



Research paper

Assessing pesticide reduction in constructed wetlands using a tanks-in-series model within a Bayesian framework

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ABSTRACT

Frequent pesticide detection at toxic levels to test organisms in California's Central Coast waterbodies has motivated regulators, resource agencies and end-users to investigate and adopt management practices and technologies to diminish agricultural chemicals entering receiving waters. Treatment wetlands are a technology of special interest because of their ability to simultaneously treat multiple pollutants commonly found in agricultural and urban runoff including nitrate, suspended sediment and pesticides. We sought evidence for transformation of three highly water-soluble pesticides (diazinon, methomyl and acephate) in a full-scale constructed treatment wetland located at the base of the Salinas Valley. We pumped water into the wetland from a slough containing agricultural runoff. The pumping rate was set to achieve a four-day mean residence time, and outlet samples were collected four days after inlet samples. We developed a dynamic tanks-in-series model and fit it to pesticide concentration data from the wetland, using parameters for number of tanks in series, mean hydraulic residence time, pesticide decay, and two parameters for inlet concentrations outside of the sampling period. We used a Bayesian analytical approach to determine the 95% credible intervals (CI) and most likely values for the five model parameters, and developed inference for pesticide decay based on the CI for the decay rate parameter. The CIs for the three pesticide decay parameters were positive and did not span zero, supporting the postulate that the wetland removed these pesticides to some extent. CIs for first-order decay rates were 0.097–0.289 day⁻¹ for diazinon, 0.068–0.232 day⁻¹ for methomyl, and 0.068–0.246 day⁻¹ for acephate. These intervals can be used in conjunction with simple decay models to optimize the design of wetlands and to estimate size requirements.

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1. Introduction

Agricultural production makes the largest economic contribution to Monterey County of all industries, grossing over \$4 billion in both 2009 and 2010, with nearly 60% of the nation's lettuce and artichokes and 85% of the strawberries grown in Monterey County (MCAC, 2011; MPCC, 2012). This agricultural productivity is achieved through a long growing period, fertile soils, innovative management practices, and advanced technologies including pest control methods. Pest control is accomplished through mechanical, biological and chemical methods, with nearly 4 million kg of pesticides applied in Monterey County in 2010 of nearly 300 different

active ingredients (CADPR, 2012). Pesticide use will likely increase as global warming changes the developmental patterns and eating habits of insects and increases the severity of invasive species' impacts, and as human population growth requires greater agricultural production (Tillman et al., 2001; Trumble and Butler, 2009).

Although rarely applied directly to water, pesticides may be carried to public waters by runoff, overspray and atmospheric deposition, and can originate from either agricultural and/or urban sources (Larkin and Tjeerdema, 2000; Schulz, 2004). Pesticide application rates are spatially correlated with concentrations found in streams in the central coast of California (Hunt et al., 2006). A summary of California Department of Pesticide Regulation (CADPR) monitoring results between 2008 and 2010 of six California counties found the organophosphate (OP) and carbamate pesticides detection frequency in waters ranged from 4% to 72%, with the highest frequency reported for diazinon (Starner, 2012). Monitoring programs by the California Department of Pesticide Regulation and the Cooperative Monitoring Program show frequent pesticide detection in Central Coast waters (CCWQPI, 2008; CCWQPI, 2010;

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CADPR, 2011). The Central Coast's Cooperative Monitoring Program evaluated organophosphate (OP) compounds in water in 2006 and 2007 in Monterey and San Luis Obispo Counties, detecting OP pesticides at all 23 sites monitored (CCWQPI, 2008). Both chlorpyrifos and diazinon were detected at concentrations above the 303(d) listing criteria (0.025 ppb and 0.16 ppb respectively) at 15 and 12 sites respectively (CCWQPI, 2008). The CADPR reported monitoring results from 33 sites for diazinon in Salinas Valley between 2005 and 2008 for a total of 244 samples, finding that 62% of samples exceeded the 0.10 ppb target concentration (Zhang and Starner, 2011). This target concentration was developed by the California State Water Resources Control Board for the San Joaquin and Sacramento Watershed and also represents the Criterion Continuous Concentration established for the Salinas watershed (CSWRCB, 2008; CCRWQCB, 2011).

Management practices under investigation worldwide to reduce pesticide entry into streams include altering the types of pesticides used, changing irrigation practices, changing application processes, and treating runoff before it enters public water ways by means such as no-spray zones, vegetated buffer strips, riparian vegetation, enzyme addition, and vegetated treatment systems (Schulz, 2004; Reichenberger et al., 2007; Anderson et al., 2011). A number of studies have demonstrated that pesticides with high adsorption coefficients and hydrophobicity, such as pyrethroids, can be reduced or removed from water passing through constructed wetlands or vegetated ditches, due primarily to adsorption to particles that settle and to plant surfaces (Bennett et al., 2005; Budd et al., 2009). More difficult to ascertain is the effectiveness of vegetated treatment systems and wetlands in removing highly water soluble pesticides (Reichenberger et al., 2007), such as those considered in this study.

The objective of our study was to establish a 95% credible interval for the decay rates of three water soluble pesticides (diazinon, methomyl, and acephate) through modeling wetland hydrology in order to distinguish decay from mixing. We postulated that a free water surface treatment wetland would reduce the concentrations of pesticides through decay processes such as hydrolysis, photolysis, and biological degradation. Specifically, we modeled a parameter representing the rate of decay of pesticides between the inlet and the outlet and estimated credible intervals for this parameter using Bayesian analysis. We inferred support for the postulate from the degree to which the credible intervals included zero.

2. Materials and methods

2.1. Wetland site and watershed

The wetland is located on a 1.2 ha parcel at the confluence of the Tembladero Slough and Old Salinas River Channel at the base of the Salinas Valley, CA, USA at Latitude (36.7718) and Longitude (-121.788). It was constructed for the purpose of field research and pumps water from the agriculturally intensive Tembladero Slough drainage area (Hogan et al., 2012). The contributing watershed covers 39,000 ha comprised of 36% agricultural, 12% urban land, and 48% forest, grassland and shrubland (CCRWQCB, 2011). Ambient year round temperature varies between 10 °C and 24 °C and morning fog is common (<http://www.nws.noaa.gov>). In 2010 a total of 17,400 kg of diazinon were applied to the watershed from farm operations (CADPR, 2012). Urban use of diazinon is no longer permitted and detections in urban areas have diminished since their final phase out in 2004 (Zhang and Starner, 2011).

The wetland channel morphology formed a long sinuous pattern 280 m in length by 6.5 m wide and 0.3 m deep (Fig. 1). It was designed to have a high length to width ratio (43:1) intended to



Fig. 1. Molera experimental wetland. This aerial photograph shows the sinuous wetland channel winding back and forth.

(Photo: Delay & Hatfield, 2010).

maximize plug-flow and minimize short-circuiting (Harris et al., 2007). Tule (*Schoenoplectus californicus*) were established on berms across the channel at periodic intervals, covering about 30% of the channel, and channel edges contain various rushes (*Juncus spp.*), a sedge (*Carex barbarae*) and dicots *Potentilla anserina* and *Jaumea carnosa*. Floating Duckweed (*Lemna minor*) and algae (primarily *Ulva intestinales*) dominated the open water between the sedge covered berms. Inlet water was pumped from the upper 10 cm of the water column of the Tembladero Slough, with a float attached to the inlet pipe to maintain its position on the surface. Floating the inlet allowed us to minimize entrainment of sea water into the wetland due to the salinity gradient in the slough. Water was pumped at a rate of 1.325 L s⁻¹ to achieve a hydraulic retention time of four days. Because water flows at different rates to the outlet over a residence time distribution (RTD), the 4 day interval matched the peak of the RTD, as established by a bromide tracer study conducted prior to pesticide sampling.

2.2. Pesticide sampling and analysis

During the summer of 2009, CADPR collected pilot samples on 13 sample dates in Tembladero Slough near the pumped inlet of the wetland to determine which pesticides to investigate for wetland mitigation and to establish the timing of 2010 sampling events (Starner, 2012). The 2010 sampling schedule coincided with times when pesticides of interest were likely to be detected in the Slough. From April 28 through July 29, 2009, diazinon samples consistently ranged between 0.08 and 0.17 ppb, with a drop to between 0.03 and 0.09 between 8/31/09 and 9/16/09 (Table 1). Methomyl showed no clear detection pattern and acephate was consistently detected in samples taken between 7/27/09 and 9/1/09.

Pesticide sampling at the Molera Wetland took place between July 5 and July 11, 2010. A total of 18 samples were collected consisting of two samples taken at the inlet on Day 1, four samples on Day 2 and three samples on Day 3, spaced throughout daylight hours. Outlet samples were taken four days later on Day 4, Day 5 and Day 6, at matching times to inlet samples (Appendix A, Table A1). Pesticide samples were also taken from Tembladero Slough water near the wetland inlet three times to allow for comparison of inlet and surface water concentrations. Water quality measurements of dissolved oxygen (mg/L), water temperature (°C), pH, specific conductivity (µs/cm), total dissolved solids (g/L), and turbidity (NTU) were taken continuously during the sampling period by three Hydrolab Sondes DS5X (Hach, Loveland, CO) immersed in the wetland. One was placed near the wetland inlet, a second

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