Department of Pesticide Regulation
Environmental Monitoring Branch

1001 I Street

Sacramento, California 95812

Study 314. Pesticide mitigation through a woodchip bioreactor at Jim May Park, Santa Maria, CA

Aniela Burant, Ph.D.

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1. Introduction

The City of Santa Maria has constructed a woodchip bioreactor in Jim May Park. The bioreactor was designed to treat water conveyed in the Bradley Channel, which is a drain for approximately 5,700 acres of irrigated agriculture. The Bradley Channel also receives runoff from 913 acres of urban areas during storm events. During storm events, the Bradley Channel is full of runoff from both agricultural and urban areas. The Bradley Channel discharges into the Bradley Stormwater Management Basin, which is located in Jim May Park. This water eventually discharges into the Santa Maria River, which is on the Federal Clean Water Act Section 303(d) list due to high levels of nitrate in the water. Historical monitoring data has shown that the Bradley Channel contains, on average, nitrate concentrations of 80 mg /L nitrate as nitrogen (mg-N/L), well above the target concentration of 10 mg-N/L, which is the United States Environmental Protection Agency's (USEPA) drinking water maximum contaminant level (US EPA, 2017a). In addition, the Bradley Channel has recently been added as a monitoring site for the California Department of Pesticide Regulation's (CDPR) environmental monitoring efforts in Central and Southern California agricultural regions since it serves as a drain for agricultural irrigation runoff. These monitoring efforts by CDPR detected an array of pesticides in the Bradley Channel in 2016 (Deng, 2016). Therefore, in addition to removing nitrate, the Jim May Park bioreactor may also serve as a treatment best management practice for removing pesticides from the agricultural tail-waters and urban runoff in the Bradley Channel.

The use of woodchip bioreactors to reduce nitrate concentrations in runoff water has been shown to be effective (Schipper et al., 2010, Krause Camilo et al., 2013; Lepine, et al., 2015; Hartz, et al, 2017). Nitrate in the bioreactors is converted to nitrogen gas (N_2) in the bioreactor by a process called heterotrophic denitrification. Woodchips in the bioreactor act as a carbon source for anaerobic bacteria in the denitrification process. The conversion of nitrate to N_2 is highly dependent on the retention time of nitrate in the reactor (Lepine, et al., 2015). The retention time of nitrate in the bioreactor is expected to be the same as the hydraulic retention time, which is expected to range from 1.5 to 2 days for the Jim May Park bioreactor. This hydraulic retention time was estimated in a design feasibility study (Wallace Group, 2013). The bioreactor is expected to treat 200 gal/min, has a surface area of 0.75 acres, and has an operating depth of six to eight feet. Preliminary studies suggest that this will provide for adequate time for conversion of nitrate to N_2 (Schipper et al., 2010; Krause Camilo et al., 2013; Lepine, et al., 2015; Hartz, et al., 2017).

There have been a few studies on the ability of bioreactors to remove pesticides from agricultural tail waters (Ranaivoson, et al., 2012; Krause Camilo, et al., 2013; Ilhan, et al., 2012). There are two

possible removal mechanisms: sorption of pesticides to woodchips and anaerobic biodegradation. Sorption of pesticides in the bioreactor is expected to be dependent on the hydrophobicity of the pesticide. Studies investigating the removal of moderately hydrophobic pesticides, such as bentazon, atrazine, and acetochlor, have confirmed that woodchips are expected to retain moderately hydrophobic pesticides (Ranaivoson, et al., 2012; Krause Camilo, et al., 2013; Ilhan, et al., 2012). Removal efficiencies have not been confirmed for hydrophilic pesticides, such as the neonicotinoids (i.e., imidacloprid) or carbamates (i.e., methomyl). Rates of anaerobic biodegradation are highly specific to each pesticide, and studies have indicated that sorption will be the primary removal mechanisms for pesticides (Ilhan, et al., 2012). In addition, the majority of this research was conducted in batch reactors or bench-sale experiments. There is a lack of peer-reviewed research on pesticide removal behavior in woodchip bioreactors at field scale. This study aims to fill this gap by determining the removal efficiency of various classes of pesticides, which have a range of hydrophobicity, on a field scale.

We aim to investigate the removal of pesticides in several bioreactors around California. In addition to Jim May Bioreactor, the Sea Mist Farms Bioreactor in Castroville, Calif., will treat irrigation runoff water. The bioreactor, which contains ~1,000 cubic yards of woodchips, will treat the tailwater before draining into a wetland. Another bioreactor in Santa Maria is under construction and will treat both agricultural tailwaters and urban runoff. All bioreactors will operate under different treatment conditions (i.e., different volume of woodchips and flow rate through the bioreactor), which will provide a comparison for removal rates between the different bioreactors.

2. Objectives

The objectives of this study are to:

1). Determine the presence and concentrations of selected pesticides at the inlet and outlet to the bioreactor.
2). Determine the removal rates of various classes of pesticides and identify which are most effectively removed by the bioreactor.
3). Evaluate the magnitude of bioreactor outlet pesticide concentrations relatively to aquatic toxicity thresholds.
4). Determine the differences in removal of pesticides between dry and wet conditions.

3. Personnel

This project is a joint effort between many state and local agencies, and will be conducted under the general direction of Nan Singhasemanon, Senior Environmental Scientist (Supervisory). Key Personnel are listed below:

- Project Leader: Aniela Burant, PhD
- Adviser: Scott Wagner
- Field Coordinator: Kevin Kelley
- Reviewing Scientist: Xin Deng, PhD
- Statistician: Dan Wang, PhD
- Laboratory Liaison: Sue Peoples
- Analytical Chemistry, water: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

- Collaborators: Shannon Sweeney, City of Santa Maria

Please direct questions regarding this study to Aniela Burant, Environmental Scientist, at (916)-445-2799 or Aniela.Burant@cdpr.ca.gov.

4. Study Plan

4.1 Selecting Pesticides for Evaluation

Pesticides that will be analyzed were selected by using the CDPR's Surface Water Monitoring Prioritization Model (Luo, 2012, 2013, 2015). The prioritization model ranks pesticides for areas or drainages of interest using use data from CDPR's Pesticide Use Reporting database and toxicological data from the US EPA Aquatic Life Benchmark database (US EPA, 2017b). The Bradley Channel primarily receives agricultural runoff from two HUC 12 drainages (HUC12 180600080503 and 180600080603) during dry season; therefore, pesticides applied within the two drainages were prioritized for monitoring. Annual average pesticide use data from 2013 – 2015 (the three most recent years available) were applied in the model, and other inputs and model parameters are given in **Table 1**. The modeling results provided a list of top-ranked 50 pesticides for both HUC 12 drainages (**Table 2**). Each pesticide is assigned a toxicity score based on its chronic or acute toxicity and a use score based on how many pounds of the pesticide was applied in the drainage area. The pesticides of interest were primarily selected based on the final score of the toxicity and use scores (**Table 3**). Groups of pesticides selected for monitoring include organophosphates (e.g. malathion), pyrethroids (e.g. permethrin and bifenthrin), neonicotinoids (e.g. imidacloprid), carbamates (e.g. methomyl), dinitroanilines (e.g. trifluralin and pendimethalin), and oxyfluorfen. Fipronil and its degradates were included in this sampling plan because the Bradley Channel receives inputs from 913 acres of urban area. Some pesticides that have high use in the area are not recommended for monitoring by the model due to a variety of physical-chemical properties, such as short persistence in water (**Table 4**).

4.2 Water Sampling

The inlet and outlet of the bioreactor will be sampled four times during the year (two dry season events and two rainstorm events). Dry season sampling will take place in September 2017 and in April – May 2018. The rain storm sampling will occur in October – November (the first flush of the 2017 – 2018 water year, if possible) and in the winter of 2018 (February – March 2018). Samples collected for this study will be grab samples collected in 1 liter amber bottles. Separate bottles will be used for each type of analysis. A separate bottle will be used to collect total suspended solids (TSS), total organic carbon (TOC), and dissolved organic carbon (DOC). To account for residence time in the bioreactor and in an effort to sample the same pulse of water, samples at the inlet will be collected 1.5 – 2 days (the expected hydraulic residence time of the reactor) before the outlet samples. Therefore, 12 samples will be collected per sampling event, six for each chemical analysis from the inlet and outlet respectively.

5. Laboratory Analysis

5.1 Chemical Analysis

A suite of pesticides will be analyzed in each sample by the Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA). Pesticide classes that will be analyzed include pyrethroids, dinitroanilines, organophosphates, carbamates (methomyl), and neonicotinoids (imidacloprid). Laboratory quality assurance and control (QA/QC) will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Segawa, 1995).

5.2 Organic Carbon, Nutrient, and Suspended Solid Analysis

TSS, TOC, DOC, ammonia, nitrate, and reactive orthophosphate will also be measured after each sampling event. Nitrate will be measured on site. A colorimetric meter (Hach DR 900 Handheld Colorimeter) will be used to measure all nutrient levels at the inlet and outlet in an effort to continue monitoring for nitrate reduction. CDPR staff will measure TSS according to Ensminger (2013a). CDPR staff will analyze water samples for TOC and DOC using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan) according to Ensminger (2013b). Given the low cost of the colorimetric measurement method, nutrient sampling is not included in the budget. Other water quality parameters, including dissolved oxygen, electrical conductivity, pH, turbidity, and temperature, will be measured *in situ* for inlet and outlet samples using a YSI EXO I multi-parameter water quality Sonde.

6. Data Analysis

The influent and effluent concentration of each pesticide will be analyzed and data will be used to determine the pesticide removal efficiency of the bioreactor. Concentrations will also be compared to the US EPA's aquatic benchmarks of pesticides, if available. This will determine the efficacy of the bioreactor. Statistical analyses will be performed to determine the removal efficiencies and differences in pesticide removal rates among pesticide classes. Since the dataset will be small (i.e. four paired data for each pesticide analyzed) and could be censored and skewed, nonparametric test and permutation test are expected to more desirable than parametric tests (Helsel, 2012). The R statistical program will be used.

7. Timetable

Field Sampling: September 2017 – May 2018
Chemical Analysis: September 2016 – July 2018
Summary Report: October 2019

8. Laboratory Budget

The expected cost for chemical analysis of samples through the CDFA lab is $28,480 (**Table 5**). All costs are estimated but do not include field blanks or laboratory QC.

9. References

CDPR (California Department of Pesticide Regulation) 2015. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. http://calpip.cdpr.ca.gov/

Central Coast Regional Water Quality Board, 2017. Agricultural Order R3-2017-0002. http://www.waterboards.ca.gov/centralcoast/water_issues/programs/ag_waivers/docs/ag_order3/ag_order3.0_approved.pdf

David, MB; Gentry, LE; Cooke, RA; and Herbstritt, 2016. Temperature and Substrate Control Woodchip Bioreactor Performance in Reducing Tile Nitrate Loads in East-Central Illinois. *Journal of Environmental Quality*, 45:822-829.

Deng, X. 2016. Surface Water Monitoring for Pesticides in Agricultural Areas of California, 2016. http://www.cdpr.ca.gov/docs/emon/pubs/ehapref/deng_report_304.pdf

Ensminger, M. 2013a. Analysis of whole sample suspended sediments in water. http://www.cdpr.ca.gov/docs/emon/pubs/sops/meth010.01.pdf

Ensminger, M. 2013b. Water TOC analysis using the Shimadzu TOC-VCSN and ASI-V autosampler. http://cdpr.ca.gov/docs/emon/pubs/sops/meth01100.pdf

Hartz T.; Smith R.; Cahn M.; Bottoms T.; Bustamante, SC.; Tourte L.; Johnson, K.; and Coletti, L. 2017. Wood chip denitrification bioreactors can reduce nitrate in tile drainage. *California Agriculture*, 71:41-47.

Helsel, D. R. (2012). Statistics for censored environmental data using Minitab® and R. 2nd ed. Hoboken, NJ: John Wiley & Sons, Inc.

Ilhan, ZE.; Ong SK.; and Moorman TB. 2012. Herbicide and Antibiotic Removal by Woodchip Denitrification Filters: Sorption Processes. *Water, Air, Soil, & Pollution.* 223: 2651-2661.

Krause Camilo B.; Matzinger, A.; Litz N.; Tedesco LP, and Wessolek, G. 2013. Concurrent nitrate and atrazine retention in bioreactors of straw and bark mulch at short hydraulic residence times. *Ecological Engineering*, 55:101-113.

Lepine C.; Christianson, L.; Sharrer, K.; and Summerfelt S. 2015. Optimizing Hydraulic Retention Times in Denitrifying Woodchip Bioreactors Treating Recirculating Aquaculture System Wastewater. *Journal of Environmental Quality*. 45:813-821.

Luo, Y., X. Deng, R. Budd, K. Starner and M. Ensminger. 2013. Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas. May 2013. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prioritization_report.pdf

Luo, Y., M. Ensminger, R. Budd, X. Deng and A. DaSilva. 2013.Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas II: Refined Priority List. July 2014. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prioritization_report_2.pdf

Luo, Y and X. Deng. 2015. Methodology for prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas III: Watershed-Based Prioritization. February 2015. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/luo_prioritization_3.pdf

Ranaivoson, A; Moncrief, J; Venterea, R; Rice, P; and Dittrich, M. Report to the Minnesota Department of Agriculture: Anaerobic Woodchip Bioreactor for Denitrification, Herbicide Dissipation, and Greenhouse Gas Mitigation. 2012.

Schipper, LA; Robertson, WD; Gold, AJ; Jaynes, DB; and Cameron, SC. 2010. Denitrifying bioreactors–an approach for reducing nitrate loads to receiving waters. *Ecological Engineering.* 36:1532-1543.

Schwarzenbach, RP.; Gschwend. PM.; Imboden, DM. (2003). Environmental organic chemistry. 2nd ed. Hoboken, NF. Wiley-Interscience.

Segawa, R. 1995. California Department of Pesticide Regulation SOP QAQC001.00: Chemistry laboratory quality control. http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc001.pdf

US EPA. (2017a). National Primary Drinking Water Standards. https://www.epa.gov/ground-water-and-drinking-water/national-primary-drinking-water-regulations

US EPA. (2017b). Aquatic Life Benchmarks for Pesticide Registration. https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-pesticide-registration

Wagner, S. 2016. Study 308: Pesticide mitigation through a woodchip bioreactor at Sea Mist Farms, Castroville, CA. http://www.cdpr.ca.gov/docs/emon/pubs/protocol/study308_sea_mist_farms.pdf

Wallace Group, 2013. Tailwater Denitrification Feasibility Analysis. Prepared for the City of Santa Maria.

Table 1. Parameter selections for the Pesticide Prioritization Model

Information from Prioritization Model	Parameter
Use Pattern	Agriculture, rights-of-way, and urban
PUR Years	2013, 2014, 2015
HUC 12	180600080503, 180600080603
Estimated Drainage area	158 km^2
Toxicity Data Type	Acute and chronic toxicity data, whichever is lower
Toxicity Data Sources	US EPA Aquatic Life Benchmark; Benchmark Equivalent
Prioritization for use ranking	• Use rate of 5 > 5.637E03 lb[AI]/year (or selected months), score=5, with 3 chemicals (2%) • Use rate of 4 > 1.438E03 lb[AI]/year (or selected months), score=4, with 6 chemicals (4%) • Use rate of 3 > 5.753E02 lb[AI]/year (or selected months), score=3, with 10 chemicals (7%) • Use rate of 2 > 1.663E02 lb[AI]/year (or selected months), score=2, with 22 chemicals (16%) • Use rate of 1 < 1.663E02 lb[AI]/year (or selected months), score=1, with 94 chemicals (70%)
Tox score rankings (where TOX is toxicity value in ppb)	8, TOX ≤0.001 7, 0.001<TOX ≤0.01 6, 0.01<TOX ≤0.1 5, 0.1<TOX ≤1 4, 1<TOX ≤10 3, 10<TOX ≤100 2, 100<TOX ≤1000 1, TOX>1000 0, No Data
Months of interest	Annual

Table 2. Results from the Prioritization Model for HUC 12 areas 18060008503 and 180600080603

Pesticide Name	Use (lbs)	Use-score	Benchmark (µg/L)	Tox-score	Final-score	Recommended for Monitoring?
MALATHION	26416.9	5	0.295	5	25	TRUE
OXYFLUORFEN	5221.3	4	0.29	5	20	TRUE
NALED	2518.5	3	0.07	6	18	FALSE
PERMETHRIN	2507.4	3	0.0106	6	18	TRUE
CHLOROTHALONIL	3559.4	4	1.8	4	16	FALSE
PROMETRYN	3093.1	4	1.04	4	16	TRUE
CAPTAN	51625.7	5	13.1	3	15	FALSE
MANCOZEB	13462.3	5	47	3	15	FALSE
IMIDACLOPRID	9132.2	5	34.5	3	15	TRUE
LAMBDA-CYHALOTHRIN	306.9	2	0.0035	7	14	TRUE
METHOMYL	2582	3	2.5	4	12	TRUE
PYRACLOSTROBIN	2435	3	1.5	4	12	TRUE
LINURON*	1558.6	3	2.5	4	12	TRUE
TRIFLURALIN	1513.9	3	7.52	4	12	TRUE
BIFENTHRIN	946.8	2	0.075	6	12	TRUE
NOVALURON*	652.5	2	0.075	6	12	TRUE
CHLORPYRIFOS	445.1	2	0.05	6	12	TRUE
FENPROPATHRIN	854.4	2	0.265	5	10	TRUE
FENBUTATIN-OXIDE	536.5	2	0.85	5	10	TRUE
HYDROGEN PEROXIDE	2749.6	3	11	3	9	FALSE
CYPRODINIL	2685.1	3	16	3	9	TRUE
THIRAM	2509	3	21	3	9	FALSE
FLUDIOXONIL	1763.9	3	70	3	9	TRUE
AZOXYSTROBIN	1355	3	49	3	9	TRUE
BENSULIDE	5117	4	290	2	8	TRUE
FENHEXAMID	4794.3	4	670	2	8	TRUE
BIFENAZATE	2915.5	4	250	2	8	FALSE
CHLORANTRANILIPROLE	955.1	2	4.9	4	8	TRUE
ACEQUINOCYL	796.5	2	1.2	4	8	FALSE
SPIROMESIFEN	579.2	2	8.4	4	8	TRUE
PENDIMETHALIN	578.2	2	5.2	4	8	TRUE
TRIFLOXYSTROBIN	308.9	2	7.15	4	8	TRUE
ACEPHATE	2493.8	3	550	2	6	TRUE
PENTHIOPYRAD	1918.6	3	145	2	6	TRUE
BUPROFEZIN	1707.6	3	165	2	6	TRUE
SPINETORAM	1005.1	2	77.9	3	6	TRUE
QUINOXYFEN	856	2	27	3	6	TRUE
HEXYTHIAZOX	831.6	2	60	3	6	TRUE
ACETAMIPRID	772.4	2	10.5	3	6	TRUE
METHOXYFENOZIDE	677.9	2	25	3	6	TRUE
PROPICONAZOLE	635.7	2	21	3	6	TRUE
AMETOCTRADIN	621.6	2	32.5	3	6	TRUE
FENAMIDONE	516.6	2	24.5	3	6	TRUE
DIMETHOATE	446.9	2	21.5	3	6	TRUE
SPINOSAD	426.4	2	90	3	6	TRUE

FLUBENDIAMIDE	398.6	2	27.4	3	6	TRUE
THIAMETHOXAM	372.9	2	17.5	3	6	TRUE
ORYZALIN	366.5	2	15.4	3	6	TRUE
GLUFOSINATE-AMMONIUM	349.6	2	72	3	6	TRUE
INDOXACARB	324.2	2	84	3	6	TRUE

*Analytical method not available

Table 3. Pesticides to be included in monitoring

Pesticide	Chronic Benchmark (µg/L)	MDL (µg/L)	RL (µg/L)
LC Multi-Residue Screen			
Malathion	0.035	0.004	0.02
Imidacloprid	1.05	0.004	0.02
Methomyl	0.7	0.004	0.02
Dimethoate	0.5	0.004	0.02
Pyraclostrobin	1.5	0.004	0.02
Azoxystrobin	44	0.004	0.02
Cyprodinil	8	0.004	0.02
Chlorpyrifos	0.04	0.004	0.02
Prometryn	1.04	0.004	0.02
Propyzamide	600	0.004	0.02
Chlorantraniliprole	4.5	0.004	0.02
Bensulide	290	0.004	0.02
Diazinon	0.105	0.004	0.02
Trifloxystrobin	2.76	0.004	0.02
Oryzalin	15.4	0.021	0.05
Fipronil	0.011	0.004	0.05
Fipronil Amide	0.59	0.005	0.05
Fipronil Sulfide	N/A	0.003	0.05
Fipronil Sulfone	0.037	0.005	0.05
Desulfinyl Fipronil	0.11	0.003	0.05
Desulfinyl Fipronil Amide	N/A	0.005	0.05
Pyrethroid-6			
Permethrin	0.0014	0.00105	0.002
Fenpropathrin	0.064	0.00132	0.005
Bifenthrin	0.0013	0.00091	0.001
Lambda-Cyhalothrin	0.002	0.00174	0.002
Cyfluthrin	0.0074	0.00146	0.002
Esfenvalerate	0.017	0.00166	0.005
Dinitroanilines and Oxyfluorfen			
Oxyfluorfen	0.29	0.023	0.05
Trifluralin	1.14	0.015	0.05
Benfluralin	1.9	0.015	0.05
Ethafluralin	0.4	0.017	0.05
Pendimethalin	5.2	0.019	0.05
Prodiamine	1.5	0.02	0.05

Table 4. Pesticides to be excluded from monitoring due to physical-chemical parameters

Pesticide	**Reason for Exclusion**
Naled	Low soil runoff potentials, based on vapor pressure
Chlorothalonil	Short persistence in water, based on hydrolysis or other degradation processes
Captan	Short persistence in water, based on hydrolysis or other degradation processes
Mancozeb	Short persistence in water, based on hydrolysis or other degradation processes
Thiram	Low bioavailability in the water-sediment system
Flumioxazin	Short persistence in water, based on hydrolysis or other degradation processes
Diquat Dibromide	Low bioavailability in the water-sediment system

Table 5. Budget for the project

Analyte Group	September 2017	May 2018	July 2018	September 2018	Total Number of Samples	Cost Per Sample	Total Cost per Analyte Group
LC Multi-Residue Screen	2	2	2	2	8	$1700	$13,600
Malathion	2	2	2	2	8	$540	$4,320
Dinitroanilines/Oxyfluorfen	2	2	2	2	8	$720	$5,760
PY-6	2	2	2	2	8	$600	$4,800
Total Cost							$28,480