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SUBJECT: RESULTS FOR STUDY 234: THE EFFECTIVENESS OF A CONSTRUCTED WETLAND AT REDUCING ORGANOPHOSPHATE PESTICIDES IN IRRIGATION RUNOFF

I. SUMMARY

This study was conducted on a constructed wetland in Stanislaus County, California. The wetland was constructed to capture and reduce sediment from entering into the San Joaquin River and to provide habitat for wildlife. We examined whether this wetland would also be effective in reducing dissolved pesticides in tailwater runoff. The primary objective was to determine the wetland's effectiveness in reducing the mass of organophosphate (OP) pesticides in discharge, under flow-through conditions, during an irrigation season. A reagent grade sodium bromide salt was used as a tracer to determine the residence time within the wetland. Water samples were collected every two hours over a 70-hour period at the wetland outfall. The median residence time was estimated as the time at which one-half of the initial bromide load initially applied at the inlet was recovered at the outlet. Water samples for pesticide analyses were collected to determine the total pesticide mass entering and exiting the wetland. Samples were collected every seven hours over a 20-day period. All water samples were collected using ISCO® autosamplers. Dimethoate was detected in 87% of the samples collected. There were few other OP pesticide detections; concentrations for all but one were below laboratory reporting limits. Dimethoate concentrations were to be used to determine mass loads due to the significant number of detections. However, dimethoate laboratory continuing quality control data were outside recovery control limits in 36% of samples. Also, while total discharge was measured at the inlet and the first outlet, this data was not available for the second outlet. These two factors compromised the use of the pesticide analytical data for estimating mass loads within the wetland. Therefore, the effectiveness of this constructed wetland at reducing mass loads of OP pesticides from agriculture tailwaters is inconclusive.

II. INTRODUCTION

This project was a cooperative study between the Department of Pesticide Regulation (DPR) and the San Luis and Delta Mendota Water Authority. Funds were provided by the Pesticide Research and Identification of Source and Mitigation Grant Program, authorized through California State Proposition 13 (2000 water bond).

The study was conducted on a constructed wetland in Stanislaus County, California (Wingsetter Ranch). It was constructed to capture and reduce sediment from entering into the San Joaquin River, and to provide habitat for wildlife. This study examined whether the constructed wetland also was effective in reducing dissolved pesticides in tailwater runoff.

III. STUDY OBJECTIVE

The primary objective was to determine the effectiveness of a constructed wetland in reducing the mass of chlorpyrifos or other OP pesticides in discharge water, under flow-through conditions, during the irrigation season.

IV. STUDY DESIGN

Study Site

Wingsetter Ranch is located directly adjacent to the west bank of the San Joaquin River in Stanislaus County. It was once approximately three to five acres of mostly barren, flood-prone farmland that has now been restored to a productive wetland (Figure 1). Restoration was possible in part due to Natural Resources Conservation Service 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 constructed wetland intercepts and filters sediment from agricultural tailwaters from approximately 2800 acres of row and orchard croplands, such as walnuts, corn and alfalfa. It also provides habitat for wildlife.

Figure 1. Wingsetter Ranch constructed wetland, Stanislaus County, California

V. MATERIALS AND METHODS

Sampling Plan

Sample collection for pesticide analyses began July 10th and continued until July 26th. Samples were collected every seven hours, seven days a week. Total pesticide mass entering and exiting the wetland in a 20-day period was to be estimated. Mass was to be calculated by multiplying the measured pesticide concentrations with the measured volume of water over time (discharge) at each sampling point, and then summing the data over time. Staff from the University of California, Davis, Department of Land, Air and Water Resources (UCD LAWR) measured discharge at the sampling points. Monitoring occurred during peak pesticide applications to surrounding agricultural areas, when the irrigation season had begun (July, 2007). Historically, July has been the month with the highest reported chlorpyrifos use in Stanislaus County, with 33,042 pounds active ingredient applied in 2006 (DPR PUR, 2006). All pesticides monitored are presented in Table 1.

Background samples

Water samples were collected prior to the start of the irrigation season (May 2007) from the inlet and outlet sampling points to determine typical background OP concentrations. Water samples consisted of a single grab sample using an extension pole with a one-liter amber bottle.

Tracer sampling method

A reagent grade sodium bromide salt (NaBr) was used as a tracer to determine the residence time within the wetland. NaBr was chosen due to its conservative and noncarcinogenic properties. It is not expected to be lost through evapotranspiration (water evaporation and transpiration through vegetation). Vegetation at the wetland was limit to less than 1% of the area within the wetland and along the banks (Figure 2). Therefore, binding of the tracer or soluble pesticides to vegetation in the wetland was considered negligible.

Figure 2. Outlet1 sample collection

One tracer injection was made on August 6th, 2007, ten days after monitoring for pesticides had occurred. Irrigation practices were similar to those in July when pesticide monitoring occurred. The NaBr tracer was applied and collected as follows:

1. 50 kg of reagent grade NaBr tracer was mixed with approximately 100 L of native water in a large 500 L polypropylene barrel. Two samples were collected from the barrel and analyzed for total Br. The mixture was then immediately added to the inlet (Figure 3).
2. Samples were collected from both outlets every two hours and continued for 70 hours. They were collected in 950 ml polyethylene plastic bottles using ISCO® autosamplers.
3. Samples were collected from the autosamplers and transferred to 250 ml polyethylene plastic bottles every 24 hours, and then transferred to the California Department of Fish and Game (CDFG) lab for analyses.
4. Discharge of the wetland was measured at the inlet and outlets, throughout the tracer-monitoring period by UCD LAWR.
5. Using the measured concentrations, elution time of NaBr, and the discharge data, an attempt was made to estimate the residence time (Eq. 2).

Figure 3. Inlet of wetland

Pesticide sampling method

Samples were collected using ISCO® portable, refrigerated, autosamplers as per DPR SOP #EQWA005.00 (Jones, 2000). Autosamplers were placed at each inlet and outlet. Samples were collected every 7 hours, 7 days a week, for 20 days.

Sodium bromide analyses

CDFG uses U.S. EPA method 300.0: Determination of inorganic anions in water by ion chromatography. Water samples are filtered through a 0.45 um filter prior to analysis.

A small volume of sample, typically 2 to 3 mL, is introduced into an ion chromatograph. The anions of interest are separated and measured, using a system comprised of a guard column, separator column, suppressor device, and conductivity detector.

Organophosphate pesticides analyses

The CDFG method is a modified version of the U.S. EPA method 8141A that uses liquid-liquid extraction, with methylene chloride in a separatory funnel. The extract is dried with sodium sulfate and evaporated using Kuderna-Danish concentrator apparatus and solvent exchanged into petroleum ether. The extract is concentrated with micro-snyder K-D apparatus to 1 ml and adjusted to 2.0 ml with iso-octane. If there are interferences, Florisil column cleanup or Gel Permeation Chromatography procedures are followed. The extracts are analyzed by high resolution Gas Chromatography (GC), with Flame Photometric Detector (FPD) in phosphorous mode and Thermionic Bead Specific Detector (TSD). Qualitative confirmation of unknowns can be conducted using GC with a Mass Spectrometer-Ion Trap Detector (GC/MS-ITD). The method detection limit (MDL) and the Reporting Limit (RL) for chlorpyrifos is 0.020 and 0.050 µg/l, respectively. All pesticide results are presented in Table 2.

Data Analyses

1. Theoretical residence time was determined 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

2. The median retention time was estimated as the time where the following equation was satisfied:

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

where C_M = Concentration of bromide measured
C_{Bk} = Concentration of average background bromide
Q = Discharge measured at time of bromide measurement
M_{Br} = Initial mass of bromide injected at Inlet

Quality Control

Continuing quality control (QC) spikes consist of a blank matrix control sample and a blank matrix sample that is spiked with all the analytes that are part of the screen. The matrices were either clean American River water or sediment. All continuing QC spikes are spiked the day samples are to be extracted. The full QC program is documented in DPR SOP QAQC001.00 (Segawa, 1995). QC results from this study were compared to control limits set at two and three times the standard deviation of method validation data for each analyte. Recoveries were used to assess and monitor ongoing sample analyses and random variation is expected. All continuing QC blank matrix control samples analyzed are presented in Table 3.

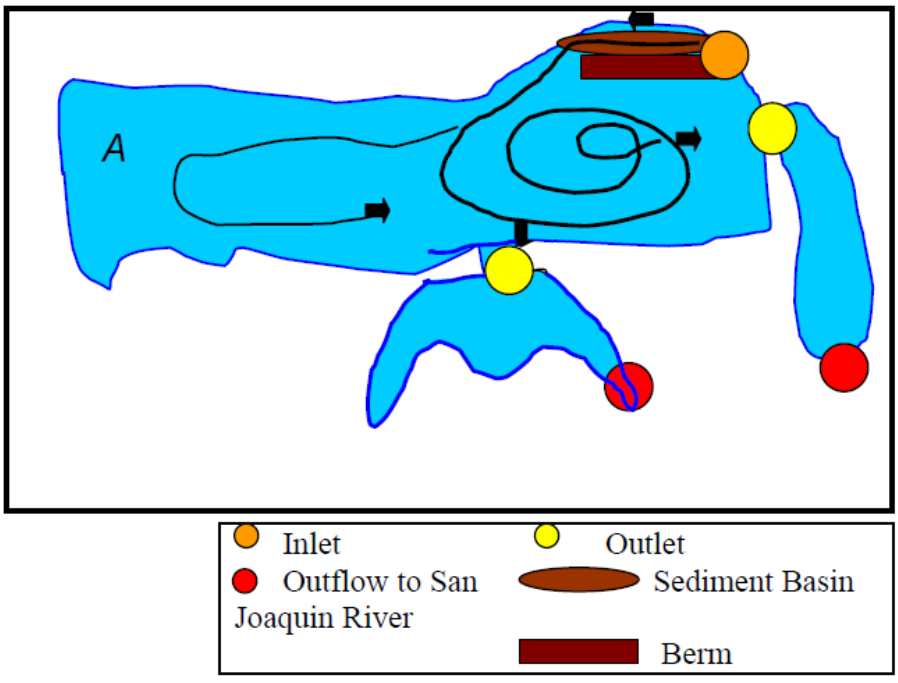
Organophosphate QC samples were generated by spiking water with the 10 screen analytes at 0.1 ppb. Chlorpyrifos and diazinon were spiked at 25 ppt to be closer to the lower reporting limit for those analytes. Twenty-two matrix spikes were conducted with the six extraction sets of samples. The average recoveries for the 10 analytes ranged from 58.7 to 113% recovery. The standard deviation of the recoveries ranged from 0.424 to 18.60%. Some analyte recoveries were beyond the warning limits in 16 QC samples, and 11 of these were beyond the upper or lower control limits.

Blind spikes are matrices spiked with standard by a chemist other than the chemist extracting and analyzing that matrix. Handling of blind spikes follows DPR SOP QAQC008.00 (Ganapathy, 2005). Twelve blind spikes containing one or two analytes were submitted for this study. Of the 14 analytes spiked, three analyte recoveries were below the lower control limit. All blind spike results are presented in Table 4.

IV. RESULTS AND DISCUSSION

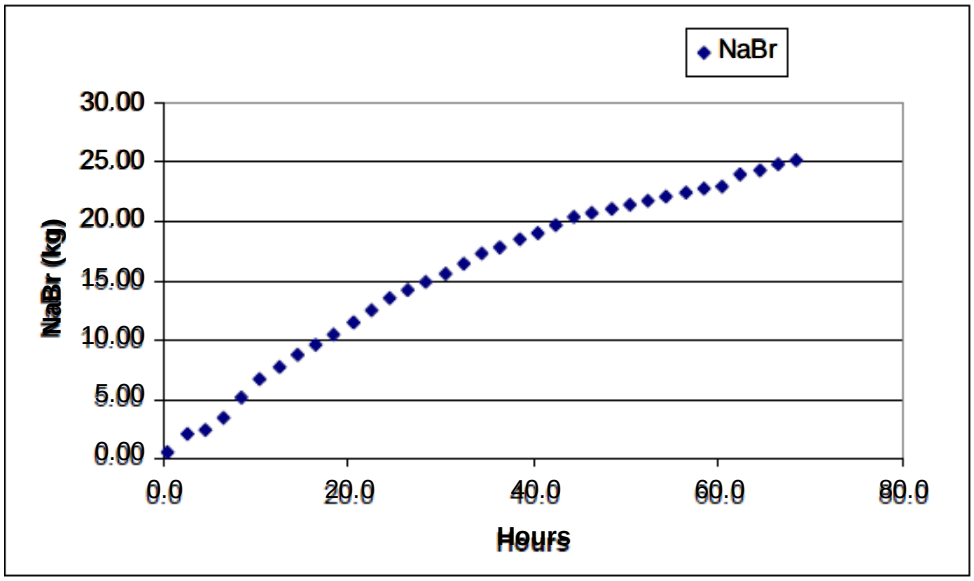
The wetland area was approximately 10.5 thousand m^3. The measured mean depth was 0.762 m. This is equivalent to approximately 10.5 million liters. Based on the mean discharge at the time of the tracer event (94.5 L/sec), the theoretical residence time was estimated as approximately 30.8 hours (Eq. 1). This estimate assumes "piston displacement" of the water in the wetland by the incoming water. This is generally a poor assumption due to mixing and dispersion. Section A of the wetland generally performs more as a pond rather than a flow-through portion, trapping and slowing inputs that enter; therefore increasing the residence time within the wetland (Figure 4). Using NaBr as a tracer, the median residence time was determined to be the time one-half of the initial bromide load (50 kg) was recovered (Eq. 2).

Figure 4. Monitored section of wetland



Collection of NaBr samples at Outlet1 began approximately 30 minutes after the input of the tracer at the inlet. Outlet2 sample collection began approximately120 minutes later. The background NaBr concentration was taken as the mean of the first two samples collected at Outlet2 (0.399 mg/L) under the assumption that the tracer had not reached this point within that time. Based on samples collected from both outlets, the wetland residence time was estimated as 67 hours, the time 25 kg of NaBr was recovered (Figure 5). NaBr results are presented in Table 5.

Figure 5. Cumulative mass of NaBr tracer over time



Many of the pesticide results were trace detections, that is, concentrations were between the method detection limit and the reporting limit (Table 3). In the 48 total samples collected there were only four trace chlorpyrifos detections (0.01ppb) at the inlet and three at Outlet1 (0.01ppb). Outlet2 also had four trace chlorpyrifos detections (0.01ppb). Dimethoate was detected in 87% of the samples collected from the inlet, and concentrations ranged from 0.033 to 0.374 ppb (19% trace detects). Both Outlet1 and Outlet2 also had high dimethoate detection frequencies (92 and 100%, respectively). Of the 12 other OP pesticide detections, only one was above the laboratory reporting limits. Due to the low number of OP pesticide detections, dimethoate was the only potential candidate for determining the mass load budget within the wetland. However, while conducting this study we encountered a number of uncertainties, including those in determining residence time and mass loads.

First, dimethoate concentrations were at or near the reporting limits, and dimethoate laboratory continuing QC samples were frequently beyond limits. Of the 22 matrix spikes for dimethoate, six were beyond the warning limit and two were beyond the control limit. Two blind spikes were also submitted for analyses (0.15 and 0.30 ppb). For one (0.15 ppb), the analyte recovery was below the control limit. Because recoveries were either above or below limits so frequently, substantial error in measured dimethoate concentrations was likely.

Next, the mean concentration of NaBr during the first 44 hours of sampling at Outlet1 was 1.70 mg/L, while one sample (second hour) was inexplicitly high (4.39 mg/L). Also, the sum of volume of water exiting Outlet1 and Outlet2 was assumed to be equal to that entering at the Inlet. This assumption was used to estimate the load of tracer and pesticides exiting at Outlet2 since discharge at this point was not monitored. Discharge at Outlet2 was negligible most of the year, however, this may not have been the case during the peak of the irrigation season. The lack of accurate discharge data may have increased the error in estimating both the residence time and the dimethoate loads.

Finally there may have been significant use of dimethoate in the surrounding area in the weeks prior to our sampling and dimethoate may have been resident in the wetland when the monitoring study began, resulting in a larger load exiting then as compared to entering during the study period.

Because of one or more of these uncertainties the difference in dimethoate mass load between the entrance and exit of the wetland was not accurately determined. Therefore, the effectiveness of this constructed wetland at reducing mass loads of OP pesticides from agriculture tailwaters is inconclusive.

IIV. ACKNOWLEDGEMENTS

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Table 1. Organophosphate pesticides analyzed, including method detection limits and reporting limits

Method: GC/FPD	**Method Detection Limit (ppb)**	**Reporting Limit (ppb)**
Azinphos methyl	0.030	0.050
Chlorpyrifos	0.010	0.020
Diazinon	0.005	0.020
Dimethoate	0.030	0.050
Disulfoton	0.010	0.050
Malathion	0.030	0.050
Methidathion	0.030	0.050
Parathion, Methyl	0.010	0.050
Phorate	0.030	0.050
Phosmet	0.030	0.050

Note: All method detection limit**'s and** Reporting Limit **s listed were determined by CDFG for DPR**

Table 2. Pesticide results Inlet (table 1 of 3)

Sample #	Date	Time	Chlorpyrifos (ppb)	Dimethoate (ppb)	Methyl Parathion (ppb)	Malathion (ppb)	Diazinon (ppb)
10	9-Jul	13:44	0.01	0.266			
12	9-Jul	20:44	0.01	0.122			
14	10-Jul	10:44	0.01	0.052	0.039		
43	10-Jul	18:11		0.042	0.032	0.038	
45	11-Jul	1:11					
47	11-Jul	15:11					
49	11-Jul	22:11		0.043			
51	12-Jul	5:11					
53	12-Jul	12:11		0.05	0.01	0.046	0.005
59	12-Jul	20:29					
61	13-Jul	3:29					
63	13-Jul	10:29		0.035		0.11	0.005
65	13-Jul	17:29					
67	14-Jul	0:29		0.081			
69	14-Jul	7:29		0.081			
93	14-Jul	14:16		0.072			
121	16-Jul	11:38		0.065			
123	16-Jul	18:38		0.053			
125	17-Jul	1:38		0.068			
127	17-Jul	8:38	0.01	0.07			
141	17-Jul	15:46		0.138			
143	17-Jul	22:46		0.065			
145	18-Jul	5:46		0.048			
147	18-Jul	12:46		0.068			0.005
149	18-Jul	19:46		0.072			0.007
151	19-Jul	2:46		0.05			
153	19-Jul	9:46		0.038			
181	19-Jul	16:36		0.073			
183	19-Jul	23:36		0.033			
185	20-Jul	6:36		0.035			
187	20-Jul	13:36		0.067			
189	20-Jul	20:36		0.055			
191	21-Jul	3:36		0.034			
192	21-Jul	10:36		0.104			
223	21-Jul	17:56		0.05			
225	22-Jul	0:56		0.035			
227	22-Jul	7:56		0.044			
229	22-Jul	14:56		0.067			
231	22-Jul	21:56		0.054			
259	23-Jul	12:18		0.04			

Table 2. Continued. Pesticide detections Outlet1 (table 2 of 3)

Sample #	Date	Time	Chlorpyrifos (ppb)	Dimethoate (ppb)
18	10-Jul	18:34		0.049
20	11-Jul	1:34		0.053
24	11-Jul	15:34		0.048
26	11-Jul	22:34		0.044
71	12-Jul	12:34		0.042
73	12-Jul	19:34		0.04
75	13-Jul	2:34		0.038
77	13-Jul	9:34		0.035
79	13-Jul	16:34		0.05
81	13-Jul	23:34		0.062
83	14-Jul	6:34		0.05
95	14-Jul	13:33		0.05
131	16-Jul	11:47		0.031
135	17-Jul	1:47		
137	17-Jul	8:47		0.043
155	17-Jul	15:48		0.06
158	17-Jul	22:48		0.046
159	18-Jul	5:48		0.045
161	18-Jul	12:48		0.04
163	18-Jul	19:48		0.044
165	19-Jul	2:48		0.032
167	19-Jul	9:48		0.034
195/194	19-Jul	16:43		0.056
196	19-Jul	23:43		0.044
199	20-Jul	6:43		0.039
201	20-Jul	13:43		0.056
203	20-Jul	20:43	0.01	0.049
205	21-Jul	3:43	0.011	
207	21-Jul	10:43	0.012	0.058
233	21-Jul	17:59		0.033
235	22-Jul	0:59		0.041
237	22-Jul	7:59		0.041
239	22-Jul	14:59		0.083
241	22-Jul	21:59		0.045
267	23-Jul	12:28		0.061
269	23-Jul	19:28		0.061
271	24-Jul	2:28		0.047
273	24-Jul	9:28		0.082
295	24-Jul	16:27		0.052
297	24-Jul	23:27		0.048
299	25-Jul	6:27		0.049
301	25-Jul	13:27		0.157
303	25-Jul	20:27		0.117

Highlighted numbers are below reporting limits

Table 2. Continued. Pesticide detections Outlet2 (table 3 of 3)

Sample #	Date	Time	Chlorpyrifos (ppb)	Dimethoate (ppb)	Methyl Parathion (ppb)	Malathion (ppb)	Diazinon (ppb)
31	10-Jul	19:16		0.062			
33	11-Jul	2:16		0.068			
37	11-Jul	16:16		0.07			
39	11-Jul	23:16		0.063			
41	12-Jul	6:16		0.057			
85	12-Jul	12:51		0.051			
87	12-Jul	19:51		0.055			
89	13-Jul	2:51		0.041			
91	13-Jul	9:51		0.041			
107	14-Jul	14:31		0.051			
139	16-Jul	11:40		0.045			
169	17-Jul	15:39		0.037			
172	17-Jul	22:39		0.047			
173	18-Jul	5:39		0.051			
175	18-Jul	12:39		0.057			
177	18-Jul	19:39		0.036			
209	19-Jul	16:37		0.06			
211	19-Jul	23:37		0.052			0.011
213	20-Jul	6:37		0.055			
215	20-Jul	13:37	0.016	0.058			0.01
217	20-Jul	20:37	0.013	0.038			
219	21-Jul	3:37	0.014	0.047			
221	21-Jul	10:37	0.014	0.122			
243	21-Jul	17:52		0.048			
245	22-Jul	0:52		0.054			
247	22-Jul	7:52		0.043			
249	22-Jul	14:52		0.079			
251	22-Jul	21:52		0.047			
275	23-Jul	12:39		0.058			
277	23-Jul	19:39		0.038			
279	24-Jul	2:39					
281	24-Jul	9:39		0.216			
309	24-Jul	16:56		0.045			
311	25-Jul	13:25		0.042			
313	25-Jul	20:25		0.055			

Highlighted numbers are below reporting limits

Table 3. Laboratory continuing quality control

	Azinphos methyl	Chlorpyrifos	Diazinon	Dimethoate	Disulfoton	Malathion	Methidathion	Parathion, Methyl	Phorate	Phosmet	Surrogate with QC	Average and SD of Surrogate in all samples in set	Method Blanks in set
sample number	Sample extraction set												
	97.0	85.8	89.5	67.3	76.2	85.1	87.3	83.9	74.2	105	103		
1,2,5,6,9,11	94.2	93.1	91.8	50.0	73.9	88.8	87.9	85.7	77.0	103	102		2 blanks ND
average	95.6	89.5	90.7	58.7	75.1	87.0	87.6	84.8	75.6	104	103	93.7	
SD	1.98	5.16	1.63	12.2	1.63	2.62	0.424	1.27	1.98	1.41	0.71	11.3	
sample number	Sample extraction set												
10,12,14,37,39,41,	119	107	118	83.3	91.6	113	133	134	115	102	111		
43,45,47,49,51,53,	79.8	85.5	95.5	72.2	80.5	125	103	106	96.5	72.5	91.5		
55,16,18,20,22,24,	79.4	82.4	89.0	58.1	74.5	85.0	99.1	99.7	87.9	70.1	90.9		
26,27,28,29,31,33,	90.3	88.3	94.3	67.0	78.5	112	113	111	94.0	81.0	99.9		2 blanks ND
average	92.1	90.8	99.2	70.2	81.3	109	112	113	98.4	81.4	98.3	97.2	
SD	18.6	11.1	12.8	10.5	7.32	16.9	15.2	14.9	11.7	14.5	9.4	5.64	
sample number	Sample extraction set												
57,59,61,63,65,67,	98.4	90.9	94.5	70.2	89.5	100	96.0	104	98.2	112	93.4		
69,71,73,75,77,79,	102	101	107	94.6	81.1	108	107	100	103	87.1	90.7		
81,83,85,87,89,91,(	101	99.3	111	79.6	97.5	109	117	103	107	115	94.5		
548),(579),93,95,9	103	96.7	97.2	96.3	85.9	99.2	98.9	91.8	99.6	100	80.2		
7,99,101,103,105,(	106	93.9	102	73.9	90.6	101	99.4	92.8	98.4	98.3	91.7		
576),(581),107,109	104	91.8	96.7	83.5	89.4	96.3	97.4	92.0	98.7	112	103		
,111,113,115,117,1													3 blanks ND
average	102	95.6	101	83.0	89.0	102	103	97.3	101	104	92.3	93.7	
SD	2.61	4.09	6.50	10.68	5.43	5.10	8.02	5.71	3.51	10.80	7.35	11.25	

	Azinphos methyl	Chlorpyrifos	Diazinon	Dimethoate	Disulfoton	Malathion	Methidathion	Parathion, Methyl	Phorate	Phosmet	Surrogate with QC	Average and SD of Surrogate in all samples in set	Method Blanks in set
sample number	Sample extraction set												
141,143,145,147,1	104	97.2	112	82.1	65.0	99.8	102	94.0	86.5	98.3	74.8		
49,151,153,155,15	118	99.6	116	76.1	70.1	102	101	94.2	89.9	75.3	98.5		
8,159,161,163,165,	143	96.1	106	85.9	68.0	99.4	96.2	99.9	90.8	59.4	74.8		
167,169,172,173,1	87.4	101	110	83.8	73.2	102	97.9	99.8	94.3	100	75.0		1 blank ND
75,177,179,180,(57													1 bnk w/ disulfoton
average	113	98	111	82.0	69.1	101	99.3	97.0	90.4	83.3	80.8	87.5	
SD	23.5	2.23	4.16	4.21	3.46	1.40	2.69	3.32	3.21	19.5	11.8	10.6	
sample number	Sample extraction set												
223,225,227,229,	93.3	93.6	102	99.7	51.9	102	98.0	98.8	92.8	108	73.2		
231,233,235,237,2	102	106	107	89.7	53.9	106	99.3	105	97.3	105	92.0		
39,241,249,251,25	95.3	95.0	99.9	77.5	61.6	101	90.9	100	89.1	98.7	89.5		
3,255,257,258,261,	89.8	92.7	100	72.5	68.7	99.3	95.8	98.4	93.0	112	82.0		2 blanks ND
average	95.1	96.8	102	84.9	59.0	102	96.0	101	93.1	106	84.2	109	
SD	5.13	6.19	3.33	12.26	7.69	2.84	3.69	3.04	3.35	5.61	8.46	15.1	
sample number	Sample extraction set												
285,	109	101	110	97.6	95.3	100	90.8	121	110	96.4	84.3		
287,289,291,293,2	107	96.1	108	82.4	93.9	98.2	102	102	98.0	97.7	97.6		1 bnk w/ disulfoton
average	108	98.6	109	90.0	94.6	99.1	96.4	112	104	97.1	91.0	115	
SD	1.41	3.46	1.41	10.75	0.99	1.27	7.92	13.44	8.49	0.919	9.40	10.1	

Control Limits from valid	Azinphos methyl	Chlorpyrifos	Diazinon	Dimethoate	Disulfoton	Malathion	Methidathion	Parathion, Methyl	Phorate	Phosmet	Surrogate
UCL	134	110	110	105	115	130	115	108	110	117	124
UWL	122	103	104	98	106	117	108	101	102	108	114
LWL	71.2	75.0	77.9	72.8	69.1	69.3	79.9	75.6	73.1	70.5	72.5
LCL	58.6	68.1	71.5	66.4	59.9	57.2	72.9	69.2	65.7	61.1	62.2

Outside the range of the warning limits **Outside the range of the control limits**

Table 4. Blind spike results

DPR sample identification	Analyte spiked	Amount spiked	Amount recovered	Percent recovery	Within control limits?
548	Phosmet	0.4	0	0	below LCL
579	Phorate	0.3	0.294	98.0	yes
543	Malathion	0.3	0.232	77.3	yes
544	Dimethoate	0.3	0.278	92.7	yes
	Methidathion	0.25	0.202	80.8	yes
545	Dimethoate	0.15	0.075	50.0	below LCL
546	Chlorpyrifos	0.1	0.089	89.0	yes
547	Malathion	0.5	0.428	85.6	yes
549	Diazinon	0.5	0.406	81.2	yes
574	Azinphos methyl	0.25	0.179	71.6	yes
576	Chlorpyrifos	0.2	0.19	95.0	yes
	Diazinon	0.1	0.105	105	above UWL
581	Disulfoton	0.25	0.146	58.4	below LCL
572	Chlorpyrifos	0.4	0.35	87.5	yes

LCL = Lower control limit, UWL = Upper warning limit
Diazinon and chlorpyrifos are ppt all others are ppb.

Table 5. Sodium bromide results

Outlet1 (hr)	Date	Time	Sample #	mg/L	Outlet2 (hr)	Date	Time	Sample #	mg/L
2	8/6/2007	13:20	602	1.58	2	8/6/2007	15:19	613	0.427
4	8/6/2007	15:20	603	4.39	4	8/6/2007	17:19	614	0.371
6	8/6/2007	17:20	604	1.04	6	8/6/2007	19:19	615	2.3
8	8/6/2007	19:20	605	1.6	8	8/6/2007	21:19	616	4.17
10	8/6/2007	21:20	606	1.79	10	8/6/2007	23:19	617	3.82
12	8/6/2007	23:20	607	1.59	12	8/7/2007	1:19	618	1.75
14	8/7/2007	1:20	608	1.75	14	8/7/2007	3:19	619	3.03
16	8/7/2007	3:20	609	1.64	16	8/7/2007	5:19	620	1.3
18	8/7/2007	5:20	610	1.7	18	8/7/2007	7:19	621	1.61
20	8/7/2007	7:20	611	1.71	20	8/7/2007	9:19	622	1.6
22	8/7/2007	9:20	612	1.79	22	8/7/2007	11:19	623	2.02
24	8/7/2007	11:27	624	1.71	24	8/7/2007	13:20	636	1.48
26	8/7/2007	13:26	625	1.98	26	8/7/2007	15:20	637	1.62
28	8/7/2007	15:26	626	1.45	28	8/7/2007	17:20	638	1.4
30	8/7/2007	17:26	627	1.5	30	8/7/2007	19:20	639	1.29
32	8/7/2007	19:26	628	1.58	32	8/7/2007	21:20	640	1.89
34	8/7/2007	21:26	629	1.88	34	8/7/2007	23:20	641	1.18
36	8/7/2007	23:26	630	1.94	36	8/8/2007	1:20	642	1.28
38	8/8/2007	1:26	631	1.34	38	8/8/2007	3:20	643	1.23
40	8/8/2007	3:26	632	1.36	40	8/8/2007	5:20	644	1.25
42	8/8/2007	5:26	633	1.32	42	8/8/2007	7:20	645	1.18
44	8/8/2007	7:26	634	1.25	44	8/8/2007	9:20	646	1.1
46	8/8/2007	9:26	635	1.3	46	8/8/2007	11:20	647	1.04
48	8/8/2007	11:35	672	0.855	48	8/8/2007	13:20	684	1.18
50	8/8/2007	13:35	673	0.904	50	8/8/2007	15:20	685	1.07
52	8/8/2007	15:35	674	0.907	52	8/8/2007	17:20	686	1.05
54	8/8/2007	17:35	675	0.785	54	8/8/2007	19:20	687	1.36
56	8/8/2007	19:35	676	0.786	56	8/8/2007	21:20	688	0.94
58	8/8/2007	21:35	677	0.847	58	8/8/2007	23:20	689	0.905
60	8/8/2007	23:35	678	0.883	60	8/9/2007	1:20	690	0.933
62	8/9/2007	1:35	679	0.847	62	8/9/2007	3:20	691	4.04
64	8/9/2007	3:35	680	0.913	64	8/9/2007	5:20	692	1.17
66	8/9/2007	5:35	681	0.881	66	8/9/2007	7:20	693	1.09
68	8/9/2007	7:35	682	0.926	68	8/9/2007	9:20	694	1.13
70	8/9/2007	9:35	683	0.813	70	8/9/2007	11:20	695	0.77