California Environmental Protection Agency
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Environmental Monitoring
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STUDY 220: PROTOCOL FOR EVENT-BASED MONITORING OF ORGANOPHOSPHORUS INSECTICIDES AND PREEMERGENT HERBICIDES IN THE SACRAMENTO VALLEY, WINTER 2003 – 2004

January 6, 2004

I. INTRODUCTION

A variety of pesticides are used to control insect and plant pests in the Sacramento Valley. For example, the organophosphate (OP) insecticides diazinon, chlorpyrifos, and methidathion are generally applied with a dormant oil to nut and stone fruit trees for control of peach twig borer, San Jose scale, and mite pests. The best time to achieve control of these pests is December through February, when trees are dormant and better pesticide coverage is possible (Zalom *et al.*, 1995). Similarly, preemergent herbicides such as simazine, a triazine, and diuron, a substituted urea, are used in winter to control grasses and broadleaf weeds in wine grapes, rights-of-ways, alfalfa, almonds and walnuts.

Because applications of both the dormant spray OP insecticides and the preemergent herbicides coincide with seasonal winter rainfall, diazinon, simazine, and diuron have the potential to wash off target areas and migrate with runoff waters to the Sacramento River. All three pesticides have been frequently detected in Sacramento Valley water bodies during winter sampling (Domogalski et al., 2000).

Previous studies of the Sacramento River by the U.S. Geological Survey (USGS) and the California Department of Pesticide Regulation (DPR) have shown that diazinon is the most frequently detected OP and that most detections occur during the dormant-spray season (Ganapathy *et al*., 1997; MacCoy *et al*., 1995). Recently, an intensive winter storm runoff study evaluated the relative contributions of Sacramento Valley sub-basins to diazinon loading in the mainstem of the Sacramento River (Dileanis *et al*., 2002). However, only limited herbicide sampling data was reported by Dileanis et al. (2002). Consequently, there is limited or no data from which to evaluate the relative contribution by sub-basin of preemergent herbicide load to the Sacramento River.

In initial efforts to better understand the relationship of pesticide loads in surface water and governing environmental factors, DPR conducted a regression analysis of the available historical data of pesticide concentrations (1991 to 2000) in surface water, river discharge, precipitation, and pesticide use in the Sacramento River watershed (Guo *et al.*, 2003). The objective of the analysis was to develop an empirical model relating winter-time pesticide loads in the Sacramento River to precipitation and pesticide use. One use of the model may be to evaluate the effect of mitigation measures on reducing pesticide runoff into surface water at the watershed scale. Guo et al. concluded that additional sub-basin monitoring data would allow better model calibration and better interpretation of the entire data set.

II. OBJECTIVE

The objectives of this monitoring study are to 1) determine the relative contributions of six Sacramento Valley sub-basins to total OP and triazine pesticide loading in the Sacramento River during winter storm events and 2) provide additional data for calibration of DPR's pesticide use/precipitation model.

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: Kevin Bennett
Field Coordinator: Roger Sava
Senior Scientist: Frank Spurlock
Statistician: Lei Guo
Laboratory Liaison: Carissa Ganapathy
Chemists: Jean Hsu and Hsiao Feng, California Department of Food & Agriculture

Questions concerning this monitoring project should be directed to Kevin Bennett at (916) 324-4200.

IV. MONITORING PLAN

To obtain finer watershed resolution in observing the potential relative contributions of pesticide loading to the Sacramento River, the larger watershed has been divided into smaller sub-basins to more accurately reflect regional and local hydrology (Figure 1).

The delineation of the Sacramento River watershed and its sub-basins is similar to that used by the Central Valley Regional Water Quality Control Board (CVRWQCB) for pesticide Total Maximum Daily Load development (McClure *et al*., 2002). The sub-basins are 1) Sacramento River above Colusa, 2) Colusa Drain, 3) Butte/Sutter Basin, 4) Feather River, 5) Natomas Cross Canal, and 6) Natomas Basin/American River (Figure 1). Sampling sites were selected to best characterize the pesticide loadings from each sub-basin into the lower Sacramento River and are presented in Table 1.

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.

Monitoring will commence prior to the onset of the dormant-spray season (December 2003) and will continue until data during two storm events are captured. Background samples will be collected for one day, beginning prior to dormant-spray applications, and then monitoring will resume during storm events, after applications have begun in the watershed. 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.

Samples will be collected twice daily at each of the eight monitoring sites to examine pesticide concentrations over the rise and fall of the hydrograph. In general, a single storm event will involve four to five consecutive days of sampling. However, sampling may be extended beyond this timeframe in order to best characterize the hydrograph. Wherever practical, a center channel, depth-integrated water sample will be collected from bridges or road crossings. This will be done using a D-77 sampler with a Teflon® bottle and nozzle. 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. COCs will be completed and submitted for each sample. All samples will be stored at 4^{o}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 USGS and/or the DWR for five of the eight monitoring sites (Table 1). The Natomas East Main Drain and Cross Canal sites will be manually gauged by monitoring crews at the time of sample collection. These discharges will be determined 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. Method titles and reporting limits for this study 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 (OP, triazine) x 8 sites x 1 day …………………………………………. 16
4 (2 OP, 2 triazine) x 8 sites x 5 days/storm x 2 storms ………………… …………… 320
Continuing QC (min. 10% of total chemical analyses) ………………………………….. 34
Total …………………………………………………………………………………….. ***370***

VII. LOAD ESTIMATIONS

Pesticide loads will be calculated by generating a mass curve for the period of observation. This is accomplished by developing a discharge curve from data obtained from either the discharge station or measurements from sampling crews. Daily pesticide concentrations will be averaged. This concentration is then multiplied by the discharge volume for the corresponding timeframe to obtain a value for the mass. In case of isolated detections that have no detected concentrations on sampling days immediately preceding and following the date of detection, one-half the detection limit will be used to calculate the mass for those days. 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.

One of the sampling sites representing the Natomas Cross Canal sub-basin – Natomas East Main Drain Canal – discharges to the Sacramento River downstream of the integrator site, Alamar Marina. To evaluate this sub-basin's contribution to total pesticide loading in the Sacramento River, DPR will coordinate sampling efforts with the CVRWQCB who is conducting similar research on the Sacramento River at the Tower Bridge during the same timeframe. Pesticide data collected by CVRWQCB will allow DPR to compare loads between all of the sub-basins. Discharge at the Tower Bridge site will be determined by adding real-time data from stations on the Sacramento and American rivers at I Street and Fair Oaks, respectively.

VIII. DATA ANALYSIS

Pesticide loading will be estimated as previously mentioned. Upon continuing consultation with senior DPR staff, appropriate statistical analysis will be used to best investigate potential relationships between loading, discharge, rainfall, pesticide use, and physiographical features within each of the sub-basins. Final analysis and evaluation of the data will also be used to further develop pesticide management plans and calibrate existing DPR hydrological models.

IX. TIME TABLE

Field Sampling – December 2003 and application onset for two storm events.
Chemical Analysis – December 2003 through April 2004
Preliminary Memorandum – June 2004
Final Report – September 2004

X. REFERENCES

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XI. BUDGET

Chemical Analysis Costs ($300/sample)	
Background: 8 OP + 8 triazines = 16 samples:	$4,800
OPs: 10 samples x 8 sites x 2 storm events = 160 samples:	48,000
Triazines: 10 samples x 8 sites x 2 storm events = 160 samples:	48,000
Quality Control = 34 samples	10,200
Total Chemical Analysis Costs:	$111,000
Personnel: 40 hours each estimated per storm event	
(4) Assoc. Env. Scientist @ $25/hr for 88 hours:	8,800
(4) Env. Scientist @ $20/hr for 88 hours:	7,040
(2) Senior Env. Scientist @ $32/hr for 10 hours:	640
Staff Benefits @ 31%:	5,109
Total Staff Costs:	$ 21,589
Total Study Costs:	***$ 132,589***

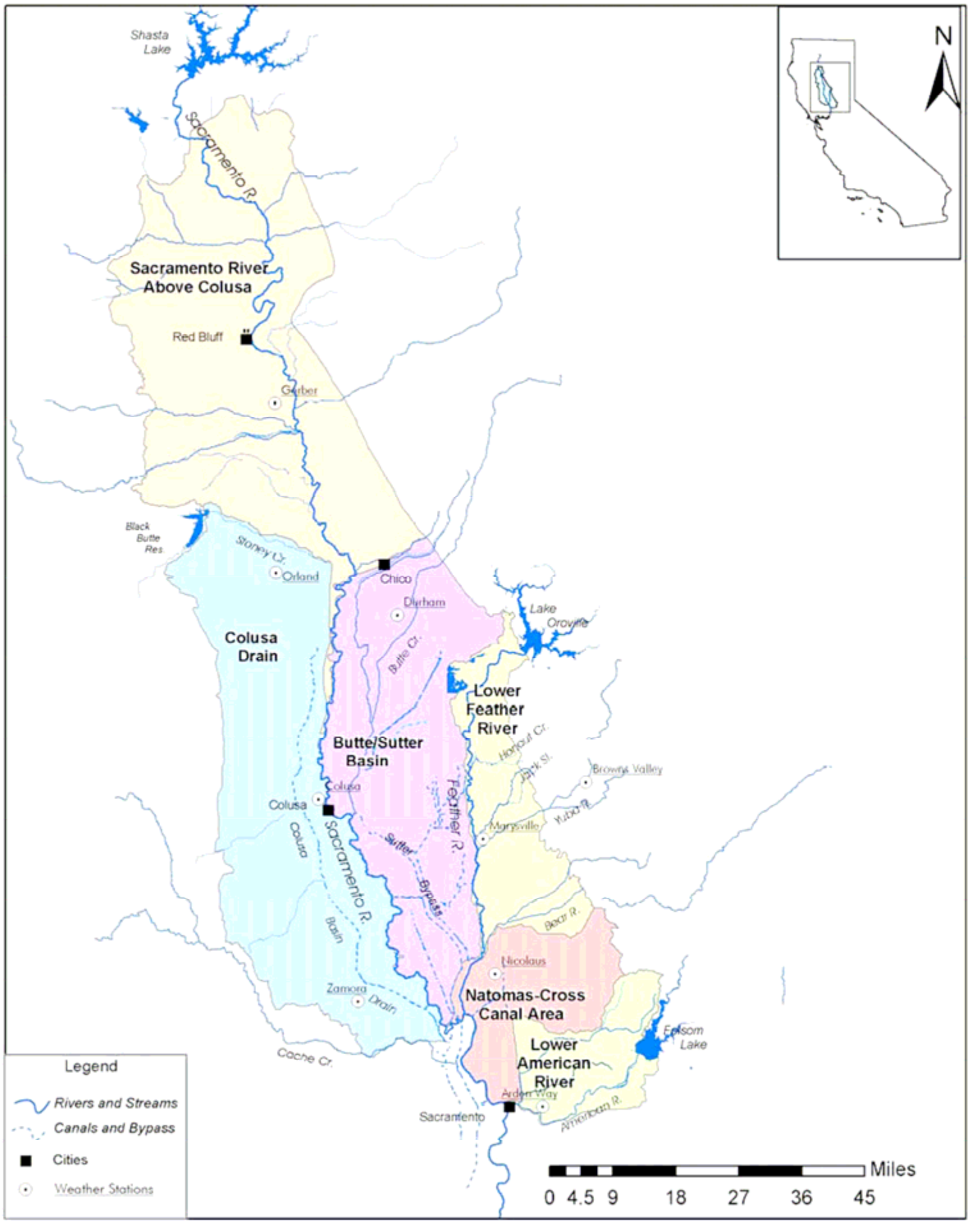

Figure 1. Delineation of the Subbasins in the Sacramento River Watershed - Sacramento Valley

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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	Sub-basin	Discharge Source[1]
1	Sacramento R. @ Alamar Marina	Integrator Site	VON
2	American R. @ Sunrise Blvd.	Natomas Basin/ American R.	AFO
3	Natomas E. Main Drain Canal @ Northgate Blvd.	Natomas Cross Canal	Manually Gage
4	Cross Canal @ Garden Hwy.	Natomas Cross Canal	Manually Gage
5	Sacramento Slough @ Karnak	Butte/Sutter Basin	SSK
6	Colusa Basin Drain @ Rd. 99E	Colusa Drain	CDR
7	Feather R. near Hwy. 99	Feather R.	GRL + MRY + BRW
8	Sacramento R. @ Colusa	Sacramento R. above Colusa	COL

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

Table 2. California Department of Food and Agriculture, Center for Analytical Chemistry: organophosphate and triazine pesticide screens.

Organophosphate Pesticides in Surface Water Method: GC/FPD/MSD		**Triazine Pesticides in Surface Water Method: LC/MS/MS**	
Compound	Reporting Limit (ug/L)	Compound	Reporting Limit (ug/L)
Diazinon	0.04	Simazine	0.05
Chlorpyrifos	0.04	Diuron	0.05
Methidathion	0.05	Atrazine	0.05
Ethoprop	0.05	Prometon	0.05
Disulfoton	0.04	Bromacil	0.05
Malathion	0.05	Prometryn	0.05
Fenamiphos	0.05	Hexazinone	0.05
DDVP (Dichlorvos)	0.05	Metribuzin	0.05
Phorate	0.05		
Fonofos	0.04		
Dimethoate	0.05		
Profenofos	0.05		
DEF (Tribufos)	0.05		
M. Parathion	0.03		
Azinophos Methyl	0.05		