California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring
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STUDY 227: PROTOCOL FOR EVENT-BASED MONITORING OF ORGANOPHOSPHORUS INSECTICIDES AND PREEMERGENT HERBICIDES IN THE SACRAMENTO VALLEY, WINTER 2004 – 2005

Lei Guo and Kevin Kelley

I. INTRODUCTION

Transport of pesticides by rainfall-driven surface runoff is a major process leading to pesticide contamination in rivers. This occurs when application of pesticides coincide with precipitation. Previous studies have shown frequent detections of pesticides in the Sacramento River and its tributaries, especially organophosphorus (OP) insecticides and preemergent herbicides (Domagalski et al., 2000; Dileanis et al., 2002; Spurlock, 2002; Guo et al., 2004). These pesticides were applied during winter storm seasons and subsequently carried by runoff water into the streams during storm events.

Adequately characterizing the source and transport of pesticides in the Sacramento River is an important component of any mitigation strategy to reduce pesticide loads to surface water in the Sacramento Valley. Despite a substantial body of surface water monitoring data for the Sacramento Valley, as documented in the Surface Water Database of the California Department of Pesticide Regulation (DPR), a complete conceptual picture of pesticide transport within the Sacramento River watershed and its subbasins is still lacking.

II. OBJECTIVE

The objective of this monitoring study is to determine the relative contributions of pesticide load to the Sacramento River from its major subbasins during winter storm events. The information is necessary for understanding pesticide fate and transport at the watershed scale in the Sacramento River watershed, and can be used for calibrating DPR's watershed model of pesticide transport and prioritizing the mitigation efforts in the Sacramento Valley.

III. PERSONNEL

Monitoring will be conducted by DPR staff, and the project will be under the general direction of Kean Goh, Agricultural Program Supervisor IV. The roles and responsibilities of project personnel are defined in DPR's Standard Operating Procedure (SOP): ADMIN002.00 – Personnel organization and responsibilities for studies (http://www.cdpr.ca.gov/docs/empm/pubs/sops/admn002.pdf). Key personnel are listed below:

Project Leader: Lei Guo
Field Coordinator: Kevin Kelley
Senior Scientist: Frank Spurlock
Laboratory Liaison: Carissa Ganapathy
Chemists: Jean Hsu and Hsiao Feng, California Department of Food & Agriculture

Questions concerning this monitoring project should be directed to Lei Guo at (916) 324-4186.

IV. MONITORING PLAN

The monitoring plan is designed to monitor four of the six subbasins in the Sacramento River watershed – Sacramento Valley (Figure 1). Pesticide loading from the American River subbasin will not be monitored due to the extremely low use of dormant spray pesticides in the area. For example, the American River subbasin historically received <0.05% of the total agricultural use of diazinon in the Sacramento River watershed.

Pesticide load from the other five subbasins will be estimated by monitoring at five sampling locations: four of them for the subbasins of 1) Sacramento River above Colusa; 2) Colusa Drain; 3) Feather River; and 4) Natomas Cross Canal; and one for the main stem of the Sacramento River at the Alamar Marina Dock. The main stem site characterizes the total load of pesticides to the Sacramento River from the upstream five subbasins, excluding the American River subbasin (Figure 1). The subbasin of Butte/Sutter Basin will not be monitored due to the difficulty in locating a suitable monitoring site for accurately characterizing drainage. Its loading to the Sacramento River, however, will be calculated by taking the difference between the load obtained at the Alamar Marina Dock and the sum of the other four subbasins

The sampling of surface water will be undertaken during one storm event after dormant spray of pesticides started, most likely in later January or February based on historical pesticide use data. One background sampling will be taken prior to the onset of the dormant-spray season in December 2004. Monitoring will commence during the first significant storm event following the beginning of dormant spray applications. In the event that only a portion of the study area is to receive rainfall, the project leader will determine which sites will be sampled. In the event of a false start, the project leader will recall sampling personnel and determine whether or not any collected samples should be analyzed.

The project leader will be responsible for following weather forecasts, evaluating and tracking storm fronts throughout the watershed. Precipitation data from the California Data Exchange Center (CDEC) – operated by the California Department of Water Resources (DWR) – and information from local and national weather sources will be used to determine whether or not a storm constitutes a “storm event.” The triggers used to designate an impending storm front as an actual “storm event” will be defined by several factors including storm intensity, storm track, predicted rainfall, measured rainfall, and observed runoff. Upon the determination that a given storm constitutes a storm event, designated monitoring crews will be mobilized and sampling will begin.

Sampling will be conducted twice daily for the initial two days following the storm to catch the rapid change of pesticide concentration expected, especially for the subbasins.

The sampling frequency will then reduce to once daily for the rest of the hydrograph. In general, a single storm event will involve five to seven consecutive days of sampling. However, sampling may be extended beyond this time frame in order to fully characterize the hydrograph of a storm event.

Wherever practical, a center channel grab water sample will be collected from bridges or road crossings. This will be done using a 4.2-L stainless steel Kemmerer samplers (Wildlife Supply Company). The sample will then be transferred to pre-labeled amber, glass bottles. Where bank monitoring is required, a telescoping rod that holds the sample container will be used, and the sample will be collected by submersing the pre-labeled bottle to a depth of at least 1 meter. All samples will be sealed with Teflon®-lined lids and placed on wet ice until delivered to DPR's facility in West Sacramento later that day. A chain of Custody (COC) form will be completed and submitted for each sample. All samples will be stored at 4°C until delivered to the laboratory for chemical analyses.

Data collection at each site will also include *in-situ* measurements of water pH and temperature, dissolved oxygen, and specific conductance. General guidance on surface water sampling is provided on DPR's website at http://www.cdpr.ca.gov/docs/empm/pubs/sops/fswa002.pdf.

Discharge measurements are available via the United States Geological Survey (USGS) and/or the DWR for three of the five monitoring sites (Table 1). The discharge at the Colusa basin drain canal and Cross Canal sites will be manually gauged by monitoring crews at the time of sample collection, using standard USGS methods (Buchanan and Somers, 1969). The discharge on the Feather River will be estimated by adding real-time discharge measurements from the Bear and Yuba Rivers to the flow in the Feather River at Gridley which is also available in real-time.

V. CHEMICAL ANALYSIS

Chemical analyses will be performed by the California Department of Food and Agriculture's Center for Analytical Chemistry. Water samples will be analyzed for OPs and triazines. The chemical analytical method and reporting limits are reported in Table 2. The reporting limit will be used to record the lowest concentration of an analyte that the method can detect reliably in a matrix blank. Comprehensive chemical analytical methods will be provided in the final report.

VI. QUALITY ASSURANCE/QUALITY CONTROL

Quality control will be conducted in accordance with SOP QAQC001.00 (http://www.cdpr.ca.gov/docs/empm/pubs/sops/admn001.htm). Ten percent of the total number of analyses will be submitted with field samples as field blanks, rinse blanks and blind spikes.

Number of Chemical Analyses

Background: 2 samples (OP, triazine) per site x 5 sites x 1 sampling event…………. 10
Storm event: 2 samples per site x 5 sites x 2 sampling events per day x 2 days +
2 samples per site x 5 sites x 1 sampling event per day x 5 days………..…………… 90

Continuing QC (min. 10% of total chemical analyses). ………………………………….. 10

***Total** ……………………………………………………………………………………….. 110*

VII. DATA ANALYSIS

Pesticide loads, expressed as kg/day, will be calculated using the time series of pesticide concentration data and stream flow rate. The following equation will be used for the calculation:

$$Y(t) = 0.00245C(t)F(t)$$

where *Y(t)* is the estimated pesticide load (kg d^{-1}) for day *t*, *C(t)* is the pesticide concentration ($\mu g\ L^{-1}$), and *F(t)* is the stream flow rate (cfs, or cubic foot per second), and 0.00245 is a conversion factor. For samples with a concentration of lower than the method detection limit (MDL), the pesticide load will be calculated assuming one half of the MDL (Table 1). The integrated load over the period of observation is the total mass of pesticide transported past the monitoring site and will be used to compare the relative contributions of the sub-basins to total loading in the Sacramento River.

VIII. TIME TABLE

Field Sampling – December 2004 and application onset for one storm event.
Chemical Analysis – December 2004 through April 2005
Preliminary Memorandum – June 2005
Final Report – September 2005

IX. REFERENCES

Buchanan, T.J. and W.P. Somers. 1969. Discharge measurements at gaging stations. U.S. Geological Survey, Tech. Water-Resources Inv., Book 3 Chap. A8. Washington DC.

Dileanis, PD., K.P. Bennett, and J.L. Domagalski. 2002. Occurrence and Transport of Diazinon in the Sacramento River, California, and Selected Tributaries During Three Winter Storms, January-February 2000. WRIR - 02-4101. USGS, Sacramento, CA. 2002.

Domagalski, J.L., P.D. Dileanis, D.L. Knifong, C.M. Munday, J.T. May, B.J. Dawson, J.L. Shelton, and C.N. Alpers. 2000. Water-Quality Assessment of the Sacramento River Basin, California: Water-Quality, Sediment and Tissue Chemistry, and Biological Data, 1995-1998, OFR - 00-391. USGS, Sacramento, CA. 2000.

Guo, L., C. Nordmark, F. Spurlock, B. Johnson, L. Li, M. Lee, and K. Goh. 2004. Characterizing dependence of pesticide load in surface water on precipitation and pesticide use for the Sacramento River watershed. Environ. Sci. Technol. 38: 3842-3852.

Spurlock, F. 2002. Analysis of diazinon and chlorpyrifos surface water monitoring and acute toxicity bioassay data, 1991-2001. EH01-01, Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA.

X. BUDGET

<u>Chemical Analysis Costs ($300/sample)</u>	
Background (10 samples):	$3,000
Storm event (90 samples):	$27,000
Continuing QC (10 samples):	$3,000
Total Chemical Analysis Costs:	$33,000
<u>Personnel: 72 hours (16 hour per day x 2 days + 8 hours per day x 5 days) per person per storm event</u>	
(4) Assoc. Env. Scientist @ $25/hr for 72 hours:	$7,200
(4) Env. Scientist @ $20/hr for 72 hours:	$5,760
(2) Senior Env. Scientist @ $32/hr for 10 hours:	$640
Staff Benefits @ 31%:	$4,216
Total Staff Costs:	<u>$17,816</u>
Total Study Costs:	***$50,816***

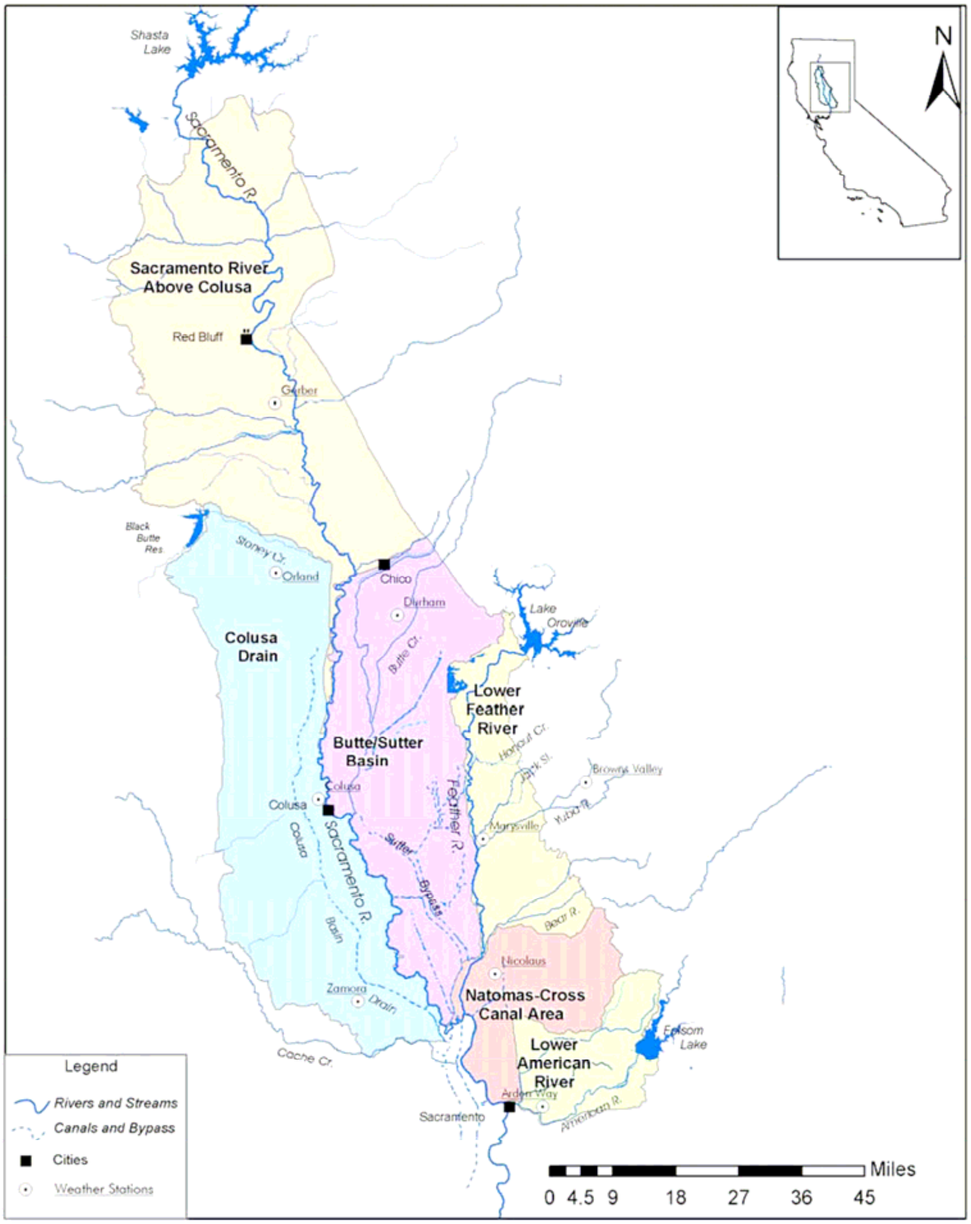

Figure 1. Delineation of the Subbasins in the Sacramento River Watershed - Sacramento Valley

CEN 7/7/03
Sacto_pesticide_modelling2
Based on Regional Water Quality Control Board map
Thanks to Gene Davis

Table 1. Sampling sites for event-based monitoring, Sacramento Valley, Winter 2003/2004

Site#	Site Name	Subbasin	Discharge Source[1]
1	Sacramento R. @ Alamar Marina	Integrator Site	VON
2	Cross Canal @ Garden Hwy.	Natomas Cross Canal	Manually Gauge
3	Colusa Basin Drain @ Rd. 99E	Colusa Drain	Manually Gauge
4	Feather R. near Hwy. 99	Feather R.	GRL + MRY + BRW
5	Sacramento R. @ Colusa	Sacramento R. above Colusa	COL

1) CDEC three letter designation of real-time discharge station.

Table 2. Method Detection Limit (MDL) and Reporting Limit (RL) of pesticides in surface water, California Department of Food and Agriculture, Center for Analytical Chemistry.

OPs-	***GC/FPD***		***Herbicides- LC/MS/MS***		
Analyte	**MDL**(ppb)	**RL**(ppb)	**Analyte**	**MDL**(ppb)	**RL**(ppb)
Ethoprop	0.0098	0.05	Atrazine	0.02	0.05
Diazinon	0.011	0.04	Simazine	0.013	0.05
Disulfoton	0.0093	0.04	Diuron	0.22	0.05
Chlorpyrifos	0.0109	0.04	Prometon	0.016	0.05
Malathion	0.0117	0.04	Bromacil	0.031	0.05
Methidathion	0.0111	0.05	Prometryn	0.016	0.05
Fenamiphos	0.0125	0.05	Hexazinone	0.04	0.05
Azinphos methyl	0.0099	0.05	Cyanazine	0.0133	0.05
Dichlorvos	0.0098	0.05	Metribuzin	0.025	0.05
Phorate	0.0083	0.05	Norflurazon	0.019	0.05
Fonofos	0.008	0.04	DEA	0.010	0.05
Dimethoate	0.0079	0.04	ACET	0.030	0.05
Methyl Parathion	0.008	0.03	DACT	0.016	0.05
Tribufos	0.0142	0.05			
Profenofos	0.0114	0.05			
OPs-	***GC/MS***				
Diazinon	1.191ppt*	10ppt			
Chlorpyrifos	0.7999 ppt*	10ppt			

**in clean American River water*