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MEMORANDUM

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SUBJECT: RESULTS FOR STUDY 231: EFFECT OF POLYACRYLAMIDE CALCIUM IN IRRIGATION WATER ON CHLORPYRIFOS MOVEMENT FROM AN AGRICULTURAL FIELD

Scope of the Memorandum

This memorandum summarizes results of a field experiment designed to investigate the effect of polyacrylamide (PAM) on chlorpyrifos movement from a fallow field. This study was conducted pursuant to an agreement (05-0071R) between the Department of Pesticide Regulation (DPR) and the San Luis and Delta-Mendota Water Authority, under which DPR was to assess the efficacy of various mitigation measures to prevent runoff of chlorpyrifos from agricultural uses. Chemical analysis of water samples was performed by the Water Pollution Control Laboratory of the Office of Spill Prevention and Response of the Department of Fish and Game in Rancho Cordova, California.

Background

Orestimba Creek originates in the Coast Range Mountains in western Stanislaus County, passes through irrigated farmland in the San Joaquin Valley, and terminates at it's confluence with the San Joaquin River. The Orestimba Creek watershed encompasses approximately 18,000 acres devoted to production agriculture. The most important crops in the watershed are alfalfa, walnuts, almonds, and dry beans. Irrigation return flows from agricultural lands in the Orestimba Creek watershed flow into Orestimba Creek, a tributary to the San Joaquin River, and ultimately the San Francisco Bay/Delta. Drainage from farmlands, either from surface water flows (irrigation tailwater) or storm runoff, carries pesticides, nutrients, salts, and other constituents into Orestimba Creek and subsequently the San Joaquin River. Chlorpyrifos has been detected in Orestimba Creek samples at concentrations high enough to cause toxicity in concommitant Ceriodaphnia dubia bioassays. Detections of the organophosphate pesticides diazinon and chlorpyrifos, during both the winter dormant spray period and the summer growing season, have prompted the listing of Orestimba Creek on the Clean Water Act § 303(d) list (Foe, 1995).

One practice thought to be effective in reducing the movement of pesticides offsite in water is application of PAM (Aase et al., 1998; Bjorneberg et al., 2003; Lehrsch et al., 1996; Lentz and Sojka, 1996; McElhiney and Osterli, 1996). PAM is a flocculent that causes sediments to bind into larger aggregates which are more resistant to movement by the force of flowing water. In fields where pesticides have been applied, PAM has also been suggested to reduce pesticide movement offsite by reducing sediment movement (Agassi et al., 1995; Bahr and Steiber, 1996; Singh et al., 1996).

The goal of this study was to determine what effect PAM added to irrigation water has on the mass of chlorpyrifos leaving a fallow treated field in irrigation runoff. To achieve this goal, a chlorpyrifos-treated field was irrigated, and the total mass of chlorpyrifos recovered in runoff water from both PAM-treated and PAM-untreated (control) rows within the field was determined. For this study, a liquid formulation of PAM, PAM–Calcium, was added to irrigation water as it was applied to the field. PAM-Calcium is a formulation of polyacrylamide and calcium carbonate.

Materials and Methods

Site Description

The experimental field was located in western Stanislaus County near the city of Crows Landing (Figure 1). The fallow field represented a worst-case scenario with 100% of the chlorpyrifos reaching the soil surface, thereby creating the highest potential for runoff. The field was bordered by tomatoes (east), walnuts (north), and corn (west). Orestimba Creek bordered the field to the south. The dimensions of the field were approximately 300 meters by 60 meters (80 rows); the southernmost 100 meters was utilized for this study (Figure 2). The field was prepared and bedded following local farm practices. Row width was approximately 30 inches furrow to furrow, with the length of each row 100 meters. Four blocks of ten rows each (five paired rows) were identified within the field for use in the study. Four- to six-row buffers separated blocks. The field was pre-irrigated approximately 20 days before chlorpyrifos application. Chlorpyrifos (Lorsban 4-E) was applied to the bare field at the rate of one pound of active ingredient per acre, using ground-based application equipment and following all label directions. Chlorpyrifos was applied to the upper 95 meters of each row, allowing a 5-meter buffer between applied chlorpyrifos and sample collection equipment and personnel at the bottom of sampled rows (Figure 3). The application was completed 36 hours prior to initiation of the first irrigation event.

Figure 1. Location of field site in Stanislaus County, California.

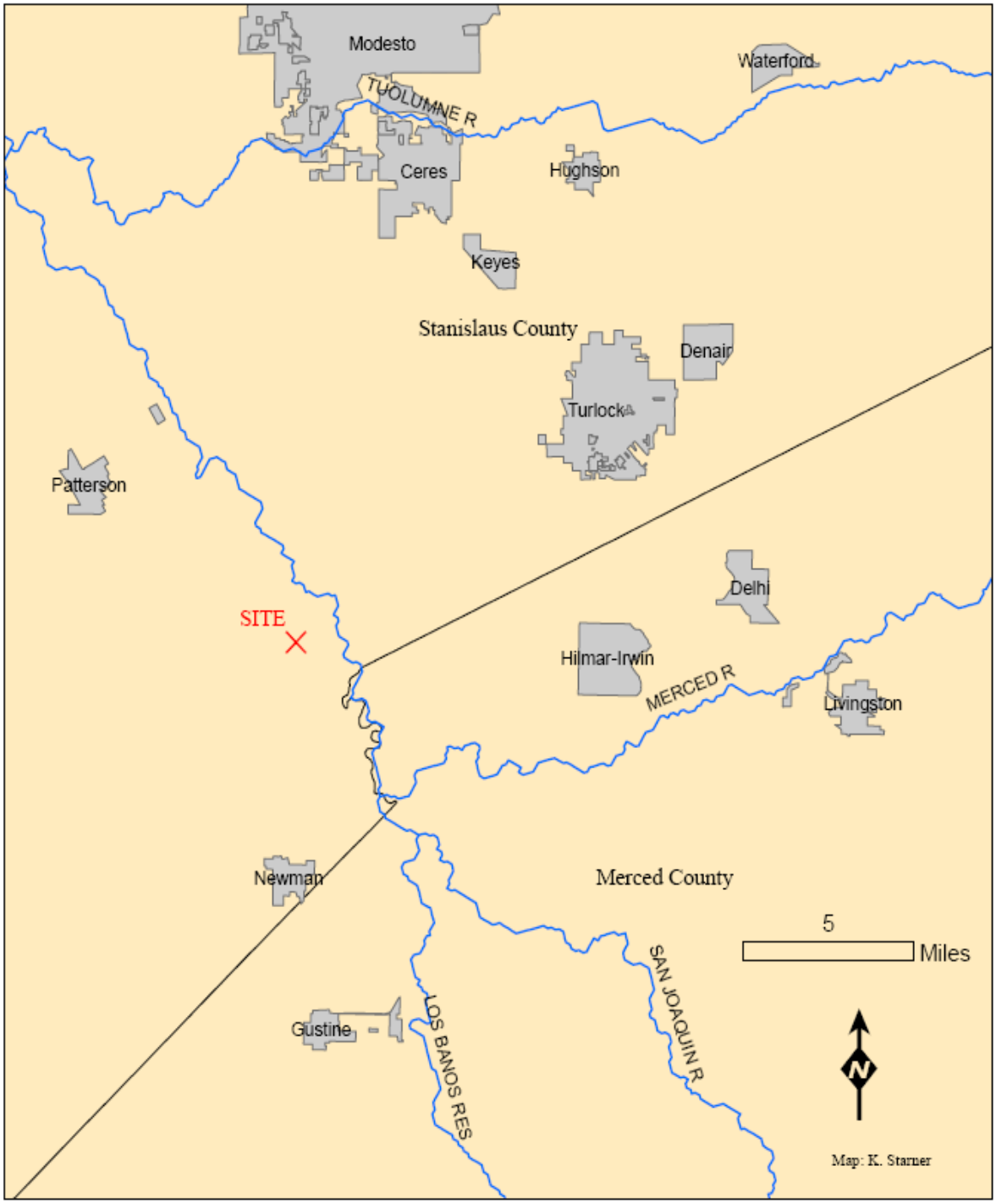


Figure 2. Experimental field, facing south, at the onset of irrigation on Day 2. Riparian zone along banks of Orestimba Creek is in the background.

Figure 3. Sampling equipment *in situ*

Irrigation Procedures

Irrigation of portions of the chlorpyrifos-treated field was completed over four successive days beginning on August 14, 2006. Each day, one of the four blocks (ten rows/block=five paired rows) was irrigated. For the first day, irrigation water was obtained from a well located near the experimental site. On subsequent days, irrigation water was delivered through surface irrigation canals in the Crows Landing area. All irrigation water was first delivered to a cistern, and then to the field via nine-inch irrigation pipes with flow control gates. Gates were equipped with sleeves to reduce erosion. During the irrigation events, flow was monitored and adjusted to deliver comparatively uniform flow to each furrow. Irrigation water flowed 100 meters down the field to the sampling and monitoring stations.

PAM Application

For each PAM treated row, a 5% solution (v/v) of PAM was applied to the irrigation stream at approximately one gallon per hour over the irrigation event (Figure 4). Application of the solution to each row was achieved by plastic buckets equipped with adjustable drip irrigation valves connected to 24 inches of ¼ inch drip tubing (Figure 5). The ends of the irrigation tubing were inserted into irrigation sleeves to ensure thorough mixing of PAM solution with irrigation water. The PAM solution in the application buckets was replenished as needed during the irrigation process. The total amount of PAM solution applied to each row was recorded.

Sampling and Flow Monitoring

At the base of the paired rows, irrigation water was collected in plastic buckets embedded in the ground (Figure 7). Buckets were equipped with submersible water pumps controlled by float switches, and pumps were enclosed in environmental mesh cloth debris screens. As irrigation runoff filled the collection bucket, water was pumped through a calibrated in-line flow meter (Precision) and subsequently through a calibrated 1:100 (v:v) splitter valve (Figure 6). The smaller portion of the water from the splitter valve was continuously collected in one-gallon containers (flint glass) for subsequent analysis; three to five one-gallon samples were collected from each furrow. The larger portion of the water from the splitter valve was passed from the sample collection area and discharged onto the untreated lower portion (200 meters) of the field. Over the course of the study, no discharged water reached the tail water ditch at the end of the field. Flow meter readings were recorded prior to the onset of sample collection, following the collection of each one-gallon sample, and at the completion of the sample collection process for that row. Readings were used to calculate runoff volume for each sample and to calculate total runoff volume for each row. Each one-gallon continuously collected composite sample was split into a one-liter sample for chemical analysis and a one-liter “backup” sample. The one-liter samples were then stored on wet ice and transported to DPR’s facility in West Sacramento,

California. Samples were then refrigerated at 4 ºC overnight and transported (on wet ice) the following day to the Department of Fish and Game's Water Pollution Control Laboratory.

Sampling equipment was rinsed at the end of each day. Debris screens were rinsed until no debris or fine sediment remained. Pumps, in-line flow meters, splitter valves, and all clear hose were reassembled, and 20 gallons of clean water were passed through each system. Sample buckets were not rinsed as new buckets were used on a daily basis.

QA/QC

Numerous samples were collected for quality control purposes. These samples included: duplicate samples, irrigation water input (collected from gated irrigation pipes), equipment rinse blanks, consisting of either splitting funnel rinsate or sampling equipment rinsate, field blanks, and blind matrix spikes. Results and discussion of QA/QC analysis is presented in an attachment to this memorandum.

Figure 4. PAM application apparatus setup at head of field prior to onset of irrigation.

Figure 5. PAM application buckets and irrigation sleeves.

Figure 6. Sampling equipment, showing bucket/pump assembly in ground, battery, in-line flow meter, splitter (left side of PVC "T"), sample collection jars, and discharge water return (right side of PVC "T").

Figure 7. Placement of sample collection buckets in ground

Results

Summary

The total mass of chlorpyrifos and the total volume of water discharged from each row over the course of each day's irrigation regimen are shown in Table 1. For a majority of rows, five samples were collected. In control rows, the mass of chlorpyrifos discharged in tailwater ranged from 1789.24 μg to 14,342.24 μg. The mass of chlorpyrifos discharged from PAM-treated rows ranged from 3,179.36 μg to 10,455 μg.

The total movement of chlorpyrifos from the field and runoff volume for each day is shown in Table 2; Figure 8 shows chlorpyrifos in runoff by day and treatment. On day one, the total mass of chlorpyrifos leaving the field was greater on control rows than on PAM-treated rows. On days two, three, and four, this reversed, with the total mass of chlorpyrifos leaving the field greater on PAM-treated rows than on control rows. Over all four days, average water flow rates were higher on PAM-treated rows than on control rows (Figure 9). Averaged over the course of all four irrigation/sampling events, concentrations of chlorpyrifos were 5.04 μg/L and 4.94 μg/L in tailwater discharged from control and PAM-treated rows, respectively.

Over the course of the experiment, the amount of PAM (dry weight) applied to each row varied slightly (Table 3); the average PAM applied was 0.124 g (σ= 0.035).

Table 1: Data used for statistical analysis†.

Row	Treatment	Total (µg) Chlorpyrifos	Runoff Volume (L)	Day #	Notes
1	Control	1,789.24	1203.3	1	
2	PAM-Ca Treated	3,179.36	1508.7	1	
5‡	PAM-Ca Treated	7,709.40	1630.2	1	
6	Control	14,342.24	1523.8	1	
7	Control	6,651.99	1093.9	1	4 Samples
8	PAM-Ca Treated	8,188.44	1053.4	1	3 Samples
9	PAM-Ca Treated	4,809.28	1267.2	1	4 Samples
10	Control	6,786.29	1643.4	1	
11	PAM-Ca Treated	5,925.42	1591.6	2	
12	Control	4,579.86	1252.5	2	
13	Control	3,717.93	689.2	2	
14	PAM-Ca Treated	3,976.98	947.4	2	
15	PAM-Ca Treated	6,710.24	1107.1	2	
16	Control	7,498.54	1028.4	2	
17	Control	3,359.19	644.6	2	2 Samples
18	PAM-Ca Treated	4,803.58	1023.5	2	
19	Control	4,441.32	985.6	2	
20	PAM-Ca Treated	7,503.77	1121.1	2	
21	PAM-Ca Treated	7,522.32	1489.4	3	
22	Control	4,730.31	1197.2	3	
23	PAM-Ca Treated	4,418.87	868.3	3	
24	Control	4,343.86	937.9	3	
25	PAM-Ca Treated	5,644.08	1162.0	3	
26	Control	2,145.50	911.0	3	
27	Control	3,094.63	638.5	3	
28	PAM-Ca Treated	6,178.79	972.4	3	
29	PAM-Ca Treated	3,735.04	872.8	3	
30	Control	4,594.18	1005.7	3	
31	PAM-Ca Treated	5,882.86	1674.1	4	
32	Control	6,170.23	806.6	4	
33	Control	3,619.56	883.8	4	
34	PAM-Ca Treated	10,455.23	925.4	4	
35	PAM-Ca Treated	8,464.02	1089.3	4	
36	Control	3,936.10	951.2	4	
37	PAM-Ca Treated	3,456.24	773.7	4	
38	Control	6,530.53	1060.2	4	
39	Control	5,594.61	953.8	4	
40	PAM-Ca Treated	3,849.69	994.3	4	

† Data used for statistical analysis based on total mass of chlorpyrifos leaving field and the total volume of water recorded during sample collection.
‡ Data for rows 3 and 4 are not presented due to equipment failure on row 3.

Table 2. Amounts of chlorpyrifos and water measured on a daily basis. Total for all rows of a specific treatment for each day

Date	**Chlorpyrifos (µg)**			**Water (L)**	
	Control	PAM-treated		Control	PAM-treated
14/August	29,569.76	27,557.89		5,464.4	6,903.90
15/August	23,596.84	28,919.99		4,600.3	5,790.70
16/August	18,908.48	27,499.10		4,690.3	5,364.90
17/August	25,851.03	32,108.04		4,655.6	5,456.80
total	97,926.11	116,085.02		19,410.6	23,516.3

Figure 8. Box plot of chlorpyrifos (µg) in runoff water from PAM–treated and control rows by day and treatment.

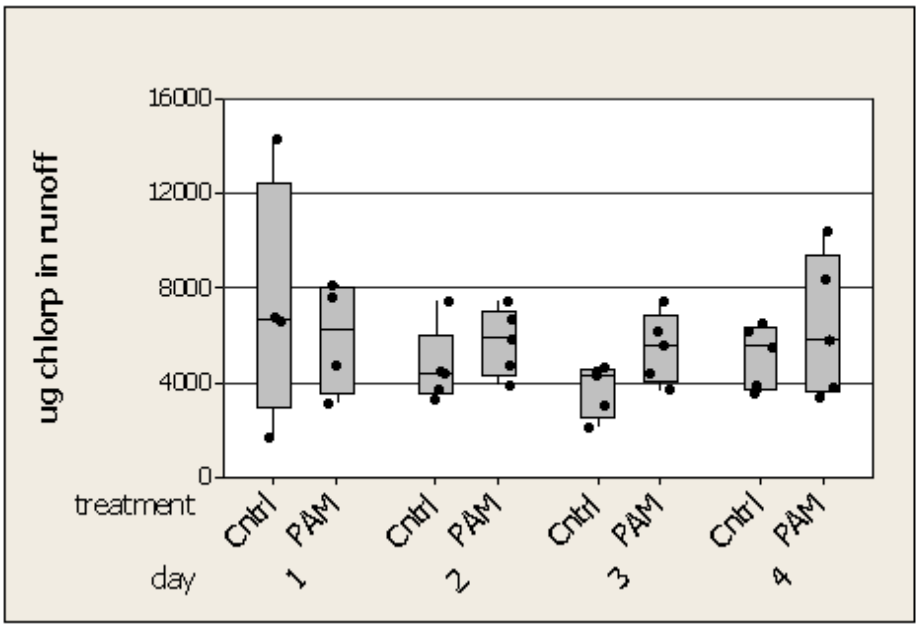


Figure 9. Box plot of runoff volume (Liters) from PAM–treated and control rows by day and treatment.

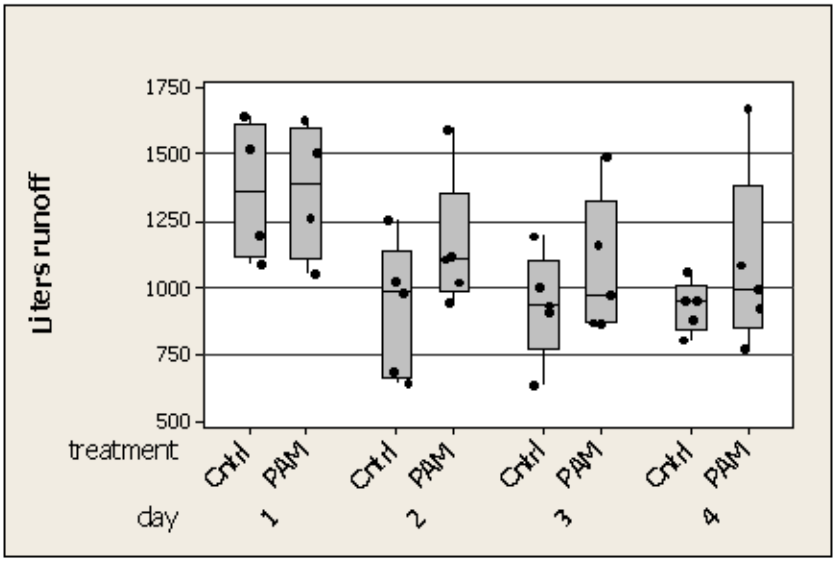


Table 3. Total amount of PAM–Ca applied.

Date	Row #	PAM Applied (g)
14/August	2	194.08
	4	129.39
	5	147.87
	8	157.11†
	9	147.87†
15/August	11	129.39
	14	157.11
	15	129.39
	18	110.90
	20	147.87
16/August	21	184.84
	23	147.87
	25	184.84
	28	184.84
	29	157.11
17/August	31	129.39
	34	92.42
	35	110.90
	37	73.94
	40	101.66

† At onset of application, the 5 gallons Pam-Ca solution for row 8 spilled into these two rows. A fresh solution was created and metered into row 8 over the course of the irrigation event.

Data Analysis

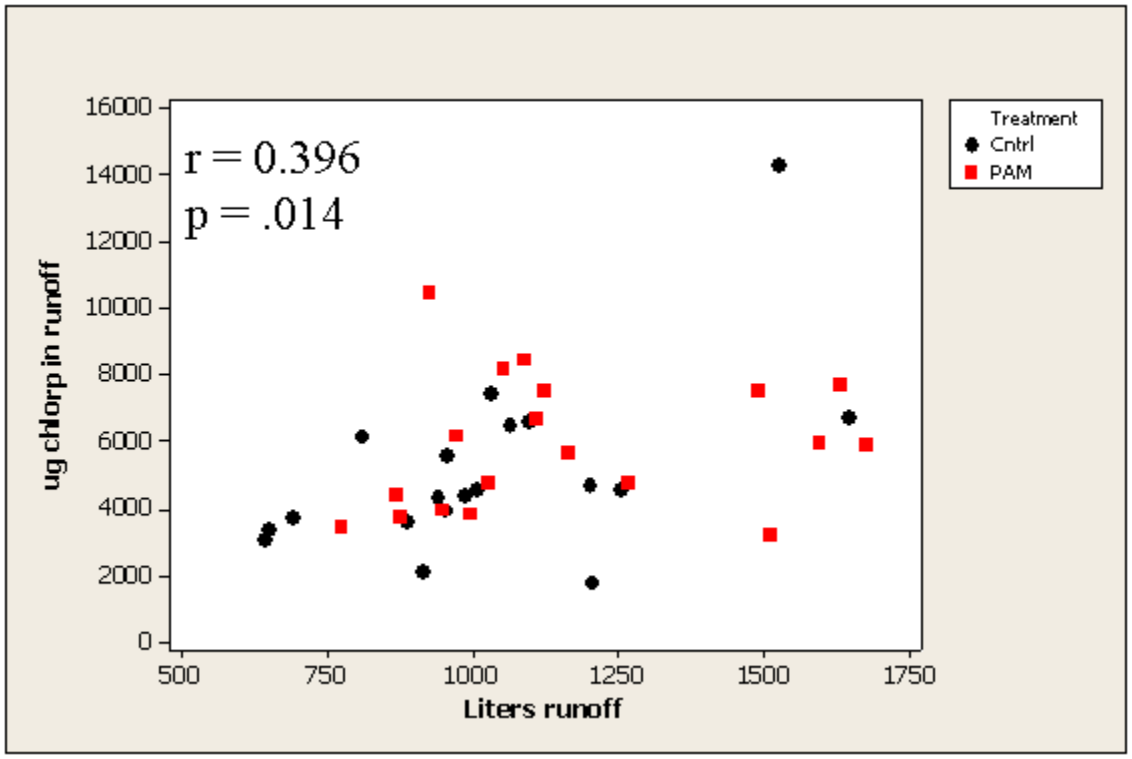
The chlorpyrifos mass and runoff volumes recovered from rows were variable (Figures 8 & 9). Coefficients of variation across all mass chlorpyrifos and runoff volume measurements were 43 % and 26 %, respectively. The total mass of chlorpyrifos recovered in runoff from individual rows ranged from approximately 1800 µg (control row, day 3) to 14000 µg (control row, day 1), with a grand mean of 5500 µg. This mean mass is approximately 0.07% of the 1 lb/acre nominal application to each row/bed unit. Runoff volume from the furrows ranged from 638 L (control row, day 3) to 1674 L (PAM-treated row, day 4) with a mean of 1090 L (Figure 9). Mean runoff for control rows was 1025.5 L (range 638 L to 1643 L). Mean runoff for PAM-treated rows was 1161.6 L (range 773 L to 1674 L).

The study design consisted of 20 experimental units of paired rows, each pair including a row of PAM application and a nonPAM control (Table 4). While the experiment was conducted over 4 consecutive days by sampling 4 field blocks consisting of 5 paired rows each, equipment failure on day 1 resulted in data being collected for only four experimental units (i.e. row pairs) that day, leaving a total of 19 experimental units. Based on a paired t-test, there was a small but significant difference in mean runoff water volume between control and PAM treatments within all row pairs ($p=0.04$). The mean control runoff water volume was 1022 L ($\sigma=246$), compared to 1162 L ($\sigma=282$) in the PAM-treated rows, a difference of 140 L. In addition, there was significant positive correlation between runoff volume and total chlorpyrifos recovered from each row (Figure 10). Consequently, either the use of PAM or the amount of runoff could affect the amount of chlorpyrifos moving off-site. Therefore the analysis accounts for both possible effects.

Table 4. General Linear Model: log (µg chlorpyrifos) versus treatment, event, and row pair.

Factor	Type	Levels	Values
day	fixed	4	1, 2, 3, 4
row pair (day)	fixed	19	a, b, c, d, e, f, g, h, i, j, k, l, m, n, o, p, q, r, s
treatment (day)	fixed	8	Ctrl, PAM; Ctrl, PAM; Ctrl, PAM; Ctrl, PAM.

Figure 10. Positive correlation between runoff volume and total chlorpyrifos recovered from each row.

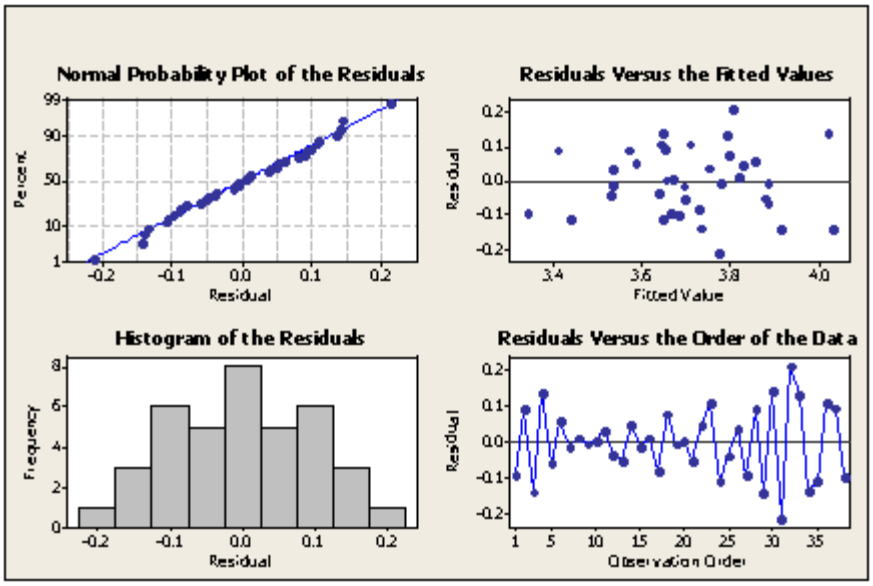


We analyzed the data using analysis of covariance (ANCOVA) where log (µg chlorpyrifos) recovered was the response variable, the total runoff volume was a covariate, and three factors were day (1-4), row pair (19 pairs designated a-s, nested within day), and treatment (PAM and no-PAM control nested within day) (Table 4).

Effect of PAM

The diagnostic plots for ANCOVA (Figure 11) demonstrate normality of the residuals and their variance is independent of log µg chlorpyrifos in runoff, supporting the use of log transformation. In contrast, preliminary analysis of the untransformed chlorpyrifos data demonstrated severe nonnormality of residuals and a marked dependence of residuals on chlorpyrifos concentration.

Figure 11. Diagnostic plots for ANCOVA.



There was no significant effect of PAM on offsite movement of chlorpyrifos (p=0.80, Table 5). This means that there is insufficient evidence to reject the null hypothesis that PAM had no effect on chlorpyrifos movement off-site. A second interesting result of the analysis is the lack of any significant effect due to day (p=0.62). Delaying post- application irrigations has been suggested as a potential mitigation measure for off-site movement of chlorpyrifos in irrigation tailwater. Based on data here, such delays are unlikely to be effective in reducing chlorpyrifos movement off-site in furrow-irrigated soils.

Table 5. Analysis of Variance for log (µg chlorpyrifos), using adjusted SS for tests

Source	**DF**	**Seq SS**	**Adj SS**	**Adj MS**	**F**	**P**
Liters (runoff)	1	0.18882	0.04895	0.04895	1.99	0.181
day	3	0.04667	0.04456	0.01485	0.60	0.624
row pair (day)	15	0.58139	0.57335	0.03822	1.55	0.209
Treatment (day)	4	0.04049	0.04049	0.01012	0.41	0.798
Error	14	0.34495	0.34495	0.02464		
Total	37	1.20233				

Discussion

A fallow field was chosen for this experiment to represent a worst-case scenario, with 100% of the applied chlorpyrifos reaching the soil surface to create a situation with the highest potential for runoff. Starting irrigation soon after the application further develops the worst-case scenario.

The average mass of chlorpyrifos in runoff from each irrigation event was a small fraction (~ 0.07% of the entire furrow + bed application) of the total chlorpyrifos applied to the field. Levels of chlorpyrifos in edge-of-field runoff averaged 2.5 μg/L for control rows (range 0.6 μg/L to 13.2 μg/L) and averaged 2.2 μg/L for PAM-treated rows (range 1.76 μg/L to 16.0 μg/L). These levels are very high when compared to the acute and chronic water quality criteria for chlorpyrifos: 0.025 μg/L and 0.015 μg/L, respectively.

PAM was very effective in reducing sediment runoff based on visual observation. PAM causes soil particles to aggregate and thereby reduce soil particle movement off-site. Reduced movement of soil particles is quite evident *in vitro* (Figure 12) and from observations of irrigation water *in situ* (Figure 13). For pesticides of low water solubility and with a correspondingly high propensity to bind to soil particles, one would expect to see a decrease in the amount of those pesticides moving off-site from fields treated with PAM due to the lack of sediment movement. However, for pesticides like chlorpyrifos (which is moderately water soluble and has only a moderate tendency to bind to soil) the presence or absence of PAM in irrigation water would not be expected to dramatically reduce chlorpyrifos offsite movement under typical conditions (e.g., appendix 1). Our experiment supports this conclusion, with no significant difference in the mass of chlorpyrifos detected in runoff water from PAM-treated rows or control (nonPAM-treated) rows.

With respect to onset of irrigation, there was no measurable effect on chlorpyrifos movement off-site due to irrigation delay (1.5 versus 5.5 days) (Figure 9). Thus, delaying the onset of irrigation does not appear to be an effective means for slowing chlorpyrifos movement from similar low vegetation or bare ground-type scenarios. This result is consistent with results of Gill (2007), who found that delaying the onset of irrigation up to four days following application had no effect on subsequent runoff of chlorpyrifos.

Figure 12. Sample bottles with runoff water. PAM-treated water (left) control water (right).

Figure 13. Irrigation water in situ showing immediate effect of PAM on suspended sediment in irrigation water. Control furrow (left) with the PAM-treated furrow (right).

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Appendix 1. Estimating Dissolved versus Sediment-bound **Chlorpyrifos**

The purpose of this exercise is to estimate the fraction of chlorpyrifos associated with sediment in "typical" California runoff water, assumed here to be runoff containing 1 g L^{-1} suspended sediment and 1% organic carbon in that suspended sediment. The fraction of chlorpyrifos associated with sediment in runoff is estimated using simple equilibrium sorption assumptions (Spurlock et al., 2005).

The fraction chlorpyrifos dissolved in runoff at equilibrium is:

$$\frac{C_{dissolved}}{C_{total}} = \frac{1}{(1+[0.001\times f_{oc}\times\rho\times K_{oc}])}$$

where:

$C_{dissolved}$ = dissolved concentration (i.e. not associated with sediment, μg L^{-1})
C_{total} = total concentration in runoff (dissolved + sediment adsorbed, μg L^{-1})
f_{oc} = fraction organic carbon of sediment [g OC (g sediment)$^{-1}$]
ρ = sediment concentration in runoff (g L^{-1})
K_{OC} = organic carbon normalized soil partition coefficient, L (Kg OC)$^{-1}$]

Then, in the typical runoff water:

$f_{oc} = 0.01$
$\rho = 1$ g sediment L^{-1}
chlorpyrifos $K_{OC} = 6925$ (Footprint, European pesticide properties database, <http://www.herts.ac.uk/aeru/footprint/)>.

the dissolved fraction = $C_{dissolved}/C_{total} \approx 0.94$.

Thus, in this scenario using sediment concentration and percent organic carbon typical of California tailwater, 94% of the total chlorpyrifos is dissolved in water, and remaining 6% is bound to sediment. Since only a small fraction of the total chlorpyrifos is associated with sediment, this example suggests that removing sediment from runoff via the addition of PAM would provide only minor reductions in the offsite movement of chlorpyrifos.

Attachment: Quality Assurance /Quality Control Data

Numerous samples were collected for quality control purposes. These samples included: duplicate field samples, irrigation source water samples, funnel rinse blanks, sampling equipment rinse blanks, field blanks, and blind matrix spikes.

Duplicate Field Samples

Results of chlorpyrifos detections in duplicate samples are presented in Table 1. A total of nine duplicate samples were analyzed, and the difference in analytical results for these duplicate sample sets ranged from 0.87 to 1.27 ug/L. These results of the duplicate samples are within the 50-150% range of the nominal sample as required by the Quality Assurance Project Plan.

Table 1: QA/QC Data: Duplicate Samples

Date	Sample #	Chlorpyrifos (ug/L)	Difference[†]
16/August/2006	2300[‡]	5.38	0.98
	2301	5.50	
	2500[‡]	5.90	0.95
	2501	6.24	
	2700[‡]	5.80	1.27
	2701	4.56	
	3000[‡]	5.88	1.05
	3001	5.60	
17/August/2006	3100[‡]	5.20	0.87
	3101	6.00	
	3300[‡]	5.20	0.93
	3301	5.60	
	3500[‡]	9.8	1.09
	3501	9.0	
	3700[‡]	5.00	0.96
	3701	5.20	
	3900[‡]	7.20	0.92
	3901	7.80	

[†] Difference represented as the chlorpyrifos concentration in duplicate sample (XX00 sample) divided by the chlorpyrifos concentration in "nominal sample" (XX01 sample).

[‡] Sample designated as the duplicate sample.

Irrigation Source Water– Headwater Samples

Concentrations of chlorpyrifos in three headwater samples are shown in Table 2. Chlorpyrifos was detected at the reporting limit (0.020 ug/L) in one sample. Estimated residues are shown for two other samples as the detected concentration was below the reporting limit of 0.020 ug/L.

Table 2: QA/QC Data: Irrigation Source Water – Headwater Samples.

Date	Sample #	Chlorpyrifos (ug/L)†
17/August/2006	1711	0.017†
17/August/2006	1811	0.020
17/August/2006	1911	0.018†

† Estimated residue below the reporting limit (0.020 ug/L)

Funnel Rinse Blanks.

Results for analyses of rinse blanks for funnel rinses are presented in Table 3. Funnels were used on days 2 through 4 of the study to facilitate equitable splitting of samples into primary and backup. Chlorpyrifos residues were detected in all funnel rinse blanks with concentrations of chlorpyrifos ranging from 0.021 ug/L to 0.058 ug/L. The impact of cross contamination of samples occurring at levels reported in rinse blanks was minimal: The highest amount of chlorpyrifos in funnel rinse blanks was 0.058 ug/l, which was approximately 3% of the lowest reported concentration of chlorpyrifos (1.80 ug/L in sample 2609) detected, the concentration in any funnel-split sample.

Table 3: QA/QC Data: Funnel Rinse Blanks

Date	Sample #	Chlorpyrifos (ug/L)
16/August/2006	2400	0.023
16/August/2006	2800	0.058
16/August/2006	2900	0.047
17/August/2006	3111	0.021
17/August/2006	3811	0.050

Sampling Equipment Rinse Blanks

Following each day's sampling, all sampling equipment (except buckets) was triple rinsed with clear well water and dried overnight. Sample buckets were not rinsed as new buckets were used daily. On August 18, 2006 (18 hours post rinse following April 17, 2006 sampling event), approximately 50 gallons of clear tap water was run through each sampling apparatus and collected in 1-gallon bottles per field practice. Collecting the samples 18 hours following rinse approximated field collection practices. Each bottle was split into primary and backup samples per field practice.

No chlorpyrifos was detected in any sample from rinsed field equipment (Table 4). In the field, equipment was rinsed at approximately 15:00 each day, and the initial samples the subsequent day were collected about 10:00 (approximately 20 hours post-rinse).

Table 4: QA/QC Data: Sampling Equipment Rinse Blanks.

Date	Sample #	Chlorpyrifos (ug/L)
18/August/2006	4501	ND†
18/August/2006	4503	ND
18/August/2006	4505	ND
18/August/2006	4507	ND
18/August/2006	4509	ND
18/August/2006	4601	ND
18/August/2006	4603	ND
18/August/2006	4605	ND
18/August/2006	4607	ND
18/August/2006	4609	ND

† ND = Not Detected in samples.

Field Blanks

Field blanks were collected in the following manner: Deionized water from 5-gallon bottles was used fieldside to rinse equipment. Periodically during splitting of samples and rinsing of funnels, a field blank was collected from this deionized rinse water. Chlorpyrifos was not detected in any field blank collected Table 5.

Table 5: QA/QC Data: Field Blanks.

Date	Sample #	Chlorpyrifos (ug/L)
17/August/2006	3411	ND†
17/August/2006	3511	ND
17/August/2006	3611	ND

† ND = Not Detected in samples.

Blind Matrix Spikes

Table 6 shows the results of blind spike analysis. Blind matrix spikes were made by the California Department of Fish and Game, Office of Spill Prevention and Response's Water Pollution Control Laboratory (WPCL) with a chlorpyrifos standard containing 86.6% chlorpyrifos. Recoveries are based on comparison with ultra pure chlorpyrifos analytical standard containing >99.9% chlorpyrifos. Values presented in "Recovery" (and "% Recovery" are actual data based on WPCL chlorpyrifos standard. "Actual recovery" and "% Actual Recovery" are values corrected to account for the 13.4% disparity in WPCL standards as compared to the high-purity analytical standard. In all cases, the % actual recovery exceeds minimum values required by the QAPP.

Table 6: QA/QC Data: Blind Matrix Spikes

Sample #	Spiked amount (ug/L)	Recovery (ug/L)	% Recovery	Actual Recovery (ug/L)†	% Actual Recovery
1611	5	3.9	78.0	4.50	90.1
1612	10	9.0	90.0	10.4	104
1707	25	19.4	77.6	22.4	89.6
1709	10	8.40	84.0	9.70	97.0
1710	25	20.6	82.4	23.8	95.2
3400	50	40.0	80.0	46.2	92.4
3800	100	68.0	68.0	78.5	78.5
3200	5	3.4	68.0	3.93	78.5
4000	15	11.0	73.3	12.7	84.7
3600	30	22.0	73.3	25.4	84.7
		mean	**77.5**	**mean**	**89.5**

† Recovery based on Ultra Scientific Chlorpyrifos Std (100ppm in MeOH) used to prepare the blind water spikes (86.6% Chlorpyrifos based on WPCL stds) (see Note).

Note: The Ultra Scientific Dursban (chlorpyrifos) standard was analyzed using WPCL chlorpyrifos standard purchased from Accustandard (100 ppm in hexane; lot number B3120050).

Surrogate Effects

Prior to analysis, the surrogate triphenyl-phosphate was added to every field and QA/QC sample at a concentration of 0.20 µg/L. The mean recovery of the surrogate in field samples was 106.6% with a standard deviation of 8.4%. Triphenyl-phosphate recoveries ranged from 84.2% to 125%. The mean recovery of the surrogate in lab samples was 100.4% with a standard deviation of 7.2% and a range of 79.2% to 115%. These results indicate that there was minimal effect of water source (matrix effects) and analysis procedures on triphenyl-phosphate recovery.