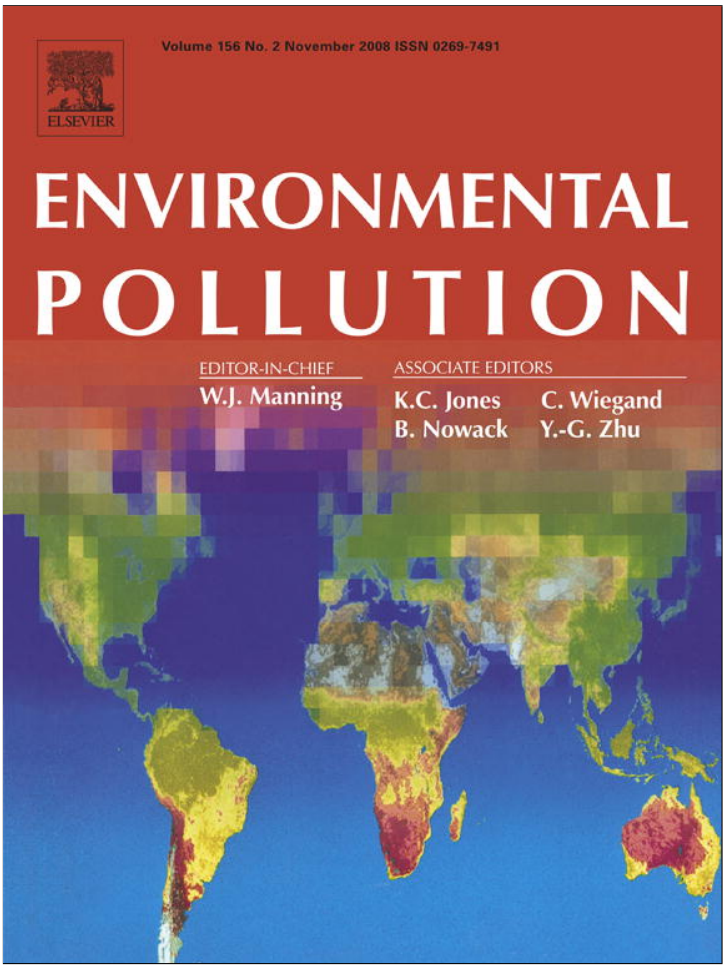

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Use of toxicity identification evaluations to determine the pesticide mitigation effectiveness of on-farm vegetated treatment systems

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Toxicity identification evaluations identified key pesticides in agricultural runoff, and their concentrations were reduced by farmer-installed vegetated treatment systems.

Abstract

Evidence of ecological impacts from pesticide runoff has prompted installation of vegetated treatment systems (VTS) along the central coast of California, USA. During five surveys of two on-farm VTS ponds, 88% of inlet and outlet water samples were toxic to *Ceriodaphnia dubia*. Toxicity identification evaluations (TIEs) indicated water toxicity was caused by diazinon at VTS-1, and chlorpyrifos at VTS-2. Diazinon levels in VTS-1 were variable, but high pulse inflow concentrations were reduced through dilution. At VTS-2, chlorpyrifos concentrations averaged 52% lower at the VTS outlet than at the inlet. Water concentrations of most other pesticides averaged 20–90% lower at VTS outlets. All VTS sediment samples were toxic to amphipods (*Hyalella azteca*). Sediment TIEs indicated toxicity was caused by cypermethrin and lambda-cyhalothrin at VTS-1, and chlorpyrifos and permethrin at VTS-2. As with water, sediment concentrations were lower at VTS outlets, indicating substantial reductions in farm runoff pesticide concentrations.

Keywords: Agricultural management practice; Pyrethroid pesticide; Organophosphate pesticide; Sediment TIE; Agricultural runoff

1. Introduction

Agricultural production currently utilizes over 12 million km^2 of the Earth's surface, and requires extensive commitments of labor and materials (FAO, 2007). Many costs of agriculture are external to farm operations, and accrue as losses in ecosystem services, including the beneficial uses of uncontaminated water. A variety of techniques are being evaluated worldwide to limit degradation of waterways from runoff of agricultural chemicals into aquatic habitats (Popov et al., 2006; Vu et al., 2006; Wang et al., 2005; Yates et al., 2007). In the USA, a number of studies have evaluated vegetated treatment systems (VTS), such as buffers, filter strips, ditches, ponds, and wetlands, to improve water quality (Dabney et al., 2006; Moore et al., 2006). Along the central coast of California, VTS are being installed by some of the 2500 operators who farm over 250 000 hectares year-round,

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producing nearly 200 different crops worth over $5 billion (CCRWQCB, 2004), while applying 7500 MT of pesticides annually (active ingredient; PAN, 2007).

Numerous studies have documented pesticide toxicity and ecological impacts in central coast streams (e.g., Anderson et al., 2003; CCAMP, 2007; Hunt et al., 1999; Phillips et al., 2006). An innovative regional program has been established to regulate non-point source pollution through adoption of conditional agricultural discharge permit waivers. Waiver conditions require farm water quality management plans, which often include installation of VTS to mitigate runoff of nutrients and pesticides (CCRWQCB, 2007). Many local farmers have installed VTS with assistance from the county Resource Conservation Districts and the National Resource Conservation Service. In this study, VTS built by growers were evaluated to provide feedback for system design and information for other growers considering VTS projects. Because this study evaluated VTS on working farms that receive intermittent runoff containing mixtures of unknown chemicals, it is distinct from previous studies that administered specific pesticides under controlled conditions into experimentally constructed VTS prototypes (e.g., Moore et al., 2001, 2006; Sherrard, 2004). For this reason, toxicity identification evaluations (TIEs) were employed here to identify chemicals most likely to cause biological impacts, so that VTS improvements could emphasize mitigation of these constituents. A number of advanced water and sediment TIE procedures were employed (e.g., Anderson et al., 2007; Wheelock et al., 2004).

We investigated two vegetated pond systems to evaluate their effectiveness in reducing concentrations of pesticides and nutrients. Both systems were originally constructed by the farm operators to retain sediment. Vegetation, primarily floating pennywort (*Hydrocotyle ranunculoides*), was established to provide shade and a carbon source for denitrification, as well as plant and microbial substrate for pesticide retention and breakdown. The fields draining to these VTS ponds have been treated with numerous pesticides, each potentially best mitigated by different VTS components that promote photolysis, hydrolysis, volatilization, sorption to plant surfaces, microbial metabolism, or deposition in sediments (Hapeman et al., 2003). To evaluate mitigation of these mixtures, this study employed a phased approach that began with toxicity testing of VTS inlets and outlets, followed by TIEs of water and sediment to identify chemicals of concern, and then chemical analysis to measure the differences in contaminant concentrations at the VTS inlets and outlets.

2. Methods

2.1. Vegetated treatment systems (VTS)

VTS-1 is a two-pond system vegetated with floating pennywort (*Hydrocotyle ranunculoides*), which formed a floating mat of roots and stems 0.5 to 1.0 m thick, with a typical biomass of 800 g/m^2. The primary inlet drained 50 hectares, and the secondary inlet drained 3.5 hectares of irrigated row crop vegetables. Water samples were collected just above the inlet (Fig. 1, A) and near the pond outlets (Fig. 1, B and C). Sediment samples were collected just above the inlet at A, and in the pond at C. VTS-2 is a single pond system vegetated with three aquatic plants: duckweed (*Lemna* sp.), watercress (*Nasturtium* sp.), and pennywort (*Hydrocotyle ranunculoides*), which formed a floating mat of roots and stems 0.01 to 1.0 m thick. The main inlet drained 35 hectares of greenhouse flower growing operations, and the secondary inputs drain three 1-hectare outdoor flower nursery areas. Water samples were collected just above the inlet (Fig. 2, A), and just below the outlet (Fig. 2, B). Sediment samples were collected in the input ditch at A, and in the pond immediately in front of the outlet culvert at B.

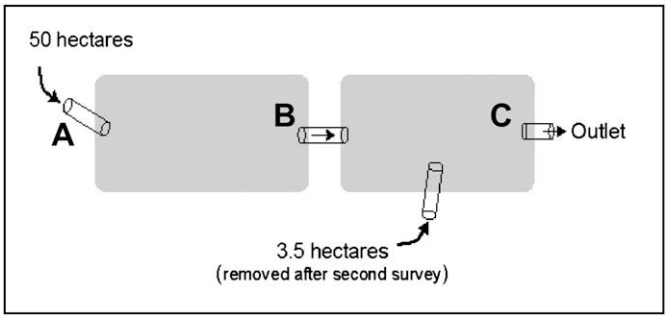

Fig. 1. Schematic diagram of ponds at VTS-1, with sampling stations A, B, and C. Upper pond is 27 m × 12 m × 1 m deep, and lower pond is 24 m × 12 m × 2 m deep.

To evaluate VTS effectiveness in reducing pesticide concentrations, water samples were collected at VTS inlets and outlets during five surveys, and sediment was collected once. Water samples at VTS inlets were collected as composites of three daily grab samples, while outflows were characterized by a single grab sample taken on the third day. This was done because parcels of water were presumed to channel through the ponds at rates faster than nominal residence times (Table 1). Compositing was selected as a means of obtaining an inlet sample that might be adequately compared to a day 3 outlet sample, in which constituent concentrations were "smeared" by mixing as the parcels passed through the ponds. Continuous sampling devices were not used because of the inconsistent pulsed nature of the runoff inflows. All sampling and analysis followed protocols and met objectives described by Puckett (2002). Details for all methods are given by Hunt et al. (2007).

Flow at the VTS-1 inlet was measured in an HS flume (Brakensiek et al., 1979), with an estimated error of less than 10%. Outflow at VTS-1 and inflow at VTS-2 were calculated from depth measured near the pipe inlets and rating curves developed using the broad crested weir equation and HEC-RAS 3.1.3 software (Brunner, 2002), with an estimated error of <25%.

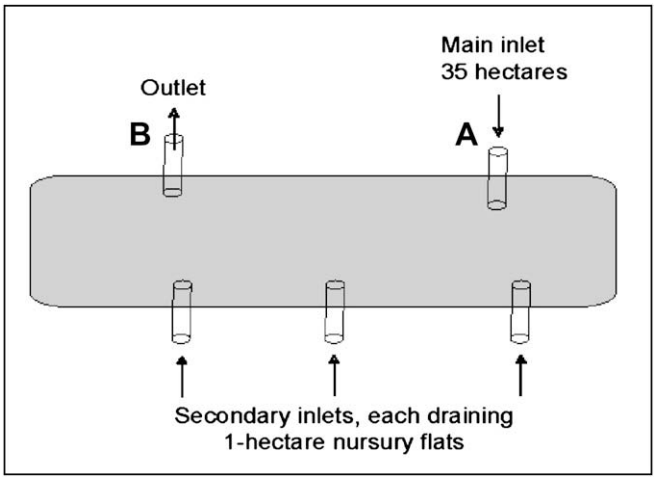

Fig. 2. Schematic diagram of pond at VTS-2, with sampling stations A and B. The pond is 70 m by 12 m × 1 to 2.5 m deep.

Table 1
Summary of hydrologic data for sites VTS-1 and VTS-2

	VTS-1	VTS-2
Production type	Row crops	Greenhouses
Drainage area (hectares)	50	35
Vegetated treatment system area including perimeter roads (hectares)	0.15	0.2
Vegetated treatment system volume (m^3)	640	1350
Mean flow rate (L/s)	1.0	6.8
Nominal residence time (volume/flow rate in days)	7.4	2.3

2.2. Toxicity testing and toxicity identification evaluation

Water toxicity was evaluated using the 7-day chronic test with the planktonic crustacean *Ceriodaphnia dubia* (USEPA, 2002). Sediment toxicity was assessed using the 10-day growth and survival test with the epibenthic amphipod *Hyalella azteca* (USEPA, 2000).

Toxicity identification evaluations (TIEs) were performed on water samples using *C. dubia*, and on sediment solid-phase and interstitial water samples using *H. azteca*. Each TIE manipulated the original sample (baseline) using specific treatments to increase, decrease, or transform the bioavailable chemical fractions of the sample to provide lines of evidence to identify constituents causing observed test organism mortality (USEPA, 1991, 1993). The following treatments were performed on a dilution series for both water and sediment interstitial water samples (0% (treatment blank), 10%, 25%, 50%, and 100%).

1. Centrifugation – to reduce toxicity associated with particulates, and as a pre-treatment for the solid-phase extraction columns.
2. Cation solid-phase extraction (SPE) column (Supelco Supelclean LC-WCX, 3 mL, St. Louis, MO, USA) – to remove cationic metals.
3. Cation column eluate – 1 N hydrochloric acid (HCl) passed through column to recover metals. The HCl was then added to 150 mL of clean water and neutralized for toxicity testing.
4. HLB column (Oasis Hydrophilic-Lipophilic Balance (HLB)®, 6 mL, 500 mg, Waters Corporation, Milford, MA, USA) – to remove non-polar organic chemicals.
5. HLB column eluate – methanol passed through the column to recover sorbed organics. The methanol was evaporated to 1.5 mL and added to 150 mL of clean water for toxicity testing.
6. Sequential cation and HLB SPE columns – used in sequence to determine if toxicity was caused by both metals and organics.
7. Sequential column eluate – each column was individually eluted, as above, to recover chemicals and toxicity.
8. Carboxylesterase enzyme (Sigma-Aldrich, St. Louis, MO) – added to hydrolyze pyrethroid pesticides and reduce their toxicity (Wheelock et al., 2004).
9. Bovine serum albumin (BSA, Sigma-Aldrich, St. Louis, MO) – added as a control for the carboxylesterase enzyme, to differentiate between carboxylesterase-specific pyrethroid hydrolysis and any general sequestration of contaminants by proteins (Wheelock et al., 2004).
10. Piperonyl butoxide (PBO, Sigma-Aldrich, St. Louis, MO) – added to the interstitial water to block metabolic transformation of organophosphate (OP) pesticides into the toxic oxon form, thus reducing their toxicity. PBO also synergizes pyrethroid toxicity (Kakko et al., 2000).
11. Carboxylesterase/PBO combination to resolve effects due to mixtures of OP and pyrethroid pesticides.

Treatment blanks were employed for all treatments, and consisted of control water that underwent the same manipulation as the sample.

For solid-phase sediment TIEs, a baseline sample was tested, and the following treatments were performed on undiluted solid-phase sediment (see Anderson et al., 2007 for complete methods):

1. Ambersorb 563® (Rohm and Haas, Spring House, PA, USA) – carbonaceous, non-polar resin added to sorb non-polar organic compounds from the sediment.
2. Ambersorb eluate – Ambersorb was sieved from the sediment at test termination, and eluted in a column with acetone. After evaporation and concentration, 1 mL of acetone was added to 100 mL of clean water for toxicity testing.
3. Powdered coconut charcoal (PCC; 90–96%, Calgon Carbon, Pittsburgh, PA, USA) – pyrolized, activated coconut husk ground to <45 μm. Like Ambersorb, PCC is added to sediment to sorb organics, but its greater surface area increases efficiency (Ho et al., 2004).
4. SIR-300 (ResinTech, West Berlin, NJ) – a macroporous weak acid cation exchange resin added to chelate heavy metal ions.
5. SIR-300 eluate – SIR-300 was sieved from the sediment, then eluted in a column with 1 N hydrochloric acid. One milliliter of acid was then combined with 100 mL of clean dilution water and neutralized for toxicity testing.

6–8. Carboxylesterase enzyme, BSA, and PBO were added to sediment overlying water as in the water treatments described above.

Each TIE included a dilution control, which consisted of 90% sample sediment and 10% control sediment (v:v). This control was used to measure any effects due to simple toxicant dilution arising from addition of treatment resins. Control sediment was equal parts reference site sediment and kiln-dried sand, with 0.75% added organic peat moss.

The magnitude of sample toxicity was characterized using toxic units (TU). A sample TU equals 100 divided by the LC_{50} calculated using mortality data from the sample dilution series. (LC_{50} is the median lethal concentration, at which test organism mortality is 50%.) To characterize the potential toxicity of individual chemicals measured in a sample, chemical specific TUs were calculated as the concentration of the chemical in the sample divided by that chemical's known LC_{50} value.

2.3. Chemical analysis

Water samples were analyzed by gas chromatography mass spectrometry (GCMS) using the following methods: organochlorines (USEPA, Method 8080), organophosphates (USEPA, Method 8140/8141), pyrethroids (USEPA, 8081BM). Chlorpyrifos and diazinon were also measured using enzyme-linked immunosorbent assays (ELISA, Strategic Diagnostics Inc, Newark, DE), following recommendations by Sullivan and Goh (2000). The following methods were used for sediment analysis: organochlorines (USEPA, Method 8081), organophosphates (USEPA, Method 8141), and pyrethroids (USEPA, Method 1660). All sediment concentrations are given in dry weight units, except when normalized to organic carbon, as indicated.

To describe differences in contaminant concentrations between VTS inflows (A) and outflows (B), the relative percent difference (RPD) was calculated as:

$$100\% \times \left(0 - \frac{[A] - [B]}{[A]}\right)$$

with negative results indicating a decrease. RPD values for water samples are presented as the average for the five surveys.

3. Results

3.1. VTS hydrology

Runoff flow rates and pond residence times were calculated to better interpret differences between inlet and outlet

pesticide concentrations. No rain events or stormwater runoff occurred during the study; discharge to the ponds consisted solely of irrigation runoff. Tile drainage was not used on either farm, and there was no evidence of groundwater seepage into the ponds.

The runoff hydrology on the two sites varied considerably. VTS-1 was characterized by highly variable inlet flow rates. Irrigation events typically lasted about 12 h, and runoff stopped within 4 h of the end of irrigation. Irrigation events occurred as frequently as three times in 4 days, and as infrequently as once in 5 days. Absent an irrigation event, no flow occurred. The mean flow rate measured during the study period (including periods of no flow) was 1.0 L/s (Table 1). VTS-2 was characterized by continuous and relatively consistent flow averaging 6.8 L/s.

3.2. VTS-1 water toxicity and chemistry

In all five surveys, samples from all three VTS-1 stations were highly toxic to *C. dubia* (100% mortality), with the exception of 80% survival at station A in the last survey. A TIE was conducted on the inlet sample from the fourth survey in which *C. dubia* mortality was 100% even when the sample was diluted to 10% strength. The TIE baseline sample contained >20 toxic units. ELISA measurements indicated 11.135 μg/L diazinon, or approximately 35 diazinon TUs (using a diazinon LC_{50} of 0.320 μg/L; Bailey et al., 1997). The TIE treatments also provided lines of evidence to identify cause. Removing particulates through centrifugation removed some of the diazinon, but none of the toxicity (Fig. 3). Passing the sample through an HLB column, which sorbs organics, removed the toxicity and all of the diazinon; and the HLB eluate returned the toxicity and 83% of the diazinon. The carboxylesterase enzyme did not reduce toxicity, nor did the addition of BSA, indicating that pyrethroids either did not contribute to toxicity or their contribution was overwhelmed by other chemicals. The addition of PBO individually and with carboxylesterase reduced toxicity to 2.7 and 2.9 TUs, respectively, indicating toxicity caused by an organophosphate pesticide. Subsequent GCMS chemical analysis confirmed the high diazinon concentration (9.620 μg/L), along with high concentrations of the OP pesticide dimethoate (8.400 μg/L), though this was much lower than the dimethoate LC_{50} (600 μg/L; Beusen and Neven, 1989).

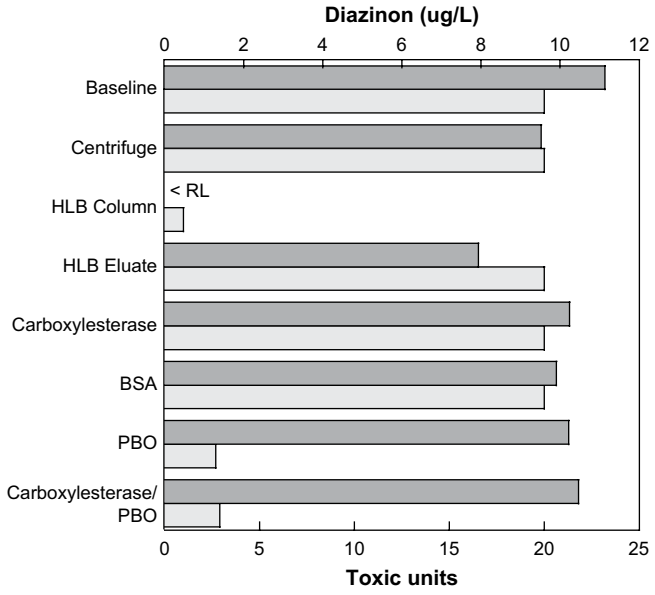

Fig. 3. Toxicity identification evaluation of a water sample from the VTS-1 inlet collected October 4. Dark bars are diazinon concentration, lighter bars are sample toxic units. Treatments are described in Section 2.2. <RL, less than reporting limit.

3.3. VTS-1 mechanism of diazinon reduction

Differences between inlet and outlet diazinon concentrations were variable (Fig. 4). During the fourth survey, however, the inlet concentration was markedly higher than the outlet concentration. To determine whether this reduction in diazinon concentration was the result of breakdown or dilution, the VTS-1 ponds were intensively sampled to develop a mixing model (Fig. 5). Diazinon concentrations were measured at the inlet and outlet twice daily for 2 weeks, while flow was measured continuously at the inlet flume using a recording water level logger.

The continuous flow record indicated a rapid response between inflow and outflow: the water levels in the ponds rose and fell rapidly, but the ponds retained 1–2 m of water between tailwater events. Simplified models of wet detention basins (discussed in Haan et al., 1994) assume that incoming water displaces resident water. This was not evident in the record of diazinon concentrations. During the intensive sampling period (October 19 to November 1), inflowing diazinon concentrations were consistently low, and concentrations at the outlet of the upper pond were also low while flow was occurring, but were higher during periods of no flow. This indicated that during quiescent conditions diazinon was entering the water column at the outlet of the upper pond. Mixing from backwater areas or from interstitial water among the plants may be the most likely source. Diazinon was not detected in bed sediment samples, but some diazinon may have desorbed into the water column from thin layers of recently deposited sediment.

Flow model simulations were superimposed on the continuous dataset collected at the end of October (Fig. 5),

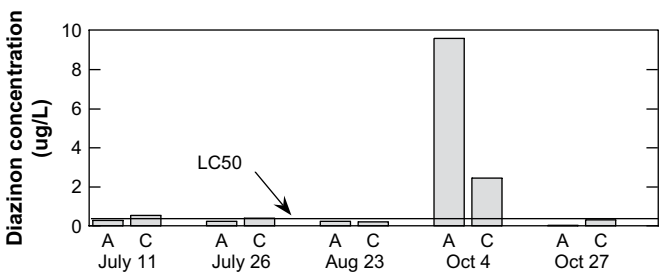

Fig. 4. Concentrations of diazinon measured by GCMS in water samples from VTS-1 stations A, at the system inlet, and C, at the system outlet. Line indicates the diazinon median lethal concentration (LC_{50}).

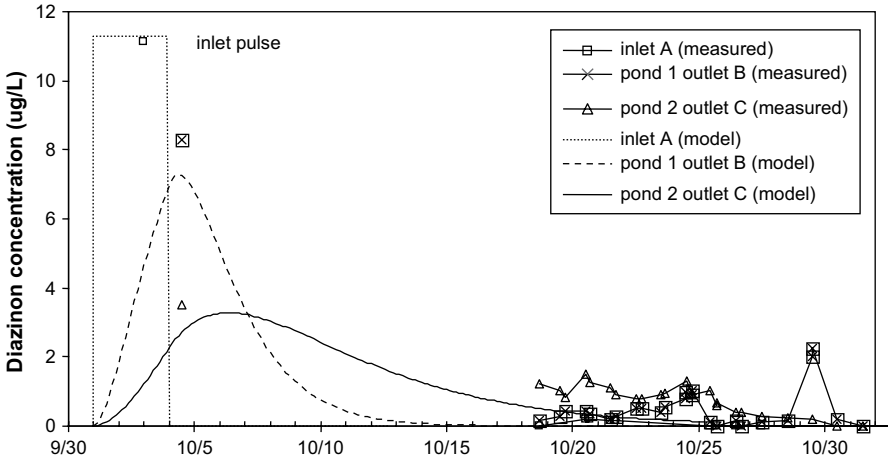

Fig. 5. VTS-1 diazinon concentrations from field measurements and as predicted by a hydraulic mixing model, assuming diazinon behavior as a non-reactive tracer (i.e., no degradation). Measured diazinon concentrations are indicated by the symbols, which are connected by "measured" curves for the 2-week intensive sampling period, lower right. Smooth curves indicate modeled concentrations at stations B and C, assuming the measured elevated diazinon inflow pulse, shown by the rectangular curve for the 3-day composite sample at the inlet A.

and illustrated the dominant effect of the October 4 spike on concentration data collected through the rest of the month. It is likely that the change in concentration between inlet and outlet was due primarily to in-pond dilution of the October 4 spike, despite other potential loading events and degradation of diazinon during this period. Diazinon photolysis half-lives in water are on the order of weeks to months at pH 7–9 (Novartis, 1997). It therefore appears that for this water soluble pesticide, the critical function of the pond was to serve as a reservoir to dilute peak inflow concentrations. Other treatment mechanisms likely apply to the more hydrophobic compounds discussed below.

3.4. Overall changes in water pesticide concentrations at VTS-1

Twenty-three synthetic organic pesticides were detected by GCMS analysis of VTS-1 water samples, including five organophosphates, three carbamates, four pyrethroids, and ten organochlorines (Hunt et al., 2007). Of these, only diazinon (9.620 μg/L) and *p′,p′*-DDT (0.094 μg/L) were measured above available LC_{50} values (Bailey et al., 1997; Phipps et al., 1995, respectively). While changes in diazinon concentrations were variable, other OP pesticides and carbamates (carbaryl and carbofuran) had lower average concentrations in the outlet samples than in the corresponding inlet samples (Fig. 6). The same was true for the organochlorines, which were generally found at low concentrations. The average difference in pyrethroids reflects generally low concentrations, including many non-detects at one station or the other that tended to skew the mean. In the one case in which a relative high pyrethroid concentration was measured (608 ng/L cypermethrin at the inlet), this compound was not detected at the outlet (Hunt et al., 2007). (Note that all pyrethroid concentrations are given here in units of ng/L.) Chlorpyrifos, diazinon, permethrin, dacthal, DDE(*p,p′*) and methomyl were detected in some outlet samples when not found in the corresponding inlet samples. Possible explanations for this include flux from pond sediments or variability in residence times for contaminants entering the ponds in pulse runoff events.

3.5. VTS-1 sediment toxicity and chemistry

Amphipod mortality was high in sediments collected from both VTS-1 stations (A and C), with 100% mortality at the inlet, and 72% mortality at the outlet. A sediment TIE was conducted on the inlet sample, and produced the following lines of evidence to identify the cause of toxicity. The addition of powdered coconut charcoal to the sediment decreased mortality to 50%, indicating toxicity was caused by a non-polar organic compound (Fig. 7). Addition of Ambersorb did not reduce toxicity, but the Ambersorb eluate caused 100% mortality, further supporting the implication of a non-polar organic. In separate treatments, the addition of carboxylesterase to the sediment overlying water reduced mortality to 22%, indicating toxicity caused by a pyrethroid.

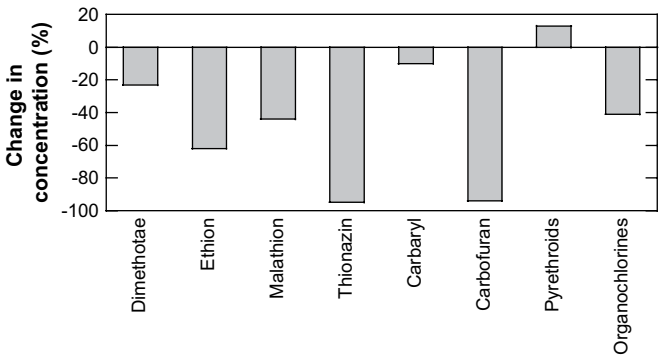

Fig. 6. Relative percent difference between VTS-1 inlet and outlet concentrations for all pesticide compounds or classes detected in water samples. Values are means for all surveys in which chemicals were detected. Negative values indicate lower outlet concentrations.

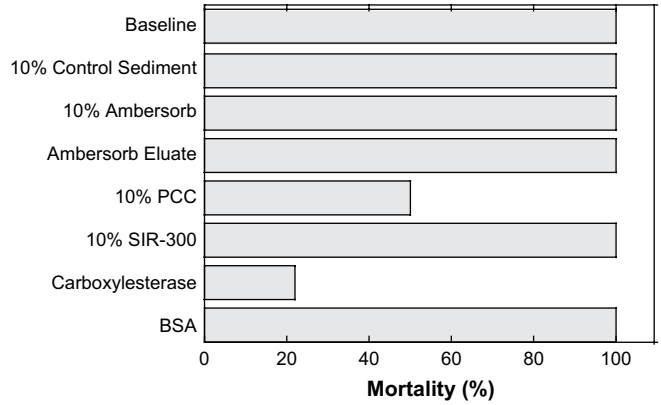

Fig. 7. Toxicity identification evaluation of the solid-phase sediment sample collected near the VTS-1 inlet. Treatments are described in Section 2.2.

In the corresponding interstitial water TIE, water extracted from VTS-1 sediment contained 6.3 TUs, but only 0.234 μg/L diazinon, well below the amphipod *H. azteca* LC_{50} of 6.210 μg/L (Phipps et al., 1995). The HLB column reduced toxicity to 2.4 TUs, and baseline toxicity was recovered in the HLB eluate (Fig. 8). Addition of the enzyme to the interstitial water removed nearly all toxicity, while the addition of BSA reduced toxicity by only 1.5 TUs. Addition of PBO, which synergizes pyrethroid toxicity, increased toxicity to 20 TUs, and the addition of carboxylesterase and PBO in combination reduced the toxicity to 3.5 TUs. These results provide strong evidence that toxicity was caused by a pyrethroid. Subsequent GCMS analysis measured 66.4 ng/g of the pyrethroid pesticide cypermethrin in the sediment. This dry weight value is equivalent to an organic carbon normalized concentration of 2800 ng/g OC, which is well above the LC_{50} of 400 ng/g OC (Maund et al., 2002). The pyrethroid pesticide lambda-cyhalothrin was also present at toxic concentrations in this sample: 18.8 ng/g dry weight, compared to an LC_{50} of 5.6 ng/g (Amweg et al., 2005), and an organic carbon normalized concentration of 0.79 ng/g OC, compared to an LC_{50} value of 0.45 ng/g OC.

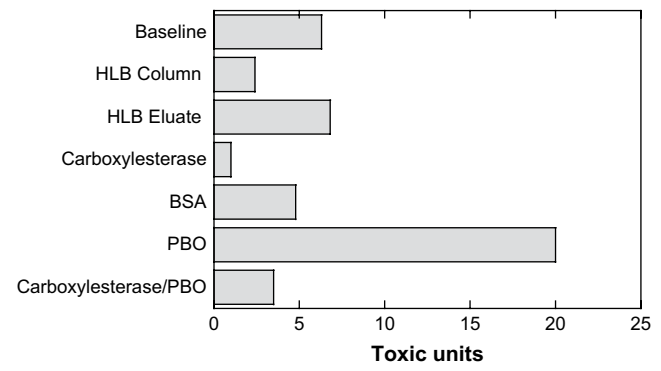

Fig. 8. Toxicity identification evaluation of interstitial water from the sediment sample collected near the VTS-1 inlet. Treatments are described in Section 2.2.

Trends in sediment chemical concentrations at VTS-1 were most pronounced for the pyrethroid pesticides. Cypermethrin and lambda-cyhalothrin, both implicated as causes of sediment toxicity, were measured at higher concentrations in sediments collected at the inlet than at the outlet. Cypermethrin was measured at 66.4 ng/g at the inlet, and was below the 2 ng/g detection limit at the outlet. Lambda-cyhalothrin was measured at 18.8 ng/g at the inlet and 5.75 ng/g at the outlet. There was little change in the already lower concentrations of other pyrethroids, and there was only a slight decrease in the total organic carbon concentration (2.37% inlet; 2.07% outlet). Organophosphate compounds were not detected in VTS-1 sediments, and organochlorine pesticide concentrations were generally low, with mixed trends between inlet and outlet. Total DDT declined from an inlet sediment concentration of 0.546 μg/g to an outlet concentration of 0.470 μg/g, perhaps reflecting ambient variability for this ubiquitous compound.

3.6. VTS-2 water toxicity and chemistry

Water samples collected from both VTS-2 stations in four of five surveys were significantly toxic to *C. dubia*. However, in the second survey, survival was 80% at both stations. A TIE was conducted on a water sample from the fourth survey, in which 100% mortality was observed. There were nearly 5 TUs and 0.238 μg/L chlorpyrifos in the baseline sample (Fig. 9). Toxicity was reduced by centrifugation, the cation column, and the HLB column. Chlorpyrifos was decreased to 0.168 μg/L by centrifugation, and to non-detectable levels by treatment with the cation and HLB columns. Nearly 2 TUs were returned in the HLB eluate, along with a detectable

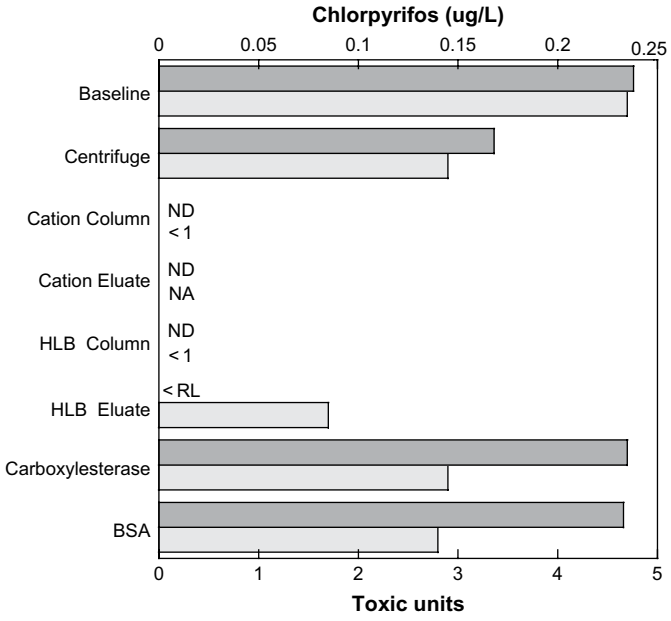

Fig. 9. Toxicity identification evaluation of a water sample from the VTS-2 inlet collected Oct 2. Dark bars are chlorpyrifos concentration, lighter bars are sample toxic units. Treatments are described in Section 2.2. ND, not detected; <RL, less than reporting limit; NA, not applicable due to blank toxicity.

level of chlorpyrifos (below reporting limit). Subsequent chemical analysis found that the chlorpyrifos concentration in this sample was 0.762 μg/L, about 14 times the *C. dubia* LC_{50} of 0.053 μg/L (Bailey et al., 1997). The carboxylesterase enzyme partially reduced toxicity in the TIE, but so did BSA, which controls for contaminant binding by proteins, providing no strong evidence to implicate pyrethroids.

Chlorpyrifos was measured at toxic concentrations in all VTS-2 water samples, but concentrations declined substantially from inlet to outlet in all five surveys (Fig. 10). The more water soluble OP diazinon, on the other hand, was consistently measured well below toxic concentrations, but differences between inlet and outlet concentrations were variable, and there was no indication that diazinon was reduced in VTS-2. All other pesticide compounds or classes had lower average concentrations at the VTS-2 outlet than at the inlet (Fig. 11). Chlorpyrifos, diazinon, dioxathion, and oxadiazon were the most frequently measured OP pesticides in the system. Pyrethroids and organochlorines were generally present in water at very low concentrations (Hunt et al., 2007). Methomyl was detected once at the outlet but not in the corresponding inlet sample.

3.7. VTS-2 sediment toxicity and chemistry

There was 100% amphipod mortality in both inlet and outlet VTS-2 sediment samples collected on October 27. Solid-phase and interstitial water TIEs were conducted on the inlet sample. None of the solid-phase treatments reduced toxicity, but the Ambersorb eluate was toxic, indicating sediment toxicity due to a non-polar organic chemical. No toxicity was observed in the SIR-300 eluate, indicating that toxicity was not due to metals. Sediment chemical analysis found chlorpyrifos at 11.258 μg/g, about 30 times greater than the published *H. azteca* LC_{50} of 0.399 μg/g (Brown et al., 1997). This concentration apparently overwhelmed the ability of solid-phase TIE treatments to reduce toxicity, but chlorpyrifos and toxicity were recovered through elution of the Ambersorb resin.

Interstitial water extracted from the VTS-2 sediment was highly toxic, with a sample LC_{50} of 5.4% (18.6 toxic units;

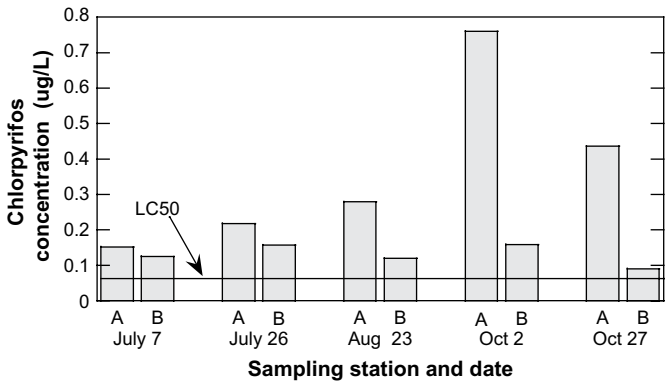

Fig. 10. Chlorpyrifos concentrations at the inlet A and outlet B of VTS-2. Line indicates the chlorpyrifos median lethal concentration (LC_{50}).

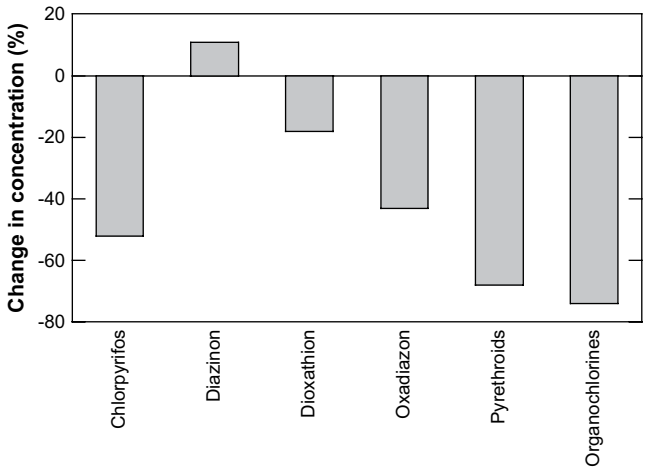

Fig. 11. Relative percent difference in concentration for all chemicals detected in water at both the inlet and outlet of VTS-2. Values are mean RPDs for all surveys in which chemicals were detected.

Fig. 12). Passing the sample through a cation column reduced the chlorpyrifos concentration to 0.105 μg/L, but only reduced the toxicity to 14.7 TU. The cation eluate did not return chlorpyrifos or toxicity, providing no evidence to implicate trace metals. The HLB column completely removed the chlorpyrifos but only reduced the toxicity to 16.4 TUs, indicating the presence of other toxic compounds. The HLB eluate returned toxicity and 95% of the chlorpyrifos. The sequential columns removed the toxicity, but toxicity was only recovered in the HLB eluate. Addition of the carboxylesterase enzyme reduced toxicity to 6 TUs, but did not reduce the chlorpyrifos concentration. This result implicates a pyrethroid pesticide as partially responsible for toxicity. The addition of BSA (a control for the enzyme treatment) did not reduce toxicity. The

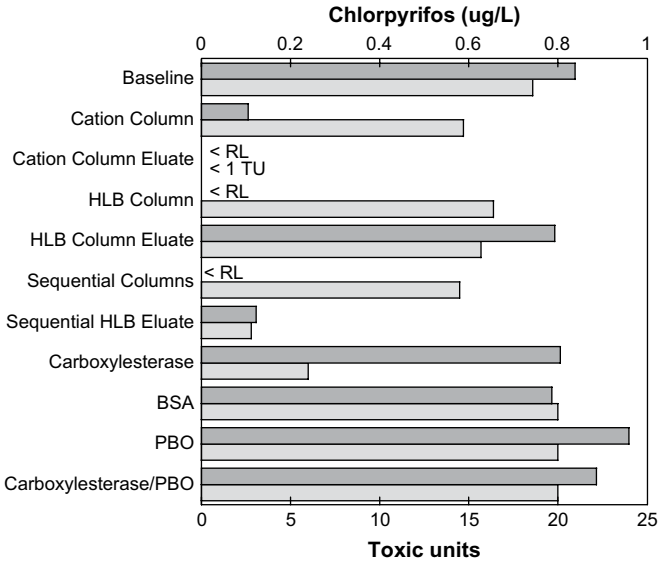

Fig. 12. Toxicity identification evaluation of interstitial water from the sediment sample collected near the VTS-2 inlet. Dark bars are chlorpyrifos concentration, lighter bars are toxic units. Treatments are described in Section 2.2. <RL, less than reporting limit. <1 TU, less than 1 toxic unit.

addition of PBO individually and in combination with the enzyme increased toxicity to the maximum measurable with this dilution series (>20 TU). Based on these lines of evidence, the probable cause of toxicity is a combination of chlorpyrifos and a pyrethroid. Chlorpyrifos was measured by ELISA in interstitial water at 0.839 μg/L. The interstitial water was not analyzed by GCMS, so concentrations of chemicals other than chlorpyrifos are not known. However, 2003 ng/g permethrin was measured in the solid-phase sediment, about 10 times the LC_{50} of 200 ng/g (Amweg et al., 2005). The TIE evidence implicates chlorpyrifos and permethrin as the toxic constituents in the VTS-2 sediment.

There were differences between the inlet and outlet sediment concentrations of a number of chemicals (Hunt et al., 2007). Chlorpyrifos was measured at 11.258 μg/g at the inlet and 2.199 μg/g at the outlet, an 80% reduction. Permethrin was also higher near the inlet (2003 ng/g) than the outlet (412 ng/g), as were diazinon (0.128 μg/g to 0.057.2 μg/g) and total organic carbon (6.96% to 2.48%). Most organochlorine pesticides had lower concentrations in the outlet sediment, but DDT was higher (0.304 μg/g inlet, 0.505 μg/g outlet), perhaps reflecting ambient variability of this ubiquitous compound. In general, it appears that most sediment-associated pesticides, including those responsible for toxicity, decreased in concentration in VTS-2.

3.8. Turbidity and nutrients

While pesticide treatment was the primary focus of this study, management practices are most useful when they address multiple water quality stressors, including nutrients and turbidity. Both nutrient concentrations and turbidity were lower at the VTS-1 outlet than at the inlet, while results at VTS-2 were more variable. Turbidity at the VTS-1 inlet consistently exceeded the instrument range of 1000 nephelometric turbidity units (NTU), and decreased markedly in the VTS. The average RPD for turbidity was −96% (using an input value of 1000; Table 2). The average total nitrate RPD was −34%, and the average total phosphate RPD was −86%. VTS-2 inflow turbidity averaged 40 NTU, with lower levels at the outlet in four of five surveys (Table 3). Differences in total nitrate concentration between VTS-2 inlet and outlet samples were variable, as were differences in total phosphate. This may be a result of the multiple inlets to the system, with only the main inlet measured, and with secondary inlets located closer to the outlet.

4. Discussion

Inflows to both VTS pond systems contained mixtures of numerous pesticides. At VTS-1, 15 pesticides were detected in water, including organophosphates (OPs), organochlorines (OCs), pyrethroids, and carbamates. Sediments from VTS-1 contained 14 OC and pyrethroid pesticides. Similarly, 23 pesticides were detected in water at VTS-2, and 15 OPs, OCs, and pyrethroids were detected in sediment (Hunt et al., 2007). While chemical concentrations can be matched with standards, guidelines, or literature LC_{50} values to estimate potential effects, the TIEs conducted in this study provided direct experimental evidence for the causes of toxicity, and helped to identify chemicals of concern for runoff mitigation.

Newer TIE techniques, including resin treatments of solid-phase sediment and addition of carboxylesterase, proved useful for toxicant identification, particularly for pyrethroid pesticides, which have been used increasingly over the past decade. Combining solid-phase and interstitial water TIEs provided complimentary lines of evidence, as in the case of the VTS-1 sediment sample. Addition of carboxylesterase to overlying

Table 2
Turbidity, total nitrate (as NO_3), and total phosphate (as PO_4) concentrations in water samples from the three VTS-1 stations, with relative percent differences (RPD) in concentrations between stations A (inlet) and C (outlet)

Date	Station	Turbidity (NTU)	Total nitrate (mg/L)	Total phosphate (mg/L)
7-Jul-06	A	>1000	25.6	8.61
	B	21.3	16.4	3.63
	C	6.5	18.3	3.35
	RPD (%)	−99	−29	−61
26-Jul-06	A	>1000	24.8	95.9
	B	38.5	17.4	5.58
	C	10.4	16.9	4
	RPD (%)	−99	−32	−96
23-Aug-06	A	>1000	32.4	73.6
	B	403	19.7	20.9
	C	159	20.4	11.9
	RPD (%)	−84	−37	−84
4-Oct-06	A	>1000	54.4	236
	B	310	42.2	19
	C	6.2	23.4	3.6
	RPD (%)	−99	−57	−98
27-Oct-06	A	>1000	30.6	48
	B	144	22.7	9.6
	C	18.4	25.5	3.4
	RPD (%)	−98	−17	−93
Mean RPD (%)		−96	−34	−86

Table 3
Turbidity, total nitrate (as NO_3), and total phosphate (as PO_4) concentrations in water samples from the two VTS-2 stations, with relative percent differences (RPD) in concentrations between stations A (inlet) and C (outlet)

Date	Station	Turbidity (NTU)	Total nitrate (mg/L)	Total phosphate (mg/L)
7-Jul-06	A	18.3	34	4.93
	B	3.4	45.2	8.73
	RPD (%)	−81	33	77
26-Jul-06	A	4.8	38.4	6.84
	B	5.6	50.6	10.48
	RPD (%)	17	32	53
23-Aug-06	A	7.4	22.6	6.9
	B	1.6	18.9	6.3
	RPD (%)	−78	−16	−9
2-Oct-06	A	157	51.2	26.2
	B	1.5	4.2	23.5
	RPD (%)	−99	−92	−10
27-Oct-06	A	13.8	56.4	17.9
	B	3.7	42.8	14.3
	RPD (%)	−73	−24	−20
Mean RPD (%)		−63	−14	18

water in the solid-phase TIE reduced toxicity, while addition of PBO to the interstitial water strongly increased toxicity, both providing strong complimentary evidence to implicate pyrethroids.

The findings of water toxicity due to diazinon and chlorpyrifos were consistent with previous results from agricultural watersheds on the central coast and elsewhere (e.g., Anderson et al., 2003; de Vlaming et al., 2000; Hunt et al., 2003; Schulz, 2004). Chlorpyrifos concentrations were consistently lower at the VTS-2 outlet (Fig. 10), indicating retention or breakdown in the pond. Chlorpyrifos is less water soluble than diazinon, and is more likely to sorb to plant surfaces and settling particulates (e.g., Sherrard et al., 2004). In contrast, there was little evidence that VTS-1 reduced diazinon concentrations by any process other than dilution of high pulse concentrations (Figs. 4 and 5). The relatively high solubility of diazinon limits its retention in VTS systems, and mitigation depends on hydrolysis and photolysis (Watanabe and Grismer, 2001). Because diazinon half-lives are on the order of weeks to months at neutral pH (Novartis, 1997), VTS systems would need to be large to increase residence time or shallow to promote photolysis, both requiring increased dedication of valuable farm land. A recently proposed solution is the addition of enzyme to catalyze hydrolysis in VTS mixing basins, resulting in rapid breakdown of OP pesticides (unpublished data, Orica Watercare, Inc., Watkins, CO, USA). This additional treatment step may be necessary for chlorpyrifos as well, since concentrations were markedly reduced in VTS-2, but not to a level low enough to eliminate toxicity to *C. dubia*.

Implication of pyrethroid pesticides as causes of sediment toxicity is also consistent with recent studies (e.g., Amweg et al., 2005; Anderson et al., 2006; Hendley et al., 2001; Weston et al., 2004). These hydrophobic compounds readily sorb to plant surfaces and sediments and tend to settle out in retention systems (e.g., Moore et al., 2001; Schultz, 2004). In VTS-1, cypermethrin and lambda-cyhalothrin were both measured at higher concentrations in inlet sediments; and the same was observed for permethrin at VTS-2, indicating early deposition of pyrethroids in both ponds. Based on half-lives in water, pyrethroids would have to remain in the VTS for weeks to months to allow significant degradation (Hendley et al., 2001). However, Bennett et al. (2005) calculated half-lives of bifenthrin and lambda-cyhalothrin to be 6.1 and 1.4 days, respectively, in vegetated ditch systems, with ditch plants being the major sink and/or sorption site responsible for the rapid aqueous pyrethroid dissipation. The present study did not have the resources to characterize chemical fate in VTS water, vegetation, or sediment.

Overall, the VTS installed by farmers were effective at reducing pesticide concentrations in agricultural runoff (Figs. 6 and 11). Effectiveness could be increased by careful positioning of inlets and outlets to minimize short circuiting, by ensuring that vegetation extends throughout the water column, and perhaps by enzyme additions to treat organophosphates. The conditional discharge permit waiver program has required all farm operations to develop and implement water quality management plans that may include installation of VTS. Currently 93% of the irrigated acreage in the region has been enrolled in the program. As management practices, including vegetated treatment systems, are adopted, effectiveness monitoring will allow continued VTS modifications to increase the effectiveness of treatment systems for the specific chemicals of concern in agricultural runoff.

5. Conclusions

Inflows of agricultural runoff to both VTS ponds were highly toxic to *C. dubia*. Toxicity identification evaluations were successful in identifying the chemicals responsible for toxicity, including diazinon and chlorpyrifos in water; and chlorpyrifos, permethrin, cypermethrin, and lambda-cyhalothrin in sediment. VTS-2 outlet water concentrations of chlorpyrifos were substantially lower than inlet concentrations, while differences in diazinon at VTS-1 were variable and likely affected mainly by dilution. Concentrations of most pesticides, pesticide classes, turbidity, and nutrients were lower at VTS outlets than at inlets, indicating overall VTS effectiveness in reducing non-point source pollution. Monitoring VTS effectiveness and identifying chemicals of concern are key components in the design and optimization of conservation practices to mitigate the effects of agricultural runoff.

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