Mitigation Strategies for Reducing Aquatic Toxicity from Chlorpyrifos in Cole Crop Irrigation Runoff

Final Report for DPR contracts 13-C0027 and 14-C0012

Prepared by:
Bryn Phillips, Brian Anderson, Michael Cahn,
Jennifer Voorhees, Katie Siegler, and Ron Tjeerdema

University of California, Davis
Department of Environmental Toxicology
Marine Pollution Studies Laboratory
34500 Coast Route One, Granite Canyon
Monterey, CA 93940

Submitted to:

Robert Budd

California Department of Pesticide Regulation

Date submitted: January 27, 2016

Introduction

Pesticide use continues to be a primary tool for increasing crop yields in intensive industrial scale agriculture operations in central California's Salinas Valley. This is one of the most productive agriculture regions in the United States and produces much of the country's lettuce, cauliflower, asparagus, and broccoli. Pesticides associated with irrigation runoff continue to impact central California streams and rivers, and many of the region's watersheds are listed as degraded due to surface water toxicity (Central Coast Regional Water Quality Control Board, 2011).

Chlorpyrifos is one of several organophosphate (OP) pesticides responsible for surface water toxicity in central California coastal watersheds. Use of chlorpyrifos to control root maggots ensures increased crop productivity for central coast broccoli growers, and there are currently no viable alternative pesticides for control of this pest. Traditional integrated pest management (IPM) strategies are not adequately effective in meeting the goals of maintaining broccoli crop productivity and reducing chlorpyrifos in runoff. It is likely that an integrated approach of improving procedures to reduce pesticide loading in broccoli runoff, combined with treating residual chlorpyrifos before it enters receiving waters is the most practical approach to addressing pest control and water quality objectives. California's Central Coast Regional Water Quality Control has set a chlorpyrifos target of 25 ng/L to reflect the Criterion Maximum Concentration developed by the California Department of Fish and Wildlife (Siepmann and Finlayson, 2000).

Research has demonstrated that vegetative treatment systems reduce pesticide loads in tailwater runoff (Bennet et al., 2005; Moore et al., 2008; Vymazal and Bfezinova, 2015). While these systems reduce pesticides, vegetation alone is only partially effective for OPs. Integrated vegetated treatment systems consisting of multiple treatment areas or installations can provide additional pesticide reduction, and the use of the Landguard™ enzyme can remove residual OP concentrations (Anderson et al., 2011; Phillips et al., 2012). Landguard is effective, but is not currently available to growers, and its future availability is uncertain.

Alternative mitigation practices are therefore needed to reach water quality goals for OP pesticides. In the current study, installations consisting of compost and granulated activated carbon (GAC) were tested individually and as part of an integrated system with vegetation to reduce chlorpyrifos loading. Compost mats have shown promise as a pesticide removal treatment option in previous studies (OMIT, 2009). Preliminary trials conducted in Salinas during 2011 indicated that compost mats spaced at 15 meter intervals in a ditch could reduce chlorpyrifos concentration in run-off by 40% over a distance of 75 meters (M. Cahn, unpublished data). Activated carbon filtration is commonly used in industrial applications as a method to remove organic compounds from wastewater and has been suggested for surface water treatment (Pryor et al., 1999; Kalmykova et al., 2014).

An on-going issue constraining widespread implementation of vegetated treatment systems has been the perception that vegetated drainage ditches provide habitat for organisms that may contain pathogens. These species could serve as pathogen vectors to adjacent fields. While the magnitude of this threat is the subject of on-going research at the Western Center for Food Safety - wcfs.ucdavis.edu

(Gorski et al., 2011; Atwill et al., 2015), the perception among produce buyers and farm auditors is that food safety takes precedence over surface water quality. Until conclusive evidence dispels the threat of pathogen vectors in vegetated ditches, widespread use of vegetated treatment systems may be limited. Another alternative is the use of recycled plastics as a replacement for vegetation. Organic chemicals preferentially bind to discarded plastic waste in the environment (Rochman et al., 2012), and the sorptive capacity of polyethylene plastic is the characteristic behind their use in environmental monitoring (e.g., semi-permeable membrane devices). There are also concerns over food web contamination through consumption of discarded plastic waste in the environment by biota. These characteristics suggest that certain plastics may present useful alternatives to vegetation in runoff treatment systems as they are unlikely to provide the same habitat refugia as plant systems.

The goal of this project was to refine an integrated treatment approach to reduce chlorpyrifos loads and associated toxicity in irrigation runoff. We evaluated several practices to reduce chlorpyrifos in tailwater, with the final goal of reducing concentrations to below the regulatory threshold (<25 ng/L). Individual trials of chlorpyrifos-dosed irrigation water were treated with a vegetated ditch, compost mats, and GAC filtration. Each of these treatments were conducted individually in three replicate trials, and were compared to three replicate trials of a no-treatment control (bare ditch). Replicate trials were also conducted to determine the effectiveness of an integrated system comprised of a vegetated ditch with compost and GAC installations. Additionally, laboratory experiments were conducted with two forms of recycled low density polyethylene plastic to determine proof of concept before replicate field trials were conducted with chlorpyrifos-dosed irrigation water.

Methods

Individual and Integrated Treatments

All field trials were conducted at the USDA-ARS Spence research farm, in Salinas CA. Year 1 field trials were conducted between December 2013 and January 2014. Trials were conducted on parallel vegetated and bare ditches of 550 meter lengths and a slope of approximately 3%. The vegetated ditch was constructed in 2010 and has a semi-V-shaped cross-section of 5 meters in width at the top, and one meter in depth. The ditch was seeded with a combination of native grass species, including red fescue, tufted hair grass, bent grass, and june grass. A bare ditch of 2 meters in width and one-half meter in depth was established adjacent to the vegetated ditch before beginning the trials. All treatment evaluations were replicated three times. The bare ditch was divided into individual plots of 90 meter lengths and randomly assigned treatments of 1) bare, 2) bare ditch with compost mats, and 3) bare ditch with GAC filters. The vegetated ditch was also divided into 90 meter length plots where simulated runoff events were conducted. Five compost mats were constructed from 2 meter long permeable geo-textile sleeves (Filtrexx®, Grafton, OH) filled with compost from a local supplier, and secured to the bed of the bare ditch, perpendicular to the water flow direction at approximately 15 meter intervals using wooden stakes. Activated charcoal filters consisted of 6 two-meter Filtrexx SafteySoxx® sleeves filled with approximately 30 liters of AC830 of GAC (Siemens Corp., Oakland, CA) and placed in the bare ditch in pairs between the sampling points. Sleeves were anchored with wire stakes on the upstream edge. During the trials, the GAC sleeves were each fronted on the downstream side with a section of 2.5 meter long pine board. The boards were dug into the two sides and bottom of the channel to minimize water bypassing and undercutting the carbon sleeves. These boards also which provided vertical support to maximize water contact time with the carbon (Figure 1).

During Year 1, each plot was subjected to three-hour simulated runoff events at a target flow of 1.9 L/s. Randomized replicate trials were conducted using simulated runoff containing chlorpyrifos dosed at a target concentration of 3,300 ng/L. Runoff was simulated using ground water mixed with suspended sediment. Chlorpyrifos stock solutions were prepared fresh for every trial by adding certified stock solution (Accustandard, New Haven CT), to a known volume of Nanopure™ water. A metering pump provided a consistent volume of stock solution to the runoff water before entering the inlet of the ditch. Stock solution was delivered at 50 mL/minute to the flow of simulated irrigation water. The water inflow flow rate was monitored with a digital meter and this rate was used to quantify total volume of runoff water applied to the inlet of the ditch. Water at the outlet of the ditch flowed through a weir and then through a digital flow meter to record the volume of runoff exiting the ditch. Flow meters were interfaced with data loggers to record flow at 5 minute intervals. Automated samplers located at the input and at 23, 45, and 68 meters below the input of the ditch collected subsamples of runoff into stainless steel containers at 5 minute intervals (Figure 2).

Year 2 integrated trials were conducted between October 2014 and December 2014, and consisted of the GAC and compost treatments integrated with the vegetated ditch (Figure 2). Five compost filters and six carbon filters were installed as described above in 152 meter sections of the vegetated ditch. The integrated system was evaluated at two higher flow rates that represented more typical off-field discharge, 3.2 L/s and 6.3L/s. The target chlorpyrifos dose was approximately 2,600 ng/L. The flow rates and target chlorpyrifos concentrations used in the Year 1 and 2 trials were within the ranges previously measured in local irrigation runoff (Anderson et al., 2011; Phillips et al., 2012).

Composite samples of the runoff water from both sets of trials were transferred into amber glass bottles at the end of the runoff event and maintained at 4°C for toxicity and chemical analyses. Composite samples were analyzed for total suspended solids (TSS) and chlorpyrifos using enzyme-linked immunosorbent assays (ELISA, Strategic Diagnostics Inc., Newark, DE). Six ELISA concentrations were confirmed with GC/MS (EPA Method 8141). The ELISA method detection limit was 50 ng/L and the reporting limit was 100 ng/L. All analytical blanks were non-detect. External standard recoveries for the ELISA method ranged from 93% to 133%, and ELISA duplicates had relative percent differences between 0% and 19%. Recovery of GC/MS laboratory control standards ranged from 99.2% to 105%. Relative percent differences between the ELISA and GC/MS methods ranged from 0.2% to 33%.

Water column toxicity was evaluated in composite samples from the inlet (pre-treatment) and outlet (post-treatment) of each trial using 96-hour *Ceriodaphnia dubia* toxicity tests (U.S. EPA, 2002). Tests were conducted in five replicate 20 mL glass scintillation vials, each containing 15 mL of test solution and five organisms. Test solutions were fed daily with a combination of algae and YCT (yeast, cerophyll and trout chow mixture) two hours prior to renewal. Daily survival was recorded. Dissolved oxygen, pH, and conductivity were measured with an Accumet meter and appropriate electrodes (Fisher Scientific, Pittsburgh, PA). Un-ionized ammonia was measured using a Hach 2010 spectrophotometer (Hach, Loveland, CO). Water temperature was recorded with a continuous recording thermometer (Onset Computer Corporation, Pocasset, MA). Additional daily temperatures were measured using a glass spirit thermometer. Toxicity data was analyzed using the test for significant toxicity (TST) to determine statistically significant toxicity (U.S. EPA, 2010).

Figure 1. Examples of the Year 1 treatments on the USDA Spence Road farm. Clockwise from top left: bare ditch, compost sleeve, granulated activated carbon sleeves, and vegetated ditch.

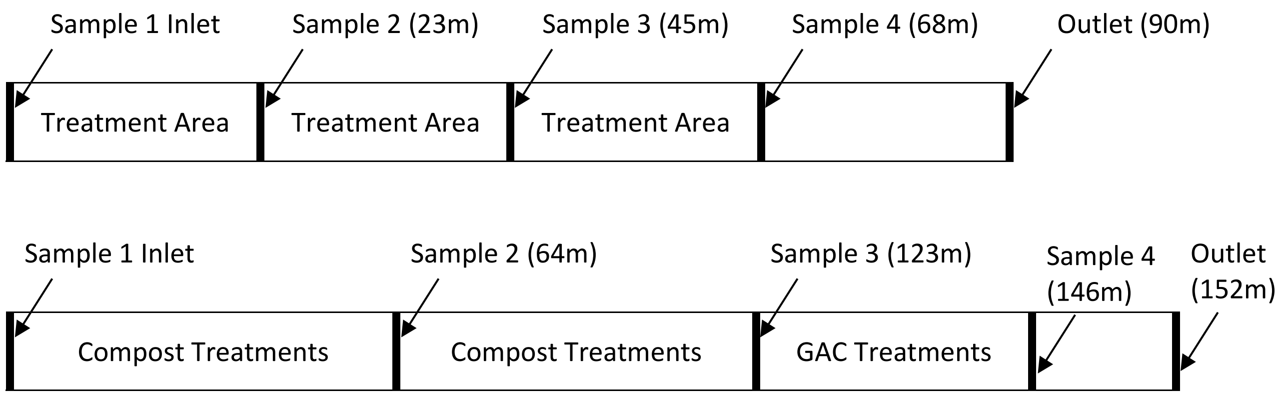

Figure 2. Top: Schematic of Year 1 ditch system (90 meter length, not to scale). Treatment areas contained either compost or GAC installations. There were no treatments during the bare ditch trials, and during the vegetated trials the entire ditch contained vegetation. Bottom: Schematic of Year 2 ditch system (152 meter length, not to scale). Entire ditch was vegetated. Compost and GAC installations were as shown.

Plastics Trials – Laboratory and Field

The efficacy of recycled low density polyethylene plastic for removing pesticides from irrigation runoff was evaluated using laboratory and field experiments. Plastic was evaluated as a possible alternative to vegetation. A series of laboratory trials were conducted with each of two types of recycled plastic: shredded low density polyethylene (LDPE) and polyethylene plastic pellets. Plastic materials were supplied by Encore Plastics (http://encore-recycling.com/company/), an agriculture plastics recycling company based in Salinas, California. The shredded LDPE came from berry hoop houses and had been subjected to water rinsing and spin drying as part of the recycling process. The LDPE pellets were the final product of the recycling process and were formed by heating the recycled plastic material to 500 °F, prior to extrusion into pellets.

Preliminary tests determined whether either of the recycled plastic materials released toxic chemicals into the water. For these trials, clean dilution water was pumped through polycarbonate food containers (approximately 700 mL) loosely packed with either pellets or shredded plastic. Containers were fitted with three horizontal PVC plastic baffles to force water up and down through the entire volume of the containers. Flow rates were controlled with a digital peristaltic pump adjusted to a bench scale flow rate of 136 ml/min. This flow rate was comparable to the 30 gal/min rate used in the Year 1 field trials. Water was pumped through the recycled plastic for 180 minutes and a composite sample consisting of water collected at the initiation of the trial (Time 0), and at 30, 90, and 180 minutes was assessed for residual toxicity. Toxicity was assessed using toxicity tests with the cladoceran *Ceriodaphnia dubia* and the amphipod *Hyalella azteca* (U.S. EPA, 2002). These two test species were used because of their variable sensitivities to OP and pyrethroid pesticides. *Ceriodaphnia dubia* tests were conducted as described above. Amphipod exposures were conducted in five replicate 300 mL beakers containing 100 mL of test solution and ten organisms. Amphipods were fed YCT at 48 hours, two hours prior to renewal. Daily survival was recorded, and water quality was measured as described above.

After experiments confirmed plastic treated water was not toxic to standard test organisms, the sorptive capacity of each type of plastic was assessed with spiked chlorpyrifos and bifenthrin in mixture. The target spiking concentration for chlorpyrifos was 3000 ng/L and the target concentration for bifenthrin was 500 ng/L. Pesticide mixtures were pumped through containers of loosely packed material as described above, and removal rates were determined using ELISA (chlorpyrifos) and confirmed with GC/MS (bifenthrin and chlorpyrifos). Samples were collected for toxicity testing and chemical analyses at 30, 90 and 180 minutes of the simulated treatment.

Based on the results of the laboratory trials, three replicate field trials with the LDPE plastic pellets were conducted with chlorpyrifos to compare the relative effectiveness of vegetated and plastic treatment systems to reduce pesticide loading. Pellets were loaded into Filtrexx SafteySoxx sleeves in the same manner as the GAC, and staked to the bottom of the bare dirt ditch. Trials were conducted in Year 2, but utilized the same ditch length and design described above for Year 1.

Results

Year 1 – Individual Treatments

Concentrations of chlorpyrifos in the input varied considerably among the trials (Table 1). Although the target concentration was approximately 3300 ng/L, the concentrations measured in the composite samples from the input ranged from 858 to 2840 ng/L. Stock solutions were prepared in a consistent manner, and made fresh for every trial. The only input that was variable was the particle load that was introduced to the irrigation water to simulate suspended sediments in actual furrow runoff. Particle load was generated by injecting highly turbid water from an adjacent irrigation ditch. The turbid water was injected with a gasoline powered water pump. The variable TSS concentrations had a significant relationship with the variable chlorpyrifos concentrations, and may be due to binding of chlorpyrifos by suspended sediments (Table 1).

Chlorpyrifos concentrations from each subsequent composite sample after the initial measurement showed steady declines in all treatments but the bare ditch, and the GAC and the vegetated ditch were the most effective at removing chlorpyrifos from runoff. The average reduction in chlorpyrifos concentration between the inlet and outlet of the bare ditch, GAC, compost, and vegetation treatments was 16%, 95%, 18%, and 82%, respectively (Table 1). The average reductions in the bare ditch and compost trials reflect the fact that no reduction was observed in one of the three trials for each these treatments.

Runoff infiltration also varied depending on the treatment. The greatest infiltration was observed using the GAC and compost. Average infiltration was 73% and 67% for GAC and compost, respectively (Table

1). Greater infiltration using these treatments reflected the fact that runoff flow slowed as water was dammed behind the GAC and compost Filtrexx installations. Average infiltration in the bare ditch and vegetated ditch trials was 31% and 48%, respectively. Infiltration was also influenced by the condition of the ditch. Greater infiltration was observed when the trials were initiated with a dry ditch. This will be an important consideration for on-farm applications because some ditches are likely to be wet at all times depending on the irrigation schedule.

The combination of increased infiltration and chlorpyrifos removal resulted in average load reductions of 44%, 99%, 77% and 90% in bare ditch, GAC, compost and vegetation, respectively. Carbon had the highest rates of chlorpyrifos reduction and infiltration, and therefore the highest rate of load reduction. The average infiltration rate for the vegetated treatment was less than 50%, but because of the high rate of chlorpyrifos reduction, the overall load reduction was only 9% less than the load reduction of GAC. Although compost had a low rate of chlorpyrifos reduction, the treatment had the second best infiltration rate which resulted in the third highest load reduction.

The highest average reduction of TSS occurred in the vegetated ditch treatment. This resulted as the water slowed during its passage through the grass. The bare ditch treatment reduced TSS by as much as 64%, but in one trial increased the TSS by 84%. This marked increase was likely caused by loose dirt suspended as water flowed through the ditch.

All toxicity tests met the test acceptability criterion of 90% or greater survival in the control treatments, and all toxicity test water quality parameters were within acceptable limits defined in the test protocols. Complete mortality was observed in all input samples, and in all but one of the output samples. Carbon was the only treatment that reduced chlorpyrifos below reporting limits for ELISA (<100 ng/L), and in one trial GAC reduced chlorpyrifos to a non-toxic concentration.

Table 1. Chlorpyrifos concentrations, total suspended solids concentrations (TSS), and percent *C. dubia* survival in composite samples from replicate trials comparing effectiveness of compost, carbon and vegetated treatments to bare ditch treatment. ELISA analyses conducted 24-48 hours after sample collection. Bold values are below the ELISA reporting limit but above the detection limit. Shaded cells indicate a significant reduction in toxicity.

	Bare Ditch			Carbon			Compost			Vegetated		
Composite	1	2	3	1	2	3	1	2	3	1	2	3
Chlorpyrifos ELISA (ng/L)												
Sample 1 Input	858	1352	1204	2840	1340	1148	1516	1006	1534	2720	1828	1612
Sample 2	857	1064	1086	1020	884	539	1368	938	1572	1916	848	868
Sample 3	803	1040	1178	240	354	193	1308	1178	1422	1368	562	510
Sample 4	956	940	868	**92**	**59**	**69**	792	1236	1110	524	244	358
Percent Change	11	-30	-28	-97	-96	-94	-48	23	-28	-81	-87	-78
TSS (mg/L)												
Sample 1 Input	1460	968	788	386	1110	546	1090	725	1160	440	565	690
Sample 4	524	1780	379	439	451	754	596	655	515	58	240	131
Percent Change	-64	84	-52	14	-59	38	-45	-10	-56	-87	-58	-81
Toxicity (% Survival)												
Sample 1 Input	0	0	0	0	0	0	0	0	0	0	0	0
Sample 4	0	0	0	96	0	0	0	0	0	0	0	0
Control	96	92	96	100	92	100	96	100	96	100	96	100
Average Reduction	16%			95%			18%			82%		
Average Infiltration	31%			73%			67%			48%		
Average Load Reduction	44%			99%			77%			90%		

Year 2 – Integrated Treatments

Compost and GAC treatments were installed in the vegetated ditch to create an integrated treatment system for the second year of the study. The evaluated treatment areas of the integrated system were over twice as long as those of the individual trials conducted in Year 1, and the input rates were 1.6 and 3.3 times greater. Input concentrations of chlorpyrifos were generally lower than those of the individual trials (Table 2), and ranged from 282 ng/L to 973 ng/L. The input chlorpyrifos concentrations did not have a significant relationship with the input TSS concentrations, as in the Year 1 trials, but there were similar coefficients of variation among the different flow rates. The cause of the variability is unknown.

Greater average chlorpyrifos reduction was observed at the 3.2 L/s flow rate (Table 2). Chlorpyrifos was reduced from an average of about 750 ng/L to less than detection (<50 ng/L) in two of three trials at 3.2 L/s, and to less than the reporting limit (<100 ng/L) in the third trial. At the higher flow rate chlorpyrifos was reduced from an average of 707 ng/L to less than 100 ng/L in all three trials. When infiltration rates were taken into consideration, the average load reduction was 98% and 94% for 3.2 L/s and 6.3 L/s flow rates, respectively.

All Year 2 toxicity tests also met the test acceptability criteria, and water quality parameters were within acceptable. Complete mortality was also observed in all Year 2 input samples (untreated), but two of the 3.2 L/s outlet samples, and one of the 6.3 L/s outlet samples were not toxic (Table 2). These samples also had the three lowest output concentrations of chlorpyrifos.

Table 2. Chlorpyrifos concentrations, total suspended solids concentrations, and percent survival of *C. dubia* in composite samples from replicate trials evaluating the effectiveness of the integrated ditch treatments at two flow rates (3.2 L/s and 6.3 L/s). Bold values are below the ELISA reporting limit but above the detection limit. Shaded cells indicate a significant reduction in toxicity.

	3.2 Liters/second			6.3 Liters/second		
Composite	1	2	3	1	2	3
Chlorpyrifos ELISA (ng/L)						
Sample 1 Inlet	638	738	879	282	973	966
Sample 2	168	118	649	197	696	404
Sample 3	**50**	**51**	281	**65**	213	162
Sample 4	ND	ND	**78**	**52**	**82**	**58**
Percent Change	-100	-100	-91	-82	-92	-94
TSS (mg/L)						
Sample 1 Inlet	422	588	448	238	218	258
Sample 4	46	66	176	40	52	31
Percent Change	-89	-89	-61	-83	-76	-88
Toxicity (% Survival)						
Sample 1 Inlet	0	0	0	0	0	0
Sample 4	96	100	0	100	0	4
Control	96	100	100	96	100	100
Average Reduction	97%			89%		
Average Infiltration	52%			43%		
Average Load Reduction	98%			94%		

Plastic Laboratory and Field Trials

Clean laboratory water was filtered through a scaled-down benchtop treatment system containing either shredded or pelletized low density polyethylene plastic. Water passing through the system throughout the three-hour simulated treatment remained non-toxic to *C. dubia and H. azteca*, demonstrating that both types of plastic did not impart contaminants and toxicity to the water. The benchtop experiments were repeated with laboratory water spiked with chlorpyrifos and bifenthrin to determine proof of concept for treatment of pesticides using recycled plastic. The inlet concentration for chlorpyrifos was approximately 1,600 ng/L and the inlet concentration for bifenthrin was approximately 200 ng/L. Results were similar between shredded and pelletized plastic for reduction of chlorpyrifos (75% and 77%, respectively), but shredded plastic reduced bifenthrin concentrations to a greater extent (64% vs. 55% for pelletized plastic, Table 3). Both plastic types reduced both pesticides consistently throughout the three-hour simulation, but neither plastic reduced the pesticides below toxic concentrations. Complete mortality was immediately observed in all *C. dubia* tests, but some survival was observed in the *H. azteca* tests (Table 3).

Table 3. Percent survival of *C. dubia* and *H. azteca*, pesticide concentration, and percent reduction in benchtop plastic trial. Data presented for timed intervals.

	C. dubia	*H. azteca*	Chlorpyrifos		Bifenthrin	
	% Survival	% Survival	ng/L	% Reduction	ng/L	% Reduction
Initial	0	0	1605	NA	197	NA
Pellets						
30 Minutes	0	0	405	75	83.4	58
90 Minutes	0	0	351	78	95.8	51
180 Minutes	0	8	354	78	87.7	55
Shredded						
30 Minutes	0	0	366	77	60.7	69
90 Minutes	0	0	333	79	76.8	61
180 Minutes	0	0	483	70	77.3	61
Control	92	100	NA	NA	NA	NA

Field trials were conducted with pelletized plastic because there was no difference between the plastic types for chlorpyrifos reduction in the laboratory experiment, and the pelletized plastic was easier to install in the field and available at the time of the trials. Although three replicate trials were conducted using plastic installations in a bare ditch, each installation was constructed differently. The first two trials mimicked the GAC installation, where pairs of plastic-filled Filtrexx sleeves were placed between each composite sample station. The first trial utilized plastic sleeves staked behind short riser boards, as with the GAC. There was a steady decline in the concentration of chlorpyrifos as the water passed through the plastic, and the final reduction was 42% (Table 4). The second trial attempted to increase the flow of water through the plastic by draping the sleeves over the riser boards, but water still bypassed the sleeves and percent reduction of chlorpyrifos was much lower at only 25%.

The design was altered for the third trial to increase pesticide sorption by maximizing contact time with the pellets. Eighteen plastic sleeves were placed in sequence between sampling stations 3 and 4. This installation created a "bed" of plastic that was more similar to a short section of the vegetated ditch. This installation method reduced the concentration of chlorpyrifos by 60%, but the percentage infiltration was only 9%, compared to 62% and 29% for the first and second plastic trials, respectively. Note that the first two trials were conducted when the ditch was relatively dry, resulting in greater infiltration.

Table 4. Chlorpyrifos concentrations, percent survival of *C. dubia*, and average chlorpyrifos reduction, infiltration and load reduction in composite samples from individual trials evaluating the effectiveness of plastic treatments.

Composite	Plastic Trials 1	2	3
Chlorpyrifos ELISA (ng/L)			
Sample 1 Input	1017	1059	1062
Sample 2	904	1040	906
Sample 3	774	868	1012
Sample 4	594	792	423
Percent Change	-42	-25	-60
Toxicity (% Survival)			
Sample 1 Input	0	0	0
Sample 4	0	0	0
Control	96	100	100
Average Reduction	42%		
Average Infiltration	33%		
Average Load Reduction	63%		

Discussion

The advantages and limitations of on-farm vegetated treatment systems have been widely reported (Hunt et al., 2007; Moore et al., 2008; Kroger et al., 2009; Anderson et al., 2011; Moore et al., 2014; Vymazal and Bfezinova, 2015). While vegetated treatment systems almost always reduce chemical loads to some extent, vegetation alone can be limited depending on treatment system design and the characteristics of the chemicals being treated. Although vegetated systems increase hydraulic and chemical residence time (Kroger et al., 2009), more soluble OP pesticides are less likely to be removed by vegetation alone. Moore et al. (2014) evaluated vegetated wetland buffers and determined that the presence of vegetation did nothing to improve the removal of the organophosphate diazinon, but concentrations of the pyrethroid permethrin were reduced by 84%. Similarly, Anderson et al. (2011) demonstrated that a sedimentation section coupled with a length of ditch vegetated with pennywort and grasses significantly reduced organochlorine and pyrethroid pesticides, but a final enzyme treatment was necessary to treat chlorpyrifos and diazinon. When correctly designed, these systems are more effective at removing hydrophobic pesticides and less effective at removing more soluble pesticides, such as the most common OPs.

Anderson et al. (2011) demonstrated that treatment with Landguard enzyme was effective at removing residual concentrations of diazinon and chlorpyrifos when used as a final step in an integrated ditch system. Because the Landguard enzyme is currently not commercially available (Phillips et al., 2015), the current project was designed to evaluate alternative polishing treatments that could be combined with vegetation. The effectiveness of compost, GAC, and vegetation were evaluated as stand-alone treatments by measuring load reduction. This combines pesticide loss through sorption to plant surfaces and sediments as well as infiltration. The current vegetated system alone reduced the chlorpyrifos concentrations by an average of 82% in the Year 1 trials, and while average infiltration was only 48%, the final load reduction was 90%. Since vegetation cover is expected to be 100% and flow rates and infiltration can be variable depending on irrigation patterns, pesticide removal can likely be increased by extending the vegetated ditch length The parameters of the current vegetated system have been submitted to Xuyang Zhang (California Department of Pesticide Regulation) for application to the Vegetated Filter System modeling program (VFSMOD). Modeling should allow us to calculate the optimum ditch length to maximize pesticide removal.

In comparison, the bare ditch (control) reduced the concentration of chlorpyrifos by 16%, had an average infiltration of 31%, and reduced the load of chlorpyrifos by 44%. The addition of compost treatments to the bare ditch reduced pesticide concentrations by an additional two percent. The compost sleeves acted as a dam which forced pooling of the runoff and reduced pesticide load by a total of 77% through increased infiltration. The GAC sleeves also caused pooling, and infiltration with this treatment was increased by the same amount as the compost. In addition, the carbon was more permeable and the active sorption of pesticide with this material was more effective at removing chlorpyrifos. Pesticide concentrations were reduced by an average of 95% and the GAC installation reduced chlorpyrifos load by an average of 99%.

The Year 2 integrated trials combined compost, GAC, and vegetation. These trials were conducted in longer ditch sections and evaluated treatments at two flow rates higher than the Year 1 trials. Infiltration rates in the integrated trials were similar to those of the individual vegetated trials, indicating that the addition of the compost and GAC sleeves did not increase infiltration. In addition, runoff residence time was expected to increase using longer vegetated ditch lengths, but this was likely offset by the higher flow rates. Load reductions among the integrated trials and the individual GAC trials steadily decreased in relation to flow rate. In individual trials at 1.9 L/s, the GAC reduced the highest input concentration of chlorpyrifos to non-toxic levels, and had an average load reduction of 99%. The integrated trials conducted at 3.2 L/s reduced load by 98% and the 6.3 L/s trials reduced load by 94%. It should be noted that input concentrations for the integrated trials were on average 50% lower than the input concentrations from the individual trials.

Total suspended solids varied among the individual treatments, but was consistently reduced in the individual vegetated trials and the integrated trials (58-89% reduction). Input TSS concentrations for all trials with vegetation varied from about 200-700 mg/L, which were comparable to previous studies of actual agricultural runoff in this region (Anderson et al., 2011; Phillips et al., 2012). Vegetated and integrated trials did not completely remove TSS, but significant reduction of suspended particles has been shown to also reduce loading of particle-associated hydrophobic chemicals, such as pyrethroids (Anderson et al., 2011; Phillips et al., 2012). This study did not evaluate the effectiveness of pre-treatment sedimentation traps, but ponds and sedimentation zones incorporated upstream of integrated treatment ditches have proven to be effective at reducing TSS and would likely extend the operational lifespan of any treatment system by preventing sedimentation of vegetation, and reducing clogging of compost and granulated activated carbon sleeves.

Granulated activated carbon shows the most promise for treating agricultural runoff containing chlorpyrifos and meeting this pesticide's regulatory target of 25 ng/L. This was the only treatment to reduce chlorpyrifos concentrations below toxic levels, and chlorpyrifos concentrations were reduced below detection limit in two of the low flow integrated trials. We were not able to definitively determine if chlorpyrifos concentrations were below the 25 ng/L target because the method detection limit for the ELISAs was 50 ng/L. Future evaluations should confirm low output concentrations with GC/MS methods that have adequately low method detection limits.

The cost of installing and maintaining these treatments are a concern for growers, and in some cases need to be further investigated. The vegetated ditch evaluated in this study was approximately 550 meters long and 5 meters wide (total area = 0.27 hectare). Including grading, seeding, irrigation and maintenance, the final cost to create the ditch was approximately $10,100, or approximately $37,500 per hectare of ditch area. The vegetated ditch requires some yearly maintenance, but at minimal cost to a grower. As suggested above, inclusion of a sedimentation basin upstream of the vegetation will reduce clogging and prolong the sorption capacity of the plant material. The rolls of Filtrexx mesh material used in this project were donated by Filtrexx, but are available commercially for approximately $100 per 40 meter roll. Compost was obtained gratis from the local landfill.

New GAC was purchased for $2 per pound. Total cost of providing two 55 gallon drums of A380 GAC (400 lbs. total GAC) and disposing of the drums of used/contaminated carbon was estimated to be $500 (Siemens-Evoqua Water Technologies). The effective operational life of A380 GAC for removing pesticides from real-world runoff depends on several factors, including pesticide loads, pesticide mixtures, and particle loads in run-off. The current integrated design assumes GAC will be used as a final polishing step to prolong carbon life. Carbon effectiveness over time should be the subject of future modeling exercises and field trials. The Evoqua representative who consulted on this project also discussed the option of using recycled GAC from municipal drinking water treatment systems. This form of activated carbon will likely perform similarly to A380 for pesticide sorption, and is available at half the cost if purchased in bulk. This option could be explored if more wide-spread use of GAC is being considered for treatment of irrigation water in the Salinas Valley. Future work should also evaluate biochar as a potential alternative to GAC. Depending on the source, biochar is less costly to obtain and might not require disposal as hazardous waste if it can be used as a soil amendment after use (Smernik, 2006).

The efficacy of recycled plastics in irrigation runoff treatment was evaluated in this project because of ongoing food safety concerns in the Salinas Valley (Gorski et al., 2011). There is concern that vegetated ditches may provide habitat to rodents and amphibians which may convey pathogens to adjacent fields. A primary benefit of this approach is that plastics are unlikely to provide the same habitat refugia to pathogen vectors as plant systems. In addition, thousands of tons of waste plastic are generated by the California agriculture industry yearly and these materials are now being recycled for other industrial applications. Laboratory bench-scale trials demonstrated greater than 70% removal of chlorpyrifos by recycled low density polyethylene plastic, and subsequent field trials showed up to 60% removal of chlorpyrifos in simulated run-off with an average of 63% load reduction. These reductions were lower than the individual vegetated trial results of 82% chlorpyrifos reduction and 90% load reduction, but the results from the plastic trials cannot be directly comparable to the current vegetated trials because much less ditch length was treated in the plastic trials (8m in plastic vs. 90m in vegetated). The results suggest that once the field design is optimized, use of an inexpensive and readily available recycled plastic resource can be applied as a replacement material in farm runoff treatment systems to circumvent food safety concerns. After use, it is anticipated the plastic used in the treatment system can be returned to the recycling facility for reintegration into the recycling recovery process, or get recycled through other means. Thus, this material may provide an effective and inexpensive treatment alternative to vegetation while generating no waste.

Conclusions

These experiments demonstrated that a 150m grass-lined ditch combined with compost and granulated activated carbon treatments reduced loading of chlorpyrifos by 98% at a flow rate of 3.2 L/sec and by 94% at a flow rate of 6.3 L/sec. Given that chlorpyrifos is a moderately soluble pesticide, we anticipate greater load reductions could be achieved with less soluble pesticides using the same system (e.g., organochlorine and pyrethroids pesticides). The effectiveness of this system to treat more soluble pesticides is uncertain. Given the increased use of highly soluble neonicotinoid pesticides such as imidacloprid, treatment of this class of pesticide should be confirmed in future studies. In addition, effectiveness of the integrated vegetated system described in this study should be confirmed in replicate trials under real-world runoff conditions. This would allow system evaluation using irrigation runoff events containing mixture of pesticides, herbicides, nutrients, and particulates. Additional studies should also include further design and evaluation of recycled plastics as an alternate treatment method.

References

Anderson, B.S., Phillips, B.M., Hunt, J.W., Largay, B., Shihadeh, R., Berretti, M., 2011. Pesticide and toxicity reduction using an integrated vegetated treatment system. Environ Toxicol Chem, 1036-1043.

Atwill, E.R., Chase, J.A., Oryang, D., Bond, R.F., Koike, S.T., Cahn, M.D., Anderson, M., Mokhtari, A., Dennis, S., 2015. Transfer of Escherichia coliO157:H7 from simulated wildlife scat onto Romaine lettuce during foliar irrigation. J. Food Prot. 78, 240-247.

Bennet, E.R., Moore, M.T., Cooper, C.M., Smith, S., Shields, F.D., Drouillard, K.G., Shulz, R., 2005. Vegetated Agricultural Drainage Ditches for the Mitigation of Pyrethroid-associated runoff. Environ Toxicol Chem 24, 2121-2127.

Central Coast Regional Water Quality Control Board, 2011. Total Maximum Daily Loads for Chlorpyrifos and Diazinon in Lower Salinas River Watershed in Monterey County, California. California Environmental Protection Agency and California Regional Water Quality Control Board Central Coast Region. Final Project Report For the May 4-5, 2011 Water Board Meeting.

Gorski, L., Parker, C.T., Liang, A., Cooley, M.B., Jay-Russell, M.T., Gordus, A.G., Atwill, E.R., Mandrell, R.E., 2011. Prevalence, Distribution, and Diversity of Salmonella enterica in a Major Produce Region of California. Applied and Environmental Microbiology 77, 2734-2748.

Hunt, J.W., Anderson, B.S., Phillips, B.M., Largay, B., 2007. Effectiveness of Agricultural Management Practices in Reducing Concentrations of Pesticides Associated with Toxicity to Aquatic Organisms: Data Summary and Final Report. California Water Quality Control Board, Central Coast Region.

Kalmykova, Y., Moona, N., Stromvall, A.-M., Bjorklund, K., 2014. Sorption and degradation of petroleum hydrocarbons, polycyclic aromatic hydrocarbons, alkylphenols, bisphenol A and phthalates in landfill leachate using sand, activated carbon and peat filters. Water Research 56, 246-257.

Kroger, R., Moore, M.T., Locke, M.A., Cullum, R.F., Steinriede, R.W., Jr., Testa, S., III, Bryant, C.T., Cooper, C.M., 2009. Evaluating the influence of wetland vegetation on chemical residence time in Mississippi Delta drainage ditches. Agricultural Water Management 96, 1175-1179.

Moore, M.T., Denton, D.L., Cooper, C.M., Wrysinski, J., Miller, J.L., Reece, K., Crane, D., Robins, P., 2008. Mitigation Assessment of Vegetated Drainage Ditches for Collecting Irrigation Runoff. J Environ Qual 37, 486-493.

Moore, M.T., Kroeger, R., Locke, M.A., Lizotte, R.E., Jr., Testa, S., III, Cooper, C.M., 2014. Diazinon and Permethrin Mitigation Across a Grass-Wetland Buffer. Bull. Environ. Contam. Toxicol. 93, 574-579.

OMIT, 2009. Ontario Ministry of Transportation. Compost Biofilters for Highway Stormwater Runoff Treatment. Ministry of Transportation, Provincial Highways Management Division Report Highway Infrastructure Innovation Funding Program. p. 103.

Phillips, B.M., Anderson, B.S., Siegler, K., Voorhees, J.P., Tjeerdema, R.S., 2012. Optimization of an Integrated Vegetated Treatment System Incorporating Landguard A900 Enzyme: Reduction of Water Toxicity Caused by Organophosphate and Pyrethroid Pesticides. Final Report. Resource Conservation District of Monterey County and the United States Department of Agriculture Natural Resources Conservation Service and The California Department of Pesticide Regulation. http://www.cdpr.ca.gov/docs/emon/surfwtr/contracts/ucdavis_09-C0079_final.pdf.

Phillips, B.M., Anderson, B.S., Voorhees, J.P., Siegler, C., Budd, R., Tjeerdema, R., 2015. The Effects of the Landguard™ A900 Enzyme on the Macroinvertebrate Community in the Salinas River, California, U.S.A. Arch Environ Contam Toxicol In Press.

Pryor, M.J., Nozaic, D., Freese, S.D., Rajagopaul, R., 1999. The use of granular activated carbon for the treatment of impounded surface water. Water Science and Technology 39, 197-200.

Rochman, C.M., Hoh, E., Hentschel, B., Teh, S., 2012. Discarded plastics and priority pollutants: A multiple stressor in marine habitats. Abstracts of Papers American Chemical Society, pp. 35-ENVR.

Siepmann, S., Finlayson, B.J., 2000. Water quality criteria for diazinon and chlorpyrifos. California Department of Fish & Game, Office of Spill Prevention and Response, Administrative Report 00-3.

Smernik, R.J., 2006. Biochar and Sorption of Organic Chemicals. in: Lehmann, J., Joseph, S. (Eds.). Biochar for Environmental Management. Earthscan, New York, pp. 289-300.

U.S. EPA, 2002. Methods for measuring acute toxicity of effluents and receiving water to freshwater and marine organisms. EPA-821-R-02-012. Office of Research and Development, Washington, D.C.

U.S. EPA, 2010. National Pollutant Discharge Elimination System Test of Significant Toxicity Technical Document. EPA 833-R-10-004. Office of Wastewater Management. Washington DC.

Vymazal, J., Bfezinova, T., 2015. The use of constructed wetlands for removal of pesticides from agricultural runoff and drainage: A review. Environment International 75, 11-20.