



Report TP 02-08

**City of Stockton Mosher Slough and Five Mile Slough
Diazinon and Chlorpyrifos
Aquatic Life Toxicity Management Report**



Prepared by

G. Fred Lee, PhD, DEE and Anne Jones-Lee, PhD
California Water Institute
California State University, Fresno

for the
Central Valley Regional Water Quality Control Board
Sacramento, California

and the
State Water Resources Control Board
Sacramento, CA

December 2002

DISCLAIMER

This publication is a technical report by staff of the California Water Institute to the California State Water Resources Control Board and the Regional Water Quality Control Board, Central Valley Region. No policy or regulation is either expressed or intended.

Disclosure Statement

Funding for this project has been provided in part by the U.S. Environmental Protection Agency (US EPA) pursuant to Assistance Agreement No. C9-989268-99-0 and any amendments thereto which has been awarded to the State Water Resources Control Board (SWRCB) for the implementation of California's Nonpoint Source Pollution Control Program. The contents of this document do not necessarily reflect the views and policies of the US EPA or the SWRCB, nor does mention of trade names or commercial products constitute endorsement or recommendation for use.

This project was conducted by Drs. G. Fred Lee and Anne Jones-Lee as employees of the California Water Institute, California State University, Fresno. In addition to the support provided to this project by the California Water Institute and the Central Valley Regional Water Quality Control Board, it was supported by G. Fred Lee & Associates, El Macero, California.

Acknowledgment

We wish to acknowledge the assistance provided in developing this report by Dr. Val Connor, formerly with the Central Valley Regional Water Quality Control Board, now with the State Water Resources Control Board; William Jennings (the DeltaKeeper); and Joe Karkoski, Les Grober, Shakoora Azimi-Gaylon, Jerrold Bruns, Karen Larsen and Kelly Briggs of the Central Valley Regional Water Quality Control Board staff. We also wish to acknowledge the assistance of Mary McClanahan of the California Water Institute, California State University, Fresno, and Linda Deanovic and other staff of the University of California, Davis, Aquatic Toxicology Laboratory, Davis, CA.

California Water Institute California State University, Fresno

The California Water Institute was started with seed money provided by the Proposition 13 Water Bond Measure, approved by voters in 2000. The Institute is housed at the California State University, Fresno.

The goal of the Institute is to provide a place where agricultural, urban, and environmental interests can be brought together in an unbiased, open, collaborative process to develop a shared vision of how to best utilize our water resources. It is the stated purpose of the Institute to work on collaborative solutions to pressing water issues facing the State. The staff of the Institute includes economists, chemists, crop water usage specialists, resource specialists, and environmental engineers. In addition, faculty at the California State University, Fresno, collaborate with the Institute in important research efforts.

Executive Summary

Mosher Slough and Five Mile Slough are stormwater drainage ways located in the city of Stockton, California. Monitoring studies conducted by the Central Valley Regional Water Quality Control Board (CVRWQCB) and the DeltaKeeper from 1994 through 2000 have found measurable, potentially toxic concentrations of diazinon and, at times, chlorpyrifos, as well as aquatic life toxicity to *Ceriodaphnia dubia* during and for a short time after stormwater runoff events. The concentrations of diazinon and chlorpyrifos are sufficient to cause the aquatic life toxicity found. Mosher Slough and Five Mile Slough have CVRWQCB designated beneficial uses of municipal and domestic supply, agricultural supply, industrial supply, contact and non-contact water recreation, freshwater aquatic habitat, fish migration, fish spawning, and wildlife habitat. The presence of aquatic life toxicity in these sloughs represents a violation of the CVRWQCB Basin Plan water quality objective of “no toxics in toxic amounts.”

Mosher Slough receives stormwater runoff and irrigation tailwater discharges upstream of the City. Within the City, it receives stormwater runoff from residential and commercial areas. Five Mile Slough receives runoff from residential and commercial areas. Mosher Slough and Five Mile Slough are freshwater tidal tributaries with about a three-foot tide that discharge to the San Joaquin River Deep Water Ship Channel, via Fourteen Mile Slough or Disappointment Slough. They are part of the San Joaquin River-Sacramento River Delta.

Mosher Slough and Five Mile Slough are listed on the Federal Clean Water Act’s 303(d) list as impaired for diazinon and chlorpyrifos. The impairment is expected to extend throughout Mosher Slough and Five Mile Slough within the city of Stockton and for some undefined distance into the San Joaquin River Deep Water Ship Channel and the Delta via Fourteen Mile Slough or Disappointment Slough. The 303(d) listing requires development of a Total Maximum Daily Load (TMDL) for diazinon and chlorpyrifos for Mosher Slough and Five Mile Slough. This report has been developed to present information that is pertinent to managing the aquatic life toxicity that is due to diazinon and chlorpyrifos in Mosher Slough and Five Mile Slough associated with stormwater runoff events.

Since information is not available on the loads of diazinon and chlorpyrifos to Mosher Slough and Five Mile Slough and within these sloughs during a stormwater runoff event, it was necessary to consider an alternative US EPA recommended approach of using the water quality management goal (proposed water quality objective) for protection of aquatic life from diazinon and chlorpyrifos toxicity as the allowable loading capacity (concentration) for Mosher Slough and Five Mile Slough. This translates for diazinon allowed loading capacity concentrations for Mosher Slough and Five Mile Slough to 0.08 µg/L for a 1-hour average (acute exposure), and 0.05 µg/L for a 4-day average (chronic exposure). For chlorpyrifos, the corresponding allowed loading capacities, expressed as concentrations, are 0.020 µg/L for acute exposure and 0.014 µg/L for chronic exposure.

In addition to urban stormwater-runoff-derived diazinon and chlorpyrifos from urban, residential and commercial properties, some unquantified loads of these pesticides to Mosher Slough and Five Mile Slough are believed to be due to atmospheric transport of diazinon and chlorpyrifos used in agricultural areas in San Joaquin County and in the Central Valley. Further, during stormwater runoff events there is a potential for upstream of the City agricultural use of diazinon and chlorpyrifos to be transported to Mosher Slough within the City via Mosher Creek, and thereby contribute to the loads of these pesticides within Mosher and Five Mile Sloughs. The magnitude of this loading is unknown. It is believed, however, that the primary sources of diazinon and chlorpyrifos for Mosher Slough and Five Mile Slough within the city of Stockton are storm sewers that drain residential and commercial properties within these sloughs' urban watersheds.

Table of Contents

Disclaimer	ii
Disclosure Statement and Acknowledgment	iii
California Water Institute, California State University, Fresno	iii
Executive Summary	iv
Table of Contents	vi
List of Tables	vii
List of Figures	vii
List of Acronyms and Abbreviations	viii
City of Stockton Mosher Slough and Five Mile Slough	
Diazinon and Chlorpyrifos Aquatic Life Toxicity Management	
Introduction and Background	1
The Problem	1
Beneficial Uses	1
Water Quality Objectives	1
Pesticides	1
Toxicity	4
Climate and Hydrology	5
Chemical and Physical Properties and Biological Effects	5
Sources of Diazinon and Chlorpyrifos	5
Monitoring Data	6
Summary of Results	7
Discussion	13
Mosher Slough	13
Five Mile Slough	13
City of Stockton NPDES Stormwater Permit OP Pesticide and Aquatic Life	
Toxicity Monitoring Data 1992-2000	13
Comparison between City of Stockton and CVRWQCB/DeltaKeeper Sampling	15
November 1999 Studies	16
January 1998	20
1997 Stormwater Runoff Monitoring	21
1995-1996 Stormwater Runoff Monitoring	21
Overall Evaluation	22
Estimating Loads of Diazinon and Chlorpyrifos	22
Diazinon and Chlorpyrifos Export Coefficients	23
Chlorpyrifos and Diazinon Use Data	25
Relationship between Sources and Concentrations in the Sloughs	29
Allocations	30
Background Load	30
Margin of Safety	30
Waste Load Allocation	31
Load Allocation	31
Conclusions	31
Recommendations	32
References	32

List of Tables

Table 1	CDFG Freshwater Aquatic Life Criteria for Diazinon and Chlorpyrifos.....	4
Table 2	Climate Summary for Stockton	5
Table 3	Summary of Aquatic Toxicity Test Data, Mosher Slough, Stockton, CA (1994-1999).....	8
Table 4	Summary of Aquatic Toxicity Test Data, Five Mile Slough, Stockton, CA (1994-1998).....	11
Table 5	City of Stockton Precipitation Data for Sampling Events.....	12
Table 6	Stockton Stormwater NPDES Monitoring Sites.....	14
Table 7	City of Stockton Stormwater Runoff Pesticide Monitoring 1998-2000.....	14
Table 8	Effects of City of Stockton Stormwater Runoff Sample MS-14 on Growth of <i>Selenastrum capricornutum</i> Using Laboratory Water as the Diluent	16
Table 9	Effects of Receiving Water on Growth of <i>Selenastrum capricornutum</i> Using Laboratory Water as the Diluent	17
Table 10	Effects of City of Stockton Stormwater on Survival and Reproduction of <i>Ceriodaphnia dubia</i> Using Lab Water as the Diluent	17
Table 11	Effects of PBO Addition on Mortality of <i>Ceriodaphnia dubia</i> (Acute Toxicity Testing).....	18
Table 12	Summary of Phase I Acute TIE Performed on Stormwater Runoff Collected on November 8, 1999, Using <i>Ceriodaphnia</i>	19
Table 13	Summary of Phase I Acute TIE Performed on Stormwater Runoff Collected on November 8, 1999, Using <i>Selenastrum</i>	19
Table 14	Summary of Phase II TIE Performed on Stormwater Runoff Collected on November 8, 1999, Using <i>Selenastrum</i>	20
Table 15	Toxicity Testing Results for City of Stockton Stormwater Runoff Collected on January 14, 1998.....	20
Table 16	Diazinon and Chlorpyrifos Stormwater Runoff Export from City of Stockton Mosher Slough at Kelly Drive (MS-14) Watershed.....	24
Table 17	Diazinon and Chlorpyrifos Stormwater Runoff Export from City of Stockton Mosher Slough at Thornton Road (MS-18) Watershed.....	24
Table 18	Diazinon Use in San Joaquin County During 1999-2000.....	26
Table 19	Chlorpyrifos Use in San Joaquin County During 1999-2000.....	27
Table 20	Incorporated Cities and Populations, January 1, 2002.....	28

List of Figures

Figure 1	Location Map.....	2
Figure 2	Monitoring Station and Rain Gage Locations.....	3

List of Acronyms and Abbreviations

µg/L	micrograms per liter (0.10 µg/L = 100 ng/L)
ai	active ingredient of a pesticide
Basin Plan	Water Quality Control Plan (Basin Plan) Central Valley Region ; Sacramento River and San Joaquin River Basins
BL	background load
CCC	criterion continuous concentration
CDFG	California Department of Fish and Game
CMC	criterion maximum concentration
CV	coefficient of variation
CVRWQCB	Central Valley Regional Water Quality Control Board
CWA	Federal Clean Water Act
CWC	California Water Code
Delta	Sacramento-San Joaquin Delta
DPR	California Department of Pesticide Regulation
DWR	California Department of Water Resources
EDTA	ethelene diamine tetraacetic acid
ELISA	enzyme-linked immunosorbent assays
g/day	grams/day
in.	inches
K _{OC}	equilibrium constant, normalized for organic carbon
LA	load allocation
lbs	pounds
LC	loading capacity
LC ₅₀	lethal concentration which kills 50 percent of test organisms in a given period of time
LOQ	limit of quantification
MOS	margin of safety
mPa	milliPascals
NCDC	National Climatic Data Center
ng/L	nanograms per liter (100 ng/L = 0.10 µg/L)
NOEC	no observed effect concentration
NPDES	National Pollutant Discharge Elimination System
OP	organophosphorus
PBO	piperonyl butoxide

List of Acronyms and Abbreviations

PUR	Pesticide Use Report
SWRCB	California State Water Resources Control Board
TIE	toxicity identification evaluation
TMDL	total maximum daily load
TUa	toxic units, acute
UCD-ATL	University of California, Davis, Aquatic Toxicology Laboratory
US EPA	United States Environmental Protection Agency
WLA	waste load allocation

City of Stockton Mosher Slough and Five Mile Slough Diazinon and Chlorpyrifos Aquatic Life Toxicity Management

Introduction and Background

The Problem

The city of Stockton stormwater runoff collection system discharges to several drainage ways (sloughs, rivers or canals) that are connected either directly or via other sloughs/rivers to the San Joaquin River Deep Water Ship Channel. This Channel is part of the San Joaquin-Sacramento River Delta. Mosher Slough and Five Mile Slough are two of the waterbodies within the city of Stockton that receive stormwater runoff from City residential and commercial areas. These sloughs have been found to contain sufficient diazinon and chlorpyrifos concentrations to cause aquatic life toxicity during and for a short time after stormwater runoff events. Diazinon and chlorpyrifos are organophosphorus pesticides used for urban and agricultural pest control in the Mosher Slough watershed and for residential purposes in the Five Mile Slough watershed.

The toxicity in Mosher and Five Mile Sloughs during stormwater runoff events has caused them to be placed on the Clean Water Act Section 303(d) list as impaired waterbodies for which a TMDL must be developed to control the toxicity. Figure 1 presents a map of Stockton, showing the location of the study area. Figure 2 provides additional details on the location of Mosher and Five Mile Sloughs.

Beneficial Uses

Mosher Slough's and Five Mile Slough's designated beneficial uses are those for the San Joaquin River Deep Water Ship Channel, except for navigation. These include MUN (Municipal and Domestic Supply), AGR (Irrigation), PROC (Industrial Processes), REC-1 (Contact, Canoeing and Rafting), REC-2 (Other Noncontact), WARM (Freshwater Habitat – Warm), COLD (Freshwater Habitat – Cold), MIGR (Warm, Cold), SPWN (Warm), and WILD (Wildlife Habitat). Mosher Slough and Five Mile Slough are potentially important nursery areas for larval fish and other aquatic life. They are part of the shallow water habitat of the Delta.

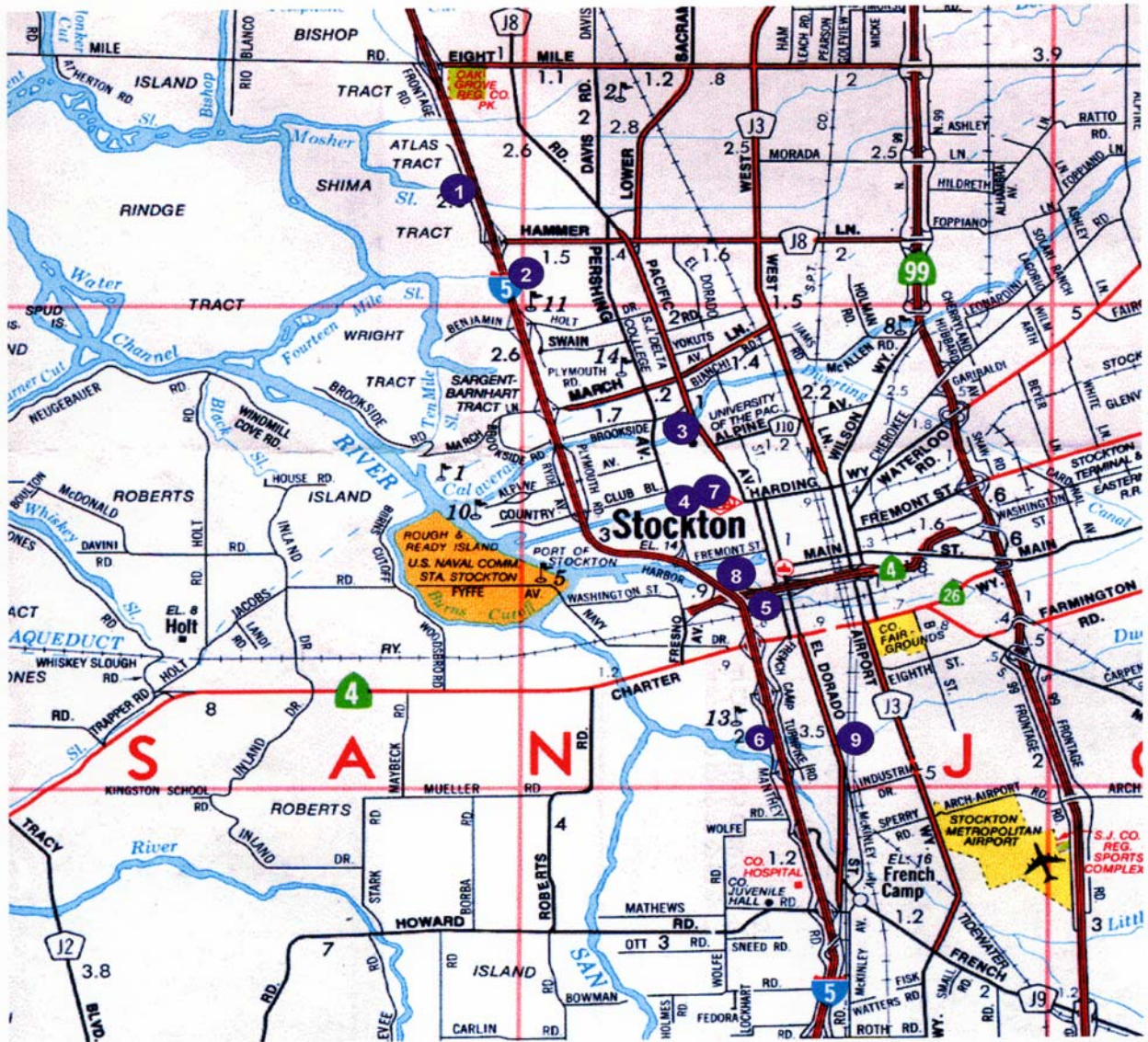
Water Quality Objectives

Water quality objectives in the current CVRWQCB (1998) Basin Plan that are relevant to diazinon and chlorpyrifos in Mosher Slough and Five Mile Slough are presented below.

Pesticides

- *“No individual pesticide or combination of pesticides shall be present in concentrations that adversely affect beneficial uses*
- *Discharges shall not result in pesticide concentrations in bottom sediments or aquatic life that adversely affect beneficial uses*
- *Pesticide concentrations shall not exceed those allowable by applicable antidegradation policies*
- *Pesticide concentrations shall not exceed the lowest levels technically and economically achievable”*

Figure 1 Location Map

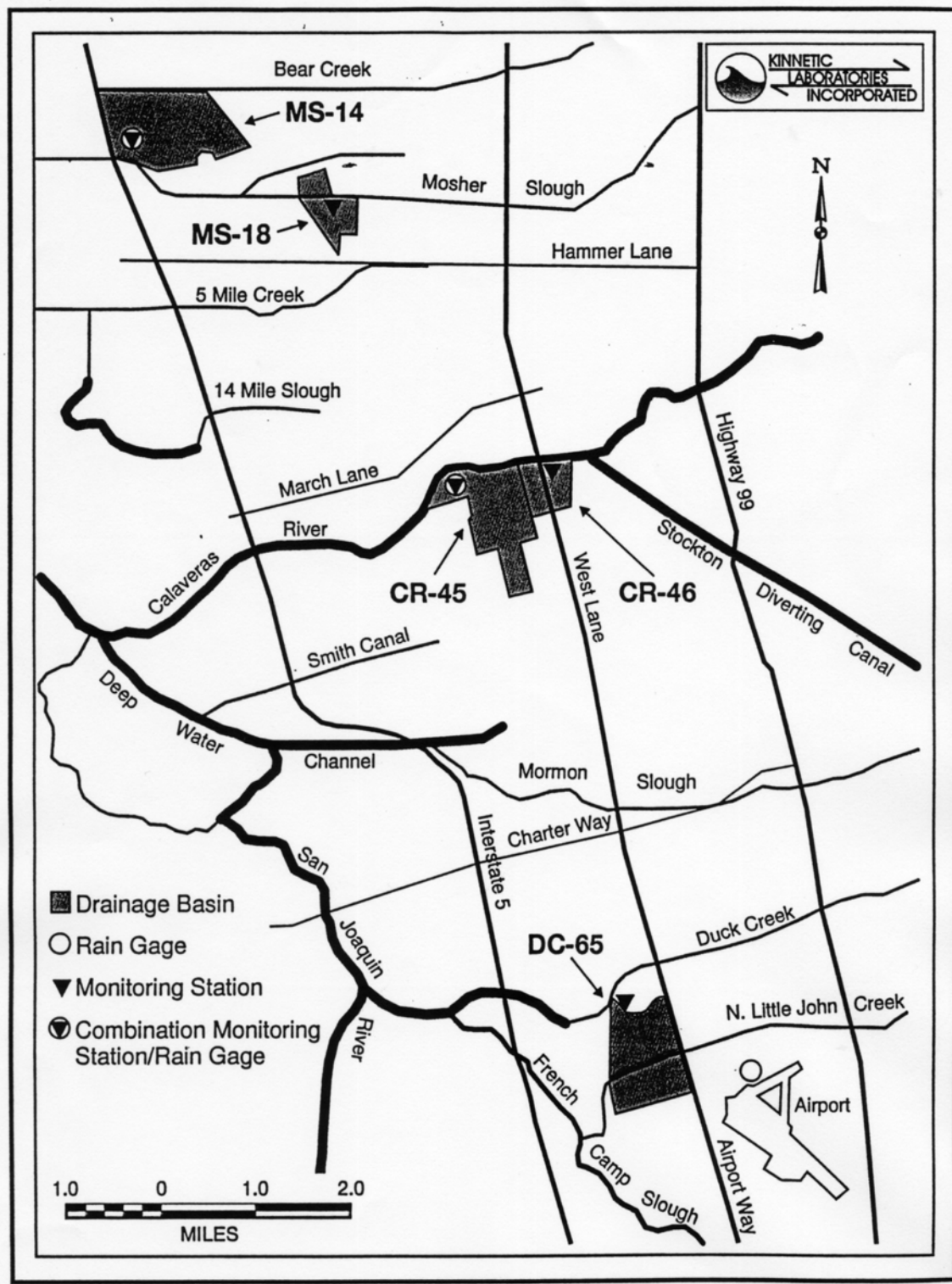


Stockton Slough Sampling Sites

- 1 Moshier Slough - Mariner's Drive bridge at I-5
- 2 Five-Mile Slough - at Plymouth Road bridge
- 3 Calaveras River - at Woods Bridge, north of UOP campus
- 4 Smiths Canal - at Pershing Avenue bridge
- 5 Mormon Slough - at Lincoln Street bridge
- 6 Walker Slough - at Manthey Road bridge and I-5 (Van Buskirk Park)
- 7 Smiths Canal - at Yosemite Street
- 8 Mormon Slough - at Turning Basin
- 9 Walker Slough - upstream from confluence with Duck Creek

Source: Lee and Jones-Lee (2001).

Figure 2 Monitoring Station and Rain Gage Locations



Source: San Joaquin County (1997)

“For purposes of these objectives, the term pesticide shall include: (1) any substance, or mixture of substances, which is intended to be used for defoliating plants, regulating plant growth, or for preventing, destroying, repelling, or mitigating any pest, which may infest or be detrimental to vegetation, humans, animals, households, or be present in any agricultural or nonagricultural environment whatsoever, or (2) any spray adjuvant, or (3) any breakdown products of these materials that threaten beneficial uses. Note that discharges of ‘inert’ ingredients included in pesticide formulations must comply with all applicable water quality objectives.”

Toxicity

The CVRWQCB Basin Plan narrative objective for pesticides states, “No individual pesticide or combination of pesticides shall be present in concentrations that adversely affect beneficial uses.” The narrative toxicity objective in the Basin Plan states, in part, “All waters shall be maintained free of toxic substances in concentrations that produce detrimental physiological responses in human, plant, animal, or aquatic life.”

The narrative toxicity objective further states that,

“The Regional Water Board will also consider ... numerical criteria and guidelines for toxic substances developed by the State Water Board, the California Office of Environmental Health Hazard Assessment, the California Department of Health Services, the U.S. Food and Drug Administration, the National Academy of Sciences, the U.S. Environmental Protection Agency, and other appropriate organizations to evaluate compliance with this objective.” (CVRWQCB, 1998).

The Regional Board has not established numerical water quality objectives for diazinon or chlorpyrifos. The California Department of Fish and Game (CDFG) has developed acute and chronic toxicity criteria for diazinon and chlorpyrifos (Siepmann and Finlayson, 2000), shown in Table 1, that were determined by using methods established by the US EPA for protection of aquatic life (US EPA, 1985).

**Table 1
CDFG Freshwater Aquatic Life Criteria for Diazinon and Chlorpyrifos**

Diazinon	Criterion Values	Criterion Type	Criterion Recurrence Period
	0.080 µg/L	Acute -- Criteria Maximum Concentration (CMC)	1-hour average; not to be exceeded more than once every 3 years
	0.050 µg/L	Chronic -- Criteria Continuous Concentration (CCC)	4-day average; not to be exceeded more than once every 3 years
Chlorpyrifos	0.020 µg/L	Acute -- Criteria Maximum Concentration (CMC)	1-hour average; not to be exceeded more than once every 3 years
	0.014 µg/L	Chronic -- Criteria Continuous Concentration (CCC)	4-day average; not to be exceeded more than once every 3 years

From Azimi-Gaylon, *et al.* (2002)

Climate and Hydrology

The city of Stockton website contains a climate summary for Stockton which is presented in part in Table 2. About 90 percent of the precipitation falls during the months of November through April. Normal annual precipitation ranges from about 12 to 15 inches.

**Table 2
Climate Summary for Stockton**

STOCKTON, CALIFORNIA :STA 724920 :LAT 37 54N : LONG 121 14W :
ELEV 36(ft) 00011(m) :TYPE NOAA SMOS V3 091 1948-1992

	TEMPERATURE (DEG F)					PRECIPITATION (INCHES)		
	MEANS			EXTREME		MEAN	MAX	MIN
	MAX	MIN	AVG	MAX	MIN			
JAN	53	37	45	71	16	2.7	7.1	.1
FEB	61	40	51	78	22	2.1	6.0	0
MAR	6	42	54	87	27	2.1	6.5	T
APR	73	46	60	100	32	1.2	3.5	0
MAY	81	52	66	107	38	.3	2.3	0
JUN	88	57	73	111	45	.1	.7	0
JUL	94	61	78	114	49	T	.6	0
AUG	92	60	76	109	47	0	.8	0
SEP	88	57	73	108	42	.3	3.0	0
OCT	78	50	65	101	33	.7	2.2	0
NOV	64	42	53	85	25	1.8	6.2	T
DEC	53	37	46	73	17	2.3	8.0	T
ANN	74	48	62	114	16	13.7	26.6	5.4

T = TRACE AMOUNTS (< .05 < .5 INCHES

Chemical and Physical Properties and Biological Effects

Azimi-Gaylon, *et al.* (2002) have recently summarized the chemical and physical properties and biological effects of diazinon and chlorpyrifos that are pertinent to TMDL development. Their review should be consulted for further information on these issues.

Sources of Diazinon and Chlorpyrifos

There are both agricultural and urban sources of diazinon and chlorpyrifos in surface waters of the Mosher Slough watershed. For Five Mile Slough, only urban sources are known. Azimi-Gaylon, *et al.* (2002) have recently summarized the sources and effects of diazinon and chlorpyrifos associated with their agricultural use in the San Joaquin River watershed upstream of Vernalis. It is expected that much of what is presented by them would be applicable to the Mosher Slough watershed upstream of the city of Stockton.

Diazinon and chlorpyrifos are used in urban areas for a variety of purposes, including for termite and ant control near foundations and for landscape applications. This use leads to the presence of a small amount of the applied pesticide in stormwater runoff and irrigation water releases, which, during stormwater runoff events, enters Mosher Slough and Five Mile Slough.

Monitoring Data¹

Beginning in 1994, the Central Valley Regional Water Quality Control Board (CVRWQCB) collected an extensive set of stormwater runoff and some dry weather flow samples of city of Stockton sloughs/rivers. The US EPA standard toxicity tests and selected chemical analyses focusing on the OP pesticides diazinon and chlorpyrifos were conducted on these samples. Additional sampling/analyses were done by the CVRWQCB in 1995. Beginning in 1996 through 1999, the DeltaKeeper continued the sample collection and supported the toxicity testing and chemical analysis of the samples. During 1998-1999, CALFED provided the DeltaKeeper with a grant to help support toxicity testing of Delta waters, which included sampling some of the same city of Stockton sloughs/rivers as had been sampled previously. A total of about 160 toxicity tests have been conducted on these samples over this time. Figure 1 shows the location of the sampling stations. In general, the samples of each waterbody were taken at the location where it crosses I-5, which is near the downstream end of the sloughs and creeks.

The CVRWQCB and the DeltaKeeper studies included collecting stormwater runoff samples from Mosher Slough, Five Mile Slough, Calaveras River, Smith Canal, Mormon Slough, and Walker Slough. Only the data for Mosher Slough and Five Mile Slough are included in this OP pesticide management report since these were the only waterbodies located in the city of Stockton that were placed on the 303(d) list of waterbodies as impaired due to aquatic life toxicity associated with diazinon and chlorpyrifos. The data for the other waterbodies sampled showed similar toxicities and diazinon and chlorpyrifos concentrations as reported herein for Mosher Slough and Five Mile Slough (see Lee and Jones-Lee, 2001, for the complete data set).

All samples were analyzed for aquatic life toxicity by the University of California, Davis, Aquatic Toxicology Laboratory, using the US EPA standard three species toxicity test (Lewis, *et al.*, 1994) with *Ceriodaphnia dubia* (freshwater zooplankton), *Pimephales promelas* (fathead minnow larvae) and *Selenastrum capricornutum* (freshwater alga) as the test organisms. Some of the samples were processed through a toxicity testing dilution series in order to estimate the total amount of toxicity present in the sample. Some of the undiluted and diluted samples were treated with piperonyl butoxide (PBO). PBO interacts with organophosphorus pesticides such as diazinon and chlorpyrifos to eliminate and/or reduce their toxicity (Bailey, *et al.*, 1996).

In general, the samples were analyzed for the OP pesticides diazinon and chlorpyrifos using the enzyme linked immunosorbent assay (ELISA) procedure. Details of the sampling and analytical procedures are provided by the UCD-ATL QAPP.

While not involved in the original studies, the authors of this report, Drs. G. Fred Lee and Anne Jones-Lee, were asked to assist the DeltaKeeper/CVRWQCB in developing a report summarizing the data obtained in these studies. Their report (Lee

¹ The Monitoring Data section is derived from a report by Lee and Jones-Lee (2001).

and Jones-Lee, 2001) presents an overview assessment of the information available from the 1994-2000 city of Stockton urban stormwater runoff aquatic life toxicity studies. Appendix A of this report presents the UCD-ATL test results for the CVRWQCB/DeltaKeeper-collected samples. Some of the data used in this report have previously been reported by Connor (1994, 1995), Fong, *et al.* (2000) and Werner, *et al.* (2000).

In addition to the CVRWQCB/DeltaKeeper/UCD-ATL data, the city of Stockton holds an NPDES stormwater permit that requires monitoring of stormwater runoff. Stormwater monitoring data were available for 1996, 1997, 1998, 1999 and 2000 (San Joaquin County, 1997; Stockton, 1998, 1999, 2000). Summaries of the data were presented by Lee and Jones-Lee (2001) in Appendix B of their report. The city of Stockton data were similar to those found by the CVRWQCB and the DeltaKeeper for the 1998-2000 studies.

Summary of Results

A summary of the data obtained in these studies for Mosher Slough and Five Mile Slough is presented in Tables 3 and 4. The rainfall data reported in Table 5 were collected from the city of Stockton Metro as retrieved from www.ncdc.noaa.gov/onlineprod/g sod/temp/g sod_28393.txt. At times, precipitation in Stockton can be highly localized, where the amount of precipitation collected at a particular gage may not be representative of the amount of precipitation that occurred at other locations within the city of Stockton. The rainfall record of data for Stockton indicates that there was no recording of rainfall data during weekends.

Tables 3 and 4 provide information on the toxicity test results and chemical analyses obtained in these studies for each of the dates for which samples were collected. The *Ceriodaphnia* data set “% Sample” column indicates whether there was any dilution of the sample or any additions such as PBO or EDTA. The “Toxic Response” column provides the percent kill information on the day indicated in parentheses. The “Comments” column provides a brief summary of the most outstanding feature of that particular data set. The “Diazinon” and “Chlorpyrifos” concentrations are based on the ELISA testing where the “<” value was the indicated detection limit of the test. The “Calculated TUa” column represents a value obtained by dividing the concentration of diazinon or chlorpyrifos by the LC₅₀ value and summing the two quotients. For diazinon, a *Ceriodaphnia* LC₅₀ value of 450 ng/L was used. For chlorpyrifos, the LC₅₀ value used was 80 ng/L. “TUa” refers to the acute toxic units.

For the fathead minnow larvae tests, the “% Mortality” is provided with a comment as to whether it was statistically significant. The *Selenastrum* tests were summarized in terms of whether there was a toxic response based on a decrease in the number of *Selenastrum* cells in the test samples compared to the control. The “Comment” section indicates whether the algae in the test samples grew to a greater degree than the reference, indicating a “stimulation” of growth by nutrients in the samples.

Table 3
Summary of Aquatic Toxicity Test Data
Mosher Slough, Stockton, CA (1994-1999)

Ceriodaphnia

Date	% Sample	Toxicity Response %kill in (days)	Comments	Diazinon (ng/L)	Chlorpyrifos (ng/L)	TUa Est. Meas.
2/6/94	100	100 (1)		900	--	2
2/6/94	100	100 (1)		--	--	
2/6/94	100+200µg/L PBO	20 (2)	PBO reduced toxicity	--	--	
2/7/94	100	100 (1)		630	--	1.4
2/7/94	100	100 (1)		--	--	
2/7/94	100+200µg/L PBO	0 (7)	PBO reduced toxicity	--	--	
10/5/94	100	100 (2)		459	<80	1 1
10/5/94	100	100 (3)		--	--	
10/5/94	100	50 (2)		--	--	
10/5/94	50	0 (4)		--	--	
10/5/94	100+200µg/L PBO	10 (4)	PBO reduced toxicity	--	--	
11/6/94	100	100 (2)		--	--	
11/6/94	100	100 (3)		499	<80	1
11/6/94	100+200µg/L PBO	0 (4)	PBO reduced toxicity	--	--	
5/3/95	100	100 (2)	At Don Ave.	417	120	2.4
5/3/95	100+200µg/L PBO	0 (4)	PBO reduced toxicity	--	--	
10/29/96	100	100 (7)	No information on kill rate	486	103	2.4
10/29/96	100+200µg/L PBO	100 (7)		--	--	
10/29/96	100	100 (1)	(H36)	--	--	
10/29/96	50	80 (4)		--	--	
10/29/96	50+100µg/L PBO	0 (4)	PBO reduced toxicity	--	--	
10/29/96	50+200µg/L PBO	13 (4)	PBO activated toxicity	--	--	
10/29/96	25	0 (4)		--	--	
10/29/96	25+100µg/L PBO	0 (4)		--	--	
10/29/96	25+200µg/L PBO	77 (3)	PBO activated toxicity	--	--	
10/29/96	12.5	7 (4)		--	--	
10/29/96	100+15mg/L EDTA	93 (4)	Not metal toxicity	--	--	
10/29/96	100+30mg/L EDTA	100 (1)		--	--	

(continues)

Table 3 (continued)
Summary of Aquatic Toxicity Test Data
Mosher Slough, Stockton, CA (1994-1999)

Date	% Sample	Toxicity Response %kill in (days)	Comments	Diazinon (ng/L)	Chlorpyrifos (ng/L)	TUa Est. Meas.
11/13/97	100	100 (3)		461	59	2
11/13/97	100+ 100 µg/L PBO	90 (3)		--	--	
9/9/98	100	0 (7)		--	--	
10/24/98	100	100 (3)	At Mariner	310	--	
10/24/98	100+ 100 µg/L PBO	20 (7)		--	--	
12/7/98	100	60 (7)		--	--	
12/7/98	100	90 (7)		--	--	
12/7/98	100+ 100 µg/L PBO	0 (7)	PBO reduced toxicity	--	--	
1/20/99	100	100 (1)		--	--	
1/20/99	100+100 µg/L PBO	100 (6)	PBO slowed kill rate	--	--	
1/20/99	100	100 (1)	At I-5	1,200	50	3
1/20/99	100	100 (1)	At Don Ave	--	--	
2/8/99	100	100 (1)	At I-5	820	40	2.3 2
2/8/99	100+ 100 µg/L PBO	0 (4)	At I-5	--	--	
2/8/99	50	100 (2)	At I-5	--	--	
2/8/99	25	0 (4)	At I-5	--	--	
2/8/99	25+ 100 µg/L PBO	0 (4)	At I-5	--	--	
2/8/99	12.5	0 (4)	At I-5	--	--	
2/8/99	100	100 (1)	At Don Ave	860	30	2.3 1.6
2/8/99	100+ 100 µg/L PBO	5 (3)	At Don Ave; PBO reduced toxicity	--	--	
2/8/99	50	100 (1)		--	--	
2/8/99	25	0 (4)		--	--	
2/8/99	25+ 100 µg/L PBO	0 (4)		--	--	
9/22/99	100	100 (3)				
9/22/99	100+100 µg/L PBO	20	PBO reduced toxicity			

J – Estimated < detection limit

-- -- Not measured

(table continues)

Table 3 (continued)
Summary of Aquatic Toxicity Test Data
Mosher Slough, Stockton, CA (1994-1999)

Fathead Minnow Larvae

Date	% Mortality	Comment
10/5/96	0	
10/29/96	5	Not statistically significant
11/13/97	22	Not statistically significant
9/9/98	0	
10/24/98	2.5	Not statistically significant
12/7/98	0	
2/8/99	5	at I-5; Not statistically significant
2/8/99	10	at Don Ave; Not statistically significant

Selenastrum capricornutum

Date	Toxic Response	Comment
10/5/94	No	Stimulation
11/6/94	No	
10/29/96	No	Stimulation
11/13/97	No	
9/9/98	No	Stimulation
10/24/98	No	Stimulation
12/7/98	No	
1/20/99	No	
2/8/99	Yes	At I-5
2/8/99	Yes	At Don Ave

Table 4
Summary of Aquatic Toxicity Test Data
Five Mile Slough, Stockton, CA (1994-1998)

Ceriodaphnia

Date	% Sample	Toxicity Response %kill in (days)	Comments	Diazinon (ng/L)	Chlorpyrifos (ng/L)	TUa Est. Meas.
2/6/94	100	100 (2)		1,000	--	2
2/6/94	100	100 (1)		--	--	
2/6/94	100+200µg/L PBO	80 (4)	PBO reduced toxicity	--	--	
2/7/94	100	100 (1)		>1,000	--	> 2
2/7/94	100	100 (1)		1,200	--	2.5
2/7/94	100+200µg/L PBO	20 (4)	PBO reduced toxicity	--	--	
10/5/94	100	100 (2)		278	<80	0.5 1
10/5/94	100	100 (3)		--	--	
10/5/94	50	0 (4)	Between 1 and 2 TUa	--	--	
10/5/94	100+200µg/L PBO	60 (7)	PBO reduced toxicity	--	--	
11/6/94	100	0 (4)		80	<80	1
10/29/96	100	100 (7)	No information on rate of kill	304	84	1.5
10/29/96	100+100µg/L PBO	0 (7)	PBO reduced toxicity	--	--	
11/13/97	100	100 (5)		359	52	2
11/13/97	100+100µg/L PBO	0 (7)	PBO reduced toxicity	--	--	
10/24/98	100	0 (7)		--	--	
10/24/98	100+100µg/L PBO	10 (7)		--	--	
9/22/99	100	100 (7)				
9/22/99	100+100µg/L PBO	0				

-- Not measured

Fathead Minnow Larvae

Date	% Mortality	Comment
10/5/94	7	Not statistically significant
10/29/96	42	Not statistically significant
11/13/97	75	Statistically significant
10/24/98	0	

Selenastrum capricornutum

Date	Toxic Response	Comment
10/5/94	No	Stimulation
11/6/94	No	
10/29/96	No	Stimulation
11/13/97	No	Stimulation
10/24/98	No	Stimulation

Table 5
City of Stockton Precipitation Data for Sampling Events

Date	Precipitation
2/7/94	0.08
10/5/94	0.42
10/6/94	0.00
11/8/94	0.00
11/9/94	0.00
11/25/94	0.33
3/2/95	0.08
4/27/95	0.04
4/28/95	0.00
4/29/95	0.00
5/1/95	0.33
5/3/95	0.00
12/11/95	0.00
10/29/96	1.28
11/16/96	0.60
11/17/96	1.06
11/18/96	0.71
1/22/97	0.28
11/10/97	0.20
11/13/97	0.12
1/4/98	0.24
1/14/98	0.04
2/19/98	0.08
9/9/98	0.00
10/24/98	0.67
12/7/98	0.00
12/12/98	0.00
1/19/99	0.56
1/20/99	0.00
2/8/99	0.16
3/8/99	0.20
6/7/99	0.00
6/16/99	0.00
8/18/99	0.00
9/22/99	0.24

Source: Stockton Metro precipitation gage, as reported at
www.ncdc.noaa.gov/onlineprod/g sod/temp/g sod_28393.txt

The estimated *Ceriodaphnia* TUa (acute toxicity) presented in Tables 3 and 4 is based on the *Ceriodaphnia* LC₅₀ normalized diazinon and chlorpyrifos concentrations, summed for their additivity. The *Ceriodaphnia* LC₅₀ for diazinon used was 450 ng/L and for chlorpyrifos, 80 ng/L. For many samples, chlorpyrifos was not measured. This would tend to give the estimated TUa lower than was actually present. Typically, when measured, diazinon contributed from 0.5 to 1 TUa for the sample.

Discussion

Mosher Slough. Table 3 presents the toxicity data for the three test organisms for samples of Mosher Slough during times of stormwater runoff. In general, the undiluted sample of Mosher Slough during runoff events killed 100 percent of the *Ceriodaphnia* within one to seven days. The addition of PBO to the sample reduced the toxicity. The concentrations of diazinon ranged from about 310 ng/L to 1,200 ng/L. Chlorpyrifos was found to range from about 30 ng/L to 120 ng/L. The estimated TUa based on diazinon concentrations for *Ceriodaphnia* toxicity ranged from 1 to 2.4. The three samples for which there were diazinon and chlorpyrifos concentrations measured and a dilution series of the toxicity conducted, showed that there was reasonable agreement between the estimated TUa and the measured TUa.

There was no toxicity to fathead minnow larvae or *Selenastrum* in the Mosher Slough samples. The algal test showed stimulation apparently due to the nutrients in the sample.

Five Mile Slough. Table 4 presents the Five Mile Slough toxicity test results. Examination of the data in Table 4 shows that the toxicity and the diazinon concentrations found in Five Mile Slough were similar to those reported for Mosher Slough. In general, the undiluted stormwater-runoff-impacted Five Mile Slough sample killed all *Ceriodaphnia* within four days. The addition of PBO greatly reduced the toxicity. The concentrations of diazinon and chlorpyrifos produced an estimated TUa of 0.5 to 2.5 TUa of *Ceriodaphnia* toxicity. The one sample on October 5, 1994, where diazinon and chlorpyrifos were measured and a toxicity test dilution series was conducted showed reasonable agreement between the estimated and measured TUa.

There was no toxicity to fathead minnow larvae or *Selenastrum* found in the Five Mile Slough samples.

City of Stockton NPDES Stormwater Permit OP Pesticide and Aquatic Life Toxicity Monitoring Data 1992-2000

As part of the city of Stockton Stormwater NPDES permit conditions, the City is required to monitor for aquatic life toxicity and a suite of organophosphorus and other pesticides. The city of Stockton stormwater runoff sampling focuses on five storm sewers that discharge to a City slough or river. These are listed in Table 6. Only the data obtained by the City for the Mosher Slough/Kelly Drive watershed and the Mosher Slough/Thornton Road watershed are included in this table. A complete set of data is available in Lee and Jones-Lee (2001).

Table 6
Stockton Stormwater NPDES Monitoring Sites

Monitoring Site	Outfall Code	Predominant Land Use	Area (acres)
Mosher Slough/Kelly Drive	MS-14	Residential	533
Mosher Slough/Thornton Road	MS-18	Residential	106
Calaveras River/Sutter Street	CR-45	Residential	360
Calaveras River (South)/West Lane	CR-46	Commercial	169
Duck Creek/W. Pacific Industrial Park	DC-65	Industrial	343

Table 7 presents the results of the chemical analysis and the measured toxicity for the samples evaluated beginning in the fall 1996 through the winter 2000. The expected TUa column in Table 7 is based on the LC₅₀ normalized diazinon and chlorpyrifos concentrations in the samples, assuming that the toxicity for these two pesticides are additive. A *Ceriodaphnia* LC₅₀ of 450 ng/L was used for diazinon and 80 ng/L for chlorpyrifos. It was assumed that the concentrations for the pesticides less than the detection limit were zero and did not contribute to the expected TUa. This approach could cause the expected TUa to be somewhat lower than actually present.

Table 7
City of Stockton Stormwater Runoff Pesticide Monitoring 1998-2000

Date	Location	Diazinon (ng/L)	Chlorpyrifos (ng/L)	Expected TUa*	Measured TUa (48 hr)*
11/16/96	MS-14	640/830	80/120	2.4/3.3	
	MS-18	760	70	2.6	
11/10/97	MS-14	2,300	150	8.0	6.0
	MS-18	1,500	100	4.6	
1/14/98	MS-14	830	< 50	1.8	2.5
	MS-18	360	< 50	0.8	
2/19/98	MS-14	430	< 50	1.0	
	MS-18	320	< 50	0.7	
11/8/98	MS-18	830	< 50	1.8	
2/6/99	MS-14	1000	140	4.0	
	MS-18	800	< 50	1.8	
2/17/99	MS-14	430	60	1.8	
	MS-18	630	< 50	1.4	
3/25/99	MS-14	680	80	2.3	
	MS-18	210	60	1.2	
11/8/99	MS-14	1600	30	4.0	> 16
	MS-18	1000	30	2.6	
2/9/00	MS-14	30	100	1.2	
	MS-18	300	30	1.0	
2/27/00	MS-14	150	80	1.3	
	MS-18	30	30	0.4	

*See text for discussion of how Estimated and Measured TUa were developed for *Ceriodaphnia* toxicity.

In general, it was found that many of the stormwater runoff samples collected by the City contained sufficient diazinon and, in some instances, chlorpyrifos, to be expected to be toxic to *Ceriodaphnia*. Examination of Table 7 shows that many of the stormwater runoff samples had about 1 TUa of acute *Ceriodaphnia* toxicity over the 48-hour test period. Some of the samples had OP pesticide (diazinon and chlorpyrifos) expected TUa on the order of 4. These samples contained from 1,000 to 1,600 ng/L diazinon.

It is important to note that the city of Stockton sampling focuses on stormwater runoff, while the CVRWQCB and DeltaKeeper sampling, summarized in Tables 2 and 3, was of the receiving waters for the stormwater runoff, i.e., the sloughs and rivers within the City. The City's stormwater sampling results would be expected to have higher concentrations than those reported above, to the extent that there was dilution of the stormwater runoff by slough/river water which did not contain stormwater runoff.

It is of interest to compare the concentrations of diazinon and chlorpyrifos found by the City in its stormwater runoff sampling with the data presented in Table 3 for samples collected by the DeltaKeeper. The MS-14 samples were collected of stormwater runoff at Kelly Drive, while the DeltaKeeper sampled Mosher Slough at Kelly Drive. According to the City, MS-14 storm sewer has a 533-acre newer residential watershed. The MS-18 watershed is reported to be 106 acres, which is devoted to older residential use.

The stormwater runoff samples collected by the city of Stockton on February 6, 1999, at MS-14 contained 1,000 ng/L diazinon, while the DeltaKeeper-collected Mosher Slough sample on February 8, 1999, contained 820 ng/L diazinon. For the one occasion where DeltaKeeper sampled Mosher Slough water and the city of Stockton sampled stormwater runoff to Mosher Slough (MS-14) on the same day, there was reasonable agreement for the concentrations of diazinon found.

Comparison between City of Stockton and CVRWQCB/DeltaKeeper Sampling

It is of interest and concern that the sampling of Mosher Slough or stormwater runoff to Mosher Slough on February 6 and 8, 1999, was found by the city of Stockton and DeltaKeeper to contain over 2 TUa of expected *Ceriodaphnia* toxicity based on diazinon concentrations. This situation is of particular concern because of the high level of toxicity and the fact that it extended over a several-day period.

While the city of Stockton did not conduct toxicity tests on the February 6, 1999, sample of stormwater runoff to Mosher Slough, the DeltaKeeper 100-percent sample of Mosher Slough collected on February 8, 1999, killed all *Ceriodaphnia* in one day while the 50-percent dilution of the sample killed all *Ceriodaphnia* in two days (see Table 3). A 25-percent dilution of this sample was nontoxic to *Ceriodaphnia* over four days. Therefore, this sample contained between 2 to 4 TUa of acute *Ceriodaphnia* toxicity. This level of measured toxicity is somewhat less than that predicted based on the diazinon concentrations found. This difference, however, is not enough to indicate that there was unknown-caused toxicity in the sample. It was also of interest to find that the

addition of PBO to the sample eliminated the toxicity over the four-day test period, indicating that an OP pesticide was likely responsible for the toxicity.

There were no other duplicate sampling of stormwater runoff events at the same sampling location in the city of Stockton (Table 7) and DeltaKeeper (Table 3) data sets.

November 1999 Studies

The city of Stockton collected stormwater runoff samples on November 7-8, 1999, from MS-14, CR-46, and DC-65. Samples were also collected of the receiving water for these discharges on November 5, 1999, prior to stormwater runoff. The November 7, 1999, sample was the first major runoff event of the water year.

The MS-14 sample was sent to Pacific EcoRisk, Martinez, California, for toxicity testing and TIEs to identify toxic components. Pacific EcoRisk (2000) found that the November 8, 1999, sample of MS-14 was acutely toxic to *Ceriodaphnia*, and significantly reduced the growth of *Selenastrum*.

Table 8 presents the results of the MS-14 stormwater runoff sample toxicity testing to *Selenastrum*. Examination of the data in this table shows that there was statistically significant decreased growth of *Selenastrum* in the 100-percent sample. The 50-percent sample using laboratory water as the diluent showed increased growth, indicating that the toxicity had been diluted out and that the nutrients present in the stormwater runoff stimulated the growth of algae. Similar patterns were seen in the 25-percent, 12.5-percent and 6.25-percent samples, compared to the control.

**Table 8
Effects of City of Stockton Stormwater Runoff Sample MS-14 on
Growth of *Selenastrum capricornutum* Using Laboratory Water as the Diluent**

Treatment	Algal Population Density (cells/ml x 10 ⁶)				Mean (cells/ml x 10 ⁶)
	Rep A	Rep B	Rep C	Rep D	
Control	0.404	0.340	0.341	0.395	0.370
100%	0.251	0.227	0.225	0.218	0.230*
50%	1.007	1.150	1.107	0.953	1.054
25%	0.807	0.943	0.975	0.863	0.897
12.5%	0.827	0.739	0.730	0.713	0.752
6.25%	0.862	0.640	0.660	0.770	0.733

* Significantly less than the Control treatment at p < 0.05.

Table 9 presents the results of the studies using the November 5, 1999, sample of receiving water for the MS-14 discharge. At the time of sampling, there was no stormwater runoff, and therefore this represented ambient pre-stormwater runoff conditions. Table 9 shows that the 100-percent receiving water sample significantly stimulated the growth of *Selenastrum*, likely because of the nutrients present.

Table 9
Effects of Receiving Water on Growth of *Selenastrum capricornutum*
Using Laboratory Water as the Diluent

Treatment	Algal Population Density (cells/ml x 10 ⁶)				Mean (cells/ml x 10 ⁶)
	Rep A	Rep B	Rep C	Rep D	
Control	0.404	0.340	0.341	0.395	0.370
100%	1.247	1.118	1.182	1.248	1.199
50%	0.677	0.714	0.631	0.720	0.685
25%	0.442	0.466	0.429	0.350	0.422
12.5%	0.347	0.331	0.315	0.316	0.327
6.25%	0.162	0.117	0.027	0.055	0.090

*Significantly less than the Control treatment at p < 0.05.

Table 10 presents the toxicity test results for MS-14 for the November 8, 1999, stormwater runoff sample. The data in this table show that there was 80-percent mortality in 48 hours to *Ceriodaphnia* down to the 6.25-percent sample. There was chronic toxicity, as evidenced by impaired reproduction, in the 25-percent sample. Therefore, there were over 16 TU of 48-hour acute toxicity. Examination of Table 10 shows that the expected TUs, based on normalized diazinon and chlorpyrifos concentrations, was about 4. Therefore, there was appreciable toxicity in this sample that could not be accounted for based on the diazinon and chlorpyrifos concentrations. This is the first time that this situation has occurred in the Stockton stormwater runoff samples. It is reminiscent of the situation that Lee and Taylor (1999) and Lee, *et al.* (2001a,b) found in the Upper Newport Bay, Orange County, California, stormwater runoff studies, where there were significant amounts of unknown-caused toxicity in the samples.

Table 10
Effects of City of Stockton Stormwater on Survival and Reproduction of
***Ceriodaphnia dubia* Using Lab Water as the Diluent**

Treatment	Survival (%)	Reproduction (# neonates/female)
Control	100	30.1
100%	0*	0*
50%	0*	0*
25%	0*	5.8*
12.5%	10*	26.9
6.25%	20*	28.8

*Significantly less than the Control treatment at p < 0.05.

Table 11 shows that the addition of 125 µg/L of PBO to the November 7, 1999, MS-14 sample eliminated the 24-hour toxicity. There was still 90-percent mortality in 48

hours. The toxicity associated with the higher concentrations of PBO shown in Table 11 is likely due to PBO, and not to the sample.

Table 11
Effects of PBO Addition on Mortality of *Ceriodaphnia dubia*
(Acute Toxicity Testing)

PBO Treatment	24-hr Mortality	48-hr Mortality
Control	0	0
Methanol Control	0	0
Stormwater Runoff	100	100
Stormwater Runoff + 62.5 µg/L	80	90
Stormwater Runoff + 125 µg/L	0	90
Stormwater Runoff + 250 µg/L	60	100
Stormwater Runoff + 375 µg/L	100	100
Stormwater Runoff + 500 µg/L	100	100
Stormwater Runoff + 750 µg/L	100	100

Pacific EcoRisk subjected the November 8, 1999, MS-14 sample to a TIE. The results of the TIE show that OP pesticides are a likely cause of the toxicity. The results of the TIE (see Table 12) show that the PBO and the C₁₈SPE treatment removed the toxicity. According to Pacific EcoRisk, the TIE studies show that the toxicity to *Ceriodaphnia* in the November 8, 1999, MS-14 sample was likely due to diazinon and malathion. There may have been other compounds that were responsible for the toxicity, but they were not identified in the study.

Pacific EcoRisk conducted a characterization study for the toxicity to *Selenastrum* on the November 8, 1999, MS-14 sample. The results of the testing are shown in Tables 13 and 14. The results of the *Selenastrum* TIE studies indicate that possibly zinc is responsible for the toxicity to *Selenastrum*. It is also possible that an herbicide, EPTIC, was a cause of this toxicity.

Table 12
Summary of Phase I Acute TIE Performed on Stormwater Runoff
Collected on November 8, 1999, Using *Ceriodaphnia*

Fraction Treatment	Treatment Method	Response
Baseline Test*	An aliquot of sample was tested for toxicity.	Toxicity Still Present
Aeration Treatment	An aliquot of sample was aerated and tested for toxicity removal.	No toxicity removal.
Filtration Treatment	An aliquot of sample was 0.45 µg filtered and tested for toxicity removal.	No toxicity removal
Centrifugation Treatment	An aliquot of sample was centrifuged and tested for toxicity removal.	No toxicity removal
C ₁₈ SPE Treatment	An aliquot of centrifuged sample was passed over a C18SPE column and tested for toxicity removal.	Removed 100% of the Baseline toxicity
EDTA	EDTA, a metal chelating agent, was added to an aliquot of sample and tested for toxicity removal.	No toxicity removal
STS	STS, a metal chelating agent, was added to an aliquot of sample and tested for toxicity removal. STS will also reduce chlorine and sulfide.	No toxicity removal
PBO	PBO was added to an aliquot of sample. PBO blocks the cytochrome P450 enzyme system, preventing activation, and therefore toxicity, to the organism.	Removed 50% of the Baseline toxicity

* All treatments are compared to the Baseline treatment with respect to toxicity removal.

Table 13
Summary of Phase I Acute TIE Performed on Stormwater Runoff
Collected on November 8, 1999, Using *Selenastrum*

Fraction Treatment	Treatment Method	Mean Cell Density (1 x 10⁶)	Treatment Response
Baseline Test	An aliquot of filtered sample was tested for toxicity.	0.198	
Estimated Growth Potential	Estimated Growth Potential for Stormwater Sample	1.18	
Aeration Treatment	An aliquot of filtered sample was aerated and tested for toxicity removal	0.840	<ul style="list-style-type: none"> • >100% toxicity removal relative to the Laboratory Control • 48% toxicity removal relative to the Stormwater Growth Potential exhibited by Cation Exchange treatment.
C ₁₈ SPE Treatment	An aliquot of filtered sample was passed over a C ₁₈ SPE column and tested for toxicity removal.	0.967	<ul style="list-style-type: none"> • >100% toxicity removal relative to the Laboratory Control • 56% toxicity removal relative to the Stormwater Growth Potential exhibited by Cation Exchange treatment.
Cation Exchange	An aliquot of filtered sample was passed over a cation exchange column (Chelex) and tested for toxicity removal.	1.744*	<ul style="list-style-type: none"> • >100% toxicity removal relative to the Laboratory Control. • >100% toxicity removal relative to the Stormwater Estimated Growth Potential.

* Since algal growth was greater at the Cation Exchange treatment, all subsequent evaluations of toxicity removal are made against this algal growth value of 1.74 x 10⁶ cells/mL.

Table 14
Summary of Phase II TIE Performed on Stormwater Runoff
Collected on November 8, 1999, Using *Selenastrum*

Fraction Treatment	Treatment Method	Mean Cell Density (1 x 10 ⁶)	Toxicity (% Reduction in Cell Density)*	Treatment Response
Baseline Test	An aliquot of filtered sample was tested for toxicity.	0.198	88.6	
Observed Growth Potential	Observed Growth Potential for Stormwater Sample.	1.74	0	
Cation Exchange Eluate	Cation exchange resin was eluted with 4M HCl and tested for toxicity recovery.	0.515	70.5	<ul style="list-style-type: none"> 89% of the toxicity was recovered relative to observed growth potential for stormwater sample.
C ₁₈ SPE Treated Cation Exchange Eluate	An aliquot of the cation exchange eluate sample was passed over a C ₁₈ SPE column and tested for toxicity removal.	0.526	69.8	<ul style="list-style-type: none"> No toxicity was removed with this treatment indicating that the toxicity recovered in the eluate was inorganic.

* Relative to observed growth potential in the Cation Exchange treatment.

January 1998

Table 15 presents a summary of the toxicity testing results for MS-14, CR-46, and DC-65 for samples collected on January 14, 1998.

Table 15
Toxicity Testing Results for City of Stockton Stormwater Runoff
Collected on January 14, 1998

Sample %	Mortality %			Neonate Reproduction, No.		
	MS-14	CR-46	DC-65	MS-14	CR-46	DC-65
Control	0	0	10	21.4	18.4	17.5
100	100	10	50	0	14.6	6.8
50	80	10	0	9.1	12.3	11.1
25	10	10	0	16.5	17.5	17.7
12.5	20	0	0	15.5	17.5	14.4
6.25	10	30	30	14.7	13.3	8.1

Examination of the data for MS-14 shows that the 100-percent sample killed all *Ceriodaphnia* in 48 hours. The 50-percent sample killed 80 percent and the 25-percent sample killed 10 percent of the *Ceriodaphnia* during the test period. This mortality translates to a TUa between 2 and 3. As shown in Table 7, based on diazinon concentrations, the expected TUa was about 2. This is approximately what was found in the sample based on toxicity testing. Therefore, it may be concluded that the toxicity of the MS-14 sample collected on January 14, 1998, could be accounted for based on

diazinon concentrations. There were no other toxicants in the sample that significantly contributed to the *Ceriodaphnia* mortality. The DeltaKeeper did not collect samples of the January 14, 1998, stormwater runoff event and, therefore, it is not possible to compare the results between the city of Stockton sampling and the DeltaKeeper sampling of this event.

As expected, Table 15 shows there was impairment of reproduction of *Ceriodaphnia* in all of the samples collected on January 14, 1998.

The contract laboratory conducting the toxicity test for the city of Stockton also conducted a series of tests with a MS-14 undiluted sample (100 percent) and various concentrations of piperonyl butoxide (PBO) ranging from 0 to 1,000 µg/L. The MS-14 100-percent sample with zero PBO killed all *Ceriodaphnia* within 48 hours. The addition of 125 µg/L PBO to the sample reduced the 48-hour mortality to 20 percent. Therefore, essentially all of the 48-hour toxicity to *Ceriodaphnia* would be expected to be due to organophosphorus pesticides. This is additional confirmation that diazinon is likely the primary cause of aquatic life toxicity in the January 14, 1998, sample collected from MS-14. The toxicity reported by the City for the MS-14 sample for the elevated concentrations of PBO was likely due to PBO toxicity to the *Ceriodaphnia*. It is known that concentrations much above 200 µg/L of PBO are toxic to *Ceriodaphnia*.

1997 Stormwater Runoff Monitoring

In addition to fairly comprehensive data for aquatic life toxicity in stormwater runoff for 1998 through 2000, the Stockton (1998) report provides a summary of the toxicity testing data for the November 11, 1997, samples collected at MS-14, CR-46 and DC-65. The MS-14 sample killed 100 percent of the *Ceriodaphnia* within 24 hours.

The MS-14 sample had a *Ceriodaphnia* TUa of about 6. The addition of PBO to this sample significantly reduced this toxicity but did not eliminate it. Examination of the data presented in Table 7 for the MS-14 sample collected on November 10, 1997, showed that it had 2,300 ng/L diazinon and 150 ng/L chlorpyrifos for an estimated TUa of 8.

Therefore, the estimated TUa, based on diazinon and chlorpyrifos concentrations, is considerably greater than that measured in the toxicity test conducted by the City's contract laboratory. This is one of the few occasions where this type of situation has occurred. The City's contract laboratory TIE studies were inconclusive with respect to identifying the cause of any unknown-caused toxicity. They did determine, through the addition of EDTA, that the toxicity in the sample was not due to heavy metals.

1995-1996 Stormwater Runoff Monitoring

In addition to the data presented in Table 7, part of the city of Stockton's NPDES permit report covering the City's stormwater runoff monitoring during 1995-1996 was available for review (Stockton, 1996). Three stormwater runoff events were sampled during 1996. These occurred on January 15-16, 1996, March 3-4, 1996 and April 16-17, 1996. Based on three samples of three different stormwater runoff events collected at MS-14, the arithmetic mean and median diazinon concentrations were about 1,000 ng/L.

For the same set of samples, the chlorpyrifos mean and median concentrations were about 100 ng/L. The diazinon data had a coefficient of variation (CV) of 0.19. For chlorpyrifos, the CV was 0.38, indicating that there is considerable variability in the concentrations of diazinon and chlorpyrifos found between stormwater runoff events.

The MS-18 monitoring during 1995-1996 had mean and median diazinon concentrations of 860 and 730 ng/L, respectively. The chlorpyrifos mean and median concentrations were 130 and 100 ng/L, respectively.

The 1995-1996 stormwater runoff monitoring report contained a summary of the diazinon and chlorpyrifos data collected in stormwater runoff from 1992 through 1996 (Stockton, 1996). During this period, the City took eight samples of stormwater runoff in residential areas, presumably from MS-14, MS-18 and CR-45. The arithmetic mean diazinon concentration in these samples was 930 ng/L, with a median of 760 ng/L. The chlorpyrifos mean concentration from seven samples from residential areas from 1992 through 1996 was 110 ng/L, with a median of 100 ng/L.

In summary, it appears that the concentrations of diazinon and chlorpyrifos found in the city of Stockton stormwater runoff from residential areas have been in the range of about 30 ng/L to 2,300 ng/L from 1992 through 2000. From the data available, it does not appear that there is any significant trend in the data through the monitoring period.

Overall Evaluation

The city of Stockton stormwater runoff toxicity and organophosphorus pesticide monitoring shows similar results to those found by the CVRWQCB and the DeltaKeeper. It is clear that, with few exceptions, stormwater runoff in the city of Stockton and the receiving water sloughs for this runoff are toxic to *Ceriodaphnia* and, at times, are toxic to *Selenastrum*. The *Ceriodaphnia* toxicity is primarily due to diazinon, with some contributions by chlorpyrifos. There was limited indication of any unknown-caused toxicity to *Ceriodaphnia*. The cause of the toxicity to *Selenastrum* has not been identified.

Estimating Loads of Diazinon and Chlorpyrifos

Typically, through a combination of monitoring and stream gaging, the sources and magnitudes of pollutants of concern are defined for a TMDL. The situation with respect to defining the magnitude of the sources of diazinon and chlorpyrifos for Mosher Slough and Five Mile Slough is somewhat different, since determination of the flow of Mosher Slough and Five Mile Slough has not been done. Flow measurements of Mosher Slough and Five Mile Slough, associated with stormwater runoff events, is complicated by the fact that both of these sloughs have about a three-foot tide, which means that, depending on whether the tide is ebb or flood, large amounts of tidal exchange water pass a monitoring point on each tidal cycle. To distinguish a net stormwater runoff downstream flow from the tidal flow requires sophisticated flow measurements. Therefore, the total loads of diazinon and chlorpyrifos present in these sloughs at any time and location is not known. However, as discussed below, two subwatersheds in the

Mosher Slough watershed have been monitored by the city of Stockton as part of its stormwater NPDES permit. These watersheds include Mosher Slough at Kelly Drive and Mosher Slough at Thornton Road. Their locations are shown in Figure 2.

It is not possible, based on the data available, to relate the concentrations/loads of diazinon and chlorpyrifos of the City's monitored watersheds that discharge to Mosher Slough to the concentrations measured by the CVRWQCB staff and the DeltaKeeper in Mosher Slough. Except for one occasion, the City's measurements and the CVRWQCB/DeltaKeeper measurements were not made on the same stormwater runoff event. Further, the CVRWQCB staff and DeltaKeeper sampling consisted of a single sample collected at some time during a runoff event just "upstream" of where the City monitored OP pesticides in stormwater runoff to Mosher Slough. No sampling was done over the stormwater runoff hydrograph by the CVRWQCB or the DeltaKeeper. Further, the proximity of the CVRWQCB and DeltaKeeper point to the monitored discharge by the City is such that at times, such as on an ebb tide, none of the monitored discharge that occurs to Mosher Slough near where the slough sampling took place would be sampled by the CVRWQCB and DeltaKeeper. During flood tide events, depending on the magnitude of stormwater runoff, some of the monitored discharge could be carried "upstream" past the CVRWQCB and DeltaKeeper monitoring point. However, since the stormwater discharge is a pumped discharge to Mosher Slough that occurs on one side of the slough, it is likely that at times there is incomplete mixing between the City's measured stormwater discharge and the waters of Mosher Slough. This means that it is not possible to relate, in a meaningful way, the concentrations of OP pesticides found in the City's monitored watershed to the concentrations found in the slough.

Because of the limited area and land use within the watershed, it is known that diazinon and chlorpyrifos found in Mosher and Five Mile Sloughs are largely derived from urban residential use. Neither the Department of Pesticide Regulation nor any other agency has information on over-the-counter pesticide sales and/or residential use. While some information of this type is available for other cities, it is not likely applicable to Stockton. The Mosher Slough at Kelly Drive MS-14 studies conducted by the City provide information that can be used to develop a diazinon export coefficient (grams of diazinon per acre of watershed per stormwater runoff event), which can be used to estimate the total mass of diazinon that is contributed by a storm sewer to Mosher Slough or Five Mile Slough. From the total watersheds contributing stormwater to each of these sloughs and assuming that the export coefficient derived from the MS-14 watershed is applicable to the other watersheds for Mosher Slough and Five Mile Slough, it is possible to estimate the total loads of diazinon and chlorpyrifos contributed to Mosher Slough and Five Mile Slough during a stormwater runoff event based on the areas of the watersheds for these sloughs. Information derived from this approach is discussed below.

Diazinon and Chlorpyrifos Export Coefficients

In the early 1960s, the senior author, G. F. Lee, worked with a group of University of Wisconsin, Madison, faculty to develop nutrient export coefficients. These coefficients provide an assessment of the amount of a nutrient or other constituent that runs off in stormwater (is exported) per unit area per unit time or stormwater runoff

event. This approach has been found to be useful in relating land use to its potential impact on water quality through the export of constituents from a particular land use to a waterbody. Following this same approach, the data developed by Kinnetic Laboratories, Inc., for the city of Stockton stormwater runoff (San Joaquin County, 1997; Stockton, 1998) for 1996 through 1998, have been reviewed for the Mosher Slough at Kelly Drive (MS-14) and at Thornton Road (MS-18) watersheds. The Kelly Drive watershed consists of 533 acres ($2.2 \times 10^6 \text{ m}^2$) of residential land area. The Thornton Road watershed consists of 106 acres ($4.1 \times 10^5 \text{ m}^2$) of older residential land area. Tables 16 and 17 have been developed based on the information provided by Kinnetic Laboratories (San Joaquin County, 1997; Stockton, 1998). The data in Table 16 show that about 6 to 12 $\mu\text{g}/\text{m}^2$ /stormwater runoff event of diazinon was exported from MS-14, while the MS-18 export of diazinon in stormwater runoff was 2.7 to 23 $\mu\text{g}/\text{m}^2$ /runoff event. The MS-14 export of chlorpyrifos for the two dates when there were data was 0.4 to 1.8 $\mu\text{g}/\text{m}^2$ /stormwater runoff event, and the MS-18 exported chlorpyrifos in stormwater runoff was 0.6 to 2.0 $\mu\text{g}/\text{m}^2$ /stormwater runoff event.

Table 16
Diazinon and Chlorpyrifos Stormwater Runoff Export from City of Stockton
Mosher Slough at Kelly Drive (MS-14) Watershed

Date	Total Rainfall (in.)	Runoff Duration (hrs.)	Total Runoff ($\text{L} \times 10^6$)	EMC Conc. ($\mu\text{g}/\text{L}$)		Total OP Pest Runoff g/stm event		OP Pest Export ($\mu\text{g}/\text{m}^2/\text{event}$)	
				Diazin.	Chlorp.	Diazin.	Chlorp.	Diazin.	Chlorp.
11/16/96	1.6	15	39	0.7	0.1	27	4	12	1.8
1/20/97	0.36	33	10	--	--	--	--	--	--
11/10/97	0.46	9.8	6.8	2.3	0.15	16	1.0	7	0.4
1/14/98	0.54	3.0	17	0.83	< 0.5	14	--	6	--
2/19/98	0.81	10.4	--	0.43	< 0.5	--	--	--	--

-- not measured

Table 17
Diazinon and Chlorpyrifos Stormwater Runoff Export from City of Stockton
Mosher Slough at Thornton Road (MS-18) Watershed

Date	Total Rainfall (in.)	Runoff Duration (hrs.)	Total Runoff ($\text{L} \times 10^6$)	EMC Conc. ($\mu\text{g}/\text{L}$)		Total OP Pest Runoff g/stm event		OP Pest Export ($\mu\text{g}/\text{m}^2/\text{event}$)	
				Diazin.	Chlorp.	Diazin.	Chlorp.	Diazin.	Chlorp.
11/16/96	1.6	15	12	0.8	0.07	9.6	0.84	23	2.0
1/20/97	0.36	33	3	--	--	--	--	--	--
11/10/97	0.46	9.8	2.6	1.5	0.1	3.9	0.26	9.5	0.6
1/14/98	0.54	3.0	3.0	0.36	< 0.5	1.1	--	2.7	--
2/19/98	0.81	10.4	6.5	0.32	< 0.5	2.1	--	5.0	--

-- not measured

Lee, *et al.* (2001a) found, using a similar approach for residential watersheds in the Orange County, CA, Upper Newport Bay watershed, that diazinon was exported from this watershed at about 1 $\mu\text{g}/\text{m}^2$ /stormwater runoff event. Therefore, the Mosher Slough watersheds that were studied are exporting about 10 times as much diazinon per unit area per storm as found in a residential area in the Upper Newport Bay watershed. Lee, *et al.*, found that the export coefficient for chlorpyrifos in a residential area in the Upper Newport Bay watershed was about equal to that of diazinon (i.e., 1 $\mu\text{g}/\text{m}^2$ /stormwater

runoff event). This is about the same as that found in the Stockton Mosher Slough MS-14 and MS-18 watersheds.

The diazinon and chlorpyrifos export coefficients will likely change significantly as these pesticides are removed from residential use, associated with the US EPA ban on their sale. Ultimately, as the current residential stock is depleted, diazinon and chlorpyrifos runoff from residential areas should become low to zero since neither of these chemicals have long half-lives in soil. However, as discussed in a subsequent section, agriculturally-derived atmospheric sources of diazinon and chlorpyrifos are being found to be a significant source of diazinon and chlorpyrifos in Modesto (Azimi-Gaylon, *et al.*, 2002). The contribution of agriculturally-derived atmospheric sources of diazinon and chlorpyrifos for Stockton stormwater runoff is unknown (see discussion presented below).

Examination of the rainfall runoff data for the MS-14 watershed shows that a 1-inch rain within a day produced about 26×10^6 L of runoff, while for MS-18, a 1-inch rain produced about 7×10^6 L of runoff. This corresponds for MS-14 to 12 L of runoff per square meter and for MS-18, 17 L of runoff per square meter. A 1-inch storm over the MS-14 area represents 56×10^6 L of rainfall. Therefore, about half of the rainfall in a 1-inch storm would be expected to run off from the MS-14 watershed. For MS-18, according to the information available, about 70 percent of a 1-inch storm would run off. This value is somewhat high for stormwater runoff from residential areas.

Chlorpyrifos and Diazinon Use Data

San Joaquin County pesticide application data for chlorpyrifos and diazinon were examined using the California Department of Pesticide Regulation's (CDPR, 2002) pesticide use report (PUR) for 1999 and 2000. Information for San Joaquin County diazinon and chlorpyrifos use for these two years is presented in Tables 18 and 19. Examination of Table 18 shows that about 11,000 pounds (ai) of diazinon were applied for structural pest control. This is the amount of diazinon that was used to control termites and other structural pests, that was applied by commercial applicators and, therefore, reported to the County Agriculture Commissioner. Most of this use would likely have occurred within the cities located in San Joaquin County. Table 20 presents information on the cities within San Joaquin County and their associated populations. As a first approximation, it can be assumed that the amount of diazinon and chlorpyrifos used in a city is proportional to the population. Therefore, using this approach, approximately 40 percent of the diazinon and chlorpyrifos used in San Joaquin County for structural pest control would be expected to have been used in Stockton. For diazinon, this amounts to about 5000 pounds (ai) in 2000, and 2000 pounds (ai) in 1999. For chlorpyrifos, the estimated structural pest control use in Stockton in 2000 was about 6000 pounds (ai), and 7000 pounds (ai) in 1999.

The use report data for structural use does not distinguish between indoor and outdoor use; therefore, it is not known how much of the structural use component will be reduced by the cancellation of any indoor uses. The indoor and outdoor use (sale) of chlorpyrifos was terminated in December 2001. Outdoor uses of diazinon will continue

Table 18
Diazinon Use in San Joaquin County During 1999-2000

Commodity	Pounds Applied (ai)	
	1999 ¹	2000 ²
Almond	12,636.70	3,203.70
Animal Premise		4.00
Apple	2,857.62	1,674.07
Apricot	877.86	395.08
Cherry	8,100.43	6,130.58
Cucumber (Pickling, Chinese, Etc.)	0.63	1.15
Grapes	130.01	125.00
Landscape Maintenance	552.57	325.71
Melons	502.00	331.78
N-Grnhs Grwn Cut Flwrs or Greens	17.00	1.39
N-Grnhs Grwn Plants in Containers	22.51	8.06
N-Grnhs Grwn Trnsplnt/Prpgtv Mtrl	261.81	18.59
N-Outdr Container/Fld Grwn Plants	104.32	160.66
Nectarine	10.00	18.50
Onion (Dry, Spanish, White, Yellow, Red, Etc.)	654.15	4.10
Peach	591.07	700.36
Pear	289.00	0.50
Peppers (Fruiting Vegetable), (Bell, Chili, Etc.)	43.02	
Plum	--	2.50
Potato (White, Irish, Red, Russet)	15.51	--
Prune	44.98	--
Pumpkin	1.00	--
Rights of Way	13.97	--
Soil Fumigation/Preplant	--	22.46
Squash (All or Unspec)	33.75	14.99
Squash (Summer)	0.88	--
Strawberry	--	0.03
Structural Pest Control	4,063.53	10,931.48
Sugarbeet	--	317.83
Tomato	93.14	30.05
Tomatoes, for Processing/Canning	1,848.92	1,727.93
Uncultivated Non-Ag Areas (All or Unspec)	0.66	0.16
Walnut (English Walnut, Persian Walnut)	58.49	156.79
Watermelons	287.20	37.28
TOTAL	34,112.73	26,344.74

-- No data available

¹ Source: Department of Pesticide Regulation 1999 Annual Pesticide Use Report Preliminary Data: San Joaquin County Indexed by Chemical
<http://www.cdpr.ca.gov/docs/pur/pur99rep/chemcnty/sanjoa99.pdf>

² Source: Department of Pesticide Regulation 2000 Annual Pesticide Use Report Preliminary Data: San Joaquin County Indexed by Chemical
<http://www.cdpr.ca.gov/docs/pur/pur00rep/chemcnty/sanjoa00.pdf>

Table 19
Chlorpyrifos Use in San Joaquin County During 1999-2000

Commodity	Pounds Applied (ai)	
	1999 ¹	2000 ²
Alfalfa (Forage – Fodder) (Alfalfa Hay)	14,351.61	20,604.22
Almond	5,235.76	5,658.65
Animal Premise	--	0.93
Apple	702.70	3,168.72
Asparagus (Spears, Ferns, Etc.)	2,468.79	2,299.21
Beans (All or Unspec)	14.87	--
Cabbage	23.00	36.90
Cauliflower	3.50	15.00
Cherry	35.25	150.07
Corn (Forage – Fodder)	6,240.71	3,558.43
Corn, Human Consumption	9.29	286.87
Grapes	139.43	--
Landscape Maintenance	186.17	69.35
N-Grnhs Grwn Cut Flwrs or Greens	4.50	9.45
N-Grnhs Grwn Plants in Containers	68.68	85.53
N-Outdr Container/Fld Grwn Plants	107.02	64.95
Onion (Dry, Spanish, White, Yellow, Red, Etc.)	130.60	--
Ornamental Turf (All or Unspec)	1.60	--
Peach	5.13	--
Prune	37.17	--
Regulatory Pest Control	--	0.19
Soil Application, Preplant-Outdoor (Seedbeds, Etc.)	35.00	--
Structural Pest Control	14,176.14	13,255.87
Sudangrass (Forage – Fodder) (Sorghum Sudanese)	22.45	52.40
Sugarbeet, General	4,476.77	4,640.96
Turf/Sod	--	5.40
Walnut (English Walnut, Persian Walnut)	22,414.94	22,569.15
TOTAL	70,891.08	76,532.25

-- No data available

¹ Source: Department of Pesticide Regulation 1999 Annual Pesticide Use Report Preliminary
Data: San Joaquin County Indexed by Chemical
<http://www.cdpr.ca.gov/docs/pur/pur99rep/chemcnty/sanja99.pdf>

² Source: Department of Pesticide Regulation 2000 Annual Pesticide Use Report Preliminary
Data: San Joaquin County Indexed by Chemical
<http://www.cdpr.ca.gov/docs/pur/pur00rep/chemcnty/sanja00.pdf>

Table 20
Incorporated Cities and Populations
January 1, 2002

Escalon	6,350
Lathrop	11,600
Lodi	59,400
Manteca	55,000
Ripon	11,150
Stockton (County Seat)	253,800
Tracy	65,600
Unincorporated Area	133,000
Total County Population	596,000

Source: State Department of Finance, May Estimates, 2002

until 2003, and product cancellation for this type of use does not occur until 2004. Azimi-Gaylon, *et al.* (2002) have reviewed the changes that are scheduled to occur in diazinon and chlorpyrifos use in urban and agricultural areas. Their review should be consulted for further information on this issue.

It is evident from Tables 18 and 19 that the dominant use of diazinon and chlorpyrifos in San Joaquin County is for agricultural pest control, especially in orchards. The use of these pesticides in orchards represents a potential for atmospheric transport from the place of use to urban areas, which would add to the diazinon and chlorpyrifos found in stormwater-runoff-impacted Mosher and Five Mile Sloughs. It is, therefore, of interest to determine the amount of OP pesticide use in orchards in the Mosher Slough watershed upstream of the City that could contribute diazinon and chlorpyrifos in stormwater runoff to Mosher Slough.

There is also need to better understand the flows of Mosher Slough (called “Mosher Creek” upstream of the City on some maps) as they enter the City during stormwater runoff events. These flows could in part be responsible for some of the diazinon and chlorpyrifos found in Mosher Slough during stormwater runoff events. Based on the information available, there is no stream gaging as it enters the City/Mosher Slough. Further, there has been no monitoring of diazinon/chlorpyrifos concentrations or toxicity in Mosher Creek as it enters Mosher Slough. In addition, the monitoring that has been done on Mosher Slough occurs near where it leaves the City and enters the Delta waterways. Therefore, at this time there is no information on the contribution of agriculturally derived stormwater-runoff-associated diazinon and chlorpyrifos that occurs in the Mosher Slough watershed.

Examination of the diazinon and chlorpyrifos concentration data, as well as the toxicity data for Mosher Slough and Five Mile Slough (see Tables 3 and 4) shows that, while the data are somewhat variable, there is no major difference between these two sloughs. Since Five Mile Slough does not have a direct runoff agricultural component as a source of diazinon and chlorpyrifos, it appears that the role of the agricultural component to Mosher Slough’s diazinon and chlorpyrifos is similar in concentration to

that contributed by the City's stormwater runoff to Mosher Slough. It is possible that Mosher Slough may at times continue to have toxic concentrations of diazinon and chlorpyrifos during stormwater runoff events derived from upstream agricultural sources, even though the use of both of these pesticides on residential properties will be eliminated.

A monitoring program will need to be conducted of the upstream contributions of diazinon and chlorpyrifos to Mosher Slough within the City to define the role of upstream agriculture as a stormwater runoff source of diazinon. There is also an unquantified atmospheric transport component of diazinon and chlorpyrifos from its use in agricultural areas to the Mosher Slough and Five Mile Slough watersheds, which could cause stormwater runoff from these watersheds to continue to have concentrations of these pesticides at levels of potential concern.

Relationship between Sources and Concentrations in the Sloughs

This discussion provides the basis for determining the loads of diazinon and chlorpyrifos that can be discharged to Mosher Slough and Five Mile Slough while still attaining the management goals. While normally the assimilative capacity of a waterbody is calculated by multiplying the management goal by the anticipated flow in the various reaches of the waterbody, that approach could not be followed for Mosher Slough and Five Mile Slough. Since water volume data within Mosher Slough and Five Mile Slough is not available, and because the influence of tide is highly variable, it is not possible to determine the loading capacity of these sloughs for diazinon and chlorpyrifos that does not cause violations of the water quality objectives (management goals).

In order to relate the pesticide concentrations discharged to Mosher Slough and Five Mile Slough to the concentrations found in the Sloughs, it was necessary to adopt an alternative US EPA-recommended approach of using the management goal (proposed water quality objective) as the allowable loading capacity (concentration) for these sloughs. This was the approach that was used by the US EPA (2002a) in developing a linkage analysis for the diazinon and chlorpyrifos TMDLs that that Agency used for the Upper Newport Bay watershed and the Bay. A similar approach was used by the San Diego Regional Water Quality Control Board (Pardy, 2002) in developing a linkage analysis for a draft diazinon TMDL for Chollas Creek, which flows through part of the city of San Diego.

Following this approach, the allowed loading capacity concentrations for Mosher Slough and Five Mile Slough are 0.08 µg/L for a 1-hour average (acute exposure), and 0.05 µg/L for a 4-day average (chronic exposure). For chlorpyrifos, the corresponding allowed loading capacity, expressed as concentrations, are 0.020 µg/L for acute exposure and 0.014 µg/L for chronic exposure.

There is considerable technical merit for adopting the management goal (water quality objective) as the in-waterbody concentration that is allowed for Mosher Slough and Five Mile Slough. It would be expected that, under conditions of ebb tide, a

considerable part, if not most, of the water in Five Mile Slough and, to the extent that upstream of the City's water from Mosher Creek represents a small part of the flow in Mosher Slough during a stormwater runoff event, in Mosher Slough would be stormwater runoff from the City's storm sewers that discharge to these sloughs. Under these conditions, there would be limited dilution of the storm sewer discharges and, therefore, the assimilative capacity for these pesticides can be directly related to the allowed concentrations in the storm sewer discharges to the sloughs.

Allocations

As discussed by Azimi-Gaylon, *et al.* (2002),

“The total assimilative capacity, or TMDL, must be distributed between a background load (BL), a margin of safety (MOS), a waste load allocation (WLA) for point sources, and a load allocation (LA) for non-point sources:

$$TMDL = BL + MOS + WLA + LA ”$$

Background Load

Although pesticides have been detected in Central Valley rainfall, there is currently insufficient information to assign an explicit background loading term for this potential source within the city of Stockton or, for that matter, elsewhere in the Central Valley. Future loading attributable to rainfall can be included in a revised load allocation when information on atmospheric loads directly to the water surface of Mosher Slough and Five Mile Slough are known. The atmospheric loading to the land surfaces within the Mosher Slough and Five Mile Slough watersheds is considered as part of that loading that is present in the storm sewer discharges to the sloughs.

Margin of Safety

Following the approach adopted by the US EPA (2002a) for the Upper Newport Bay watershed's diazinon and chlorpyrifos TMDLs, a 10-percent margin of safety could be used in the allowed discharges of the city of Stockton storm sewers to Mosher Slough and Five Mile Slough. According to the US EPA (2002a),

“This explicit 10 % margin of safety was applied to the recommended criteria derived by the CDFG (2000a) [Siepmann and Finlayson, 2000] and EPA (1986) [US EPA, 1986] for diazinon and chlorpyrifos. This explicit margin of safety is intended to account for uncertainties in TMDL calculation methods and concerning pesticide effects (e.g., potential additive and synergistic impacts from exposure to multiple OP pesticides) that may aggravate water quality impacts due to diazinon and chlorpyrifos usage in the watershed.

In addition to the explicit margin of safety, conservative assumptions were used in applying the numeric targets within the watershed. These conservative assumptions serve as implicit margins of safety to provide additional protection for aquatic life and minimize aquatic toxicity.”

Waste Load Allocation

Since the city of Stockton has a stormwater runoff NPDES permit, the load allocations are for the city of Stockton's stormwater runoff point source "waste loads" that are discharged to Mosher and Five Mile Sloughs by the storm sewer system. These allocations are based on all stormwater discharges to Mosher and Five Mile Sloughs achieving the numeric water quality objectives (management goals), adjusted downward for a safety factor. The diazinon storm sewer waste load allocation for acute exposure (1-hour average) is 0.072 µg/L, and for chronic exposure is 0.045 µg/L. For chlorpyrifos, the corresponding values are 0.018 µg/L for acute exposure and 0.0126 µg/L for chronic exposure. These values are 10 percent less than the proposed management goals (proposed water quality objectives) for diazinon and chlorpyrifos.

Load Allocation

In addition to urban stormwater-runoff-derived diazinon and chlorpyrifos from residential and commercial properties, some unquantified loads of these pesticides to Mosher Slough and Five Mile Slough are believed to be derived from atmospheric transport of diazinon and chlorpyrifos used in agricultural areas in San Joaquin County and elsewhere in the Central Valley to these sloughs' watersheds. Further, during stormwater runoff events, there is a potential for upstream of the City agricultural use of diazinon and chlorpyrifos to be transported to Mosher Slough within the City via Mosher Creek, and thereby contribute to the loads of these pesticides within the City. The magnitude of this loading is unknown. It is believed, however, that the primary sources of diazinon and chlorpyrifos for Mosher Slough and Five Mile Slough within the city of Stockton are storm sewers that drain residential and commercial properties within these sloughs' urban watersheds. The significance of upstream of the City sources will need to be determined through continued monitoring of Mosher Slough and Five Mile Slough as the uses within the City are phased out.

Conclusions

The use of diazinon and chlorpyrifos on residential and commercial properties within the Mosher Slough and Five Mile Slough watersheds is believed to be the cause of aquatic life toxicity to *Ceriodaphnia dubia* in these sloughs during stormwater runoff events. The use of these pesticides for agricultural purposes in the Mosher Slough watershed upstream of the City is an unquantified additional source of these pesticides for Mosher Slough. Also, atmospheric sources from agricultural use of these pesticides may be a contributor to Mosher Slough and Five Mile Slough diazinon and chlorpyrifos stormwater-runoff-associated concentrations. It is expected that significant reductions in the amounts of diazinon and chlorpyrifos present in stormwater runoff to these sloughs and within them will occur associated with the curtailed sale of these pesticides to the residential community.

The phase-out of diazinon and chlorpyrifos for residential and commercial use will result in the use of other pesticides that need to be evaluated with respect to causing aquatic life toxicity and other adverse impacts on the beneficial uses of Mosher Slough and Five Mile Slough.

Recommendations

An aquatic life toxicity and chemical concentration monitoring program should be conducted on both Mosher and Five Mile Sloughs. This monitoring program should include evaluation of the toxicity, using the US EPA standard three species testing procedure of the slough waters at several locations in the City and into the Delta just prior to, during, and following stormwater runoff events. Chemical concentration measurements of diazinon and chlorpyrifos should be made of the samples that are tested for toxicity. Stormwater runoff events in the late fall, mid-winter and early spring should be monitored. The toxicity testing should include measurement of the total acute toxicity units through the use of toxicity test dilution series which are conducted with and without PBO. Lee (1999) and Deanovic, *et al.* (1998) have presented guidance on the approach that should be used to monitor urban stormwater runoff for aquatic life toxicity.

If a significant part of the measured toxicity cannot be accounted for by concentrations of diazinon and chlorpyrifos, then toxicity identification evaluation (TIE) studies should be conducted to identify the cause of the non-OP pesticide-caused toxicity. Particular attention should be given to evaluating the potential for the common pesticides sold over the counter for residential use to cause aquatic life toxicity in stormwater runoff from the Mosher Slough and Five Mile Slough watersheds. To the extent possible, chemical monitoring of the commonly sold pesticides within the city of Stockton should be conducted of storm sewer discharges and Mosher and Five Mile Sloughs during stormwater runoff events with analytical methods that can reliably measure their concentrations at less than 0.1 of the LC₅₀ for toxicity to zooplankton and/or fish (see US EPA, 2002b for LC₅₀ values).

A monitoring station which includes a stream gage should be established on Mosher Creek just upstream of the point where it enters the City. This location should be sampled with each rainfall runoff event that causes Mosher Creek to flow into Mosher Slough. Aquatic life toxicity and the concentrations of diazinon and chlorpyrifos should be measured in these samples.

An atmospheric loading station should be established in the Mosher Slough watershed within the City to measure the dry-fallout- and precipitation-associated concentrations of diazinon, chlorpyrifos and aquatic life toxicity.

References

- Azimi-Gaylon, S.; Grober, L.; McCarthy, M.; Reyes, E.; Leva, D. and Tadlock, T. 2002. Draft San Joaquin River Diazinon and Chlorpyrifos Total Maximum Daily Load Report. Central Valley Regional Water Quality Control Board, Sacramento, CA. July. http://www.swrcb.ca.gov/tmdl/docs_lists.html
- Bailey, H.; DiGiorgio, C.; Kroll, K.; Miller, J.; Hinton, D. and Starrett, G. 1996. Development of Procedures for Identifying Pesticide Toxicity in Ambient

- Waters: Carbofuran, Diazinon, and Chlorpyrifos. *Environ. Toxicol. Chem.* 15:837-846.
- CDPR. 2002. Pesticide Use Report Database. California Department of Pesticide Regulation, Sacramento, CA.
<http://www.cdpr.ca.gov/docs/pur/purovrw/ovr52000.pdf>
- Connor, V. 1994. Toxicity and Diazinon Levels Associated with Urban Storm Runoff. Memorandum to Jerry Bruns, Chief, Standards, Policies & Special Studies, California Regional Water Quality Control Board, Central Valley Region, Sacramento, CA.
- Connor, V. 1995. Status of Urban Storm Runoff Projects. Memorandum to Jerry Bruns, Chief, Standards, Policies & Special Studies, California Regional Water Quality Control Board, Central Valley Region, Sacramento, CA.
- CVRWQCB. 1998. The Water Quality Control Plan (Basin Plan) for the California Regional Water Quality Control Board, Central Valley Region — The Sacramento River Basin and The San Joaquin River Basin. Fourth Edition.
- Deanovic, L.; Cortright, K.; Larsen, K.; Bailey, H.; Hinton, D. E. and Connor, V. 1998. Guidelines for Conducting Toxicity Identification Evaluation Procedures in Urban Runoff, a Laboratory Manual. Draft Report Prepared for the Central Valley Regional Water Quality Control Board, Sacramento, CA. (Being updated.)
- Fong, S.; Reyes, E.; Larsen, K.; Louie, S. and Deanovic, L. 2000. Sacramento-San Joaquin Delta Toxicity Test Monitoring Report: 1998-99, The Final Report for DeltaKeeper. Aquatic Toxicology Laboratory, University of California, Davis, CA.
- Lee, G. F. 1999. Recommended Aquatic Life Toxicity Testing Program for Urban Stormwater Runoff. Comments submitted to E. Bromley, US EPA Region IX, San Francisco, CA.
- Lee, G. F. and Jones-Lee, A. 2001. Review of the City of Stockton Urban Stormwater Runoff Aquatic Life Toxicity Studies Conducted by the CVRWQCB, DeltaKeeper and the University of California, Davis, Aquatic Toxicology Laboratory between 1994 and 2000. Report to the Central Valley Regional Water Quality Control Board Sacramento, CA and the DeltaKeeper Stockton, CA, by G. Fred Lee & Associates, El Macero, CA, November.
- Lee, G. F. and Taylor, S. 1999. Results of Aquatic Life Toxicity Studies Conducted During 1997-99 in the Upper Newport Bay Watershed, and Review of Existing Water Quality Characteristics of Upper Newport Bay, Orange County, CA and its Watershed. Submitted to State Water Resources Control Board, Santa Ana

Regional Water Quality Control Board, and Orange County Public Facilities and Resources Department, to meet the requirements of the US EPA 205(j) project, Report of G. Fred Lee & Associates, El Macero, California, October. (The aquatic toxicity part of this report is available from www.gfredlee.com).

- Lee, G. F.; Taylor, S. and Palmer, F. 2001a. Results of Aquatic Toxicity Testing Conducted During 1999-2000 in the Upper Newport Bay Watersheds. Submitted to State Water Resources Control Board, Santa Ana Regional Water Quality Control Board and Orange County Public Facilities and Resources Department to meet the requirements of the US EPA 319(h) Project, G. Fred Lee & Associates, El Macero, CA and RBF Consulting, Irvine, CA.
- Lee, G. F.; Taylor, S. and Jones-Lee, A. 2001b. Synopsis of the Upper Newport Bay Watershed 1999-2000 Aquatic Life Toxicity Results with Particular Reference to Assessing the Water Quality Significance of OP Pesticide-Caused Aquatic Life Toxicity. Report of G. Fred Lee & Associates, El Macero, CA.
- Lewis, P. A.; Klemm, D. J.; Lazorchak, J. M.; Norberg-King, T.; Peltier, W. H. and Heber, M. A. 1994. Short-Term Methods for Estimating the Chronic Toxicity of Effluents and Receiving Waters to Freshwater Organisms. Environmental Monitoring Systems Laboratory, Cincinnati, Ohio; Environmental Research Laboratory, Duluth, Minnesota; Region 4, Environmental Services Division, Athens, Georgia; Office of Water, Washington, D.C.; Environmental Monitoring Systems Laboratory, Cincinnati, OH; Office of Research and Development, U.S. Environmental Protection Agency, Cincinnati, OH.
- Pacific EcoRisk. 2000. Stormwater Toxicity Characterization Study of the Stormwater Sample MS-14 (Sample Collected November 7, 1999). Report prepared for City of Stockton by Pacific EcoRisk, Martinez, CA.
- Pardy, L. 2002. Total Maximum Daily Load for Diazinon in Chollas Creek Watershed, San Diego County. California Regional Water Quality Control Board, San Diego Region. Resolution No. R9-2002-0123. San Diego, CA. April.
- San Joaquin County. 1997. 1996-1997 Fiscal Year Annual Report for the San Joaquin County National Pollutant Discharge Elimination System, Permit No. CA0083470, Stockton, CA.
- Siepmann, S. and Finlayson, B. 2000. Water Quality Criteria for Diazinon and Chlorpyrifos. California Department of Fish and Game. Office of Spill Prevention and Response. Administrative Report 00-3. Rancho Cordova, CA.
- Stockton. 1996. City of Stockton 1995-96 Annual Progress Report-NPDES Order No. 95-035. Department of Municipal Utilities, City of Stockton, Stockton, CA.

- Stockton. 1998. City of Stockton 1997-98 Storm Water Monitoring Program. Prepared by Kinnetic Laboratories, Inc. for the City of Stockton, Stockton, CA.
- Stockton. 1999. Storm Water Management Program 1998/99 Annual Report and Program Effectiveness Evaluation Report. Prepared for the City of Stockton Municipal Utilities District, Storm Water Division, County of San Joaquin Public Works, Stockton, CA.
- Stockton. 2000. City of Stockton 1999/2000 Annual Report. City of Stockton Department of Municipal Utilities, Storm Water Division, Stockton, CA.
- US EPA. 1985. Guidelines for Deriving Numerical National Water Quality Criteria for the Protection of Aquatic Organisms and their Uses. US Environmental Protection Agency, Office of Research and Development. Washington, D.C.
- US EPA. 1986. Ambient Water Quality Criteria for Chlorpyrifos. US Environmental Protection Agency, Office of Water Document 440/5-005. Washington D.C.
- US EPA. 2002a. Total Maximum Daily Loads for Toxic Pollutants, San Diego Creek and Newport Bay, California. US Environmental Protection Agency Region 9, San Francisco, CA. June.
- US EPA. 2002b. Ecotoxicity Database. US Environmental Protection Agency, Office of Pesticide Programs, Washington D.C.
- Werner, I.; Deanovic, L. A.; Connor, V.; DeVlaming, V.; Bailey, H. C. and Hinton, D. E. 2000. Insecticide-Caused Toxicity to *Ceriodaphnia dubia* (Cladocera) in the Sacramento-San Joaquin River Delta, California, USA. *Environmental Toxicology and Chemistry* 19(1):215-227.