

Effectiveness of an Integrated Wetland Treatment System in Reducing Pesticide Concentrations Associated with Agricultural Runoff

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ABSTRACT

The Salinas Valley in Monterey County, California, USA, is a highly productive agricultural region that produces much of the country's salad greens, strawberries, artichokes, and cruciferous vegetables such as broccoli, cauliflower, and Brussels sprouts. Agricultural irrigation runoff containing pesticides at concentrations toxic to aquatic organisms poses a threat to aquatic ecosystems within local watersheds. This study was designed to monitor the effectiveness of a constructed wetland treatment system with a granulated activated carbon (GAC) filter installation at reducing pesticides associated with agricultural runoff. The addition of pennywort (*Hydrocotyle* spp.) was evaluated in some trials. The Molera Road Experimental Treatment Wetland was supplied with water pumped from the Tembladero Slough, a 303(d) listed agricultural and urban drainage that eventually enters the Monterey Bay National Marine Sanctuary. Water samples collected throughout the wetland treatment system during five monitoring trials were analyzed for 170 fungicides, herbicides, and insecticides. The system's average percent reduction in detected pesticide concentrations was 52%. The wetland channel and GAC filtration component each provided significant treatment, with the latter responsible for the majority. There was also a significant effect of pesticide solubility on changes in concentration within the wetland channel and the GAC filtration. The integrated treatment system reduced nitrate by 61%, phosphate by 73%, and turbidity by 90% on average. Additionally, the samples were analyzed for toxicity to the daphnid *Ceriodaphnia dubia*, the amphipod *Hyaella azteca*, and the midge *Chironomus dilutus*. Input water was significantly toxic to *C. dubia* and *H. azteca* in the first trial. Toxicity to *C. dubia* persisted throughout the treatment system, including post-GAC filtration, whereas toxicity to *H. azteca* was removed by the channel, but there was residual toxicity post-GAC. The last trial had significant input toxicity to *H. azteca* and *C. dilutus*. The channel reduced toxicity to *H. azteca* and removed it for *C. dilutus*. GAC filtration reduced amphipod toxicity to an insignificant level. There was no input toxicity in the other three trials. The results demonstrate that a wetland treatment system coupled with GAC filtration can reduce pesticide concentrations, nutrients, suspended particles, and toxicity associated with agricultural runoff.

INTRODUCTION

Monterey County, California, USA, contains a \$4.4 billion/year agricultural industry that largely contributes to the nation's produce supply (Monterey County Agricultural Commissioner 2017). The Salinas Valley encompasses much of the county's agriculture, and yields crops such as salad greens, strawberries, artichokes, and cruciferous vegetables in the northern portion of the valley, and peppers, tomatoes, carrots, and potatoes in the southern region. Some of the diverse crops in the northern Salinas Valley can be grown year-round due to a cool, coastal climate as the valley opens toward the Pacific Ocean (UCCE 2017).

Pesticide use can greatly increase crop yields, which imposes an increased demand for irrigation (Cahn and Phillips 2019; Ippolito and Fait 2019). While some growing operations utilize modern irrigation practices such as drip irrigation tape and time clocks to better control irrigation applications, a significant amount of pesticide-laden irrigation runoff still contributes to local stream flow (Kellogg et al. 2002; Dowd, Press, and Los Huertos 2008; Phillips et al. 2012; Stout et al. 2018; Ippolito and Fait 2019). The input of pesticides into aquatic environments can have detrimental effects on ecological communities (Ankley 1992; Anderson et al. 2003; Solomon 2010; Anderson et al. 2014), as research has revealed clear relationships between pesticide concentration and surface water toxicity (Hunt et al. 2006; Antwi and Reddy 2015; Sánchez-Bayo, Goka, and Hayasaka 2016). This leads to many watersheds within central California being listed as impaired under the Clean Water Act Section 303(d) (CA SWRCB 2017). Past studies indicate that aquatic toxicity was linked to pesticide classes such as organochlorines and organophosphates (Hunt et al. 1999; Anderson et al. 2003; Hunt et al. 2003), whereas more recent research reveals increasing toxic concentrations of pesticide classes such as pyrethroids and neonicotinoids (Epstein and Zhang 2014; Morrissey et al. 2015; Anderson et al. 2017; Deng et al. 2019).

Numerous studies have explored mitigation strategies to address the presence of pesticides in agricultural runoff. Sedimentation ponds with floating aquatic plant vegetation (e.g., pennywort, *Hydrocotyle ranunculoides*) allow for sediment-associated hydrophobic pesticides to settle out of the water column, as well as facilitate plant sorption and provide breakdown pathways such as microbial metabolism, hydrolysis, and photolysis; which can also be effective at reducing concentrations of more water-soluble pesticides (Hunt et al. 2008). Vegetated waterways can also reduce pesticide concentrations. The presence of a vegetated buffer and drainage ditch can help slow water movement, allowing for increased infiltration, particle settling, plant sorption, and breakdown pathways (Hunt et al. 2008; Moore et al. 2008; Anderson et al. 2011; Hladik et al. 2017; Phillips et al. 2017; Cahn and Phillips 2019). However, utilizing vegetation waterways alone can have limitations depending on the physical properties of the system, such as soil type, ditch slope, and vegetation cover; as well as the system's holding capacity (Arora et al. 2010; Zhang and Zhang 2011; Otto et al. 2016; Stehle et al. 2016; Hladik et al. 2017).

An integrated treatment system can be an appropriate means to reduce pesticide loading providing it has components to treat hydrophobic pesticides, such as pyrethroids, as well as more soluble pesticides, such as neonicotinoids. The addition of carbon filtration to traditional vegetated systems can increase the efficacy of pesticide removal. Granulated activated carbon (GAC) has been

utilized for decades in industrial applications, such as the removal of natural and synthetic contaminants, as well as some volatile organic compounds from drinking water, and in municipal wastewater treatment plants (Karanfil and Kilduff 1999; Sophia and Lima 2018), and has long been suggested for contaminated soil amendment and surface water treatment (Pryor et al. 1999; Denyes, Rutter, and Zeeb 2013; Kalmykova et al. 2014). In bench-scale laboratory experiments, Voorhees et al. (2017) were able to completely remove environmentally relevant concentrations of imidacloprid from simulated irrigation runoff. Phillips et al. (2017) found that the use of a vegetated ditch coupled with installations of GAC filters was most effective at significantly reducing chlorpyrifos loads in simulated agricultural runoff events.

Constructed wetlands are another treatment approach for reducing pesticide loads associated with agricultural runoff. Natural wetlands provide numerous ecosystem functions, including water filtration (Mitsch and Gosselink 2000), which translate to the use of constructed wetlands in reducing surface water contamination, as well as nutrient loads and total suspended solids. Constructed wetlands have been utilized globally in municipal and industrial effluent treatment processes, and are growing in popularity to address nonpoint source pollution associated with agricultural irrigation (Díaz, O'Geen, and Dahlgren 2012; Vymazal 2013). These systems' efficacy is attributed to the creation of longer hydraulic residence times, which promote sediment settling and vegetative treatment components, as well as increased potential breakdown processes such as hydrolysis, photolysis, and microbial metabolism (Sherrard et al. 2004; Hunt et al. 2007; Budd et al. 2009; Budd et al. 2011; Díaz, O'Geen, and Dahlgren 2012; Krone-Davis et al. 2013; Vymazal 2013; Vymazal and Brezinova 2015; Carvalho, Arias, and Brix 2017; Gorito et al. 2017; Tang et al. 2017). There can be variability in the effectiveness of constructed wetlands, however, due to factors such as water level and flow, and the plant species present, which can ultimately affect the persistence of pesticide classes exhibiting different properties within the wetland system (Romain, Sylvie, and David 2015; Stang, Bakanov, and Schulz 2016; Main et al. 2017; Moore, Locke, and Kroger 2017; Tu, Jiang, and Li 2018).

The objective of this study was to evaluate the effectiveness of a constructed wetland treatment system with GAC filtration at reducing pesticide concentrations, nutrients, suspended particles, and toxicity associated with agricultural runoff. Additional vegetation in the form of pennywort (*Hydrocotyle* spp.) was included in some trials. This combination of treatments served to address the complex mixture of contaminants found in the Tembladero Slough, a water body that is listed as impaired under the Clean Water Act Section 303(d) due to contaminants associated with agricultural runoff on the central coast of California, as well as urban runoff (CA SWRCB 2017).

METHODS

Study Site

The Molera Road Experimental Treatment Wetland is located in the Lower Salinas River Watershed (Monterey County, California, USA), just above the confluence of the Old Salinas River Channel and the Tembladero Slough. During experimental trials, Tembladero Slough water was

pumped into a 285-m-long, 6.5-m-wide, and 0.3-m-deep sinuous, vegetated channel dominated by cattails (*Typha* sp.). Channel effluent drained onto approximately 0.6-ha of non-channelized marsh wetland, and returned to the slough to eventually enter the Monterey Bay National Marine Sanctuary (Figure 1) (Hunt et al. 2007).

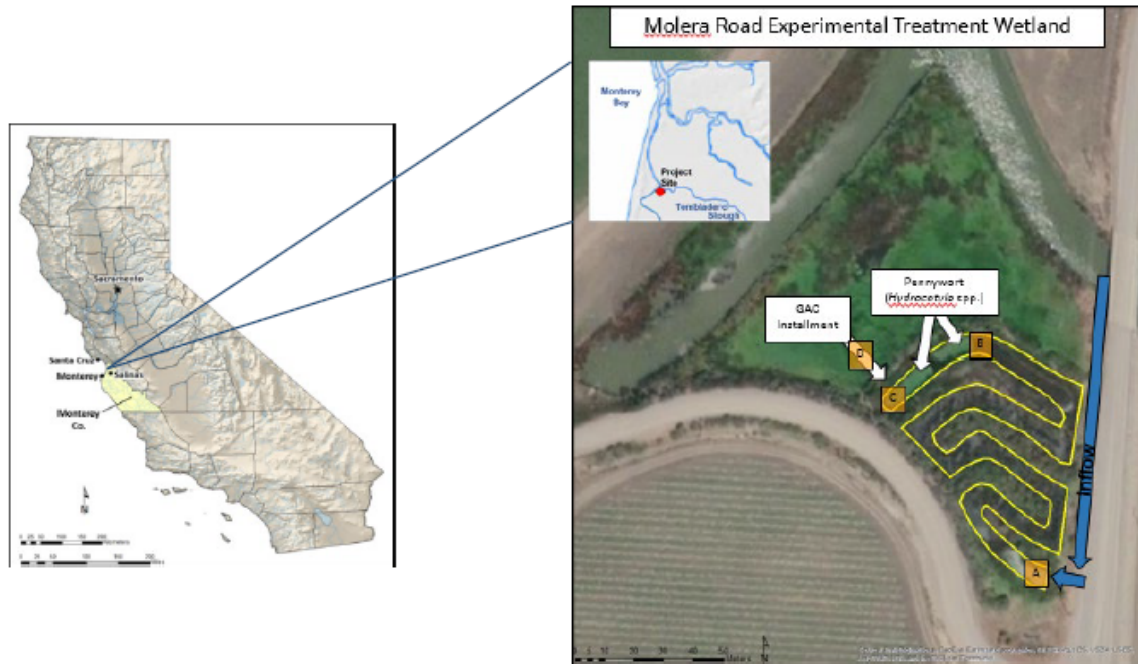


Figure 1. The Molera Road Experimental Treatment Wetland study site located in Monterey, County, California, USA. Composite samples were collected along the wetland system during the monitoring trials. Samples were collected at the wetland channel inflow (Station A), upstream of pennywort (Station B, Trials 1 and 2), the channel outflow (Station C), and the outflow of the GAC filtration installation (Station D). Adapted from Hunt et al. (2007).

A previous study evaluated this system for reducing pesticide concentrations, particularly the more frequently detected organophosphates, as well as nutrients and suspended particles (Hunt et al. 2007). For the current study, modifications were made to the wetland to optimize the treatment of current-use pesticides, some of which may not be removed by processes such as sedimentation and plant sorption due to a higher solubility, such as neonicotinoids (Phillips et al. 2017). A flow-through installation containing approximately 400 L of granulated activated carbon (GAC) was placed at the outflow of the sinuous channel in all monitoring trials to sorb more soluble pesticides. The GAC was not replaced during the five trials, however, the design of the filtration installation evolved throughout the study. For the first trial, it consisted of a wooden trough lined with Visqueen™ polyethylene sheeting. Within the trough, the GAC was contained in geotextile Filtrexx Mesh™ socks (Filtrexx, Akron, OH, USA). Improvements were made for the second trial with the introduction of a fiberglass flow-through tank in which the GAC was loosely contained. To better ensure proper water movement and treatment efficiency, the installation was further

modified for subsequent trials. The GAC was once again contained in Filtrexx Mesh socks, and a diffuser was added in the trough to evenly disperse the water flow through the carbon treatment.

The wetland was also modified by transplanting the floating aquatic plant pennywort (*Hydrocotyle* spp.) to approximately 20% of the distal end of the channel (Figure 1). Pennywort can aid treatment by slowing water flow and providing additional surface area for sorption (Hunt et al. 2008; Anderson et al. 2011). This treatment was used only in the first two trials before it was deemed unsustainable due to grazing from local fauna, as well as potential intolerance to elevated conductivity pulses in the system.

Monitoring

Five monitoring trials were conducted during two agricultural growing seasons from September 2017 through December 2018 (Table 1). The fifth trial was conducted following roughly a week of recent rain events to capture potentially increased contaminant loads from storm runoff. Tembladero Slough water was pumped through the wetland at a rate of approximately 360 L/min for 12 h/d during monitoring trials, and 4 h/d during maintenance periods. Pumping was evenly staggered throughout a 24-h period so as to disperse the inflow of water and not overwhelm the system. Pumping rates were increased from maintenance flows approximately 48 h prior to the start of each trial to allow for equilibrium within the system before sample collection. Water samples were collected using Global Water automatic samplers (Xylem, Inc., College Station, TX, USA), which were stationed at the channel inflow (Station A), upstream of the pennywort in the first two trials (Station B), at the channel outflow (Station C), and at the outflow of the GAC installation (Station D) (Figure 1). At each sampling station, the automatic samplers were programmed to collect 800 mL of sample every hour over a 24-h period (Table 1). Composite samples were collected in 5-gal glass carboys, which were kept in the dark. The start of sampling was staggered from the inflow of the channel (Station A) towards the outflow (Station C) for all trials in order to capture a 48-h hydraulic residence time through the wetland, and to better evaluate potential contaminant reductions as water progressed through the wetland treatment system (Table 1). Sampling at Station B prior to the pennywort treatment started 42 h and 40 h after the start of sampling at Station A in Trial 1 and Trial 2, respectively. The sampling start times at Stations C and D, channel outflow and post-GAC, were not staggered. The water moving through the GAC filtration installation appeared to have a short residence time, and it was assumed that collecting a composite sample over the 24-h sampling period would be sufficient in capturing the treatment of water from Station C. Following each trial, samples were transferred to Thermo Scientific™ (Thermo Fisher Scientific, Waltham, MA, USA) certified amber glass bottles and maintained at 4 °C in the dark until chemical analyses and toxicity test initiation.

Table 1. Sampling dates and times for each monitoring trial.

Trial 1	Sampling Start Date	Sampling Start Time	Sampling End Date	Sampling End Time
(A) Channel Inflow	9/23/2017	09:30	9/24/2017	09:30
(B) Pre-Pennywort	9/25/2017	03:30	9/26/2017	03:30
(C) Channel Outflow	9/25/2017	09:30	9/26/2017	09:30
(D) Post-GAC	9/25/2017	09:30	9/26/2017	09:30
Trial 2				
(A) Channel Inflow	7/15/2018	14:00	7/16/2018	14:00
(B) Pre-Pennywort	7/17/2018	06:00	7/18/2018	06:00
(C) Channel Outflow	7/17/2018	14:00	7/18/2018	14:00
(D) Post-GAC	7/17/2018	14:00	7/18/2018	14:00
Trial 3				
(A) Channel Inflow	9/16/2018	09:00	9/17/2018	09:00
(C) Channel Outflow	9/18/2018	09:00	9/19/2018	09:00
(D) Post-GAC	9/18/2018	09:00	9/19/2018	09:00
Trial 4				
(A) Channel Inflow	10/14/2018	09:00	10/15/2018	09:00
(C) Channel Outflow	10/16/2018	09:00	10/17/2018	09:00
(D) Post-GAC	10/16/2018	09:00	10/17/2018	09:00
Trial 5				
(A) Channel Inflow	12/2/2018	09:00	12/3/2018	09:00
(C) Channel Outflow	12/4/2018	09:00	12/5/2018	09:00
(D) Post-GAC	12/4/2018	09:00	12/5/2018	09:00

Chemistry

Pesticide concentrations were measured at the United States Geological Survey (USGS) Organic Chemistry Research Laboratory (OCRL) in Sacramento, California, USA, using liquid chromatography tandem mass spectrometry (LC/MS/MS) and gas chromatography mass spectrometry (GC/MS). Detailed extraction procedure and instrumental analysis of the water samples analyzed with LC/MS/MS are fully described in Hladik and Calhoun (2012). The complete extraction procedure and GC/MS instrumental analysis are described in Hladik et al. (2008, 2009) and Hladik and McWayne (2012), respectively. In summary, the composite water samples were filtered through 0.7- μm glass-fiber filters (Grade GF/F, Whatman, Piscataway, NJ, USA) to remove suspended material. The filter papers containing suspended sediments were dried at room temperature overnight in the dark, and then stored at $-20\text{ }^{\circ}\text{C}$ until extraction and analysis of pesticides in the suspended material. The recovery surrogate standards d14-trifluralin, $^{13}\text{C}^{12}$ -p,p'-DDE, and $^{13}\text{C}^6$ -permethrin (Cambridge Isotopes, Andover, MA, USA.), as well as an internal standard of a mixture of deuterated compounds acenaphthene-d10 and pyrene-d1 were added to the filter paper extracts when prepared for GC/MS analysis (Hladik, Smalling, and Kuivila 2008; Hladik and Calhoun 2012; De Parsia et al. 2018; Stout et al. 2018). The detected pesticide concentrations from the suspended sediment of the filter paper extracts were converted from ng/g to ng/L and included with the concentration detections of the filtered water samples analyzed with LC/MS/MS and GC/MS/MS, which were reported in ng/L.

Oasis Hydrophilic Lipophilic Balance (HLB) solid-phase extraction (SPE; 6-mL, 500-mg; Waters, Milford, MA, USA) cartridges were used for extraction of each filtered water sample. Prior to extraction for LC/MS/MS analysis, samples were spiked with the recovery surrogate standards monuron (Chem Service, West Chester, PA, USA) and imidacloprid-d4 (Cambridge Isotope Laboratories, Andover, MA, USA). Following extraction, the internal standard ¹³C₃-caffeine (Cambridge Isotope Laboratories, Andover, MA, USA) was added to these samples. The samples for GC/MS analysis were spiked with the recovery surrogate standards ¹³C₃-atrazine and d₁₄-trifluralin (Cambridge Isotopes, Andover, MA, USA) prior to SPE extraction, and then equipped with an internal standard of 20 µL of a 10-ng/µL solution of the deuterated polycyclic aromatic hydrocarbon compounds acenaphthene-d₁₀ and pyrene-d₁₀ following extraction. The sample extracts were stored at -20 °C until analysis, which took place up to 30 d post-extraction (Hladik, Smalling, and Kuivila 2008, 2009; Hladik and Calhoun 2012; Hladik and McWayne 2012; De Parsia et al. 2018; Stout et al. 2018).

An Agilent (Palo Alto, CA, USA) 1260 Infinity coupled to an Agilent 6430 Triple Quad LC/MS with a Zorbax Eclipse XDB-C18 column (2.1-mm by 150-mm by 3.5-mm; Agilent) was used for LC/MS/MS analysis of water extracts, and data were collected in the multiple-reaction-monitoring mode. An Agilent 7890A gas chromatograph with an Agilent 5975C inert mass-selective detector system using a DB-5MS analytical column (30-m by 0.25-mm by 0.25-µm; Agilent) for separation with helium as the carrier gas was used for GC/MS analysis of water and filter paper extracts, and data were collected in the selected ion-monitoring (Hladik, Smalling, and Kuivila 2008, 2009; Hladik and Calhoun 2012; Hladik and McWayne 2012; De Parsia et al. 2018; Stout et al. 2018). Analytical quality assurance was measured as surrogate recoveries in filtered water samples and filter paper extracts. Recoveries ranged from 72% to 125% for water samples, and 75% to 122% for filter extracts.

Method detection limits (MDLs) for detected pesticide concentrations in water samples were validated in previous work (Hladik, Smalling, and Kuivila 2008; Hladik and Calhoun 2012) by using the procedure described in 40 CFR 136, Appendix B of USEPA (1992). MDLs for pesticides in suspended sediments filtered from water samples were validated in previous studies by Hladik et al. (2009) and Hladik and McWayne (2012). The MDLs were used as quantitative reporting levels, and as analytes can sometimes be identified at concentrations less than the MDLs, concentrations of compounds detected below the MDLs were reported as estimates (Hladik, Smalling, and Kuivila 2008, 2009; Hladik and Calhoun 2012; Hladik and McWayne 2012; De Parsia et al. 2018; Stout et al. 2018).

Toxicity Tests

Toxicity tests were conducted at the Marine Pollution Studies Laboratory at Granite Canyon in Monterey, California, USA, with three invertebrate species that have varying sensitivities to agricultural pesticides. These tests included acute 96-h static renewal exposures with the cladoceran *Ceriodaphnia dubia* and the amphipod *Hyalella azteca*; as well as a chronic 10-d static renewal exposure with the dipteran *Chironomus dilutus* (USEPA 2002). Toxicity tests with *C. dubia* were conducted in five replicate 20-mL scintillation vials, each containing 15 mL of test solution and 5

neonates per replicate. Each vial was fed 0.2 mL of a mixture of the alga *Selenastrum* and YCT (yeast, cerophyll, and trout chow) 2 h prior to 100% daily renewals of test solution. Daily survival was recorded, and final survival in the water samples was compared with 96-h survival in control water with moderate hardness. Tests with *H. azteca* were conducted in five replicate 300-mL glass beakers filled with 100 mL of test solution and 10, 9-d to 14-d-old amphipods per beaker. Each beaker was fed 1.5 mL of YCT at test initiation and following a 48-h renewal of 50% of the test solution. Final survival in the water samples was compared with 96-h survival in laboratory well water. Toxicity tests with *C. dilutus* were conducted in four replicate 300-mL glass beakers containing 200 mL of test solution, and 12, 7-d-old larva. Five mL of sand was added to each beaker as substrate for larval tube building. Larvae were fed daily with an increasing amount of TetraMin™ (Tetra GmbH, Melle, Germany) slurry (4 g/L), as follows: days 0 to 3, 0.5 mL/d; days 4 to 6, 1.0 mL/d; days 7 to 10, 1.5 mL/d. Tests were conducted for 10 d, and 50% of the test solution was renewed every 48 h. Final survival in the water samples was compared with 10-d survival in laboratory well water, and growth of surviving animals was measured as ash-free dry weight. A positive control reference toxicant test was conducted concurrently with every toxicity test to bracket the lethal concentration required to kill 50% of the test organisms, the LC₅₀ value, and to demonstrate the suitability of the test methodology. The reference toxicity tests were comprised of dilutions of reagent grade copper chloride (CuCl₂) for *C. dubia*, reagent grade cadmium chloride (CdCl₂) for *H. azteca*, and reagent grade potassium chloride (KCl) for *C. dilutus*.

Dissolved oxygen, pH, and conductivity were measured at test initiation, following every renewal, and at test termination with an Accumet™ meter and appropriate electrodes (Thermo Fisher Scientific, Waltham, MA, USA). Un-ionized ammonia was measured at test initiation and termination using a Hach DR/2010 spectrophotometer (Hach, Loveland, CO, USA), and hardness and alkalinity (Hach) were measured only at test initiation. All composite water samples were also measured for nitrate and phosphate using a Hach DR/2010 spectrophotometer, as well as for turbidity with a Hach 2100P portable turbidimeter at test initiation. Water temperature was recorded with a continuous recording thermometer (Onset Computer Corporation, Pocasset, MA, USA), and additional daily temperatures were measured manually using a glass spirit thermometer.

Data Analysis

Percent changes in detected pesticide concentrations between various sampling stations were calculated for each pesticide group: fungicides, herbicides, and insecticides, as well as for all pesticides by trial. The statistical significance of changes in pesticide concentrations were analyzed using linear mixed effects models ($\alpha = 0.05$), pairwise comparisons, and linear regression models.

Linear mixed effects models were used to determine if pesticide groups or chemical classes influenced treatment effectiveness. Models were implemented in the R package “lme4” (Bates et al. 2015; R Core Team 2019), and assumed normality. An analysis of the residuals plots in this study (Appendices E – G) indicated that a log transformation of the detected pesticide concentrations was sufficient for achieving normality (Zuur et al. 2009). Linear mixed effects models contain fixed and random effects that account for the variation. Fixed effects are variables specifically chosen, and are expected to influence the response variable. Random effects are independent variables that are a subset of all possibilities. The differences between the random

effects can account for unexplained variation within an analysis, which can better help delineate the amount of variation that is due to the fixed effects (Harrison et al. 2018). In general, these models utilized the sampling stations as the fixed effect, detected analytes as the random effect, and the log-transformed pesticide concentrations as the response. In some models, analytes were nested, or grouped, within pesticide class when used as a random effect in order to account for variation so that detections of the same analyte at different sampling stations were not considered independent observations.

Pairwise comparisons were used to evaluate the effectiveness of each treatment component, and were performed with the R package “emmeans” (R Core Team 2019). Additionally, the impact of pesticide solubility on treatment effectiveness, based on log K_{ow} values, was evaluated in the wetland channel and GAC treatment components with linear regression models, where the detected analytes were the observations.

The models implemented in this study also incorporated non-detection data, or censored values, substituted with the MDLs in place of reporting limits, under the guidance of the USGS Organic Chemistry Research Laboratory in Sacramento, California, USA. For comparison of treatment efficiency within each trial, any observations of pesticides that had been detected at a measurable amount at one sampling station, but that were known to be less than the corresponding threshold value at another station were substituted with the appropriate MDL. This was done to avoid bias by deleting censored observations, increase power, and provide confidence in parameter estimates (Helsel 2012).

Toxicity data were evaluated using the Test for Significant Toxicity (TST). This statistical approach uses hypothesis testing to indicate whether the response in each sample is greater than or equal to a defined proportion of the control response (USEPA 2010b; Denton, Diamond, and Zheng 2011).

RESULTS and DISCUSSION

Changes in Pesticide Concentrations

Each composite sample was analyzed for 170 pesticides, 59 of which were fungicides, 41 herbicides, and 70 insecticides (Appendix A). Twenty-five of the targeted fungicides and degradates were detected across the five trials (Appendix B), as well as 14 of the targeted herbicides (Appendix C) and 24 of the insecticides (Appendix D). Overall percent changes in concentrations within each treatment section were calculated by trial for all detected analytes, as well as within each pesticide group (Table 2). Total fungicide concentrations tended to be higher than herbicides and insecticides, and were responsible for the high percent increase in pesticide concentrations within the channel during Trial 1, mostly driven by carbendazim (Appendices B – D). Treatment effectiveness varied across the trials, but concentrations of most pesticides decreased within the integrated system.

Table 2. Percent changes in pesticide concentrations for all detected pesticides and by pesticide group between sampling stations within each trial. Negative and positive numbers indicate percent reduction and increase, respectively.

	All Pesticides % Change	Fungicides % Change	Herbicides % Change	Insecticides % Change
Number of Detected Pesticides and Degradates	63	25	14	24
Concentration Range (ng/L)	2.6 – 9564	2.7 – 9564	2.7 – 652	2.6 – 1366
Trial 1				
(A – B) Inflow to Pre-Pennywort	4	8	19	44
(B – C) Pre-Pennywort to Outflow	127	198	-6	-3
(A – C) Inflow to Outflow	136	174	12	40
(C – D) Outflow to Post-GAC	-69	-79	-17	-29
(A – D) Inflow to Post-GAC	-26	-34	-7	-1.3
Trial 2				
(A – B) Inflow to Pre-Pennywort	-29	-35	6	-28
(B – C) Pre-Pennywort to Outflow	7	15	15	-6
(A – C) Inflow to Outflow	-24	-25	22	-32
(C – D) Outflow to Post-GAC	-90	-92	-85	-88
(A – D) Inflow to Post-GAC	-92	-94	-82	-92
Trial 3				
(A – C) Inflow to Outflow	-3	8	6	-7
(C – D) Outflow to Post-GAC	-70	-69	-68	-72
(A – D) Inflow to Post-GAC	-69	-67	-66	-74
Trial 4				
(A – C) Inflow to Outflow	-11	13	44	-30
(C – D) Outflow to Post-GAC	-24	-23	-18	-27
(A – D) Inflow to Post-GAC	-33	-13	17	-49
Trial 5				
(A – C) Inflow to Outflow	-35	-39	-36	-31
(C – D) Outflow to Post-GAC	-10	6	-22	-24
(A – D) Inflow to Post-GAC	-42	-35	-50	-47

Analysis of Pesticide Treatment Significance

1. Pennywort Treatment

To determine the statistical significance of changes in pesticide concentrations and treatment effectiveness across the wetland system, a series of linear mixed effects models were conducted with the log of pesticide concentrations as the response. The analyses were complicated, however, because only Trials 1 and 2 included the pennywort treatment component in approximately 20% of the distal end of the wetland channel. Three transplant efforts were conducted before the first trial, and by the end of Trial 2 the vegetation had been fully extracted by local fauna.

Prior to system-wide statistical analyses, an individual analysis of the pennywort treatment was conducted to determine if it significantly affected pesticide concentrations. This linear mixed

effects model included a fixed effect of Stations B and C, before and after exposure to the pennywort, a random effect of detected analytes nested in pesticide class, and the log of pesticide concentrations as the response. The analysis concluded that there was no significant effect of the pennywort on pesticide concentrations ($F(1, 122) = 0.379, p = 0.539$). Previous studies have demonstrated the benefits of implementing a floating vegetation treatment component for agricultural tailwater to slow flow, facilitate in particle-bound pesticide settling, and provide additional surface area for sorption (Hunt et al. 2008; Anderson et al. 2011). In the current study, the pennywort inconsistently provided only slight percent concentration reductions for some pesticides (Table 2), and in many cases individual pesticide concentrations were higher after the pennywort at Station C (Appendices B – D). During the transplanting efforts, it is possible that the pennywort brought pesticide residue from where it was harvested. The lack of significant treatment with pennywort could also be attributed to the vegetation not becoming fully established and rooted to the base of the channel before the first trial. This finding allowed for the inclusion of Trials 1 and 2 in the system-wide analyses, while excluding Station B (pre-pennywort) from the models.

2. Treatment Effectiveness among Pesticide Groups

A linear mixed effects model was conducted to evaluate if there was a statistically significant interaction between sampling station, or treatment sections, and pesticide group: fungicides, herbicides, and insecticides. For this model, the fixed effects were the interactions between station and group and station and trial, the random effect was detected analytes nested in pesticide class, and the response was the log of pesticide concentrations. The model produced four outputs, and the first revealed that there was a significant effect of sampling station on all pesticide concentrations ($F(2, 570) = 94.0, p < 0.001$), signifying that concentrations significantly changed as water moved through the system. There was also a significant difference in concentrations among the pesticide groups ($F(2, 38) = 3.91, p = 0.028$), indicating that the concentrations in some groups were significantly higher or lower than others. However, the model showed that there was no significant interaction between sampling station and pesticide group, revealing that there were no differences in treatment based on pesticide group ($F(4, 570) = 0.529, p = 0.715$). The model also showed that treatment effectiveness by pesticide group was variable among the trials ($F(8, 570) = 14.9, p < 0.001$). Although there was significant change in pesticide concentrations, pesticide group had no influence on treatment effectiveness.

3. Treatment Effectiveness among Pesticide Classes

An additional linear mixed effects model was conducted to assess how the detected pesticide chemical classes (Appendices B – D) may have been treated within the integrated system. This model included log of pesticide concentrations as the response, fixed effects of the interactions between station and pesticide class and station and trial, and detected analytes as the random effect. As with the previous model, there was a significant effect of sampling station on pesticide concentrations ($F(2, 512) = 96.3, p < 0.001$), showing that pesticide concentrations changed as the water moved through the system. There was also a significant difference in concentrations among the chemical classes ($F(31, 31) = 2.94, p = 0.002$), indicating that some pesticide classes had significantly higher or lower concentrations than others. However, there was no significant interaction between sampling station and pesticide class ($F(62, 512) = 1.20, p = 0.150$), meaning

that the pesticide classes did not significantly differ in response to the wetland channel and GAC filtration components. This finding could be the result of most of the variation in treatment efficiency being explained by an additive effect of both pesticide class and sampling station, or treatment type, on the pesticide concentration response variable, and not by the interaction of the two. Any remaining variation that would be explained by the interaction of class and station would likely have low statistical power due to the number of detected chemical classes and the resulting degrees of freedom in this analysis. The model also revealed that there was a significant interaction between sampling station and trial, suggesting that treatment effectiveness by class did vary across the monitoring trials ($F(8, 512) = 15.3, p < 0.001$).

4. Treatment Comparisons

Pairwise comparisons of estimated marginal means for the sampling stations were then performed to evaluate the effectiveness of each treatment component without the concern for pesticide group or chemical class-specific interaction effects. This analysis incorporated the data from all monitoring trials rather than conducting trial-specific pairwise t-tests with smaller datasets in order to reduce type I and type II errors. The contrast of Stations A to C was used to assess treatment within the wetland channel, C to D the GAC filtration, and A to D the overall treatment of the entire system. The results showed that there was significant treatment in both the channel ($p = 0.005$) and GAC filtration ($p < 0.001$). A review of each estimate value, which is the average change in log concentrations between the stations, reveals that most of the system-wide treatment occurred within the GAC filtration component (Table 3).

Table 3. Statistical results of the pairwise comparisons of sampling stations across the five monitoring trials ($\alpha = 0.05$). Stations A to C represent the wetland channel, C to D the GAC filtration, and A to D the entire system. The estimate values are the average change in log concentrations between the stations.

	estimate	SE	df	t-ratio	p-value
(A – C) Inflow to Outflow	0.315	0.101	512	3.119	0.005
(C – D) Outflow to Post-GAC	0.602	0.101	512	5.964	0.000
(A – D) Inflow to Post-GAC	0.917	0.101	512	9.083	0.000

5. Effects of Pesticide Solubility on Treatment Efficiency

Considering there was no significant difference in treatment effectiveness by pesticide group or chemical class, the impact of pesticide solubility, based on $\log K_{ow}$, or octanol/water partition coefficients, was investigated for each treatment component. Pesticides with a low $\log K_{ow}$ value are more soluble in aquatic environments, whereas those with high values are more hydrophobic and readily bind to or associate with sediment and plant material (Mackay et al. 1980; Meylan and Howard 1995; Chamberlain, Evans, and Bromilow 1996; Finizio, Vighi, and Sandroni 1997). The channel section of the system, between Stations A and C, appeared to predominately reduce the concentrations of more hydrophobic pesticides (Figure 2), whereas the inclusion of the GAC

treatment, Stations A to D, allowed the entire system to reduce pesticides over a wide range of solubility (Figure 3).

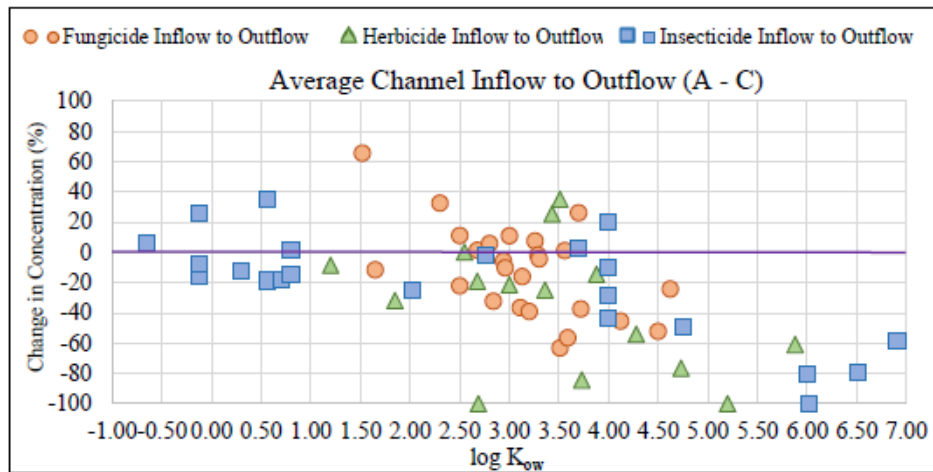


Figure 2. Average percent changes in chemical concentrations within the wetland channel (Stations A to C) across all trials compared to the $\log K_{ow}$, or octanol/water partition coefficients of the detected pesticides. Negative percent changes indicate average reduction, or treatment.

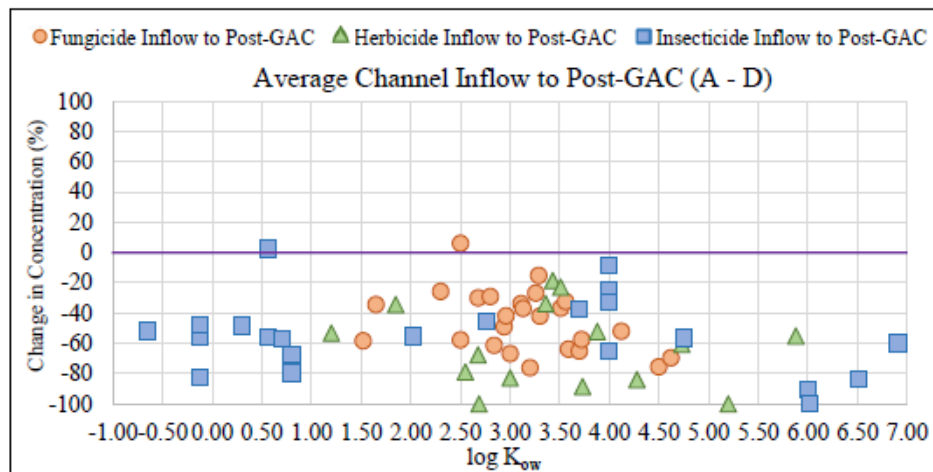


Figure 3. Cumulative average percent changes in chemical concentrations throughout the entire treatment system (Stations A to D) across all trials compared to the $\log K_{ow}$, or octanol/water partition coefficients of the detected pesticides. Negative percent changes indicate average reduction, or treatment.

Linear regression models were conducted to statistically assess the effect of solubility on detected pesticide concentrations within each treatment section. In these models, the difference between log-transformed pesticide concentrations at Stations A and C for the wetland channel and C and D for the GAC filtration were related to the detected pesticides' $\log K_{ow}$ values. The model of the channel indicated a significant effect of solubility on the change in pesticide concentrations ($F(1, 207) =$

33.2, $p < 0.001$), which seemed to be driven by some of the less soluble pesticides with higher $\log K_{ow}$ values that would more readily bind to or associate with sediment and plant material within the channel (Figure 4). This trend seemed consistent across the trials as the model revealed no significant interaction between solubility and trial ($F(4, 207) = 1.75, p = 0.141$).

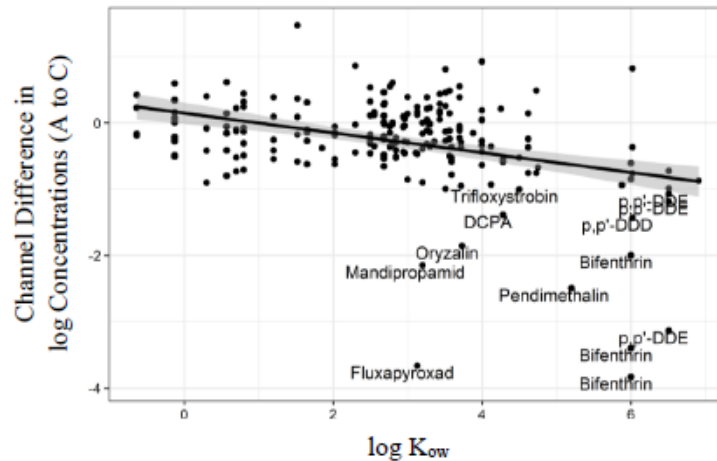


Figure 4. Difference in log-transformed pesticide concentrations across all trials within the wetland channel, between Stations A (channel inflow) and C (channel outflow), related to $\log K_{ow}$, or octanol/water partition coefficients of detected pesticides.

The model analysis for the GAC filtration component also showed a significant effect of solubility on the difference in pesticide log concentrations ($F(1, 207) = 25.3, p < 0.001$). More soluble pesticides with low to moderate $\log K_{ow}$ values exhibited greater differences in log concentrations before and after the carbon filtration system than less soluble compounds. However, the model also revealed a significant interaction between solubility and trial ($F(4, 207) = 7.62, p < 0.001$), indicating that this effect was not consistent across the trials (Figure 5).

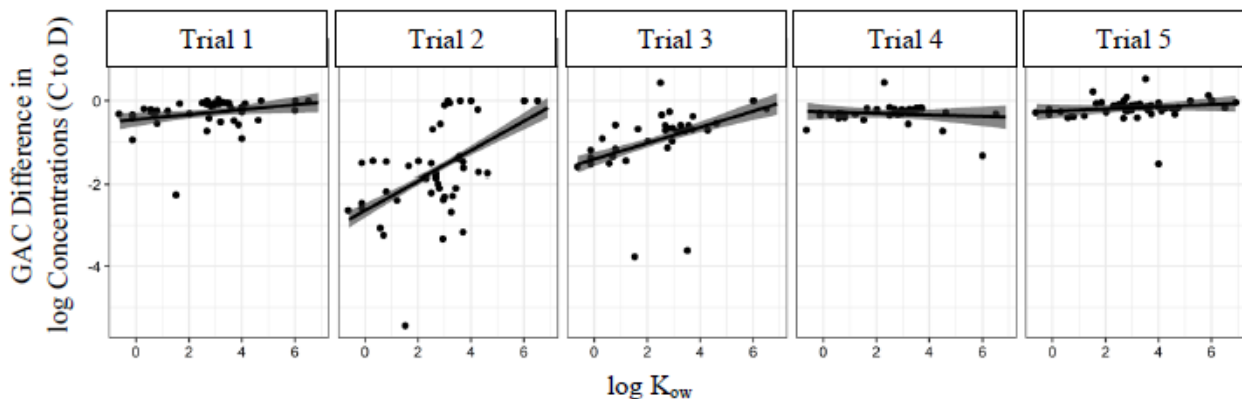


Figure 5. Difference in log-transformed pesticide concentrations by trial within the GAC filtration component, between Stations C (channel outflow) and D (post-GAC), related to $\log K_{ow}$, or octanol/water partition coefficients of detected pesticides.

The variability in treatment with GAC could be the result of several factors, including the evolving design of the filtration system throughout the study. In Trial 1, which utilized the GAC in mesh sleeves but had a fair amount of bypass in a shallower filter design, carbon filtration provided a 69% reduction in pesticide concentrations, which had increased over 100% within the channel, before and after the pennywort. GAC exhibited the best performance in Trail 2, in which the carbon was loose within a fiberglass trough, with a 90% concentration reduction. For Trials 3, 4, and 5, the carbon was contained in geotextile mesh sleeves within the trough, as it was assumed that this configuration would perform as well, or better, than loose carbon in addition to being easier to manage. However, over the course of these last three trials, GAC treatment efficiency seemed to dwindle as percent concentration reductions lessened from 70% to 10%. Simultaneously, percent reductions within the wetland channel during these trials improved from 3% to 35% (Table 2).

The adsorption capacity of the activated carbon, as it was not replaced during the study, could have also contributed to inconsistent treatment. While the lifespan of GAC being utilized in a watershed treatment system such as a constructed wetland is unclear, continual filtration of agricultural and urban drainage could account for some of the observed reduction in GAC filtration efficiency following Trial 2. Newcombe et al. (1993) described mechanisms of carbon regeneration, and found that over time high loads of organic material in source water has been shown to reduce the life of carbon filtration components.

Variable concentrations of pesticides exhibiting different physical-chemical properties entering the system, as well as influences from rain events may have also contributed to discrepancies in GAC treatment across the trials. Trial 5 followed recent rains and exhibited the highest number of pesticide detections, as well as higher input concentrations of the majority of previously detected pesticides (Appendices B – D), likely the result of elevated particle loading related to the storm events. However, this trial had the lowest percent concentration reduction with GAC filtration, and most reductions occurred within the wetland channel (Table 2), perhaps through pesticide-bound particles settling and plant sorption. Trial 5 also had the least observed spikes in pesticide concentrations as water moved through the system, which could influence GAC filtration effectiveness and overall percent reductions.

Throughout the study, some individual pesticides exhibited increases in concentration across the sampling stations, which could have been the result of not sufficiently capturing contaminant pulses during the staggered 24-hour composite sampling. Transplanting pennywort to the channel may have also introduced pesticide residue in Trials 1 and 2 from the where the pennywort was harvested, as some pesticides exhibited concentration increases just before (Station B) and immediately after (Station C) the floating vegetation mass (Appendices B – D). In Trials 1 – 4, for example, the fungicide carbendazim was detected at a higher concentration at the outflow of the channel (Station C) from that measured at the inflow (Station A). For these trials, GAC filtration reduced the elevated concentration to less than that measured at the channel inflow. However, in Trial 5 this pesticide was reduced within the wetland channel, but exhibited an increase in concentration following GAC filtration. Similarly, the fungicide azoxystrobin was also detected at higher concentrations at the outflow of the channel in Trials 1 – 4. GAC filtration provided reductions in three of the trials, but in only one was the analyte reduced to a concentration less than that observed at the channel inflow. The herbicide propyzamide was also detected in increasing concentration within the wetland channel during all five trials, and while GAC provided reductions

in each trial, concentrations were reduced to below channel inflow measurements in only three of them.

Regardless, the GAC filtration component provided percent concentration reductions in all detected pesticides across the five monitoring trials (Table 2), and significant treatment overall, particularly with the more soluble analytes. There are many variables to take into account when assessing the fluctuating efficiency of constructed wetland treatment systems, and the data reinforce the effectiveness of constructed wetlands at reducing concentrations of hydrophobic pesticides, while outlining the need for an additional treatment component to address the more soluble pesticides also found in the complex mixture of contaminants associated with modern agricultural runoff. These results demonstrate that the wetland channel with GAC filtration can significantly reduce most pesticide concentrations.

Reduction of Nutrients

The composite samples from each sampling station were also measured for nitrate, phosphate, and turbidity at toxicity test initiation for every trial, except Trial 1 in which only turbidity was measured (Table 4). On average, the integrated treatment system reduced nitrate concentrations by 61%, phosphate by 73%, and turbidity by 90%. The wetland channel, from Stations A to C, accounted for most of the average percent reductions of nutrients and suspended particles, with GAC filtration providing slight to moderate additional reductions in some trials (Table 5). As nutrients were not measured in Trial 1, an assessment of pennywort treatment effectiveness could not be completed. However, turbidity measurements increased by 71% after the pennywort in Trial 1 and decreased by 66% in Trial 2. This variation further eludes to the ineffectiveness of the pennywort treatment component, which could only be utilized in the first two trials.

Table 4. Measured nutrient concentrations and turbidity of the composite samples for the five monitoring trials. Nutrients were not measured in Trial 1.

Trial 1	Nitrate (mg/L)	Phosphate (mg/L)	Turbidity NTU
(A) Inflow	NA	NA	242
(B) Pre-Pennywort	NA	NA	11.2
(C) Outflow	NA	NA	19.1
(D) Post-GAC	NA	NA	12.2
Trial 2			
(A) Inflow	45.0	8.4	299
(B) Pre-Pennywort	21.3	4.2	129
(C) Outflow	22.2	3.4	43.6
(D) Post-GAC	21.4	3.0	17.9
Trial 3			
(A) Inflow	14.6	4.4	74.3
(C) Outflow	6.6	1.6	15.5
(D) Post-GAC	6.6	1.3	9.1
Trial 4			
(A) Inflow	11.7	6.4	91.3
(C) Outflow	4.5	0.9	11.2
(D) Post-GAC	4.3	1.0	9.2
Trial 5			
(A) Inflow	12.9	28.1	734
(C) Outflow	3.2	6.5	121
(D) Post-GAC	3.4	7.4	119

Table 5. Percent changes in nutrient concentrations and turbidity between sampling stations by trial. Negative numbers indicate percent reduction, or treatment. Nutrients were not measured in Trial 1.

Trial 1	Nitrate % Change	Phosphate % Change	Turbidity % Change
(A – B) Inflow to Pre-Pennywort	NA	NA	-95
(B – C) Pre-Pennywort to Outflow	NA	NA	71
(A – C) Inflow to Outflow	NA	NA	-92
(C – D) Outflow to Post-GAC	NA	NA	-36
(A – D) Inflow to Post-GAC	NA	NA	-95
Trial 2			
(A – B) Inflow to Pre-Pennywort	-53	-50	-57
(B – C) Pre-Pennywort to Outflow	4	-19	-66
(A – C) Inflow to Outflow	-51	-60	-85
(C – D) Outflow to Post-GAC	-4	-12	-59
(A – D) Inflow to Post-GAC	-52	-64	-94
Trial 3			
(A – C) Inflow to Outflow	-55	-64	-79
(C – D) Outflow to Post-GAC	0	-19	-41
(A – D) Inflow to Post-GAC	-55	-70	-88
Trial 4			
(A – C) Inflow to Outflow	-62	-86	-88
(C – D) Outflow to Post-GAC	-4	11	-18
(A – D) Inflow to Post-GAC	-63	-84	-90
Trial 5			
(A – C) Inflow to Outflow	-75	-77	-84
(C – D) Outflow to Post-GAC	6	14	-2
(A – D) Inflow to Post-GAC	-74	-74	-84

Reduction of Toxicity

All toxicity tests met test acceptability criteria, and water quality parameters were within acceptable limits. All accompanying reference toxicant tests produced acceptable results, indicating that test organisms responded to the positive controls in a manner consistent with previous tests. There was significant input toxicity to the daphnid *Ceriodaphnia dubia* and the amphipod *Hyalella azteca* in Trial 1. Toxicity to *C. dubia* persisted throughout the treatment system, including post-GAC filtration, whereas toxicity to *H. azteca* was removed by the channel (Table 6). However, there was residual significant toxicity to *H. azteca* at Station D following the GAC filtration. There was no significant toxicity at the inflow of the channel or at other sampling stations in Trials 2 – 4. Trial 5 was conducted after several rain events, and there was significant input toxicity to *H. azteca* and the dipteran *Chironomus dilutus*. Amphipod toxicity was reduced by the channel, but not eliminated, whereas the channel removed toxicity to *C. dilutus*. GAC filtration reduced amphipod toxicity to an insignificant level (Table 6).

Table 6. Average percent survival for 96-h *Ceriodaphnia dubia*, 96-h *Hyalella azteca*, and 10-d *Chironomus dilutus* toxicity tests, and average ash-free dry weight for the *C. dilutus* tests. Shading indicates significant toxicity.

	<i>C. dubia</i> %	<i>H. azteca</i> %	<i>C. dilutus</i> %	<i>C. dilutus</i> Growth (mg)
Trial 1	Survival	Survival	Survival	
(A) Inflow	60	34	100	3.67
(B) Pre-Pennywort	92	100	100	1.56
(C) Outflow	64	100	100	3.32
(D) Post-GAC	36	72	98	3.73
Control	100	100	100	2.45
Trial 2				
(A) Inflow	100	100	98	1.02
(B) Pre-Pennywort	100	98	98	1.18
(C) Outflow	100	100	98	1.02
(D) Post-GAC	96	96	100	1.12
Control	100	100	96	1.71
Trial 3				
(A) Inflow	100	86	98	3.19
(C) Outflow	92	100	100	2.27
(D) Post-GAC	92	98	100	2.79
Control	96	96	96	2.80
Trial 4				
(A) Inflow	100	98	100	5.89
(C) Outflow	96	100	98	5.42
(D) Post-GAC	96	100	98	5.48
Control	96	100	94	7.29
Trial 5				
(A) Inflow	100	0	6	0.02
(C) Outflow	96	68	85	5.13
(D) Post-GAC	92	80	94	5.34
Control	96	96	94	4.60

Use of toxicity testing is necessary when monitoring treatment effectiveness because toxicity can often be caused by complex mixtures of pesticides in which nonlethal concentrations of detected analytes may have additive or synergistic effects. Organisms will respond to the bioavailable fraction of multiple contaminants, and the resolution of toxicity monitoring is increased through the use of multiple species with varying sensitivities (Anderson et al. 2017).

The Molera Road Experimental Treatment Wetland has generally been used to study reductions in nutrients, but in a previous study of pesticide and toxicity reduction in this wetland, Hunt et al. (2007) determined that toxicity was related to the more frequently detected organophosphate insecticide diazinon, which was reduced as water moved through the wetland channel. Toxicity was also reduced by the channel in the current study, and further reduced with GAC filtration in Trial 5. Organophosphate insecticides were not detected in this study, but the more current use pesticides likely to contribute to toxicity are the pyrethroid and neonicotinoid insecticides. The only pyrethroid detected was bifenthrin, for which concentrations exceeded the median lethal concentration (LC50) for *H. azteca* (9.3 ng/L, Anderson et al. 2006) and *C. dilutus* (26 ng/L, Ding

et al. 2012). Trial 5 input water contained approximately 4 toxic units of bifenthrin for *H. azteca*, and about 1.6 toxic units for *C. dilutus*. A toxic unit (TU) is equal to the measured concentration divided by the LC₅₀. The neonicotinoids in Trial 5 collectively contributed about 0.3 TUs for *C. dilutus* and 0.2 TU for *H. azteca*. GAC substantially reduced neonicotinoid concentrations.

The causes of toxicity to *C. dubia* and *H. azteca* in Trial 1 are less clear, and it is hard to draw conclusions from the complex mixture of detected pesticides. The fungicide carbendazim was detected at far greater concentrations than any other pesticide, exceeding 9000 ng/L at the outflow of the channel. Carbendazim is moderately toxic to many aquatic organisms (IUPAC 2019), although the literature is lacking in the direct effects of this analyte on *C. dubia* and *H. azteca*. The daphnids *Daphnia pulex* and *Daphnia magna* have reported LC₅₀ values of 136,100 ng/L for 48 h (Encina, Escalante, and Salazar 2017) and 270,000 ng/L for 96 h (Verschuere 2001), respectively. Additionally, juveniles of the freshwater amphipod *Gammarus pulex* have been observed to have a 48-h LC₅₀ value of 77,000 ng/L and a 96-h LC₅₀ of 55,000 ng/L (Van Wijngaarden et al. 1998). Regardless, following input toxicity at Station A in Trial 1, there was no observed toxicity within the channel before the pennywort (Station B) to both *C. dubia* and *H. azteca*. Toxicity returned after the pennywort (Station C) to *C. dubia*, and to both of these organisms following GAC filtration (Station D). However, all measured pesticide concentrations at Station D were less than the measured values at Station B (Appendices B – D). It is therefore presumed that elevated conductivity pulses contributed to daphnid toxicity, and post-GAC toxicity to daphnids and amphipods was attributed to the materials used to construct the carbon installation in this trial, such as the polyethylene trough lining.

CONCLUSIONS

Constructed wetlands contain many parameters that can influence treatment efficiency, such as wetland size, water depth, flow rate, flora type and density, soil type, and contaminant input rate. The associated variability can ultimately influence the persistence of pesticides exhibiting different properties within the wetland system (Blankenberg, Braskerud, and Haarstad 2006; Olette et al. 2008; Budd et al. 2011; Vymazal and Brezinova 2015; Tu, Jiang, and Li 2018). The Molera Road Experimental Treatment Wetland contains a narrow (0.5-m), shallow (0.3-m) sinuous channel, which was excavated to greater depth at the input to serve as a sedimentation basin upon construction in 2005. The narrowness and shallowness of the channel aid in promoting contaminant treatment mechanisms such as settling with sediment particles, plant sorption, hydrolysis, photolysis, and microbial breakdown (Hunt et al. 2007). The wetland is dominated by cattails (*Typha* sp.) along the channel's margins, which are a fairly common type of vegetation for wetlands in North America (Vymazal 2013). The presence of these densely-rooted macrophytes can aid in slowing water movement, as well as the adsorption and uptake of pesticides (Stang, Bakanov, and Schulz 2016; Main et al. 2017; Moore, Locke, and Kroger 2017).

Hydraulic retention time also influences the effectiveness of constructed wetlands, with longer residence times relating to greater treatment of pesticides, particularly more hydrophobic compounds (Blankenberg, Braskerud, and Haarstad 2006; Díaz, O'Geen, and Dahlgren 2012; Romain, Sylvie, and David 2015; Gaullier et al. 2018). Hunt et al. (2007) sought to assess

treatment efficiency across varying residence times in this treatment wetland. However, because input water from the Tembladero Slough exhibited widely variable contaminant concentrations, it was difficult to fully evaluate the effect of residence time alone. The authors did determine that a 72-h residence time allowed for higher reductions of organophosphate concentrations, particularly the more frequently detected diazinon. In a more recent study, Miller (2014) assessed the effectiveness of this wetland's ability to reduce nitrate concentrations with a pumping rate of 7.5 h/d, and determined that the channel removed nitrate following an 84-h residence time. The 48-hour residence time used in the current study was chosen partially because of logistical constraints, and partially to determine if the wetland system could treat water at a higher flow rate.

The results of this study demonstrated that the Molera Road Experimental Treatment Wetland coupled with GAC filtration significantly reduced pesticide concentrations associated with agricultural runoff, as well as reduced related toxicity, nutrients, and suspended particles. These reductions were likely the result of numerous factors, including a controlled hydraulic residence time allowing for reduced flow, as well as settling of sediment, plant sorption, hydrolysis, photolysis, and microbial metabolism. The observed variability in treatment was likely influenced by factors such as physical-chemical properties and concentrations of pesticides related to local applications, changing environmental parameters, and the evolving design of the GAC filtration component.

Further research with this integrated wetland treatment system would be beneficial in better understanding the effectiveness of treating nonpoint source agricultural runoff. For instance, trials could be conducted with varying hydraulic residence times, vegetation pesticide removal could be quantitatively measured, and sediment chemical analyses and toxicity tests could be carried out periodically to evaluate pesticide accumulation within the system. Continued investigations and evaluations could also be conducted to identify other treatment methods within an integrated system. For example, biochar could be a more cost-effective and comparable alternative to GAC.

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APPENDICES

Appendix A. Target chemical analytes and method detection limits (MDLs) sorted by chemical class. An asterisk indicates a degradate.

Analyte	Chemical Class	Pesticide Type	Analytical Method	MDL (ng/L)
Fluazinam	2,6-Dinitroaniline	Fungicide	GC/MS	4.4
Benfluralin	2,6-Dinitroaniline	Herbicide	GC/MS	2.0
Butralin	2,6-Dinitroaniline	Herbicide	GC/MS	2.6
Ethalfuralin	2,6-Dinitroaniline	Herbicide	GC/MS	3.0
Oryzalin	2,6-Dinitroaniline	Herbicide	LC/MS/MS	5.0
Pendimethalin	2,6-Dinitroaniline	Herbicide	GC/MS	2.3
Prodiamine	2,6-Dinitroaniline	Herbicide	GC/MS	5.2
Trifluralin	2,6-Dinitroaniline	Herbicide	GC/MS	2.1
DCPA	Alkyl Phthalate	Herbicide	GC/MS	2.0
Benzovindiflupyr	Amide	Fungicide	GC/MS	3.4
Isofetamid	Amide	Fungicide	GC/MS	2.0
Propiconazole	Amide	Fungicide	GC/MS	5.0
Napropamide	Amide	Herbicide	GC/MS	8.2
Penthiopyrad	Amide, Pyrazole	Fungicide	LC/MS/MS	3.2
Fluopyram	Amide, Pyridine	Fungicide	GC/MS	3.8
Fenhexamide	Anilide	Fungicide	GC/MS	7.6
Flutolanil	Anilide	Fungicide	GC/MS	4.4
Fluxapyroxad	Anilide	Fungicide	GC/MS	4.8
Flufenacet	Anilide	Herbicide	GC/MS	4.7
Propanil	Anilide	Herbicide	GC/MS	10.1
Chlorantraniliprole	Anthranilic Diamide	Insecticide	LC/MS/MS	4.0
Cyantraniliprole	Anthranilic Diamide	Insecticide	LC/MS/MS	4.2
Flubendiamide	Anthranilic Diamide	Insecticide	GC/MS	6.2
Cyhalofop-Butyl	Aryloxyphenoxy Propionic Acid	Herbicide	GC/MS	1.9
Cyazofamid	Azole	Fungicide	LC/MS/MS	4.1
Cyproconazole	Azole	Fungicide	GC/MS	4.7
Difencconazole	Azole	Fungicide	GC/MS	10.5
Fenbuconazole	Azole	Fungicide	GC/MS	5.2
Flusilazole	Azole	Fungicide	GC/MS	4.5
Flutriafol	Azole	Fungicide	GC/MS	4.2
Imazalil	Azole	Fungicide	GC/MS	10.5
Ipconazole	Azole	Fungicide	GC/MS	7.8
Metconazole	Azole	Fungicide	GC/MS	5.2
Tebuconazole	Azole	Fungicide	GC/MS	3.7
Tetraconazole	Azole	Fungicide	GC/MS	5.6
Triadimefon	Azole	Fungicide	GC/MS	8.9
Triadimenol	Azole	Fungicide	GC/MS	8.0
Tricyclazole	Azole	Fungicide	LC/MS/MS	4.1
Triflumizole	Azole	Fungicide	GC/MS	6.1
Triticonazole	Azole	Fungicide	GC/MS	6.9
Zoxamide	Benzamide	Fungicide	GC/MS	3.5
Propyzamide	Benzamide	Herbicide	GC/MS	5.0
Carbendazim *	Benzimidazole	Fungicide	LC/MS/MS	4.2
Thiabendazole	Benzimidazole	Fungicide	LC/MS/MS	3.6
Acibenzolar-S-Methyl	Benzothiadiazole	Fungicide	GC/MS	3.0
Novaluron	Benzoylurea	Insecticide	GC/MS	2.9
Carboxin	Carboxamide	Fungicide	LC/MS/MS	4.5
Acetochlor	Chloroacetanilide	Herbicide	GC/MS	1.5

Appendix A. Continued.

Analyte	Chemical Class	Pesticide Type	Analytical Method	MDL (ng/L)
Metolachlor	Chloroacetanilide	Herbicide	GC/MS	1.5
Methoxyfenozide	Diacylhydrazine	Insecticide	LC/MS/MS	2.7
Tebufenozide	Diacylhydrazine	Insecticide	LC/MS/MS	3.0
Famoxadone	Dicarboximide	Fungicide	GC/MS	2.5
Iprodione	Dicarboximide	Fungicide	GC/MS	4.4
Fenamidon	Imidazole	Fungicide	GC/MS	5.1
Pyriproxyfen	Juvenile Hormone Mimic	Insecticide	GC/MS	5.2
Methoprene	Juvenile Hormone Mimic (Terpene)	Insecticide	GC/MS	6.4
Mandipropamid	Mandelamide	Fungicide	LC/MS/MS	3.3
Dimethomorph	Morpholine	Fungicide	GC/MS	6.0
Acetamiprid	Neonicotinoid	Insecticide	LC/MS/MS	3.3
Clothianidin	Neonicotinoid	Insecticide	LC/MS/MS	3.9
Dinotefuran	Neonicotinoid	Insecticide	LC/MS/MS	4.5
Flupyradifurone	Neonicotinoid	Insecticide	LC/MS/MS	3.0
Imidacloprid	Neonicotinoid	Insecticide	LC/MS/MS	3.8
Imidacloprid Urea *	Neonicotinoid	Insecticide	LC/MS/MS	4.8
Thiacloprid	Neonicotinoid	Insecticide	LC/MS/MS	3.2
Thiamethoxam	Neonicotinoid	Insecticide	LC/MS/MS	3.4
Thiamethoxam Degradate (NOA-355190) *	Neonicotinoid	Insecticide	LC/MS/MS	3.5
Thiamethoxam Degradate (NOA-407475) *	Neonicotinoid	Insecticide	LC/MS/MS	3.4
Oxyfluorfen	Nitrophenyl ether	Herbicide	GC/MS	3.1
Carbaryl	N-Methyl Carbamate	Insecticide	GC/MS	6.5
Carbofuran	N-Methyl Carbamate	Insecticide	GC/MS	3.1
Chlorothalonil	Organochlorine	Fungicide	GC/MS	4.1
p,p'-DDD *	Organochlorine	Insecticide	GC/MS	4.1
p,p'-DDE *	Organochlorine	Insecticide	GC/MS	3.6
p,p'-DDT *	Organochlorine	Insecticide	GC/MS	4.0
Tribufos	Organophosphate	Herbicide	GC/MS	3.1
Azinphos-Methyl	Organophosphate	Insecticide	GC/MS	9.4
Chlorpyrifos	Organophosphate	Insecticide	GC/MS	2.1
Chlorpyrifos Oxon *	Organophosphate	Insecticide	GC/MS	5.0
Coumaphos	Organophosphate	Insecticide	GC/MS	3.1
Diazinon	Organophosphate	Insecticide	GC/MS	0.9
Diazinon Oxon *	Organophosphate	Insecticide	GC/MS	5.0
Dichlorvos	Organophosphate	Insecticide	GC/MS	5.1
Fenthion	Organophosphate	Insecticide	GC/MS	5.5
Malathion	Organophosphate	Insecticide	GC/MS	3.7
Malathion Oxon *	Organophosphate	Insecticide	GC/MS	5.0
Methidathion	Organophosphate	Insecticide	GC/MS	7.2
Methyl Parathion	Organophosphate	Insecticide	GC/MS	3.4
Phosmet	Organophosphate	Insecticide	GC/MS	4.4
Tebupirimfos	Organophosphate	Insecticide	GC/MS	1.9
Tebupirimfos Oxon *	Organophosphate	Insecticide	GC/MS	2.8
Metalaxyl	Phenylamide	Fungicide	GC/MS	5.1
Fipronil	Phenylpyrazole	Insecticide	GC/MS	2.9
Fipronil Desulfanyl *	Phenylpyrazole	Insecticide	GC/MS	1.6
Fipronil Desulfanyl Amide *	Phenylpyrazole	Insecticide	GC/MS	3.2
Fipronil Sulfide *	Phenylpyrazole	Insecticide	GC/MS	1.8
Fipronil Sulfone *	Phenylpyrazole	Insecticide	GC/MS	3.5
Oxathiapiprolin	Piperidinyl Thiazole Isoxazoline	Fungicide	LC/MS/MS	3.2
Chlorfenapyr	Pyrazole	Insecticide	GC/MS	3.3
Fenpyroximate	Pyrazole	Insecticide	GC/MS	5.2

Appendix A. Continued.

Analyte	Chemical Class	Pesticide Type	Analytical Method	MDL (ng/L)
Tolfenpyrad	Pyrazole	Insecticide	LC/MS/MS	2.9
Sedaxane	Pyrazole-carboxamide	Fungicide	GC/MS	5.2
Allethrin	Pyrethroid	Insecticide	GC/MS	1.0
Bifenthrin	Pyrethroid	Insecticide	GC/MS	0.7
Cyfluthrin	Pyrethroid	Insecticide	GC/MS	1.0
Cyhalothrin	Pyrethroid	Insecticide	GC/MS	0.5
Cypermethrin	Pyrethroid	Insecticide	GC/MS	1.0
Deltamethrin	Pyrethroid	Insecticide	GC/MS	0.6
Esfenvalerate	Pyrethroid	Insecticide	GC/MS	0.5
Fenpropathrin	Pyrethroid	Insecticide	GC/MS	0.6
Permethrin	Pyrethroid	Insecticide	GC/MS	0.6
Phenothrin	Pyrethroid	Insecticide	GC/MS	1.0
Resmethrin	Pyrethroid	Insecticide	GC/MS	1.0
Tau-Fluvalinate	Pyrethroid	Insecticide	GC/MS	0.7
Tefluthrin	Pyrethroid	Insecticide	GC/MS	0.6
Tetramethrin	Pyrethroid	Insecticide	GC/MS	0.5
Etofenprox	Pyrethroid Ether	Insecticide	GC/MS	2.2
Boscalid	Pyridine	Fungicide	GC/MS	2.8
Dithiopyr	Pyridinecarboxylic Acid	Herbicide	GC/MS	1.6
Thiazopyr	Pyridinecarboxylic Acid	Herbicide	GC/MS	4.1
Cyprodinil	Pyrimidine	Fungicide	GC/MS	7.4
Fenarimol	Pyrimidine	Fungicide	GC/MS	6.5
Fluopicolide	Pyrimidine	Fungicide	GC/MS	3.9
Pyrimethanil	Pyrimidine	Fungicide	GC/MS	4.1
Fludioxinil	Pyrrole	Fungicide	GC/MS	7.3
Quinoxifen	Quinoline	Fungicide	GC/MS	3.3
Azoxystrobin	Strobilurin	Fungicide	GC/MS	3.1
Trifloxystrobin	Strobilurin	Fungicide	GC/MS	4.7
Fluoxastrobin	Strobin	Fungicide	GC/MS	9.5
Kresoxim-methyl	Strobin	Fungicide	GC/MS	4.0
Picoxystrobin	Strobin	Fungicide	GC/MS	4.2
Pyraclostrobin	Strobin	Fungicide	GC/MS	2.9
Pentachloronitrobenzene (PCNB)	Substituted benzene, Chlorophenyl	Fungicide	GC/MS	3.1
Ethaboxam	Thiazole	Fungicide	LC/MS/MS	3.8
Butylate	Thiocarbamate	Herbicide	GC/MS	1.8
Cycloate	Thiocarbamate	Herbicide	GC/MS	1.1
EPTC	Thiocarbamate	Herbicide	GC/MS	1.5
Molinate	Thiocarbamate	Herbicide	GC/MS	3.2
Pebulate	Thiocarbamate	Herbicide	GC/MS	2.3
Thiobencarb	Thiocarbamate	Herbicide	GC/MS	1.9
Triallate	Thiocarbamate	Herbicide	GC/MS	2.4
Captan	Thiophthalimide	Fungicide	GC/MS	10.2
Atrazine	Triazine	Herbicide	GC/MS	2.3
Indaziflam	Triazine	Herbicide	GC/MS	2.1
Prometon	Triazine	Herbicide	GC/MS	2.5
Prometryn	Triazine	Herbicide	GC/MS	1.8
Simazine	Triazine	Herbicide	GC/MS	5.0
Hexazinone	Triazinone	Herbicide	GC/MS	8.4
Myclobutanil	Triazole	Fungicide	GC/MS	6.0
Paclobutrazol	Triazole	Fungicide	GC/MS	6.2
Desthio-Prothioconazole	Triazolinthione	Fungicide	LC/MS/MS	3.0
Penoxsulam	Triazolopyrimidine	Herbicide	LC/MS/MS	3.5

Appendix A. Continued.

Analyte	Chemical Class	Pesticide Type	Analytical Method	MDL (ng/L)
Diuron	Urea	Herbicide	LC/MS/MS	3.2
DCPMU *	Urea	Herbicide	LC/MS/MS	3.5
DCPU *	Urea	Herbicide	LC/MS/MS	3.4
3,4-DCA *	Unknown	Herbicide	GC/MS	8.3
3,5-DCA *	Unknown	Herbicide	GC/MS	7.6
Cymoxanil	Unclassified	Fungicide	LC/MS/MS	3.9
Clomazone	Unclassified	Herbicide	GC/MS	2.5
Fluridone	Unclassified	Herbicide	LC/MS/MS	3.7
Oxadiazon	Unclassified	Herbicide	GC/MS	2.1
Etoxazole	Unclassified	Insecticide	GC/MS	4.2
Flonicamid	Unclassified	Insecticide	LC/MS/MS	3.4
Indoxacarb	Unclassified	Insecticide	GC/MS	4.9
Pentachloroanisole (PCA)	Unclassified	Insecticide	GC/MS	4.7
Piperonyl Butoxide	Unclassified	Insecticide	GC/MS	2.3
Propargite	Unclassified	Insecticide	GC/MS	6.1
Pyridaben	Unclassified	Insecticide	GC/MS	5.4
Sulfoxaflor	Unclassified	Insecticide	LC/MS/MS	4.4
Tetradifon	Unclassified	Insecticide	GC/MS	3.8

Appendix B. Detected fungicide concentrations reported in ng/L. Analytes are listed by ascending log K_{ow} , or octanol/water partition coefficients. An asterisk indicates a degradate. Sample A was collected at the wetland channel inflow, Sample B upstream of the pennywort (Trials 1 and 2), Sample C at the channel outflow, and Sample D at the outflow of the GAC filtration installation.

Analyte	Class	log Kow	Sampling Stations																	
			Trial 1				Trial 2				Trial 3			Trial 4			Trial 5			
			A	B	C	D	A	B	C	D	A	C	D	A	C	D	A	C	D	
Carbendazim *	Benzimidazole	1.52	2196	1891	9564	1002	1168	899	980	<4.2	716	783	18.0	225	324	203	3168	1771	2213	
Metalaxyl	Phenylamide	1.65	157	144	142	132	936	421	502	103	139	106	53.3	69.5	94.6	79.1	123	106	99.6	
Flutriafol	Azole	2.30	<4.2	<4.2	<4.2	<4.2	33.6	64.2	79.4	12.3	<4.2	<4.2	<4.2	56.4	36.1	56.6	62.9	61.2	54.1	
Azoxystrobin	Strobilurin	2.50	98.0	98.1	110	104	298	183	218	24.0	46.7	64.4	100.0	26.6	45.3	38.8	301	190	169	
Isofetamid	Amide	2.50	<2.0	<2.0	<2.0	<2.0	12.0	7.3	9.2	<2.0	<2.0	<2.0	<2.0	28.9	24.2	17.1	58.0	42.8	39.3	
Dimethomorph	Morpholine	2.68	208	197	210	191	318	155	185	29.1	67.6	107	58.8	85.8	95.4	78.5	174	137	124	
Fenamidone	Imidazole	2.80	62.8	63.1	63.1	57.4	57.2	32.5	41.4	<5.1	34.1	33.6	17.1	14.7	27.0	19.3	72.3	53.7	58.9	
Pyrimethanil	Pyrimidine	2.84	43.7	32.6	29.0	25.3	14.3	11.6	8.6	4.9	6.7	5.3	<4.1	7.7	5.7	4.3	78.6	46.4	36.4	
Myclobutanil	Triazole	2.94	191	184	179	168	153	139	168	<6.0	37.3	41.0	15.3	58.3	55.2	40.5	206	133	118	
Boscalid	Pyridine	2.96	402	403	384	344	716	498	541	50.5	174	185	95.0	173	188	151.9	469	297	264	
Iprodione	Dicarboximide	3.00	<4.4	<4.4	<4.4	<4.4	29.8	34.2	44.0	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	<4.4	105	78.2	69.8	
Paclbutrazol	Triazole	3.11	78.4	69.6	49.8	52.0	<6.2	<6.2	<6.2	<6.2	<6.2	<6.2	<6.2	<6.2	<6.2	<6.2	<6.2	<6.2	<6.2	
Fluxapyroxad	Anilide	3.13	144	155	163	150	187	<4.8	<4.8	<4.8	50.4	59.5	28.1	50.2	63.9	49.7	416	261	237	
Mandipropamid	Mandelamide	3.20	21.2	14.7	14.3	8.6	29.8	3.5	3.5	<3.3	7.0	7.1	<3.3	10.8	4.4	2.5	45.0	38.2	25.2	
Fluopicolide	Pyrimidine	3.26	170	215	211	204	398	306	354	24.3	109	115	63.1	70.8	104	85.1	150	109	94.7	
Triticonazole	Azole	3.29	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	<6.9	51.1	50.3	43.4	
Fluopyram	Amide, Pyridine	3.30	275	280	269	257	201.5	210	253	25.7	75.1	74.5	37.9	154.8	134.0	105.3	325	228	211	
Fenhexamid	Anilide	3.51	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	<7.6	171	63.3	109	
Tetraconazole	Azole	3.56	23.7	19.6	18.6	16.0	28.6	21.0	25.4	6.6	6.3	7.3	4.0	4.0	6.5	5.3	60.2	36.6	31.8	
Cyprodinil	Pyrimidine	3.59	26.5	16.6	15.7	13.1	13.3	5.8	<7.4	<7.4	<7.4	<7.4	<7.4	4.6	3.2	2.7	122	55.7	44.6	
Tebuconazole	Azole	3.70	<3.7	<3.7	<3.7	<3.7	50.6	42.0	87.6	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7	<3.7	58.0	46.2	40.4	
Propiconazole	Amide	3.72	<5.0	<5.0	<5.0	<5.0	66.7	28.9	25.8	<5.0	20.9	14.2	9.7	31.6	23.6	19.4	125	87.1	77.7	
Fludioxinil	Pyrrole	4.12	68.2	46.4	47.8	44.7	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	<7.3	122	48.2	37.6	
Trifloxystrobin	Strobilurin	4.50	<4.7	<4.7	<4.7	<4.7	<4.7	<4.7	<4.7	<4.7	<4.7	<4.7	<4.7	26.7	9.8	<4.7	53.5	31.6	26.3	
Penthiopyrad	Amide, Pyrazole	4.62	36.5	28.9	25.3	15.7	39.8	21.8	18.7	<3.2	4.8	5.6	<3.2	7.9	6.2	4.7	125	86.0	62.1	

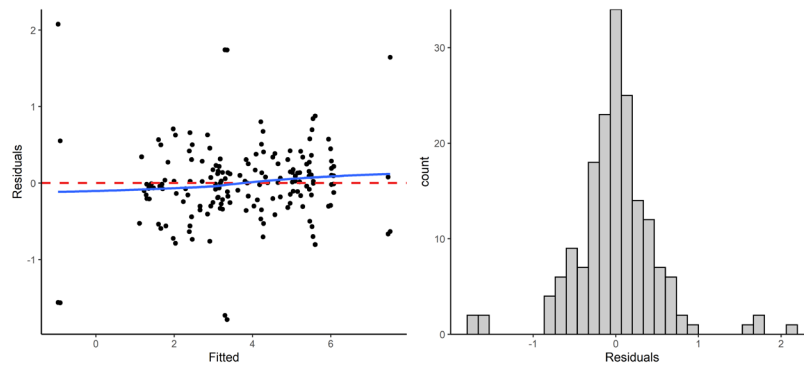
Appendix C. Detected herbicide concentrations reported in ng/L. Analytes are listed by ascending log K_{ow} , or octanol/water partition coefficients. An asterisk indicates a degradate. Sample A was collected at the wetland channel inflow, Sample B upstream of the pennywort (Trials 1 and 2), Sample C at the channel outflow, and Sample D at the outflow of the GAC filtration installation.

Analyte	Class	log Kow	Sampling Stations																		
			Trial 1				Trial 2				Trial 3			Trial 4			Trial 5				
			A	B	C	D	A	B	C	D	A	C	D	A	C	D	A	C	D		
Hexazinone	Triazinone	1.85	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	<8.4	36.0	24.6	23.6
DCPU*	Urea	2.55	<3.4	<3.4	<3.4	<3.4	5.8	7.6	6.8	<3.4	4.2	4.8	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	9.8	6.9	6.2
Diuron	Urea	2.68	20.2	27.1	26.5	12.7	24.1	20.5	18.9	<3.2	12.6	6.6	<3.2	17.2	10.6	7.9	383	313	205		
3,4-DCA*	Unknown	2.69	6.2	3.4	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	<3.2	8.5	<3.2	<3.2
DCPMU*	Urea	3.00	<3.5	<3.5	<3.5	<3.5	3.4	3.2	3.9	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	9.4	4.0	3.2
Napropamide	Amide	3.36	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	<8.2	42.9	32.3	28.4
Propyzamide	Benzamide	3.43	101	127	121	116	566	595	652	79.8	123	164	78.8	76.8	118	95.4	81.3	85.7	73.9		
Prometryn	Triazine	3.51	118	166	153	145	77.5	124	174	42.7	87.8	66.8	<1.8	43.0	68.0	57.6	132	116	97.6		
Oryzalin	2,6-Dinitroaniline	3.73	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	<5.0	140	21.9	15.9
Cycloate	Thiocarbamate	3.88	94.7	82.5	81.0	45.3	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1	<1.1
DCPA	Alkyl phthalate	4.28	<2.0	<2.0	<2.0	<2.0	45.6	9.0	11.4	<2.0	7.4	4.1	<2.0	<2.0	<2.0	<2.0	<2.0	<2.0	308	177	149
Oxyfluorfen	Nitrophenyl ether	4.73	1.9	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	<3.1	114	53.6	44.9
Pendimethalin	2,6-Dinitroaniline	5.20	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	27.9	<2.3	<2.3
Dithiopyr	Pyridinecarboxylic acid	5.88	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	6.9	2.7	3.1

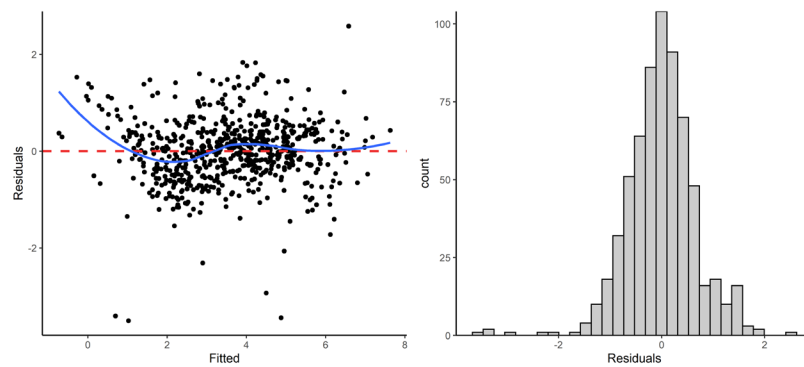
Appendix D. Detected insecticide concentrations reported in ng/L. Analytes are listed by ascending log K_{ow} , or octanol/water partition coefficients. An asterisk indicates a degradate. Sample A was collected at the wetland channel inflow, Sample B upstream of the pennywort (Trials 1 and 2), Sample C at the channel outflow, and Sample D at the outflow of the GAC filtration installation.

Analyte	Class	log K_{ow}	Sampling Stations																
			Trial 1				Trial 2				Trial 3			Trial 4			Trial 5		
			A	B	C	D	A	B	C	D	A	C	D	A	C	D	A	C	D
Dinotefuran	Neonicotinoid	-0.64	28.1	48.3	42.7	31.1	86.8	114	109	7.8	54.6	45.2	9.0	45.9	38.9	19.1	280	237	178
Thiamethoxam	Neonicotinoid	-0.13	143	159	145	103	462	283	278	23.8	101	102	21.7	111	87.0	64.5	556	448	365
Thiamethoxam Degradate (CGA-355190)*	Neonicotinoid		20.4	24.6	23.9	15.6	19.1	33.4	34.7	2.6	8.7	12.4	3.1	12.8	13.8	9.7	25.8	20.9	14.9
Thiamethoxam Degradate (NOA-407475)*	Neonicotinoid		14.3	10.1	20.1	7.8	25.3	10.6	15.5	<3.4	15.0	11.3	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4	<3.4
Flonicamid	Unclassified	0.30	94.4	151	141	116	38.6	42.3	35.4	8.2	29.0	26.9	10.6	321	211	150	494	201	154
Imidacloprid	Neonicotinoid	0.57	103	135	119	90.4	206	106	92.6	4.3	61.1	52.0	11.3	65.3	61.9	45.7	206	136	89.8
Imidacloprid Urea*	Neonicotinoid		11.1	24.0	20.5	16.5	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	12.5	10.7	7.0	<4.0	<4.0	<4.0
Clothianidin	Neonicotinoid	0.70	51.5	75.0	64.2	44.0	297	129	143	5.6	26.1	23.7	6.1	25.4	22.4	16.5	157	93.4	63.7
Acetamiprid	Neonicotinoid	0.80	11.6	17.2	18.1	10.4	39.8	32.9	29.1	<3.3	12.2	10.6	<3.3	149	73.3	49.9	641	392	265
Sulfoxaflor	Unclassified	0.80	<4.4	6.3	5.6	<4.4	26.2	21.4	19.3	<4.4	5.8	7.9	<4.4	8.6	8.0	5.3	<4.4	<4.4	<4.4
Flupyradifurone	Neonicotinoid	1.20	292	455	429	334	617	548	478	43.8	137	150	34.6	390	258	185	1366	793	549
Cyantraniliprole	Anthranilic diamide	2.02	16.4	14.0	15.5	11.4	44.4	20.2	23.7	5.5	12.9	11.1	4.2	31.4	18.2	14.8	517	428	323
Chlorantraniliprole	Anthranilic diamide	2.76	174	281	301	197	906	676	630	86.1	179	169	53.7	508	357	269	726	622	488
Methoxyfenozide	Diacylhydrazine	3.70	181	267	266	163	271	273	258	58.3	89.4	82.4	41.0	134	119	102	532	480	428
Fipronil	Phenylpyrazole	4.00	8.2	8.8	8.6	7.5	5.5	<2.9	<2.9	<2.9	<2.9	<2.9	<2.9	<2.9	<2.9	<2.9	18.7	12.1	2.6
Fipronil desulfinyl*	Phenylpyrazole		5.1	4.9	5.3	4.3	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	<1.6	6.7	5.1	4.4
Fipronil sulfide*	Phenylpyrazole		<1.8	<1.8	4.5	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8	<1.8
Fipronil sulfone*	Phenylpyrazole		5.0	5.1	6.1	4.6	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	<3.5	11.8	8.4	8.0
Tebufofenozide	Diacylhydrazine	4.25	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	3.7	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0	<3.0
Piperonyl Butoxide	Unclassified	4.75	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	<2.3	87.0	44.4	37.9
Bifenthrin	Pyrethroid	6.00	3.9	0.1	0.1	0.1	20.9	3.0	<0.7	<0.7	5.2	<0.7	<0.7	4.9	2.7	<0.7	37.6	16.1	16.4
p,p'-DDD*	Organochlorine	6.02	1.8	<4.1	<4.1	<4.1	17.2	<4.1	<4.1	<4.1	5.9	<4.1	<4.1	<4.1	<4.1	<4.1	8.8	<4.1	<4.1
p,p'-DDE*	Organochlorine	6.51	7.4	<3.6	<3.6	<3.6	82.8	<3.6	<3.6	<3.6	19.4	6.6	5.5	13.6	4.1	3.0	20.8	7.7	6.5
p,p'-DDT*	Organochlorine	6.91	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	<4.0	29.5	12.3	11.8

Appendix E. Plot of the residuals for the linear mixed effects model analysis of pennywort (*Hydrocotyle* spp.) treatment in Trials 1 and 2. A log transformation of pesticide concentrations shows that the residuals are drawn from a normal distribution with mean zero.



Appendix F. Plot of the residuals for the linear mixed effects model analysis of treatments among pesticide groups. A log transformation of pesticide concentrations shows that the residuals are drawn from a normal distribution with mean zero.



Appendix G. Plot of the residuals for the linear mixed effects model analysis of treatments among pesticide class. A log transformation of pesticide concentrations shows that the residuals are drawn from a normal distribution with mean zero.

