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Study 239: Ongoing Monitoring to Quantify Total Export of Pesticides from the Sacramento River and San Joaquin River Watersheds

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I. INTRODUCTION

The Central Valley of California is comprised of two major watersheds, the Sacramento River and San Joaquin River watersheds. It is the major fruit and vegetable production base for the nation, with more than seven million acres of intensively cultivated agricultural land, and at least 30,000 tons of pesticides applied annually for the past decade. Movement of some of the pesticides to the waterways has been a prime concern for water quality management in the Central Valley. These pesticides have a potential to impair surface water quality and cause toxicity to aquatic organisms and wildlife.

Most previous studies on monitoring pesticides in surface water were short termed, focused on pesticide transport associated with individual storm or irrigation events (e.g., Domogalski et al., 2000; Dileanis et al., 2002; Spurlock, 2002; Guo et al., 2005). We propose to monitor the total export of pesticides from the two major watersheds in the Central Valley on a continuous and long-term basis. The information will provide a temporal status and trend check on pesticide contamination in the main stem rivers of each watershed. Pesticides found in these two rivers may travel further to the Sacramento/San Joaquin Delta and therefore may present multi-regional impacts.

II. OBJECTIVES AND SIGNIFICANCE

This study will monitor the total annual and seasonal export of pesticides from the Sacramento River and San Joaquin River watersheds by sampling the main outlets of the Sacramento and San Joaquin River watershed on a continuous and regular time basis. It will help generate one of the most complete data sets of pesticide load for the two rivers and therefore will provide key evidence to demonstrate or track improvements in water quality in the watersheds and the effectiveness of management practices at the watershed scale. The results of this study will also provide calibration and validation data set for the on-going SR modeling effort of the Department of Pesticide Regulation (DPR) to simulate pesticides fate and transport and evaluate alternative management practices on reducing pesticide movement to surface water. DPR must rely on both monitoring and modeling to address pesticide-related surface water problems in the watersheds due to limited resources.

III. PERSONNEL

Monitoring will be conducted by the staff of the Environmental Monitoring Branch, DPR, and the project will be under the general direction of Marshall Lee, Senior Scientist (Supervisor). 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 Kelley
Field Coordinator:	Bill Fabre
Senior Scientist:	Frank Spurlock
Laboratory Liaison:	Carissa Ganapathy

Questions concerning this project should be directed to Kevin Kelley at (916) 324-4187 or kkelley@cdpr.ca.gov.

IV. MONITORING PLAN

The primary monitoring sites for this study are 1) the Freeport Bridge for the Sacramento River and 2) the Department of Water Resources (DWR) Vernalis Dock for the San Joaquin River. These sites are located near the outlets of the Sacramento and San Joaquin River watersheds, respectively, downstream of major inputs. On occasion, depending on flow in the Sacramento River, one of two other sites in the Sacramento River Watershed may be monitored. As the Sacramento River Watershed is a highly engineered hydrological system, water can be diverted from the Main Stem of the river as flows rise. These additional sites are located on the Knights Landing Ridge Cut and the Yolo Bypass and may be utilized as part of weekly sampling or storm event sampling.

The Knights Landing Ridge Cut connects the terminus of the Colusa Basin Drainage Canal with the Tule Canal running along the eastern edge of the Yolo Bypass. This site will be monitored when the Sacramento River at Knights Landing reaches 25 feet. At this stage the drainage from the Colusa Basin Drainage Canal is diverted from the Sacramento River into the Knights Landing Ridge Cut. The sampling location on the Knights Landing Ridge Cut is located approximately 100 meters NE of the intersection of Road 113 and County Road 102 in Knights Landing, Yolo County. Since the terminus of the Ridge Cut is the Tule Canal, and since the Tule Canal is part of the Yolo Bypass, when sampling is conducted from the Yolo Bypass, sampling will not be conducted from the Knights Landing Ridge Cut. The contribution of pesticides from the area drained by the Colusa Basin Drainage Canal to the overall load of presticide in the Sacramento Watershed will be accounted for in samples collected from the Yolo Bypass.

The Yolo Bypass (I-80 causeway between Sacramento and Davis) is a three mile-wide channel used to relieve flow pressure from the Sacramento River. Water from the Sacramento River enters the Yolo bypass through the Fremont Weir when river flow at the weir reaches 55,000 cfs (cubic feet per second). The terminus of the Bypass discharges into the Deep Water Shipping Channel, thence into the Sacramento River just upstream of Rio Vista, California. Therefore, under high flow conditions the total pesticide load from the Sacramento River watershed is the sum of loads at both the Freeport Bridge and Yolo Bypass causeway.

Figures 1 and 2 show the proposed monitoring sites for the Sacramento and San Joaquin River watersheds, respectively.

Samples will be collected on a weekly basis for the duration of this study at locations discussed above except during storm events when samples will be collected on a daily basis. A single storm event will involve ten consecutive days of sampling. However, two or more storm events may overlap in time, in which case, the 10-day sampling period will apply from the onset of the most recent storm event. The project leader will be responsible for following weather forecasts and evaluating and tracking storm fronts throughout the watersheds. Precipitation data from the California Data Exchange Center (CDEC) operated by the DWR and information from local and national weather sources will be used to determine whether 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, preceding rainfall, predicted rainfall, measured rainfall, and observed runoff. Normally, an accumulation of 0.50 inch of rain within 24 hours would be considered a likely storm event. However, isolated rainfall events of up 0.75 inch separated by dry spells will not be considered to be a storm event if observable runoff does not occur. Upon the determination that a given storm constitutes a storm event, monitoring crews will be mobilized and sampling will begin 24 hours following the major storm front.

Samples will be collected primarily using a 4.2-Liter stainless steel Kemmerer sampler (Wildlife Supply Company). At each site, a single sample will be collected in the main flow of the channel. Samples will be split into three 1-L amber glass bottles for organophosphate analysis, triazine analysis, and a backup. Bottled samples will be sealed with Teflon®-lined lids, placed on wet ice, and delivered to DPR's West Sacramento facility for storage. All samples will be stored at 4^{o}C until delivered to the laboratory for chemical analyses. A chain of custody form will be completed and submitted for each sample.

Sampling from the Yolo Bypass will be conducted using either a 4.1-L or a 1.1-L stainless steel Kemmerer sampler (Wildlife Supply Company). Multiple sub-samples will be collected, admixed in a 40-L stainless steel milk can. If the main flow through the Bypass is contained solely within the Tule Drain, four liters will be collected from the center of the Tule Drain, two liters from each side of the center piling. As flows increase, water spreads westward from the Tile Drain onto the main body of the Bypass. When this occurs, a composite sample, consisting of multiple sub-samples (minimum of six liters) will be collected with a 1.1-L stainless steel Kemmerer sampler. The composite sample will be collected as follows: two sub-samples will be collected from the center of the Tule Canal (each side of the center piling); a third sub-sample will be collected 10 meters west of this location. Subsequent sub-samples will be collected at 0.15-mile intervals proceeding west from the Tule Drain. Samples will be collected as long as a strong flow is detected at each subsequent sampling location. Following collection, the total number of liters collected will be noted, and the composite sample will be immediately transported to DPR's West Sacramento facility.

Immediately upon arrival at the facility, the composite sample will be split into three 1-L amber glass bottles for organophosphate analysis, triazine analysis, and a backup. Bottled samples will be sealed with Teflon®-lined lids. All samples will be stored at 4^{o}C until delivered to the laboratory for chemical analyses. A chain of custody form will be completed and submitted for each sample.

Environmental and flow data will be collected at each site. Data will include *in-situ* measurements of water temperature, pH, dissolved oxygen, specific conductance, and salinity. Stage heights at the DWR dock on the San Joaquin River, on the Freeport Bridge, at Colusa Basin Drainage Canal in Knights Landing, and on the Sacramento River at the SR 113 bridge in Knights Landing will also be noted at time of sampling each site. Data will be recorded on the Field Data Sheet, which will also include time of sampling, sample numbers, and comments regarding weather, flow conditions, and other pertinent information. 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 for three of the four sites are available via the United States Geological Survey (USGS) gage stations (http://waterdata.usgs.gov/nwis/sw). The discharge data for the Freeport Bridge will be estimated from the USGS gage station #11447650 located at Freeport. The discharge data for the Yolo Bypass will be calculated from the sum of the USGS gage station #11453000 near Woodland and the discharge measurements at Cache Creek and Putah Creek. The flow data for the San Joaquin River at the DWR Vernalis dock will be obtained from the USGS gauge station #11303500. Flow data is not available for the Knights Landing Ridge Cut, but will be estimated as the flow of the Colusa Basin Drain at SR 20 (http://cdec.water.ca.gov/cgi-progs/staMeta?station_id=CDR) multiplied by the quotient of the area of the entire Colusa Basin Drain watershed divided by the area of the watershed upstream from SR 20. If water flows both into the Knights Landing Ridgecut and the Sacramento River simultaneously, composited mass determined from samples collected at the Ridge Cut and at Freeport Bridge will account for mass loading from the Sacramento River Watershed.

V. CHEMICAL ANALYSIS.

Chemical analyses will be performed by the California Department of Food and Agriculture's Center for Analytical Chemistry (CDFA). Water samples will be analyzed for organophosphates (OPs) and herbicides using the CDFA's OP and triazine (TR) screens developed by the laboratory. Table 1 lists the pesticides to be analyzed for, the chemical analytical methods, and reporting limits. Comprehensive chemical analytical methods will be provided in the final report.

VI. SAMPLES.

The number of field samples for Study 239 is expected to vary and depends on the weather and hydrological conditions in the two watersheds monitored. A preliminary estimation of the total number of samples to be collected is based on the following assumptions (with no budget limitation):

1) Six storm events for the Sacramento River Watershed and four events for the San Joaquin River Watershed;
2) Ten days of sampling would be required for each storm event; and
3) Seventy days of flow (the historic median) through the Yolo Bypass.

Based on these assumptions, the maximum number of chemical analyses for both OPs and TR for each sampling site would be:

Ongoing Weekly Samples

Freeport site:		
	52 weeks – (8 weeks [rain event]) x 2 samples/week	88
Yolo Bypass/KL Ridge Cut site:		
	2 weeks x 2 samples/week	4
Vernalis site:		
	52 weeks – (6 weeks [rain event]) x 2 samples/week	92

Storm Event Sampling:

Freeport site:		
	6 events x 10 days x 2 samples/day	120
Yolo Bypass/KL Ridge Cut site:		
	6 events x 10 days x 2 samples/day	120
Vernalis site:		
	4 events x 10 days x 2 samples/day	80
	Total Field Samples	**504**

VII. 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.

QC samples (min. 10% of field samples): 50

The total number of chemical analyses will be: (504 + 50) 554

Chemical Analysis Cost:

Current laboratory charges are $650/sample for OPs, $450/sample for TRs (short screen), and $750.00/sample for TRs (full screen).

Triazine samples from the initial two storm events in the Sacramento River and the first storm event in the San Joaquin Watershed will be analyzed using the full triazine screen. Subsequent samples will be analyzed using the short screen.

554 Total samples split equally for OP and TR analyses:
277 OP samples x $650/sample = $180,050
277 TR samples:

32 samples x $750/sample = $ 24,000
245 samples x 450/sample = $110,250

Total cost: $314,300

VIII. 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:

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

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 concentrations lower than the method-reporting limit (Table 1), statistic approaches, such as maximum likelihood estimation, nonparametric methods or substitution, may be used to evaluate their values (Helsel, 2005). Concentrations for nonsampled days will be estimated using linear interpolation (Reinelt and Grimvall, 1992). The total mass of pesticide transported passing the monitoring site then is the integrated load over the period of observation. The load obtained will be analyzed together with the precipitation, pesticide use, and other watershed data to calculate event mean concentrations, runoff vulnerability, and evaluate watershed behaviors with respect to pesticide transport.

IX. TIMETABLE

Tasks	**Date**
Field Sampling	December 2006 – November 2007.
Chemical Analysis	December 2006 – December 2007
Preliminary Memorandum	June 2008
Final Report	December 2008 (or thereafter depending on the release of the 2007 Pesticide Use Report 2007.)

X. REFERENCES.

Dileanis, P.D., 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.

Helsel, D.R. 2005. Nondetects and data analysis. John Wiley & Sons, Inc., Hoboken, New Jersey.

Guo, L., K. Kelley, S. Gill, and R. Sava. 2005. A partition of pesticide loads in major sub-basins in the Sacramento River watershed: preliminary results of Study 227. Environmental Monitoring Branch, California Department of Pesticide Regulation, Sacramento, CA.

MacCoy, D., K.L. Crepeau, and K.M. Kuivila. 1995. Dissolved pesticide data for the San Joaquin River at Vernalis and the Sacramento River at Sacramento, California, 1991-94. USGS Rep. 95-110. U.S. Gov. Print. Office, Washington DC.

Reinelt, L.E., and A. Grimvall. 1992. Estimation of nonpoint source loadings with data obtained from limited sampling programs. Environmental Monitoring and Assessment. 21:173-192.

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.

XI. BUDGET

Chemical Analysis Costs	
252 OP samples ($650.00/sample):	$ 163,800
220TR samples ($450.00/sample – short screen)	$ 99,000
32 TR Samples ($750.00/sample – full screen)	$ 24,000
Continuing QC (25 OP x $650):	$ 16,250
Continuing QC (25 TR x $450):	$ 11,250
Total Chemical Analysis Costs:	**$314,300**

104 d x 8 hr = 832 hours per person per year

Personnel:	
(2) Assoc. Env. Research Scientist @ $25/hr for 832 hr/y:	$ 41,600
(1) Senior Env. Research Scientist @ $32/hr for 40 hr/y:	$ 1,280
Staff Benefits @ 31%:	$ 13,293
Total Staff Costs:	**$ 56,131**
Total Cost:	**$360,831**