Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812
Amended May 2007

STUDY #234: The effectiveness of the Wingsetter Ranch created wetland at reducing chlorpyrifos in irrigation runoff

I. INTRODUCTION

Wingsetter Ranch is located directly adjacent to the west bank of the San Joaquin River in Stanislaus County. It was once approximately 3 to 5 acres of mostly barren, flood-prone farmland that has now been restored to a productive wetland. Restoration was possible in part due to Natural Resources Conservation Service (NRCS) programs that help farmers bring flood-prone fields back to functioning wetlands. With the added help of Ducks Unlimited and the Wetland Conservation Board, the property owner was able to create a network of waterways, sediment basins, and sloughs. The created wetland intercepts and filters sediment from agricultural tailwaters from approximately 4000 acres of row and orchard croplands. It also provides habitat for wildlife. Though constructed to capture and reduce sediment from entering into the San Joaquin River, this study will test whether the created wetland is also effective in reducing dissolved pesticides in tailwater runoff.

II. OBJECTIVE

The primary objective of this study is to determine the effectiveness of a constructed wetland in reducing chlorpyrifos mass in discharge, under flow-through conditions during the irrigation season.

III. PERSONNEL

This is a cooperative study between the Department of Pesticide Regulation (DPR) and the San Luis and Delta Mendota Water Authority. Funds for this project have been provided by California State Proposition 13 (2000 water bond), Prism Grant Program. The study will be conducted by staff from DPR's Environmental Monitoring Branch, Surface Water Protection Program under the general direction of Kean S. Goh, Agricultural Program Supervisor IV. Key personnel are listed below:

Project Leader:	Juanita Bacey
Field Coordinator:	Student staff
Senior Scientist:	Frank Spurlock
Laboratory Liaison:	Carissa Ganapathy
Chemists:	California Dept. of Fish and Game

Questions concerning this monitoring study should be directed to Juanita Bacey, Environmental Research Scientist, at (916) 445-3759.

IV. STUDY PLAN

Total chlorpyrifos mass entering and exiting the wetland in a 20-day period will be estimated. Mass will be calculated by measuring chlorpyrifos concentrations and inflow and outflow volume. Monitoring will occur after peak pesticide applications to surrounding agricultural areas have occurred, and the irrigation season has begun. Additionally, other organophosphates in water will be measured (Table 1). Background sediment samples will also be collected prior to the start of the irrigation season and analyzed for organophosphates. Samples will be collected during the month of July 2006. July has been the month with the highest reported chlorpyrifos use in both 2003 and 2004 (DPR PUR, 2005) in Stanislaus County where the wetland is located. Water samples will be collected from the main inlet (back drain) and at the two outlets (Figure 1). Water quality measurements to be measured *in situ* at each sampling point include: specific conductance, pH, DO, and temperature. Additionally, staff from the U.C. Davis Department of Land, Air and Water Resources will measure the volume of water entering and exiting the wetland.

Table 1. Pesticides to be monitored

Organophosphates	
Chlorpyrifos	Ethyl parathion, also Parathion
Chlorpyrifos methyl	Methyl parathion
Diazinon	Phosphamidon
Dichlofenthion	Ethoprop (Prophos)
Dioxathion	Sulfotep
Ethion	Thionazin (Thionzin)
Fenchlorphos (Ronnel)	Tokuthion (Prothiofos)
Fenitrothion	Merphos (Tributylphosphorotrithioite)*
Fonofos (Dyfonate)	Trichloronate
Malathion	

V. SAMPLING METHOD

Background samples

Prior to the start of sampling (May), background water and sediment samples will be collected from the inlet and outlet sampling points to determine typical chlorpyrifos concentrations in the wetland. Water samples will consist of a single grab sample using an extension pole with a 1-L amber bottle.

Sediment samples will consist of one composite sample collected from each inlet and outlet, using a Teflon coated scoop. The top 2cm of sediment will be placed into a ½ pint glass jar. This will be repeated until the jar is full.

Tracer analysis samples

Prior to the start of monitoring (June 4th-8th), water residence time within the wetland will be estimated using reagent grade sodium bromide (NaBr) salt as a tracer.

The wetland residence time will be estimated during the month of June, when irrigation practices are similar to those in July, and at a time when normal irrigation runoff is occurring. The NaBr tracer will be applied and analyzed as follows:

1. Native water samples will be collected prior to the input of NaBr tracer to determine the background concentration of bromide (10, 1-L grab samples)
2. Approximately 25Kg of reagent grade NaBr tracer will be mixed with 100L of native water, then immediately added to the inlet (Figure 1)
3. Samples will be collected from both outlets every three hours and will continue for approximately 72 hours
4. Samples will be collected in 350ml glass vials using ISCO® autosamplers
5. Samples will be transferred to glass bottles after each 24 hour period and then transferred to the California Department of Fish and Game (DFG) lab for analysis
6. Flow of the wetland will be measured at the inlet and outlets, throughout the tracer monitoring period by the U.C. Davis Department of Land, Air and Water Resources
7. Using the measured concentrations, elution time of NaBr, and the discharge data, the volume of water passing through the system will be determined
8. Theoretical residence time will be determine with the following equation

$$\mathbf{T = V/Q_t}$$

where T = residence time
Q_t = total inflow rate (volume/time)
V = average volume of water storage in wetland

9. True mean retention time will be determined as the time where the following equation (or similar) is satisfied:

$$\mathbf{\Sigma\,(C_M - C_{Bk})\ x\ V) = (M_{Br}/2)}$$

where C_M = Concentration of bromide measured
C_{Bk} = Concentration of average background bromide
V = volume measured at time of bromide measurement
M_{Br} = mass of bromide at input

Upon review of residence time data, the frequency of pesticide sample collection may be modified from that described below.

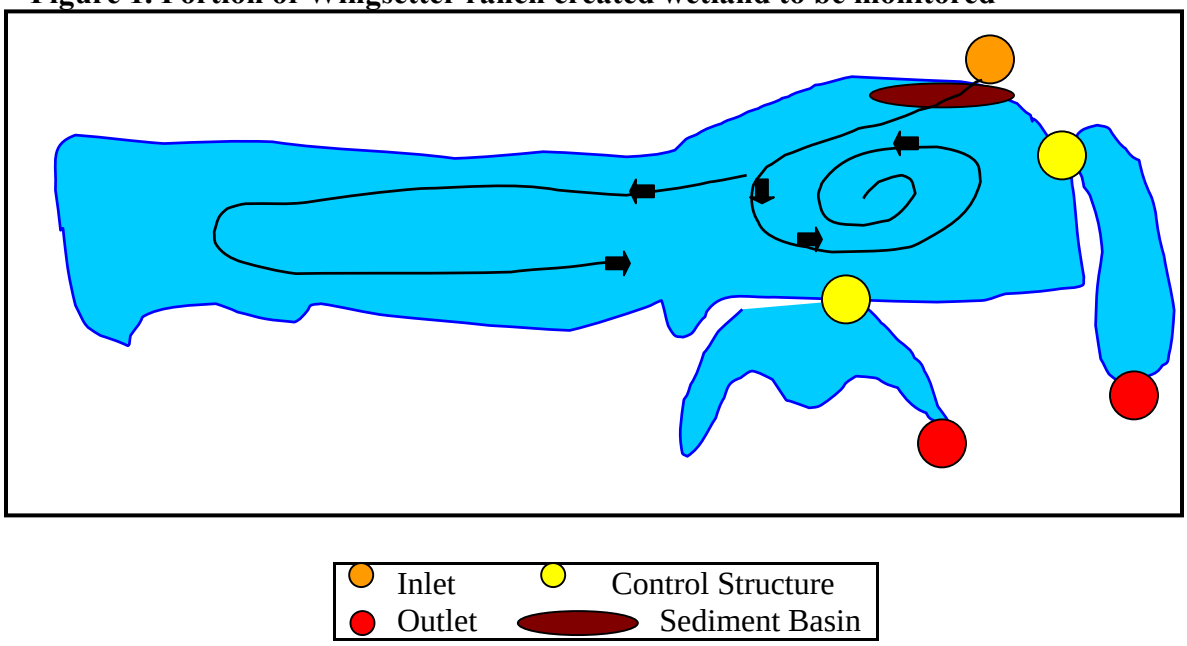
Pesticide analysis samples

Sample collection for pesticide analysis will begin July 9th and continue through July 27th. Samples will be collected using ISCO® portable, refrigerated, autosamplers as per DPR SOP #EQWA005.00 (Jones, 2000). Autosamplers will be placed at each inlet and outlet. Samples will be collected every 8 hours, 7 days a week, for 19 days, for a total of 57 samples from each sampling point.

Water quality measurements

Water quality will be measured every 2 hours using Eureka Manta® multi-parameter probes placed at the inlet and both outlets. The U.C. Davis Department of Land, Air and Water Resources will measure discharge every 15 minutes.

Figure 1. Portion of Wingsetter ranch created wetland to be monitored



Sample Handling and Custody
Samples will be retrieved from the refrigerated autosamplers every 48 hours. Samples will be transferred from the polypropelene sampler bottles to 1-L glass amber bottles, and sealed with Teflon-lined lids.

All sample types will be transported on wet ice. Water samples will be stored refrigerated at 4^{o}C until extraction for chemical analyses, and sediment samples will be stored frozen at 0^{o}C until extraction for chemical analyses. Transporting of samples will follow DPR SOP #QAQC004.01 (Jones, 1999). A chain-of-custody record will be completed and accompany each sample.

VI. CHEMICAL ANALYSIS AND QUALITY CONTROL

The California Department of Fish and Game, Fish and Wildlife Water Pollution Control Laboratory will conduct chemical analysis of all water and sediment samples. Comprehensive chemical analytical methods will be provided in the final report. Quality control (QC) will be conducted in accordance with SOP QAQC001.00 (Segawa, 1995) and will include general continuing QC. Ten percent of the total number of samples will be submitted with field samples as blind spikes and rinse blanks.

VII. DATA ANALYSIS

Pesticide concentrations in water and sediment will be reported in parts per billion (ppb). Total monthly chlorpyrifos mass entering and exiting the wetland will be estimated and compared to determine differences in concentrations.

VIII. TIMETABLE

Background sampling:	May and June 2007
Field Sampling:	July 9th through July 27th, 2007
Chemical analysis:	May through August 30, 2007
Final Report:	December 31, 2007

X. REFERENCES

DPR Pesticide Use Report Database. 2005. Available on-line: www.cdpr.ca.gov/docs/pur/purmain.htm

Jones, D. 1999. SOP #QAQC004.01 - Transporting, packaging and shipping samples from the field to the warehouse or laboratory. Available on-line: http://www.cdpr.ca.gov/docs/empm/pubs/sops/qaqc0401.pdf

Jones, D. 2000. SOP #EQWA005.00 - Instructions for operating ISCO® samplers when collecting surface water. Available on-line: http://www.cdpr.ca.gov/docs/empm/pubs/sops/FSWA016.pdf

Segawa, R. 1995. SOP QAQC001.00 - Chemistry Laboratory Quality Control. Available on-line: http://www.cdpr.ca.gov/docs/empm/pubs/sops/qaqc001.pdf

IX. BUDGET

Tracer analysis	June 4th – 8th	# of Samples		
Sodium Bromide	Water samples ($35/sample)	82		$2,870
Chemistry Analysis	July 9th through July 28th			
OPs (water)	3/day x 19 days x 3 sampling points ($294/sample)	171	=	50,274
Quality Control				
Blind spikes	5% of total water samples ($294/sample)	9	=	2,646
Field blanks	5% of total water samples ($294/sample)	9	=	2,646
Background samples	Water (June 4th)	3	=	882
Background samples	Sediment ($412/sample)	3		1,236
Lab duplicates & spikes	water & sediment	42	=	13,056
Lab overhead				12,980
Subtotal – lab analysis				$86,590
Personnel Services				
Sr. Env. Scientist	$31/hr x 20 hrs			$620
Staff benefits	(31%)			$192
Env. Scientist	$25/hr x 200 hrs			$5,000
Staff benefits	(31%)			$1,550
Scientific Aide	$11/hr x 8hrs x 3/wk x 5 wks			$1,320
Staff benefits	(11%)			$145
Student Assistant	$8.40/hr x 8hrs x 3/wk x 5 wks			$1,008
Overhead	$9,835 x 20%			$1,967
Subtotal				$12,002
Operating expenses				
Equipment/supplies	1 L Amber bottles ($40/case)	38 cases		1,520
	1 Manta multi-parameter probe			2,850
Lease	3 refrigerator autosamplers ($255/wk)	4 wks		3,060
Travel/hotel costs	Two rooms for 3 nights (during tracer sampling)			600
Per diem	2 personnel x 4 days x $40/day			320
Subtotal				$8,350
TOTAL				**$106,942**