two rice-pesticide degradates in surface waters of the Sacramento Valley and to determine the influence of pesticide use changes over the past decade on pesticide concentrations in surface water. Specific pesticides measured in this study were molinate and thiobencarb (thiocarbamate herbicides), lambda-cyhalothrin (a pyrethroid insecticide), and 2-keto-molinate and 4-keto-molinate (degradates of molinate). Sample processing and analysis techniques focused on detecting lambda-cyhalothrin at the lowest concentration possible, owing to its toxicity to aquatic organisms at low levels.

Water samples were collected weekly from May to July at three sites in 2002 and two sites in 2003 in the rice-growing region of the Sacramento Valley ([fig. 1](#), [table 2](#)). Samples were collected from tributary creeks and agricultural drains that receive water directly from rice fields, and from the Sacramento River at a site downstream of most of the rice-growing areas. Large-volume water samples to isolate suspended sediments were also collected on one occasion at two sites in 2002. All samples were analyzed for pesticides at the USGS's Organic Chemistry Laboratory in Sacramento.

Purpose and Scope

This report describes the methods used for collection and analysis of water and sediment samples collected as part of a two-year study of concentrations of rice pesticides in select streams in the Sacramento Valley of California. Pesticide concentration and ancillary data are presented. This report provides an interpretive analysis by evaluating measured concentrations in terms of current pesticide use patterns, comparing pesticide concentration data collected during the study with historical concentration data, and analyzing those factors that influence trends and patterns seen in the data.

Acknowledgments

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Study Design and Sampling

Study Area

The watershed of the Sacramento River above the city of Sacramento occupies over 23,000 mi² within northern California and includes various land use types, from heavily forested uplands to intensely agricultural and urbanized areas within the Sacramento Valley. The specific area in this study falls within the boundary of the Sacramento Valley and extends from the city of Sacramento northwards, roughly 81 mi, to the town of Durham ([fig. 1](#)). The topography of this area is predominantly low relief, with the exception of the Sutter Buttes, an extinct volcano, which rises abruptly from the center of the valley floor.

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Table 1. Amounts of lambda-cyhalothrin, molinate, and thiobencarb applied during May–July 2002 in the watersheds of each site sampled in 2002

[Amounts are reported as pounds of active ingredient applied; see figure 3 for basin locations; lb, pound]

Watershed	Lambda-cyhalothrin (lb)	Molinate (lb)	Thiobencarb (lb)
Colusa Basin Drain 1 (CBD1)	759	289,071	367,983
Sacramento Slough	970	392,031	334,645
Tower (excluding CBD1 and Sacramento Slough)	648	167,053	101,634
Tower	2,377	848,155	804,262

Table 2. Rice pesticide sampling sites, Sacramento Valley, California

[Horizontal datum, NAD 1927; mi², square mile]

Official site name (short site name)	USGS site identification No.	Latitude (degree/minute/ second)	Longitude (degree/minute/ second)	Year sampled	Basin size (mi²)
Colusa Basin Drain at Road 99E near Knights Landing (CBD1)	11390890	38°48'45"	121°46'23"	2002	1,622
Sacramento Slough near Verona (Sacramento Slough)	384649121381101	38°46'49"	121°38'11"	2002	1,250
Sacramento River at Sacramento (Tower)	11447500	38°35'12"	121°30'16"	2002	23,508
Butte Creek at Gridley Road near Butte Sink NWR (Butte Creek)	392143121532901	39°21'43"	121°53'29"	2003	593
Colusa Trough at Colusa NWR (CBD5)	391100122030101	39°11'00"	122°03'01"	2003	1,019

The Sacramento River watershed contains two main river systems, the Sacramento and Feather Rivers, which, with other tributaries, drain the western slopes of the southern Cascade mountain range and the northern Sierra Nevada and the eastern foothills of the Coast Range. On the Sacramento Valley floor, these rivers are joined by numerous smaller creeks and agricultural drains. One major agricultural drain within the study area is the Colusa Basin Drain (CBD), which receives water from over 1 million acres of farmland along the western side of the Sacramento Valley. Other important hydrologic features of the valley are the Yolo and Sutter Bypasses, which are used in the spring and summer to grow rice.

The primary land use in the Sacramento Valley is agriculture, with over 2 million acres of farmland (California Department of Water Resources, 1990, 1994a, 1994b, 1995a, 1995b, 1995c, 1995d, 2000). This region accounts for over 90 percent of the rice production in California. The Sacramento Valley also supports a large and rapidly expanding urban population of over 2.1 million people (U.S. Census Bureau, 2000).

Most precipitation in the Sacramento Valley occurs between November and March. The mean annual precipitation in the study area ranges from 15 in. per year on the valley floor to 30 in. per year in the Sierras. Typically, little or no precipitation falls during the rice planting and growing season (April–October). However, in 2002, a significant storm (1.81 in. at Sacramento) in mid-May forced some early releases of rice field water (National Oceanic and Atmospheric Administration, 2002). Rice planting was also delayed significantly in 2003 by heavy rains (3.89 in. at Durham) in mid- and late April (California Irrigation Management Information System, 2003).

Selection of Sampling Sites

Sampling sites were selected to represent watersheds that have a significant amount of rice-growing acreage and pesticide use. Other criteria for site selection included proximity to rice fields, previous surface water detections of dissolved pesticides, proximity to current and historical rice pesticide monitoring sites, and the safety of field personnel during sampling.

In 2002, three sites were sampled: two sites located on large agricultural drains—Colusa Basin Drain at Road 99E near Knights Landing (CBD1) and Sacramento Slough near Verona (Sacramento Slough), and one site downstream of all rice fields Sacramento River at Sacramento (Tower) ([fig. 1](#), [table 2](#)). Prior to sampling, water parameters (temperature, specific conductance, and pH) were measured in width and depth profile at each site to determine flow characteristics ([table 3](#)). These measurements indicated that flow was well mixed at both CBD1 and Sacramento Slough, but there was some lateral stratification at Tower as seen in the specific conductance readings. CBD1 and Sacramento Slough were used as historical monitoring sites for rice pesticides by CDPR, and CBD1 has been sampled previously by the USGS.

Lambda-cyhalothrin was not detected in water samples collected in 2002, so it was decided to relocate the sampling sites for the following year. The two new sites sampled in 2003 were Butte Creek at Gridley Road near Butte Sink NWR (Butte Creek) and Colusa Trough at Colusa NWR (CBD5) ([fig. 1](#), [table 2](#)). These sites were located farther upstream in the watershed, closer to areas of current (2003) rice production ([fig. 1](#)), to increase the likelihood of detecting lambda-cyhalothrin. CBD5 has been used as a monitoring site extensively over the past two decades by CDPR.

The Sacramento Valley watershed can be divided into five subbasin watersheds ([fig. 3](#)), which are representative of the five sampling sites. The Sacramento Slough watershed and its subbasin, Butte Creek, consist of agricultural and urban lands within the Sacramento Valley as well as large areas of nonagricultural land in the Sierra Nevada. In contrast, the CBD1 watershed and its subbasin, CBD5, are located on the valley floor and consist predominantly of agricultural lands with some areas of flooded wetlands. The Tower watershed encompasses all four subbasins, additional agricultural lands, and also receives runoff from the city of Sacramento and the American River watershed. For this report, subbasins were created by modifying larger preexisting watershed boundaries on the basis of the location of the sites sampled in the study. Where required, subbasin boundaries were delineated using USGS 1:24,000 scale digital topographic maps.

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Table 3. Site profiles of in-stream water parameters measured in 2002

[ft, feet; °C, degrees Celsius; μS/cm, microsiemens per centimeter]

Site	Date (mm/dd/yy)	Time	Distance from right bank (ft)	Depth (ft)	Temperature (°C)	Specific conductance (μS/cm)	pH
CBD1	05/16/02	1000	40	1	22.3	582	7.8
CBD1	05/16/02	1002	40	6	22.2	581	7.8
CBD1	05/16/02	1005	60	1	22.3	581	7.8
CBD1	05/16/02	1007	60	5	22.2	580	7.8
CBD1	05/16/02	1010	60	7	22.2	580	7.8
CBD1	05/16/02	1015	90	1	22.3	580	7.8
CBD1	05/16/02	1017	90	5	22.2	579	7.8
CBD1	05/16/02	1020	90	8	22.2	579	7.8
CBD1	05/16/02	1024	120	1	22.3	579	7.8
CBD1	05/16/02	1026	120	5	22.2	579	7.8
Sacramento Slough	05/15/02	1010	10	1	21.2	399	7.7
Sacramento Slough	05/15/02	1012	10	10	21.3	399	7.8
Sacramento Slough	05/15/02	1015	20	1	21.3	398	7.8
Sacramento Slough	05/15/02	1017	20	10	21.3	400	7.8
Sacramento Slough	05/15/02	1020	30	1	21.0	401	7.8
Sacramento Slough	05/15/02	1022	30	10	21.3	399	7.8
Tower	05/15/02	1245	50	1	20.1	182	7.9
Tower	05/15/02	1248	50	10	20.1	180	7.9
Tower	05/15/02	1250	50	15	19.5	171	7.9
Tower	05/15/02	1255	120	1	20.0	185	7.9
Tower	05/15/02	1300	120	10	19.5	172	7.9
Tower	05/15/02	1302	120	20	19.2	161	7.9
Tower	05/15/02	1308	220	1	19.5	168	7.9
Tower	05/15/02	1310	220	10	19.5	169	7.9
Tower	05/15/02	1312	220	20	19.0	152	7.8
Tower	05/15/02	1315	320	1	19.5	167	7.9
Tower	05/15/02	1317	320	10	19.2	159	7.9
Tower	05/15/02	1320	320	20	19.0	152	7.8
Tower	05/15/02	1325	440	1	19.0	152	7.8
Tower	05/15/02	1327	440	10	19.0	153	7.8

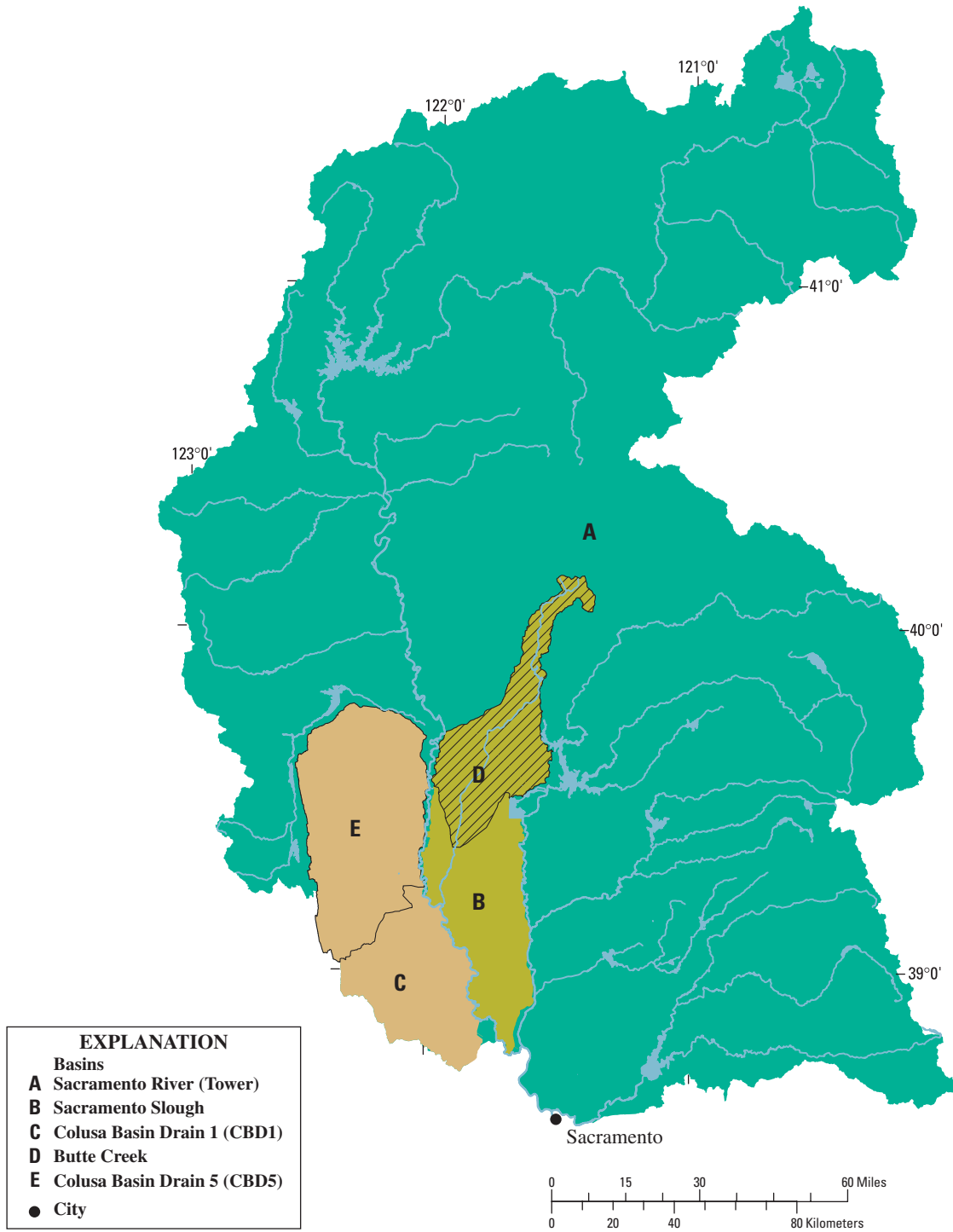


Figure 3. Drainage basins within the area under study.

Sample Collection

Surface Water 2002

Water samples were collected at three sites following pesticide application and the controlled release of water from Sacramento Valley area rice fields. Sampling occurred weekly from May 15 to July 24 at CBD1, Sacramento Slough, and Tower. Sampling at Sacramento Slough and Tower was conducted by boat, while sampling at CBD1 took place from a bridge. Water samples were collected using a 5-L, Teflon-lined Niskin bottle suspended horizontally 1 m below the water surface in the center of flow. At each site, two samples were collected using the Niskin for a total sample volume of approximately 10 L. The water sample was poured into a solvent-washed, 20-L stainless steel milk can that had been rinsed three times using water collected in the first Niskin grab. The milk can was then placed on ice and transported to the USGS's Organic Chemistry Laboratory in Sacramento. The Niskin bottle was rinsed thoroughly using deionized water and (or) native site water when changing sampling locations.

In the laboratory, each sample was split into 10 1-L fractions using a precleaned Teflon cone splitter. The milk can containing the sample water was first shaken for approximately one minute to thoroughly mix the sample and then poured at a consistent rate through the cone splitter. Care was taken to ensure that the splitter reservoir was kept filled at a constant level with sample water during the procedure. Split samples were collected for dissolved pesticides and dissolved organic carbon (DOC) in 1-L amber glass bottles and for suspended sediment concentration (SSC) analysis in 1-L plastic bottles.

To verify the suitability of using a point-sample approach in this study, additional samples were collected for comparison using a cross-section approach. Once a month, water samples were collected using a U.S. D-77 depth-integrating sampler with a 3-L Teflon bottle in three verticals, equally spaced over the width of the channel at each site. A total volume of two liters was collected at each site. The sample was then split into 1-liter fractions by manually shaking the Teflon bottle and pouring the sample into a 1-L baked amber bottle and 1-L plastic bottle for pesticide and SSC analyses, respectively.

Suspended Sediment 2002

Suspended sediments for pesticide analysis were collected by sampling large volumes of water at CBD1 and Sacramento Slough on July 10 and 11, respectively. Approximately 300 L of water were collected at each site using a large volume peristaltic pump with a single stainless steel and Teflon inlet hose suspended at approximately 0.5 m

below the water surface in the center of flow. Sample water was pumped directly into solvent-rinsed 20-L stainless steel soda kegs for transport to the USGS's Sacramento Field Office.

Suspended sediment samples were concentrated using a Westphalia continuous flow centrifuge with a flow rate of 2 L per minute. The resulting slurry was further centrifuged in the laboratory using a high-speed floor centrifuge to remove any remaining free water. The samples were then stored frozen for 18 months until analysis.

Surface Water 2003

Water samples were collected weekly from June 3 to July 22 at Butte Creek and CBD5. Sampling began approximately one month later than the previous year primarily because of late spring rains that delayed rice planting in the region. All samples were collected as mid-channel grabs from bridges using a weighted 3-L Teflon bottle sampler. At each site, a precleaned Teflon bottle was used after having been rinsed three times using native water. Samples were collected at a depth of approximately 0.5 m. Following collection, the sample was split into subsamples by manually shaking the Teflon bottle and pouring the sample into two 1-L baked amber glass bottles for pesticide analysis and one 125-mL amber glass bottle for DOC analysis.

Sample Processing and Analytical Methods

Dissolved Pesticides

In 2002, replicate water samples for pesticide analysis were processed by two different methods: solid-phase extraction (SPE) and liquid-liquid extraction. For SPE extraction, a 1-L water sample was filtered through baked, 0.7- μ m glass fiber filters within 24 hours of sampling, and a surrogate compound, terbuthylazine, was added to provide quantitative data on extraction efficiency. The sample was then extracted onto C8 solid-phase extraction cartridges. The cartridge was then dried using compressed carbon dioxide, frozen, and stored for up to six months. For analysis, the cartridges were thawed and then eluted with 9 mL ethyl-acetate. The resulting extracts were then amended with internal standards, reduced to 200 μ L, and analyzed for two rice pesticides (molinate and thiobencarb) and two degradates of molinate (2-keto-molinate and 4-keto-molinate) using a Varian Saturn GC/MS (gas chromatography-mass spectrometry) with ion-trap detection. Details of the analytical method are described in Crepeau and others (2000).

Liquid-liquid extraction was used for analysis of lambda-cyhalothrin because recovery of this pesticide is variable using SPE. During this process, a 3-L sample was filtered through a 0.7- μm glass fiber filter, transferred to a separatory funnel, and the terbuthylazine surrogate was added. The water was extracted three times with 300 mL of methylene chloride each time. Excess water was removed from the methylene chloride by passing it through sodium sulfate. The extract was reduced using a rotary evaporator to approximately 1 mL volume, passed through a 250-mg SPE activated carbon column (3 cc size barrel, Restek Corporation, Bellefonte, Pennsylvania), and eluted with an additional 10 mL of methylene chloride. The resulting extracts were further evaporated to 0.5 mL, solvent exchanged into ethyl acetate, amended with internal standards, and reduced to 200 μL . The extracts were analyzed for lambda-cyhalothrin using a Varian Saturn GC/MS with ion-trap detection. The method detection limit for lambda-cyhalothrin was calculated at 0.039 $\mu\text{g/L}$, following the procedure described in Crepeau and others, 2000.

All pesticide samples collected in 2003 were processed by liquid-liquid extraction using a sample size of 1 L. Water samples were filtered through a 0.7- μm glass fiber filter, transferred to a separatory funnel, and terbuthylazine was added as a surrogate. The sample was extracted three times with 100 mL of methylene chloride each time. The methylene chloride extract was dried using sodium sulfate, reduced to 0.5 mL, and solvent-exchanged into ethyl acetate. These samples were not cleaned up with the carbon column. The extracts were amended with internal standards, reduced to 200 μL , and analyzed for three rice pesticides (lambda-cyhalothrin, molinate, and thiobencarb) and two degradates of molinate (2-keto-molinate and 4-keto-molinate) using a Varian Saturn GC/MS with ion-trap detection. Details of the analytical method are described in Crepeau and others (2000) and method detection limits are listed in tables 4 and 5 later in this report.

Quality Assurance and Quality Control

Four types of quality control data were routinely collected: replicate samples, surrogate recovery, field equipment blanks, and matrix spikes. Replicate samples constituted 11 percent of the total samples collected, and

differences between replicates were less than 25 percent for all of the pesticides detected.

Recovery of the surrogate, terbuthylazine, was used to assess the efficiency of each extraction. The average percentage recovery and standard deviation for the surrogate compound terbuthylazine was calculated for each year. Sample data were excluded if the recovery of terbuthylazine was outside the control limit of the annual mean plus or minus one and a half standard deviations (Kathryn M. Kuivila, U.S. Geological Survey, unpub. data, 2004). This initial screening resulted in the elimination of three field samples collected in 2002 (two collected at CBD1 and one at Sacramento Slough), one 2002 field equipment blank, one 2002 matrix spike sample, and one 2003 matrix spike sample.

Five field equipment blanks (8 percent of samples) were collected over the course of the study with one taken after sampling at each site to assess potential sample contamination on a site by site basis. In 2002, there were three field equipment blanks, but one was excluded because the surrogate recovery was outside the control limit. Of the other two samples, one blank had no detections of any pesticides, while the other had a thiobencarb detection of 0.0107 $\mu\text{g/L}$. Closer examination of the sequence of samples and standards run on the GC/MS suggests that thiobencarb was carried over in the instrument from the previous injection of a much higher concentration standard. In 2003, two field equipment blanks were collected. One of these samples contained detectable concentrations of molinate (0.0165 $\mu\text{g/L}$) and thiobencarb (0.0053 $\mu\text{g/L}$). Contamination of this blank sample was likely the result of insufficient cleaning of the sampling equipment prior to collection of the blank sample. These values are more than an order of magnitude lower than any values measured in 2003 samples.

In 2002, there were three SPE matrix spike samples, but one was excluded owing to low surrogate recovery. One of the other samples had concentrations of molinate and 4-keto-molinate that were approximately 20 times that of the added spike concentration, making it difficult to accurately quantify the spike recovery. The recoveries of molinate, thiobencarb, 2-keto-molinate, and 4-keto-molinate were very good, ranging from 77 to 93 percent. Lambda-cyhalothrin did not work as well on SPE cartridges, which had recoveries from 29 to 46 percent.

Liquid-liquid extractions of samples were modified both years to improve the recovery and detection limits of lambda-cyhalothrin in the water samples. These results are discussed in detail later in this report.

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Pesticides Associated with Suspended Sediments

Suspended sediment samples were analyzed for pesticides by microwave-assisted solvent extraction (MASE) and GC/MS. Wet sediments were extracted to avoid any artifacts associated with the drying of sediment and for efficient extraction (Jayaraman and others, 2001). Approximately 5 g of sediment (by dry weight) were spiked with a surrogate solution containing 400 ng each of ^{13}C -labeled αBHC , chlorpyrifos, permethrin (*cis/trans* mixture), and simazine (Cambridge Isotope Laboratories, Inc., Andover, Massachusetts). The sediments were extracted three times by MASE with a mixture of methylene chloride and acetone (50:50 v/v) using an MSP 1000 (CEM Corporation, Matthews, North Carolina). The resulting solution was back-extracted against water, dried using sodium sulfate, and reduced to 1 mL. The extracts were cleaned using activated carbon SPE, solvent-exchanged into ethyl acetate, and further purified using a gel permeation/high pressure liquid chromatography (GPC/HPLC) system. The sample was reduced to approximately 500 μL , internal standards were added, and the sample was brought to a final volume of 200 μL using N_2 evaporation for GC/MS analysis. The details of the method and method detection limits are described in Lawrence A. LeBlanc, U.S. Geological Survey, unpub. data, 2004. Samples were analyzed for three rice pesticides: molinate, thiobencarb, and lambda-cyhalothrin. The method detection limits for molinate and thiobencarb are 2.0 and 4.4 ng/g dry weight, respectively (Lawrence A. LeBlanc, U.S. Geological Survey, unpub. data, 2004). The method is not suitable for the two molinate degradates, 2-keto-molinate and 4-keto-molinate.

Suspended sediments were analyzed for organic carbon content using a Perkin Elmer CHNS/O analyzer (Perkin Elmer Corporation, Norwalk, Connecticut). Sediments were combusted at 925°C in silver boats, after being exposed to concentrated hydrochloric acid fumes in a dessicator for

24 hours to remove carbonate minerals. Sediments were dried to a constant weight before CHN analysis. Acetanilide was used for instrument calibration of elemental carbon and nitrogen. Purified products of high temperature combustion (CO_2 for C, and N_2 for N) were detected via a thermal conductivity detector.

Analysis of Suspended Sediments and Dissolved Organic Carbon

Unfiltered water samples were analyzed for SSC at the USGS's Sediment Laboratory in Marina, California. Details of the analytical method can be found in Guy, 1969.

Water samples collected for DOC analysis were filtered in series through a 2.7- μm (Whatman GF/A) glass fiber filter, a 0.7- μm (Whatman GF/F) glass fiber filter, and a 0.45- μm polypropylene (Pall Gelman GH Polypro Membrane) filter within 24 hours of sample collection. After being filtered, the samples were stored in baked amber glass bottles at 4°C for no longer than 1 week until analysis. DOC concentrations were analyzed using a Shimadzu TOC-5000A total organic carbon analyzer. The instrument was calibrated using potassium hydrogen phthalate standards prepared in organic-free water, with standard concentrations bracketing the concentrations of the samples. Aliquots of filtered water sample (4.5 mL) were acidified using 30 μL of 2N HCl and sparged using N_2 for 3 minutes to remove inorganic carbon as CO_2 . The nonpurgeable organic carbon (NPOC) was analyzed by direct injection of liquid sample into a high temperature (680°C) combustion tube packed with Pt catalyst. The CO_2 produced by oxidation of the NPOC was detected using a nondispersive infrared photometric cell. Each value reported represents the mean of three injections of the same sample. Details of the analytical method are described in Bird and others, 2003.

Analytical Results

Pesticide Concentrations

Dissolved rice pesticides and degradates were analyzed in 30 samples in 2002 ([table 4](#)). All samples contained detectable concentrations of three pesticides (molinate, 4-keto-molinate, and thiobencarb), whereas twelve samples also contained 2-keto-molinate. Lambda-cyhalothrin was not detected in any of the samples. Molinate was detected at the highest concentration with a peak value of 11.7 µg/L (Sacramento Slough on May 30), and thiobencarb was detected at a maximum concentration of 7.16 µg/L (CBD1 on May 23). One of the molinate degradates, 4-keto-molinate, was also detected at high concentrations, with a peak concentration of 4.28 µg/L (CBD1 on June 12). Although the other molinate degradate, 2-keto-molinate, was detected in 12 of the samples, the concentrations were much lower than either 4-keto-molinate or its parent.

In 2003, 16 water samples were analyzed for dissolved rice pesticides and degradates ([table 5](#)). As in the previous year, molinate, 4-keto-molinate, and thiobencarb were detected in all of the samples, and lambda-cyhalothrin was not detected in any of the samples. Measurable concentrations of 2-keto-molinate were found only in two samples. Overall, all pesticide concentrations were two to three times lower than the previous year. Molinate was again detected at the highest concentration, but at a much lower value of 5.37 µg/L (CBD5 on June 10). The same sample contained the highest concentration of 4-keto-molinate (1.32 µg/L). In contrast, the maximum detected concentration of thiobencarb (3.81 µg/L) was detected in Butte Creek on June 3.

Two suspended sediment samples collected in 2002 were analyzed for three pesticides: molinate, thiobencarb, and lambda-cyhalothrin ([table 6](#)). Both molinate and thiobencarb were detected in the Sacramento Slough sample at concentrations of 43.4 and 108 ng/g, dry weight, respectively. The sample from CBD1 had a similar molinate concentration with a value of 38.8 ng/g dry weight, but thiobencarb could not be quantified in this sample because of

a co-eluting compound. The weight percentage of organic carbon in the sediments was 3.04 percent and 1.95 percent for CBD1 and Sacramento Slough sediments, respectively.

Suspended Sediment and Dissolved Organic Carbon Concentrations

Suspended sediment concentrations (SSC) were determined for 32 water samples collected at three sites in 2002 ([table 4](#)), which ranged from 10 mg/L to 93 mg/L. Samples collected at CBD1 had the highest overall concentration (93 mg/L) and the highest average concentration (68 mg/L) of all the sites sampled in 2002. Slightly lower concentrations were seen at Sacramento Slough (maximum of 79 mg/L and average of 63 mg/L). Samples collected from Tower, the farthest site downstream, had the lowest SSC value (10 mg/L) as well as the lowest average concentration (19 mg/L). No temporal trends are apparent in SSC values for any of the sites sampled that can be determined at the sampling interval of this study.

Dissolved organic carbon concentrations were determined in 28 and 16 water samples collected in 2002 and 2003, respectively ([tables 4](#) and [5](#)). Samples collected in 2002 ranged in concentration from 1.16 to 7.79 mg/L. Similar to SSC, DOC concentrations were generally highest at CBD1 and lowest at Tower. In 2003, DOC concentrations ranged from 2.65 to 8.68 mg/L. Water samples collected at CBD5 had consistently higher DOC concentrations than samples collected at Butte Creek.

Sampling Method Comparison

Samples were collected during 2002 to assess whether collecting mid-channel point samples was appropriate as compared with depth-integrated cross section samples for sampling dissolved pesticides and suspended sediments. A comparison of sample pairs collected using both an isokenetic depth-integrating sampler (U.S. D-77) and a point sampler (Niskin bottle) indicates that the two methods collected dissolved pesticides equally, but did not collect suspended sediments equally.

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Table 4. Pesticide, dissolved organic carbon, and suspended sediment concentrations detected in water samples collected during 2002

[Pesticide concentrations are reported as micrograms per liter; lambda-cyhalothrin was not detected in any samples; DOC, dissolved organic carbon, SSC, suspended sediment concentration, MDL, method detection limit, (), pesticide concentrations detected below the method detection limit, nd, nondetection, NA, not measured; µg/L, micrograms per liter; mg/L, milligrams per liter]

Sampling Site	Date (mm/dd/yy)	Time	2-keto-molinate (µg/L) MDL=0.0076 µg/L	4-keto- molinate (µg/L) MDL=0.0117 µg/L	Molinate\ (µg/L) MDL=0.0080 µg/L	Thiobencarb (µg/L) MDL=0.0060 µg/L	DOC Concentration (mg/L)	SSC (mg/L)
CBD1	05/16/02	1030	0.0290	1.40	11.5	5.08	NA	71
CBD1	05/23/02	1000	.0529	2.16	11.4	7.16	4.85	NA
CBD1	05/29/02	1115	.0353	1.91	11.6	4.84	4.14	56
CBD1	06/05/02	0715	.0230	3.68	9.65	2.20	7.79	84
CBD1	06/12/02	0700	nd	4.28	4.92	1.36	7.32	40
CBD1	06/20/02	1050	nd	1.60	1.67	.813	6.42	93
CBD1	06/27/02	0750	nd	1.17	1.01	.600	5.81	83
CBD1	07/02/02	0640	nd	1.70	.764	.403	NA	85
CBD1	07/10/02	1300	nd	.746	.443	.268	5.33	45
CBD1	07/18/02	1330	nd	.546	.326	.177	4.74	55
CBD1	07/24/02	0715	NA	NA	NA	NA	4.95	65
Sacramento Slough	05/15/02	1030	.0096	.367	2.81	.233	NA	66
Sacramento Slough	05/22/02	1015	.0439	.932	10.5	1.21	2.66	74
Sacramento Slough	05/30/02	0930	.0485	1.45	11.7	1.13	2.72	49
Sacramento Slough	06/06/02	0850	.0288	1.21	7.32	.635	3.02	63
Sacramento Slough	06/13/02	1000	.0111	1.41	5.42	.250	2.91	79
Sacramento Slough	06/19/02	1000	nd	.770	2.63	.158	2.99	61
Sacramento Slough	06/26/02	0845	(.0071)	1.12	1.10	.143	3.33	74
Sacramento Slough	07/03/02	0840	nd	.575	.908	.155	1.67	53
Sacramento Slough	07/11/02	0900	(.0053)	.594	.769	.102	3.38	75
Sacramento Slough	07/17/02	1020	nd	.537	.427	.0474	3.62	48
Sacramento Slough	07/23/02	0915	NA	NA	NA	NA	3.25	55
Tower	05/22/02	1330	.0137	.217	2.68	.411	2.26	53
Tower	05/30/02	1100	nd	.230	1.59	.237	1.58	15
Tower	06/06/02	1000	nd	.273	.906	.181	1.86	18
Tower	06/13/02	1115	NA	NA	NA	NA	NA	10
Tower	06/19/02	1115	nd	.0749	.156	.0465	1.23	17
Tower	06/26/02	1015	nd	.0836	.0720	.0252	1.55	17
Tower	07/03/02	1045	nd	.0597	.0388	.0154	4.17	19
Tower	07/11/02	1045	nd	.0446	.0326	.0124	1.39	15
Tower	07/17/02	1150	nd	.0343	.0797	.0271	1.16	23
Tower	07/23/02	1130	nd	.0506	.0301	.0118	1.48	17
Equipment blank	05/30/02	1340	nd	nd	nd	.0107	NA	NA
Equipment blank	07/17/02	1200	nd	nd	nd	nd	NA	NA

Table 5. Pesticide and dissolved organic carbon concentrations detected in water samples collected during 2003

[Pesticide concentrations are reported as micrograms per liter; lambda-cyhalothrin was not detected in any samples; DOC, dissolved organic carbon; MDL, method detection limit; (), pesticide concentrations detected below the method detection limit; nd, nondetection; NA, not measured; $\mu\text{g/L}$, micrograms per liter; mg/L , milligrams per liter]

Sampling site	Date (mm/dd/yy)	Time	2-keto-molinate ($\mu\text{g/L}$) MDL=0.0076 $\mu\text{g/L}$	4-keto-molinate ($\mu\text{g/L}$) MDL=0.0117 $\mu\text{g/L}$	Molinate ($\mu\text{g/L}$) MDL=0.0080 $\mu\text{g/L}$	Thiobencarb ($\mu\text{g/L}$) MDL=0.0060 $\mu\text{g/L}$	DOC concentration (mg/L)
Butte Creek	06/03/03	1015	nd	0.0676	0.712	3.81	2.65
Butte Creek	06/10/03	0930	0.0177	.329	3.13	.603	3.40
Butte Creek	06/17/03	1051	nd	.236	1.03	.507	3.16
Butte Creek	06/24/03	0800	nd	.246	.522	.149	3.57
Butte Creek	07/01/03	0915	nd	.315	.308	.100	3.04
Butte Creek	07/08/03	1100	nd	.423	.266	.104	3.55
Butte Creek	07/15/03	0730	nd	.961	.392	.129	3.31
Butte Creek	07/22/03	1100	nd	.889	.359	.110	4.86
CBD5	06/03/03	1100	nd	.610	3.38	.591	6.73
CBD5	06/10/03	1030	.0187	1.32	5.37	.513	8.20
CBD5	06/17/03	1145	nd	.906	1.31	.543	8.68
CBD5	06/24/03	0900	nd	.930	.894	.274	7.71
CBD5	07/01/03	1020	nd	1.06	.705	.331	6.45
CBD5	07/08/03	1140	nd	1.25	.588	.241	6.58
CBD5	07/15/03	0815	nd	.762	.351	.185	5.24
CBD5	07/22/03	1145	nd	.618	.263	.141	6.35
Equipment blank	06/17/03	1400	nd	nd	.0165	(.0053)	NA
Equipment blank	07/08/03	1700	nd	nd	nd	nd	NA

Table 6. Suspended sediment-associated pesticides: observed concentrations and predicted equilibrium-partitioning concentrations

[Lambda-cyhalothrin was not detected in any samples; nd, nondetection; NC, not calculated; ng/g, nanograms per gram dry weight; f_{oc} , fraction of organic carbon in sediment; K_{oc} , organic carbon: normalized sediment–water distribution coefficient; $\mu\text{g/L}$, micrograms per liter]

	Sampling site	Date (mm/dd/yy)	Time	Sediment concentration (ng/g)	f_{oc} (sediment)	K_{oc} ¹	Predicted water concentration ($\mu\text{g/L}$)	Measured water concentration ($\mu\text{g/L}$)
Molinate	CBD1	7/10/2002	1330	38.8	0.0304	83.2	15.3	0.443
	Sacramento Slough	7/11/2002	0930	43.4	.0195	83.2	26.8	.769
Thiobencarb	CBD1	7/10/2002	1330	nd	.0304	891	NC	.268
	Sacramento Slough	7/11/2002	0930	108	.0195	891	6.23	.102

¹Data from Mackay and others, 1997.

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When comparing pesticide concentrations between samples collected at the same time, the relative percent difference (RPD) between pesticides collected by the two methods was less than 25 percent (table 7). This is within the analytical variability of pesticide replicates (Kathryn M. Kuivila, U.S. Geological Survey, unpub. data, 2004), suggesting that the point sample was representative of the cross-section for dissolved pesticides at the sites sampled in 2002. For suspended sediment concentrations, the analytical method variability (Gray and others, 2000) ranges from a standard deviation of 2.6 mg/L at a concentration of 10 mg/L (26 percent) to 5.3 mg/L at 100 mg/L (5.3 percent). In three of the eight sample pairs collected, the RPD for the two methods was greater than the analytical variability. Results also seem to be biased, with the highest suspended sediment concentration per pair collected by the D-77 sampler in 75 percent of the sample sets. Previous studies have also shown discrepancies and bias in SSC values in comparing these two sampling methods (Martin and others, 1992). A further complicating factor in evaluating SSC is the limited range of flow velocity and depth within which the D-77 sampler operates isokinetically. It is likely that these limitations were a factor at CBD1 where flow velocity was low and at Tower because of channel depth. The D-77 sampler was phased out of use by the USGS at the end of 2002 after recognition of these limitations (USGS Technical Memorandum 2002.09, 2002).

Comparison of Pesticide Concentrations

Dissolved Pesticide Concentrations 2002

Concentrations of molinate were similar at CBD1 and Sacramento Slough (figs. 4A and 4B). In contrast, thiobencarb concentrations were approximately five times higher at CBD1 than Sacramento Slough (figs. 4A and 4B). This difference is most likely due to differences in use; however, concentrations cannot be calculated directly from application amounts because the factors that control concentrations can vary considerably between basins. But, if those factors influence the transport of both molinate and thiobencarb in an individual basin in a similar manner, then ratios of molinate to thiobencarb concentration can be compared with ratios of their application amounts. The average ratio of molinate to thiobencarb concentration was 11.1 for Sacramento Slough and 2.3 for CBD1. A comparison of the ratio of molinate to thiobencarb application in each

basin shows a similar pattern with Sacramento Slough having the highest ratio (1.2) and CBD1 the lowest (0.8).

The peak concentrations of 4-keto-molinate at CBD1 were double the concentrations at Sacramento Slough despite similar molinate concentrations in the two basins. The concentrations of 2-keto-molinate were much lower at all sites with respect to the other pesticides.

In all instances, concentrations of each pesticide detected were least in samples collected at Tower. Though Tower is representative of the largest basin in the study and, therefore, receives the greatest volume of pesticide exposed water, it is likely that dilution by pesticide-free runoff from the upper reaches of the watershed results in lower overall pesticide concentrations.

At each of the sites, the maximum concentrations of molinate, thiobencarb, and 4-keto-molinate were detected at approximately the same time, May 22 through May 30, 2002 (figs. 4A, 4B, and 4C). These detections took place just after an unseasonable storm (May 19–21) dropped over an inch and a half of rain throughout much of the Sacramento Valley. Minor flooding caused by this storm resulted in the release of water from rice fields just north of Sacramento that had recently been treated with thiobencarb, and which had not undergone the required holding period (Newhart, 2002). This water would have entered the Sacramento River and was likely present during the May 22 sampling at the Tower site. It is likely that this storm caused other uncontrolled releases of pesticide-treated water within the Sacramento Valley, contributing to elevated concentrations of pesticides at CBD1 and Sacramento Slough.

Dissolved Pesticide Concentrations 2003

Maximum concentrations of each of the pesticides detected were generally less than half of the maximum concentrations detected during the previous year. It is likely that multiple factors contributed to the decline in pesticide concentrations detected in 2003. Locating the sampling sites farther upstream in the watershed certainly reduced the source acreage planted in rice and the total amount of pesticides applied that could potentially be detected at each of the sites. Another factor that may have contributed to lower pesticide concentrations was delay of both rice planting and pesticide applications caused by severe spring 2003 rainstorms in the region. In response to this change in timing, water sampling for 2003 was delayed by two weeks relative to the previous year. Spring storms also contributed to a roughly 5 percent decrease in the total rice acreage from 2002 to 2003, which also may have reduced the total amounts of pesticides applied in the study area (U.S. Department of Agriculture, 2004).

Table 7. Pesticide concentrations determined in quality assurance sample pairs collected in 2002 and the relative percent difference between pairs

[Values are reported as micrograms per liter; lambda-cyhalothrin was not detected in any samples; *, samples collected with depth-integrating sampler; QA, quality assurance; RPD, relative percent difference; NA, not applicable; nd, nondetection; µg/L, micrograms per liter]

Sampling site	Date (mm/dd/yy)	Time	Sample type	2-keto-molinate (µg/L)	RPD (percent)	4-keto-molinate (µg/L)	RPD (percent)	Molinate (µg/L)	RPD (percent)	Thioben-carb (µg/L)	RPD (percent)
CBD1*	05/23/02	0945	QA	0.0528	0.2	2.02	7.0	11.9	4.4	7.36	2.8
CBD1	05/23/02	1000	Regular	.0529		2.16		11.4		7.16	
CBD1*	07/18/02	1315	QA	nd	NA	.455	18.2	.355	8.5	.184	3.9
CBD1	07/18/02	1330	Regular	nd		.546		.326		.177	
Sacramento Slough*	05/22/02	1015	QA	.0401	9.0	.849	9.3	9.58	9.2	1.16	4.5
Sacramento Slough	05/22/02	1015	Regular	.0439		.932		10.5		1.21	
Sacramento Slough*	06/19/02	1000	QA	nd	NA	.933	19.1	2.36	10.5	.159	0.6
Sacramento Slough	06/19/02	1000	Regular	nd		.770		2.63		.158	
Sacramento Slough*	07/17/02	1020	QA	nd	NA	.440	19.8	.505	16.7	.0574	19.1
Sacramento Slough	07/17/02	1020	Regular	nd		.537		.427		.0474	
Tower*	05/22/02	1330	QA	nd	NA	.202	7.1	2.47	8.3	.437	6.1
Tower	05/22/02	1330	Regular	.0137		.217		2.68		.411	
Tower*	06/19/02	1115	QA	nd	NA	.0822	9.3	.169	8.0	.0426	8.7
Tower	06/19/02	1115	Regular	nd		.0749		.156		.0465	
Tower*	07/17/02	1200	QA	nd	NA	.0424	21.1	.0981	20.7	.0302	10.8
Tower	07/17/02	1150	Regular	nd		.0343		.0797		.0271	

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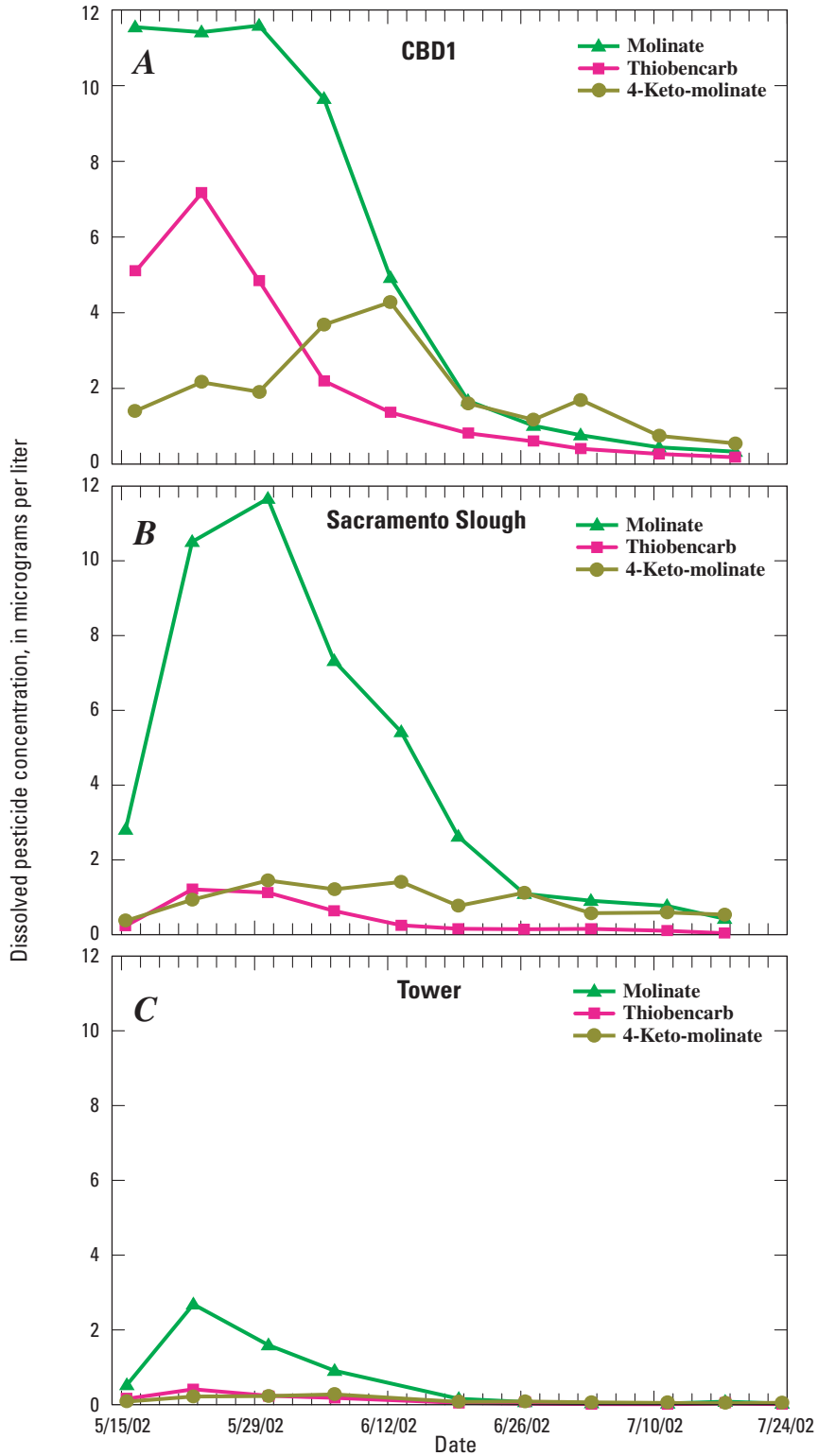


Figure 4. Dissolved pesticide concentrations at CBD1, Sacramento Slough, and Tower in 2002.

Concentrations of molinate and 4-keto-molinate were greater at CBD5 than at Butte Creek during the first six weeks of the study, but were greater in Butte Creek samples during the final two weeks. Concentrations of thiobencarb had the opposite relation. The ratio of molinate to thiobencarb concentration was higher at CBD5 (3.8) than at Butte Creek (2.9). Although pesticide use data for 2003 were not available from DPR, a general comparison can be made using the 2002 data. The ratios of application amounts in 2002 in the two basins had a pattern similar to the concentration ratios: CBD5 was higher (0.95) than Butte Creek (0.7).

The highest concentrations of molinate were detected on June 10 at both sites. Likewise, the highest concentrations of thiobencarb were seen on the same day (June 3) at both sites ([fig. 5A and 5B](#)). The fact that the highest concentrations of both molinate and thiobencarb were not observed on the same day indicates that this timing is likely pesticide dependent. It is likely that the timing of maximum concentrations is a function of the time the bulk of each pesticide was applied and, therefore, when pesticide treated waters were released after the respective holding times had past. Because detailed pesticide use data for 2003 is not yet available, this hypothesis could not be explored further.

Performance Goals and MCLs

In 2002, six water samples contained concentrations of either molinate or thiobencarb above established water quality goals. Molinate concentrations exceeded the performance goal of 10 µg/L in three consecutive weekly samples at CBD1 and in two samples at Sacramento Slough. In these samples, molinate concentrations were generally just above the performance goal. Also at CBD1, four consecutive weekly samples contained concentrations of thiobencarb that exceeded the performance goal of 1.5 µg/L. Three of these samples corresponded with the elevated molinate concentrations. The performance goal for thiobencarb was not exceeded in any samples from Sacramento Slough.

In addition, thiobencarb concentrations exceeded the secondary drinking water MCL of 1.0 µg/L in five consecutive weekly samples from CBD1 and two samples at Sacramento Slough. In these samples, the performance goal for thiobencarb was exceeded by up to 450 percent, and the secondary MCL by up to 700 percent. Water quality goals for molinate and thiobencarb were not exceeded in any samples collected at Tower.

A single water sample collected at Butte Creek during the 2003 sampling period contained thiobencarb at an elevated concentration of 3.81 µg/L. This concentration was more than double the established performance goal for

thiobencarb, (1.5 µg/L) and exceeded the secondary drinking water MCL (1.0 µg/L) by nearly four times. In all other samples collected in 2003, both thiobencarb and molinate were present at concentrations well below established water quality goals.

Historical Peak Concentrations

Using data obtained by CDPR through the Rice Pesticide Monitoring Program, it is possible to compare peak molinate and thiobencarb concentrations observed at CBD5 during this study with over two decades of similar data. The maximum concentrations of molinate and thiobencarb detected at CBD5 during the past 22 years are shown in [figure 6](#). In the early 1980s, the maximum concentrations at CBD5 were very high, with concentrations of molinate and thiobencarb reaching 697 µg/L and 170 µg/L, respectively. Once mandatory holding times for pesticide-treated field water were established in 1984, peak concentrations decreased considerably. In the past decade, peak molinate concentrations have generally continued to decrease, while peak thiobencarb concentrations increased in the late 1990s and then declined again.

Besides the holding times, another factor influencing pesticide concentrations is the change in amounts of pesticides applied over the years. Detailed pesticide use data are available from 1991 to 2002 (California Department of Pesticide Regulation, 2002) and are shown in [figure 6](#). Although maximum molinate concentrations at CBD5 show a general decreasing trend similar to the pattern of use, there is still much more variability than can be explained by changes in application amounts alone. Thiobencarb concentrations increase with increasing use until 1998, when concentrations began to decline despite a continuing increase in use ([fig. 6](#)). Some of the variability in peak concentrations may be explained by the intentional and unintentional early releases of rice field water (Crepeau and Kuivila, 2000).

Despite implementing holding times, the concentrations of both molinate and thiobencarb typically exceed the performance goals ([fig. 6](#)). Molinate concentrations measured at CBD5 were greater than the performance goal of 10 µg/L every year until 2003. In contrast, thiobencarb concentrations did not exceed the performance goal of 1.5 µg/L at CBD5 during a four-year period (1988–1991). But as use of thiobencarb began to increase, the concentrations exceeded the performance goal every year until 2003.

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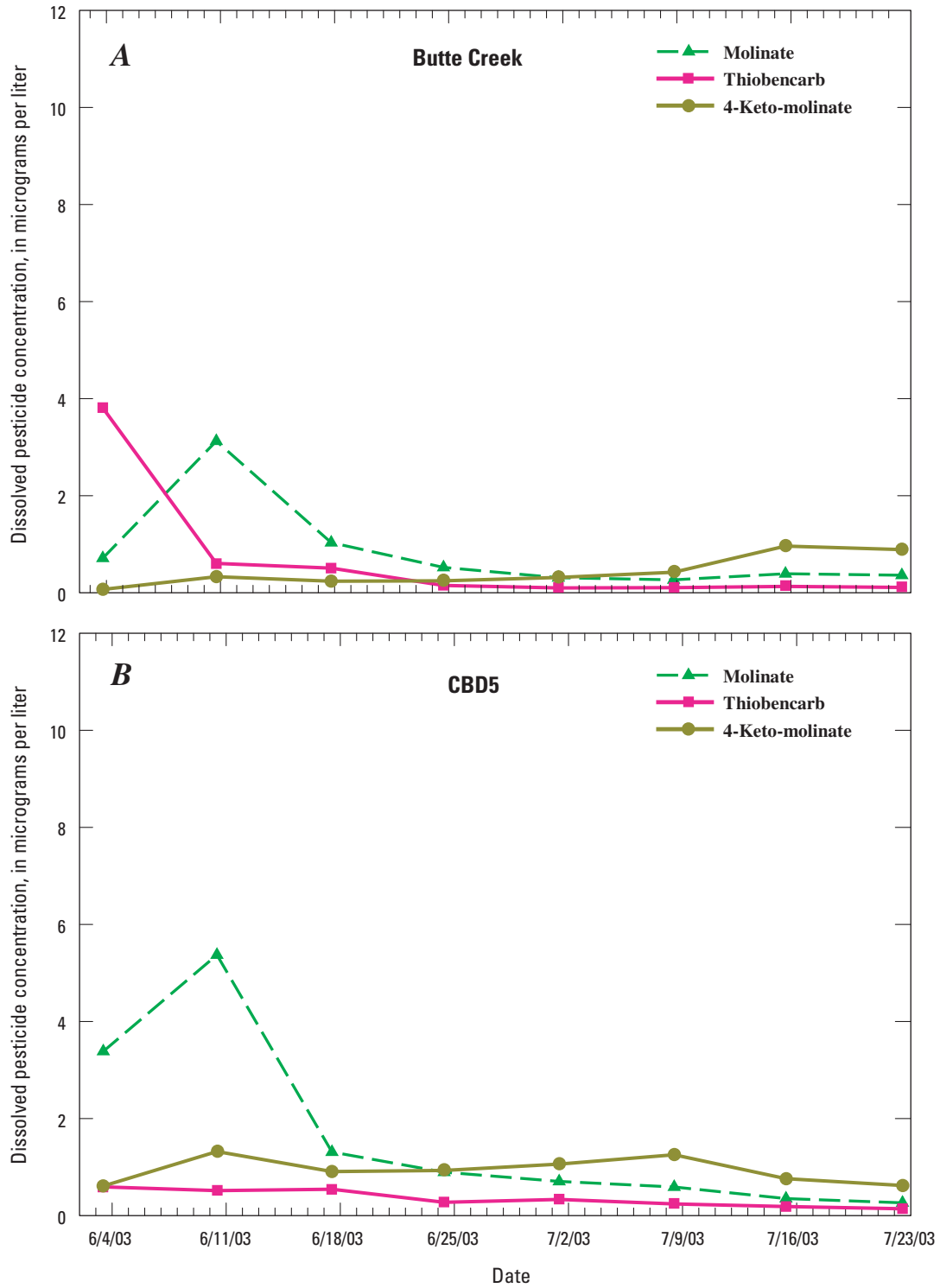


Figure 5. Dissolved pesticide concentrations at Butte Creek and CBD5 in 2003.

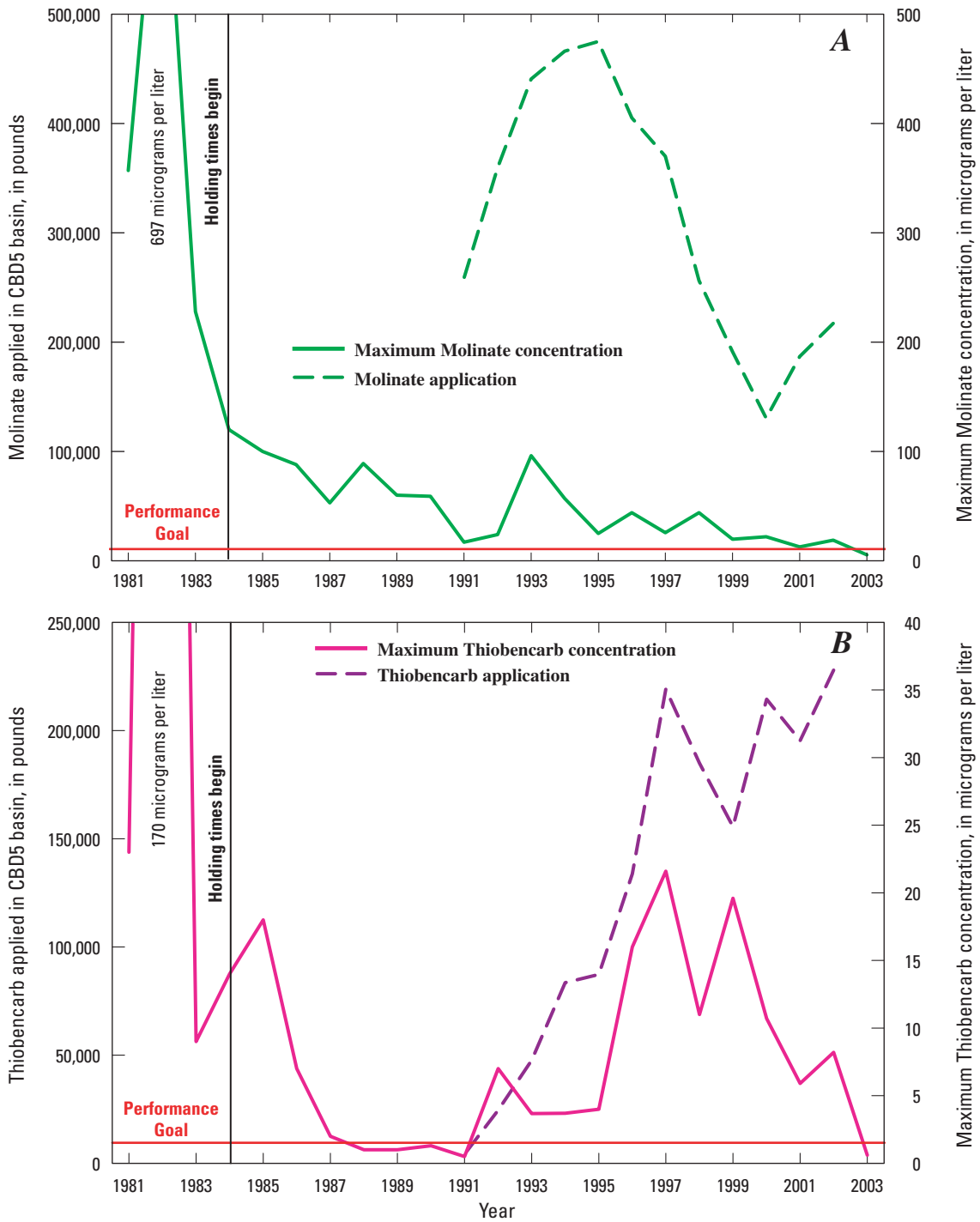


Figure 6. Pesticide application within CBD5 basin, peak pesticide concentrations at CBD5, and performance goals. Data during 1981 through 2003.

There appears to be no direct correlation between molinate and thiobencarb applications and observed maximum concentrations of these pesticides within the CBD5 basin. However, when pesticide use in the basin is plotted against the consecutive number of days during which the respective performance goals for these pesticides were exceeded, there is a very good relation ([fig. 7](#)). Examining the data in this manner indicates that the duration of potential exposure to elevated levels of molinate and thiobencarb is likely linked to the total use of these pesticides within the basin.

Analysis of Lambda-Cyhalothrin

Matrix Recoveries in 2002

Large-volume filtered water samples (3 L) were processed by liquid-liquid extraction, and analyzed to maximize recovery and lower the detection level for lambda-cyhalothrin for the 2002 samples. The drawback to extracting 3 L of water, in contrast to 1-L samples, is that more organic compounds are extracted that interfere with the analysis and cause problems with quantification. The extract was cleaned up by passing it through an activated carbon column. Method validation included testing the recovery of lambda-cyhalothrin through this cleanup step. Methylene chloride spiked using lambda-cyhalothrin and passed through the carbon column had very good recovery (107 percent). Addition of a sample matrix from the liquid-liquid extraction of 3 L of water from CBD1 decreased the recovery to 75 ± 5 percent. But, during this study, matrix spike recoveries of lambda-cyhalothrin were even lower, ranging from 49 percent to 60 percent.

One possibility is that elevated DOC concentrations decreased the efficiency of the pesticide recovery. The concentrations of DOC in these samples ranged from 2.72 to 7.79 mg/L. There is a strong trend of decreasing recovery of lambda-cyhalothrin with increasing DOC concentration ([fig. 8](#)). The apparent loss of the pesticide could have occurred during the sample processing, in either the extraction or carbon column cleanup steps or it could be an artifact of the instrumental analysis.

Additional Method Testing in 2003

Further method testing was added during the 2003 sampling. To determine if lambda-cyhalothrin was being lost during sample processing, all samples included a matrix spike, the carbon cleanup step was eliminated, and the sample size was decreased to 1 L. DOC concentrations were similar to 2002 values, ranging from 2.65 to 8.68 mg/L. Matrix spike recoveries were very good ($106 \text{ percent} \pm 9.8 \text{ percent}$). This suggests that the liquid-liquid extraction efficiency was not the problem.

Standard additions were done on all samples to determine if there was matrix interference in the GC/MS analysis. Before analysis, each eluted sample was measured precisely and a 100- μL subsample was taken. A matrix spike was added directly to the subsample as the standard addition sample. Both the unspiked and standard addition samples were analyzed by GC/MS. The amount of added matrix spike is compared with the calculated difference between the two samples. Any problems or inconsistencies with matrix interference can be identified by the standard addition method. The recoveries were very good ($104 \text{ percent} \pm 9.3 \text{ percent}$), suggesting that matrix interference was not a problem in these samples.

The results from both years suggest that the loss of lambda-cyhalothrin likely occurred during the carbon cleanup step due to elevated DOC concentrations.

Dissolved Organic Carbon

The concentrations of DOC varied considerably between the five sites sampled, with CBD5 and CBD1 being greater than Sacramento Slough and Butte Creek and all sites being greater than Tower as shown in the box plots in [figure 9](#). On the basis of a worldwide average DOC concentration in surface waters of approximately 5.8 mg/L (as reported by Boggs and others, 1985), it is possible to classify water samples collected at CBD5 as having high or above average DOC concentrations, samples from CBD1 as average to slightly below average, and those collected at Sacramento Slough, Butte Slough, and Tower as well below average.

The difference in DOC concentrations between the sites may be explained by the respective land-use practices within each watershed. Waters at CBD1 and CBD5 are almost entirely agricultural return water (mostly from flooded rice fields), whereas the Sacramento Slough and Butte Creek sites receive runoff from their respective upper watersheds where there is no agriculture in addition to rice field water. Besides runoff from both basins, the Tower site also receives runoff from the city of Sacramento and the American River watershed. The lower DOC values for the Sacramento Slough, Butte Creek, and Tower sites relative to the CBD1 and CBD5 sites are likely the result of dilution by low DOC water from the mountainous, upper reaches of the watersheds.

The results of this study suggest that dissolved organic matter, quantified in terms of DOC, influences the analysis of lambda-cyhalothrin. The concentration and type of dissolved organic matter can influence the toxicity of the contaminant by increasing or decreasing its bioavailability to aquatic species (Kukkonen and Oikari, 1987; Benson and Long, 1991; Day, 1991; Kadlec and Benson, 1995). It is, therefore, valuable to measure DOC concentrations in surface water samples especially when those same water samples may contain measurable levels of organic pesticides.

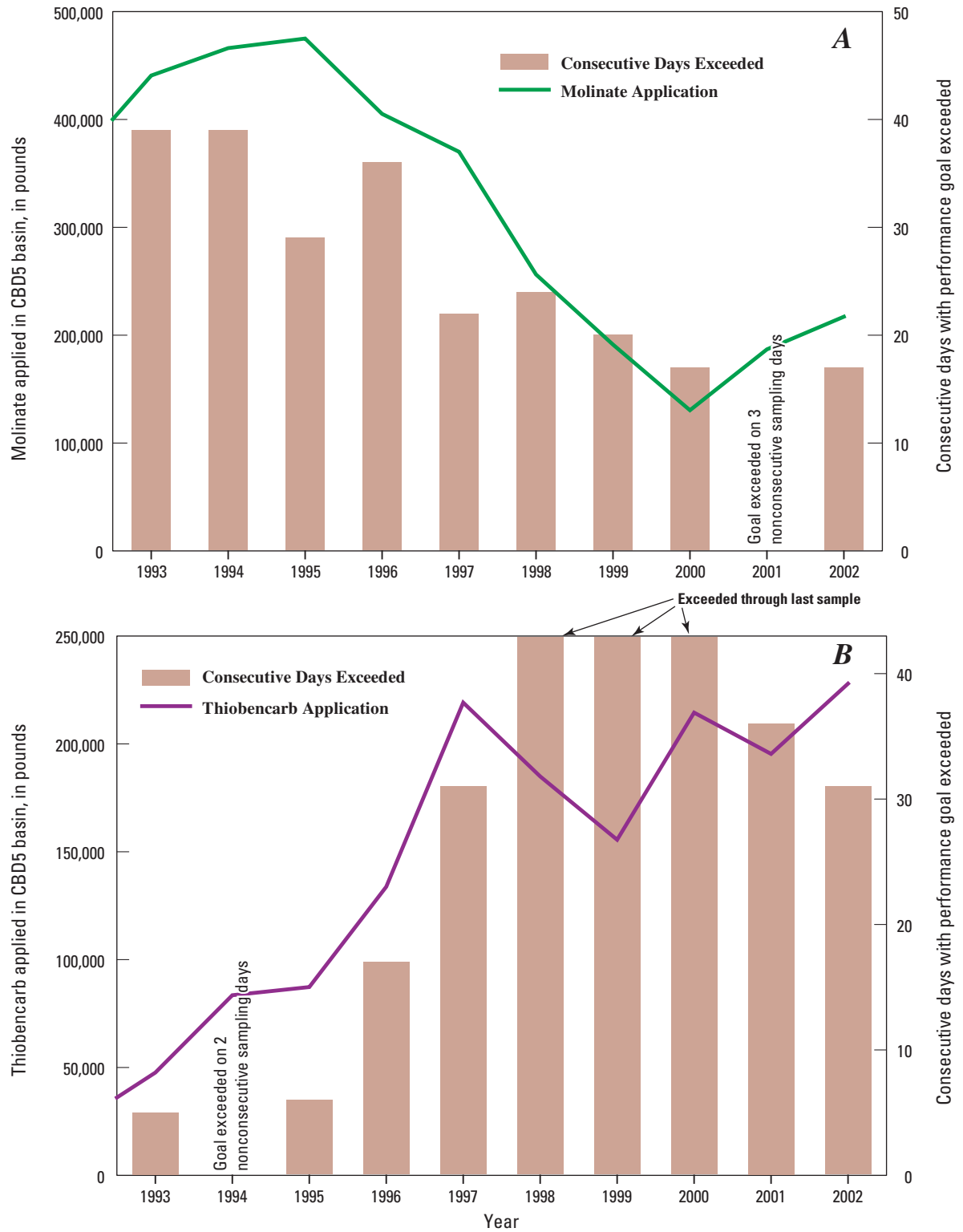


Figure 7. Days that performance goals were exceeded each year at CBD5 and the pesticide use during 1992 through 2002 in the basin.

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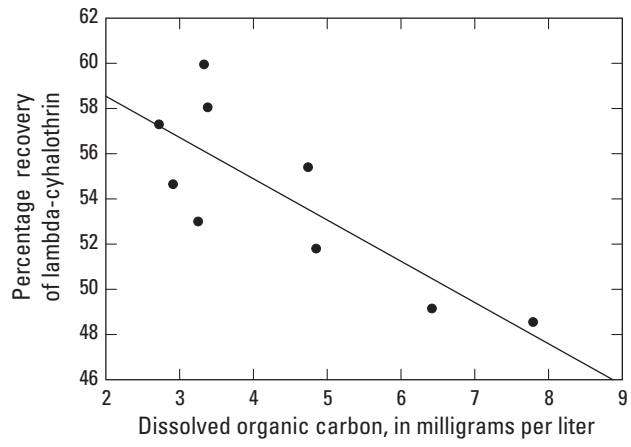
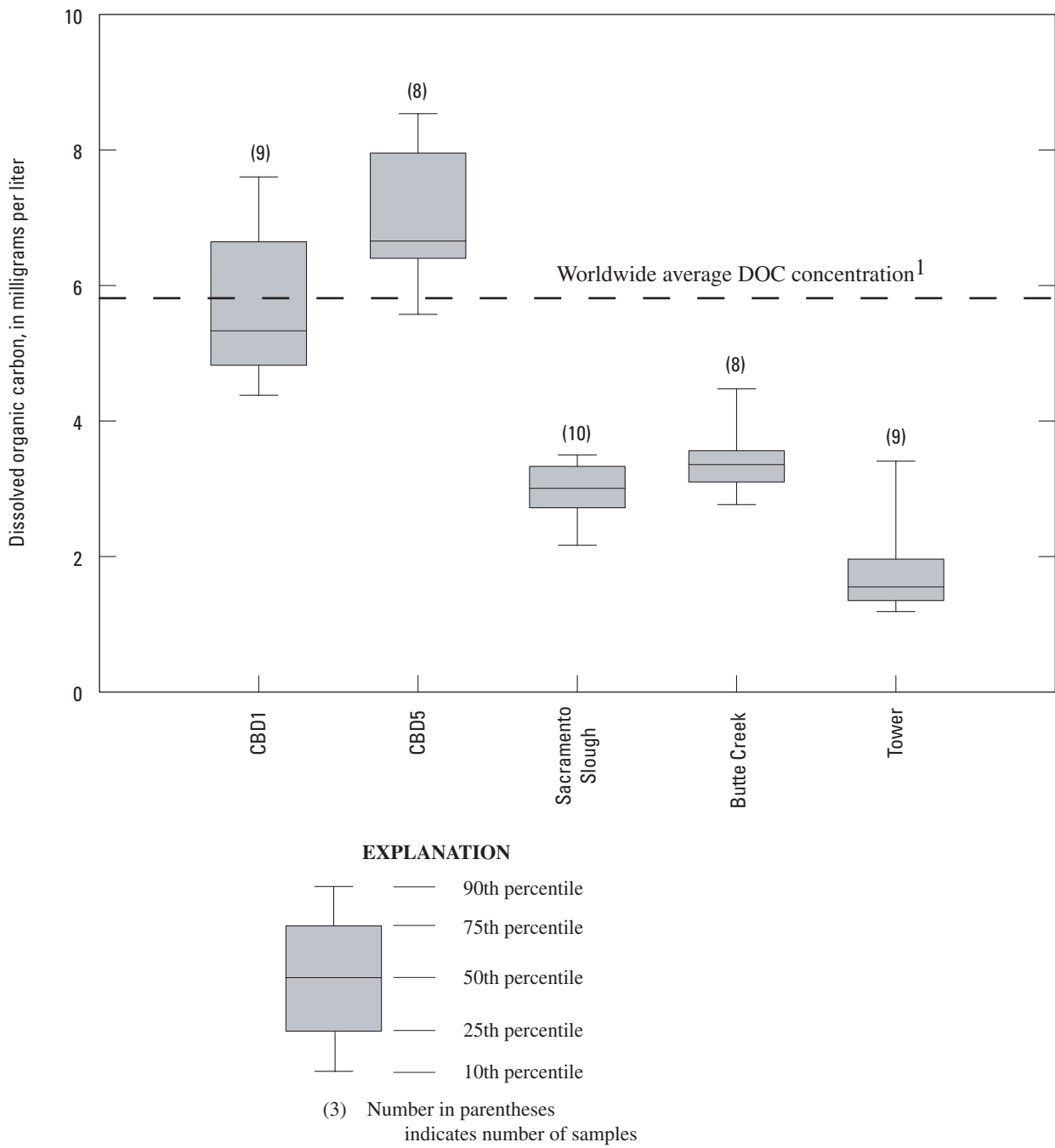


Figure 8. Recovery of lambda-cyhalothrin in samples collected in 2002 versus the dissolved organic carbon concentration (DOC).



¹ Boggs and others, 1985

Figure 9. Dissolved organic carbon (DOC) concentrations at the five sites sampled.

Pesticide Partitioning Between Water and Sediments

Sediment-Associated Pesticide Concentrations

Two suspended sediment samples collected at CBD1 and Sacramento Slough were analyzed for sediment-associated pesticides and contained detectable concentrations of molinate and thiobencarb but not lambda-cyhalothrin. A sample was not collected at Tower because of low suspended sediment and dissolved pesticide concentrations.

The concentration of molinate (43.4 ng/g) was greater in the Sacramento Slough sample than in the CBD1 sample (38.8 ng/g), which is similar to the pattern of use (tables 1 and 6). Thiobencarb also was detected in the Sacramento Slough sample, but could not be quantified in the CBD1 sample because of co-elution of interfering compounds. The concentration of thiobencarb was more than two times that of molinate in the Sacramento Slough sediment sample (table 6) despite the almost equal use of the two pesticides in the basin (table 1). This can be explained by thiobencarb having a higher organic carbon to normalized sediment–water distribution coefficient (K_{oc} ; table 6) than molinate. Lambda-cyhalothrin is more hydrophobic than molinate or thiobencarb and would be expected to preferentially sorb to sediments; however, the very low application amounts (table 1) may account for the lack of detection of lambda-cyhalothrin.

The suspended sediment sampling at CBD1 was conducted at a time corresponding to the second lowest SSC value (45 mg/L) recorded for that site during the study. In contrast, the sample collected at Sacramento Slough corresponded to the second highest SSC value (75 mg/L) at that site.

Equilibrium Partitioning

If pesticides partition between water and sediments following equilibrium partitioning models (Swarzenbach and others, 1993), the aqueous concentration can be predicted from the sediment concentration. The equation becomes:

$$C_w = \frac{C_{Sed}}{f_{oc}K_{oc}}$$

where

- C_w is the predicted concentration in water (mg/L),
- C_{Sed} is the concentration in sediment (ng/g dry weight),
- f_{oc} is the fraction of sediment organic carbon, and
- K_{oc} is the organic carbon normalized sediment–water distribution coefficient for each pesticide.

Using the measured concentrations of molinate associated with suspended sediments, the dissolved concentration can be calculated for the two samples. For molinate, the model overestimates the dissolved concentrations by a factor of 34, suggesting the sediments are not in equilibrium with the surrounding aqueous phase. Although the measured concentrations of molinate varied by a factor of two between the samples, the ratio of predicted to measured concentrations agreed very well. The predicted concentration of dissolved thiobencarb in the Sacramento Slough was also overestimated, in this case by a factor of 61. These results agree with previous studies of current-use pesticides in the Sacramento and San Joaquin Rivers (Domagalski and Kuivila, 1993; Bergamaschi and others, 1997, 2001) that showed sediment concentrations elevated above values predicted by equilibrium partitioning models.

Summary

Water samples collected during the rice growing season in 2002 and 2003 at a total of five surface water sites within the Sacramento Valley were analyzed for five currently used rice pesticides and pesticide degradates. Molinate, thiobencarb, and 4-keto molinate were detected in every sample. 2-keto-molinate was detected in less than half the samples and at much lower concentrations than the other pesticides present. Lambda-cyhalothrin was not detected in any of the samples.

Concentrations of molinate were similar at CBD1 and Sacramento Slough in 2002, but thiobencarb concentrations were five times higher at CBD1. Maximum concentrations of all pesticides detected in 2003 were less than half of the 2002 levels; this was likely due to the change in sampling locations and spring rains that delayed planting and pesticide application and may have decreased amounts of pesticides applied. Although concentrations cannot be estimated directly from application amounts in the different watersheds, the ratio of molinate to thiobencarb concentrations is comparable to the ratio of molinate to thiobencarb use in each basin during 2002.

Concentrations of molinate or thiobencarb were found to exceed established water quality performance goals of 10 mg/L and 1.5 mg/L, respectively, in six samples in 2002, but only in a single sample in 2003 (thiobencarb at Butte Creek). Performance goals for these two rice pesticides were exceeded for up to four consecutive weeks in 2002. Over the past decade, changes in pesticide use appear to influence trends in historical peak concentrations, but do not explain all of the variability in concentrations. There is a better relation between pesticide use and the period of time that performance goals are exceeded in a basin.

Sample processing and analytical methods were optimized to analyze for lambda-cyhalothrin in water. Results from cleanup steps using activated carbon SPE columns showed that recoveries decreased with increasing DOC concentrations in the water samples. Liquid-liquid extraction of 1-L samples using no cleanup appeared to yield the highest and most consistent recoveries, resulting in a method detection limit of 0.0039 µg/L and matrix spike recoveries of 106 ± 9.8 percent. Despite the method optimization, lambda-cyhalothrin was not detected in any water samples. The amounts applied are low (less than 0.5 percent of the amount of molinate or thiobencarb applied) and because lambda-cyhalothrin is hydrophobic, it is expected to partition onto sediments.

Two suspended sediment samples were collected in July 2002 at CBD1 and Sacramento Slough. Concentrations of molinate and thiobencarb associated with suspended sediments were above predicted levels when in equilibrium with dissolved pesticide concentrations. These results agree with previous studies in San Francisco Bay that have also detected elevated concentrations of molinate and thiobencarb associated with suspended sediments. Lambda-cyhalothrin was not detected in the two suspended sediment samples.

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