California Environmental Protection Agency
Department of Pesticide Regulation
Environmental Monitoring
1001 I Street, 3rd Floor
Sacramento, California 95812-4015

Study 232: Establishing permanent monitoring stations for quantifying total export of pesticides from the Sacramento and San Joaquin River Watersheds

Lei Guo

I. INTRODUCTION

The Central Valley of California is comprised of two major watersheds, the Sacramento River (SR) and San Joaquin River (SJR) 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 status and trend check on pesticide contamination overtime in the main stem rivers of the watersheds. Pesticides found in these two rivers may travel further to the Sacramento/San Joaquin Delta, and therefore may possess 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 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, Department of Pesticide Regulation (DPR), 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

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

IV. MONITORING PLAN

The primary monitoring sites for this study will be 1) the Tower Bridge for the Sacramento River, and 2) the San Joaquin River at Vernalis. These sites are located at the outlets of the Sacramento and San Joaquin River watersheds, respectively. In addition, due to the highly engineered nature of the hydrological system for the Sacramento River, two other sites may also be monitored depending on flow conditions. The first site is the Yolo Bypass at the I-80 causeway between Sacramento and Davis. The Yolo Bypass is a mile-wide channel used to divert flow from the Sacramento River when river discharge at the Fremont weir exceeds 55,000 cfs (cubic feet per second). The Bypass discharges directly to the Sacramento/San Joaquin delta, so that under high flow conditions the total pesticide load from the Sacramento River watershed is the sum of loads at both the Tower Bridge and Yolo Bypass causeway. The second Sacramento River watershed site is the Knights Landing Ridge Cut located at Road 113 in Yolo County. This site will be monitored when the Knights Landing Ridge Cut receives the drainage from the Colusa Basin Drain. The Ridge Cut is an artificial overflow channel that connects the lower end of the Colusa Basin Drain to the Yolo Bypass. Therefore, when the Yolo Bypass is sampled, the Ridge Cut will not be sampled. Figures 1 and 2 show the proposed monitoring sites for the Sacramento and San Joaquin River watersheds, respectively.

Because of the construction expected at the Tower Bridge, the sampling site may be moved 12 miles downstream to Freeport for the Sacramento River when the access to the Tower Bridge is not permissible.

Regular sampling will be conducted on a weekly basis during non-storm periods, and daily during storm events. A single storm event will probably involve seven consecutive days of sampling. 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 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, proceeding rainfall, predicted rainfall, measured rainfall, and observed runoff. Normally, an accumulative of 0.50 in of rain within 24 hours would be considered a likely "storm event". Upon the determination that a given storm constitutes a storm event, designated monitoring crews will be mobilized and sampling will begin 24 hours following the major storm front.

Surface water sampling will be conducted with a 3-L stainless steel Kemmerer sampler (Wildlife Supply Company). For both the Tower Bridge/I Street Bridge and Yolo Bypass sites, cross-section integrated samples will be taken to ensure better mixing. Six surface water sub samples will be collected across the Sacramento River at the Tower Bridge/I Street Bridge, and twelve sub samples will be collected across the Yolo Bypass. Each sub sample will be decanted into a 500-mL amber bottle after two native rinses. All samples will be sealed with Teflon®-lined lids and placed on wet ice until delivered to the West Sacramento facility for further processing. Immediately upon arrival at the facility, the sub samples from each site will be combined into a milk can, and shaken vigorously for one minute to achieve a thorough mixing. The composite sample will be split into three 1-liter amber glass bottles, and then sealed with Teflon-lined caps. For the San Joaquin River, a central channel water sample will be collected at the Vernalis site. The sample will be decanted into three pre-labeled amber bottles and stored on ice during transport to the West Sacramento Facility. A chain of Custody (COC) form 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 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 Tower

Bridge/Freeport will be estimated from the USGS gage station #11447650 located at Freeport. The Freeport site was located about 12 miles downstream from the Tower Bridge Street Bridge, but there are no major inlet or outlet flows between the two locations. 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 SJR at the Vernalis will be obtained from the USGS gage station #11303500. Flow data is not available for the Knights Landing Ridge Cut, but will be estimated by extrapolating the gauged runoff at CDR, the DWR's discharge station for the Colusa Basin Drain (http://cdec.water.ca.gov/cgi-progs/staMeta?station_id=CDR) based on the drainage ratio of the gauged area and the Colusa Basin Drainage 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 and herbicides using the CDFA's short OP and triazine screens developed by the laboratory. Table 1 presents the pesticides to be analyzed, the chemical analytical methods, and reporting limits. 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.

The number of field samples is expected to be highly variable each year, and will depend on the weather and hydrological conditions in the watersheds. The following estimation is based on the assumptions that

- there will be 4 storm events each year for the Sacramento River watershed and 3 storm events for the San Joaquin River watershed;
- seven (7) days of sampling will be required for each storm event; and
- there will be 70 days of flow in the Yolo Bypass (the median record)

Therefore, the number of chemical analyses for

the Tower Bridge/ Freeport site:

(52 wk – 4 event) x 2 sample/wk + (4 event x 7 d x 2 sample/d) = 152

the Yolo Bypass/Knights Landing Ridge Cut site:

(70 d/7 d/wk-4 event) x 2 sample/wk + (4 event x 7d x 2 sample/d) = 68

the Vernalis site:

(52 wk – 3 event) x 2 sample/wk + (3 event x 7 d x 2 sample/d) = 140

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

(152+68+140) x 10% = 36

The total number of chemical analyses will be:

(152+68+140+36) = 396

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:

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

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.

VIII. TIME TABLE

Field Sampling – starting December 2005 and throughout the following years
Chemical Analysis – starting December 2005 and throughout the following years
Preliminary Memorandum – first report June 2007 and each June thereafter
Final Report – first report December 2007 (when PUR 2006 becomes available) and each December thereafter.

IX. 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., Kelley, K., Gill, S. and Sava, R. 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.

X. BUDGET

<u>Chemical Analysis Costs ($550/sample)</u>	
Regular samples (360):	$198,000
Continuing QC (36):	$19,800
Total Chemical Analysis Cost:	$217,800
<u>Personnel: 76 d x 8 hr = 608 hours per person per year</u>	
(2) Assoc. Env. Scientist @ $25/hr for 608 hr/y:	$30,400
(1) Senior Env. Scientist @ $32/hr for 20 hr/y:	$640
Staff Benefits @ 31%:	$ 6,922
Total Staff Costs:	$40,622
Total Cost:	**$258,462**

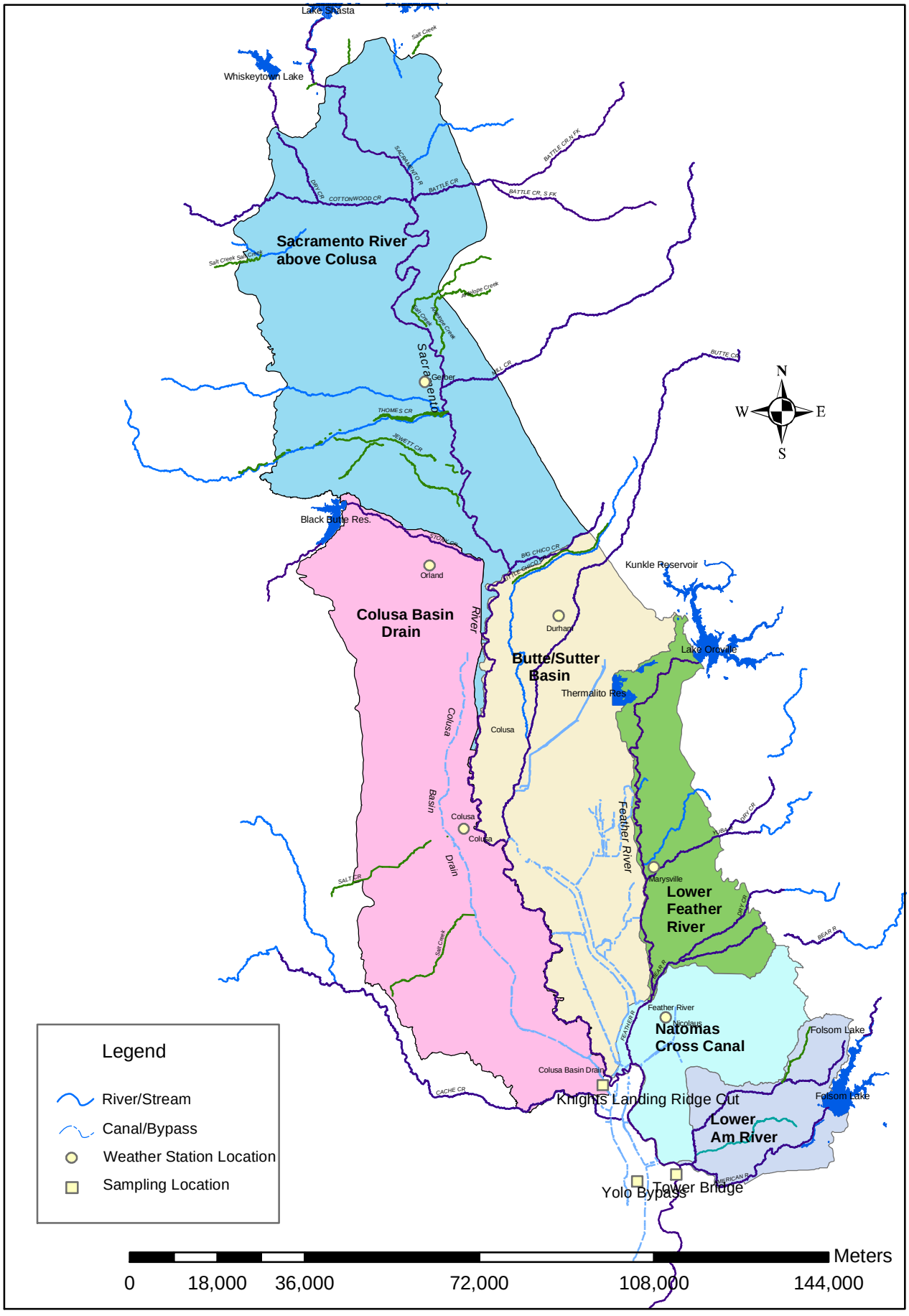

Figure 1. Sampling site locations for the Sacramento River watershed

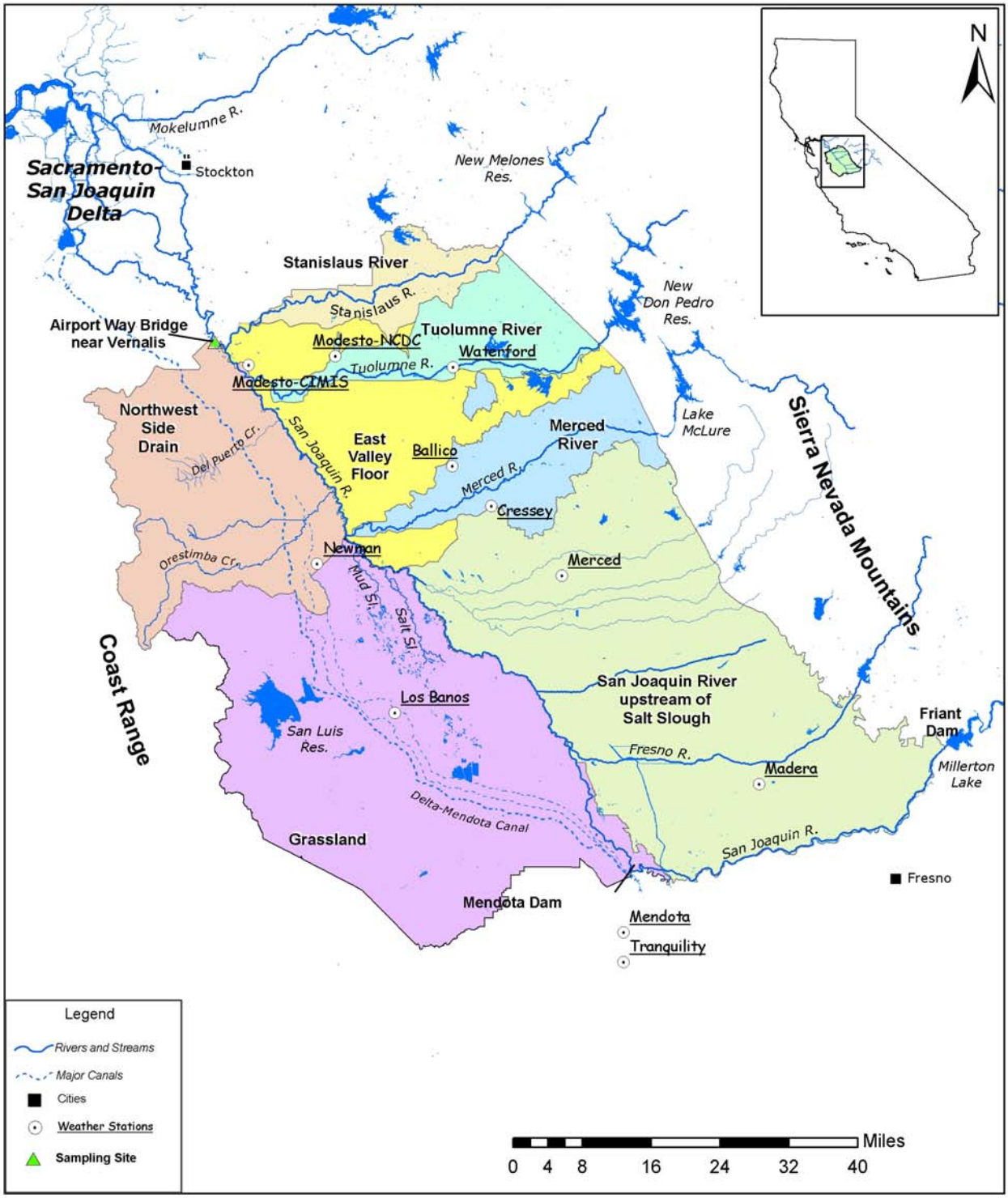

Figure 2. Sampling site location for the San Joaquin River Watershed

Table 1. List of pesticides to be analyzed for the surface water samples collected from the permanent monitoring sites in the Sacramento River and San Joaquin River watersheds.

OPs-	***GC/FPD***	
Analyte	**MDL**(ppb)	**RL**(ppb)
Diazinon	0.011	0.04
Chlorpyrifos	0.0109	0.04
Malathion	0.0117	0.04
Methidathion	0.0111	0.05
Dimethoate	0.0079	0.04

OPs-	***GC/MS***	
Diazinon	1.191ppt*	10ppt
Chlorpyrifos	0.7999 ppt*	10ppt

Herbicides- LC/MS/MS		
Analyte	**MDL**(ppb)	**RL**(ppb)
Simazine	0.013	0.05
Diuron	0.22	0.05
Bromacil	0.031	0.05
Hexazinone	0.04	0.05
DACT	0.016	0.05

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