Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street
Sacramento, CA 95812

Study 308: Pesticide mitigation through a woodchip bioreactor at Sea Mist Farms, Castroville, CA

Scott D. Wagner
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1.0 INTRODUCTION

Moss Landing Marine Laboratories (MLML) has constructed a woodchip bioreactor on Sea Mist Farms in Castroville, California. Bioreactor construction was completed in May 2016. The bioreactor is within the Elkhorn Slough watershed. Irrigation runoff water from nearby fields is continuously pumped from drainage ditches into the bioreactor, where it weaves through the ~1,000 cubic yards of woodchips in the bioreactor until it gravity drains into a wetland (Fig. 1 and 2). Irrigation runoff water throughout California has been shown to contain pesticides (Deng, 2015). As such, irrigation runoff and water release associated with agricultural production have the potential to contaminate local surface water and lead to toxicity in sensitive aquatic organisms (Ensminger et al., 2011). Regulators and stakeholders have recently been researching methods to reduce and mitigate the impacts of contaminated runoff.

Denitrifying bioreactors are currently being tested and implemented to reduce nitrate and pesticide concentrations in runoff water (Schipper et al., 2010; Zheng and Dunets). Nitrate is removed from the water and converted to nitrogen gas by denitrifying bacteria living in the anoxic woodchip bioreactor that use the wood as a carbon source (Leverenz et al., 2010). Bioreactors have been studied for their ability to reduce phosphorous and herbicide loads as well, but with a limited crop and pesticide detection list (Ranaivoson et al., 2012; Pinilla et al., 2007). One study that monitored for phosphorous and herbicide (atrazine and acetochlor) removal found that both are removed from water by the bioreactor, but likely through adsorption to woodchips (Ranaivoson et al., 2012). More specifically, 70% of acetochlor load was reduced while 53% of atrazine was removed. Moreover, phosphorous load was reduced by an average of 79% (Ranaivoson et al., 2012). The California Department of Pesticide Regulation (CDPR) conducted pesticide mitigation research in 2015 and 2016 on a woodchip bioreactor in Nipomo, California (Wagner, 2015). However, very low concentrations of pesticides were detected at the bioreactor inlet, making pesticide reductions through the bioreactor difficult to measure (Wagner, 2016- in progress). These limited studies reveal the need for further field-scale research into bioreactor pesticide removal. For example, not all pesticides passing through the bioreactor are likely to be removed at equal rates or experience similar degradation mechanisms. Those with a high Kow like pyrethroids might adsorb to the woodchips while those with a low Kow might be degraded by microbes. The unique physical-chemical properties of each pesticide could determine how well each is removed in the bioreactor; this project aims to identify which pesticides are best treated by the bioreactor.

2.0 OBJECTIVES

The objectives of the 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

3.0 PERSONNEL

This project is a joint effort between many state and local agencies. SWPP staff will be working with involved groups as it studies pesticide removal in the bioreactor. The study will be conducted by SWPP staff under the general direction of Kean S. Goh, Ph.D., Environmental Program Manager I (Supervisory). Key personnel are listed below:

- Project Leader: Scott Wagner
- Field Coordinator: Kevin Kelley
- Reviewing Scientist: Xin Deng, Ph.D.
- Statistician: Yina Xie, Ph.D.
- Laboratory Liaison: Sue Peoples
- Analytical Chemistry, water: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)
- Collaborators: Ross Clark, Jason Adelaars (Moss Landing Marine Laboratories), Pam Krone-Davis (NOAA)

Please direct questions regarding this study to Scott Wagner, Environmental Scientist, at 916-324-4087 or Scott.Wagner@cdpr.ca.gov.

4.0 STUDY PLAN

Pesticides that will be analyzed were selected based on results from queries of Pesticide Use Reporting (PUR) and CDPR's monitoring prioritization model. Runoff to the bioreactor is sourced from fields planted with artichokes and Brussels sprout. Thus, pesticides applied to these crops (sourced from PUR data) in this watershed will be prioritized. Some of the most commonly used pesticides in the Elkhorn Slough watershed are in the pesticide classes of pyrethroids, organophosphates, and neonicotinoids (imidacloprid) (Table 1, Fig. 3). These top detections are supported by the monitoring prioritization model (Table 2). Many of the insecticides in the prioritization model with the highest final score are pyrethroids (e.g. permethrin and bifenthrin), organophosphates (e.g. methidathion), neonicotinoids (e.g. imidacloprid), and dinitroanilines. The organophosphate multi-residue analytical list includes dimethoate, methidathion, malathion, and chlorpyrifos. Six pyrethroids were chosen based on results from the monitoring prioritization model for Elkhorn Slough (Table 2) and include bifenthrin, lambda-cyhalothrin, permethrin, cyfluthrin, fenvalerate/esfenvalerate, and cypermethrin. Pesticides in the dinitroaniline screen

include oryzalin, ethalfluralin, trifluralin, benfluralin, prodiamine, pendimethalin, and oxyfluorfen.

Preliminary samples were collected from the bioreactor inlet and outlet on July 12, 2016. Results from this preliminary sampling could refine this protocol to refocus efforts on certain pesticides or remove others from the monitoring list.

Samples from the inlet and outlet will be collected in September 2016 and May, July, and September 2017. 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 2 days (the expected hydraulic residence time of the bioreactor) before outlet samples.

5.0 CHEMICAL ANALYSIS

A suite of pesticides in each class of organophosphates, pyrethroids, dinitroanilines and neonicotinoids (imidacloprid) will be analyzed by CDFA. Classes were chosen based on PUR data (Table 2) and CDPR's monitoring prioritization model (Table 3) (Luo et al. 2013, 2014, 2015). Laboratory QA/QC will follow CDPR guidelines and will consist of laboratory blanks, matrix spikes, matrix spike duplicates, surrogate spikes, and blind spikes (Segawa, 1995).

Ammonia, NO_3-N, 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. Given the low cost of the colorimetric measurement method, nutrient sampling is not included in the budget.

6.0 DATA ANALYSIS

The concentration and mass of each pesticide analyzed will be estimated and compared to determine the removal efficacy of the bioreactor. Statistical analysis will be performed to test 1) the difference in pesticide concentration between inlet and outlet and 2) the difference in pesticide removal rate among different pesticide classes. Possible procedures may include parametric tests, nonparametric tests, and permutation tests. Since the dataset will be quite small (i.e. eight paired data for each pesticide analyzed) and could be censored and skewed, nonparametric tests and permutation tests are expected to be more desirable than parametric tests (Helsel, 2011). The R statistical program will be used.

7.0 TIMETABLE

Field Sampling: July 2016 – September 2017
Chemical Analysis: July 2016 – September 2017
Summary Report: January 2018

8.0 LABORATORY BUDGET

The expected cost for chemical analysis of samples through the CDFA lab is $21,120 (Table 3). All costs are estimated but do not include field blanks or laboratory QC.

9.0 LITERATURE CITED

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Fig. 1. Woodchip bioreactor, with inlet in foreground, on Sea Mist Farms in Castroville, CA. July 2016.

Fig. 2. Woodchip bioreactor on Sea Mist Farms in Castroville, CA. July 2016. Picture taken while sampling inlet water.

Table 1. Sea Mist Bioreactor HUC12 (Elkhorn Slough, Fig. 3) 2013-2014 Combined Brussels Sprout and Globe Artichoke Pesticide Use (DPR#, CAS#).

Pesticide	Pounds Applied
1,3-Dichloropropene (573; 542-75-6)	38,563
Sulfur (560; 7704-34-9)	20,023
Naled (418; 300-76-5)	2,481
Metaldehyde (379; 108-62-3)	2,453
Diuron (231; 330-54-1)	2,131
Chlorothalonil (677; 1897-45-6)	1,946
Diflubenzuron (1992; 35367-38-5)	1,716
Paraquat Dichloride (1601; 1910-42-5)	1,708
Methidathion (1689; 950-37-8)	1,381
Permethrin (2008; 52645-53-1)	1,236
Pendimethalin (1929; 40487-42-1)	1,187
Oxyfluorfen (1973; 42874-03-3)	1,132
Dimethoate (216; 60-51-5)	1,118
Oxydemeton-Methyl (382; 301-12-2)	1,067
Ferric Sodium EDTA (5950; 15708-41-5)	985
Bifenthrin (2300; 82657-04-3)	890
Margosa Oil (6065; 8002-65-1)	611
Pyraclostrobin (5759; 175013-18-0)	574
Chlorpyrifos (253; 2921-88-2)	511
Chlorantraniliprole (5964; 500008-45-7)	395
Imidacloprid (3849; 105827-78-9)	368
Spinetoram (5946; 187166-15-0)	363
Malathion (367; 121-75-5)	311
Bacillus thuringiensis (Berliner), Subsp. Aizawai, Gc-91 Protein (3843; null)	311
Acephate (1685; 30560-19-1)	309
Thiamethoxam (5598; 153719-23-4)	291
Methoxyfenozide (5698; 161050-58-4)	260
Methomyl (383; 16752-77-5)	255
Aluminum Phosphide (484; 20859-73-8)	254
Azoxystrobin (4037; 131860-33-8)	235
Myclobutanil (2245; 88671-89-0)	209
Esfenvalerate (2321; 66230-04-4)	192
Trifloxystrobin (5321; 141517-21-7)	189
Indoxacarb (5331; 173584-44-6)	180
Penthiopyrad (6020; 183675-82-3)	142
Glyphosate, Isopropylamine Salt (1855; 38641-94-0)	122
Flonicamid (5886; 158062-67-0)	119
Boscalid (5790; 188425-85-6)	119
Spirotetramat (5955; 203313-25-1)	108
Pymetrozine (5232; 123312-89-0)	105
Fenamidone (5791; 161326-34-7)	102

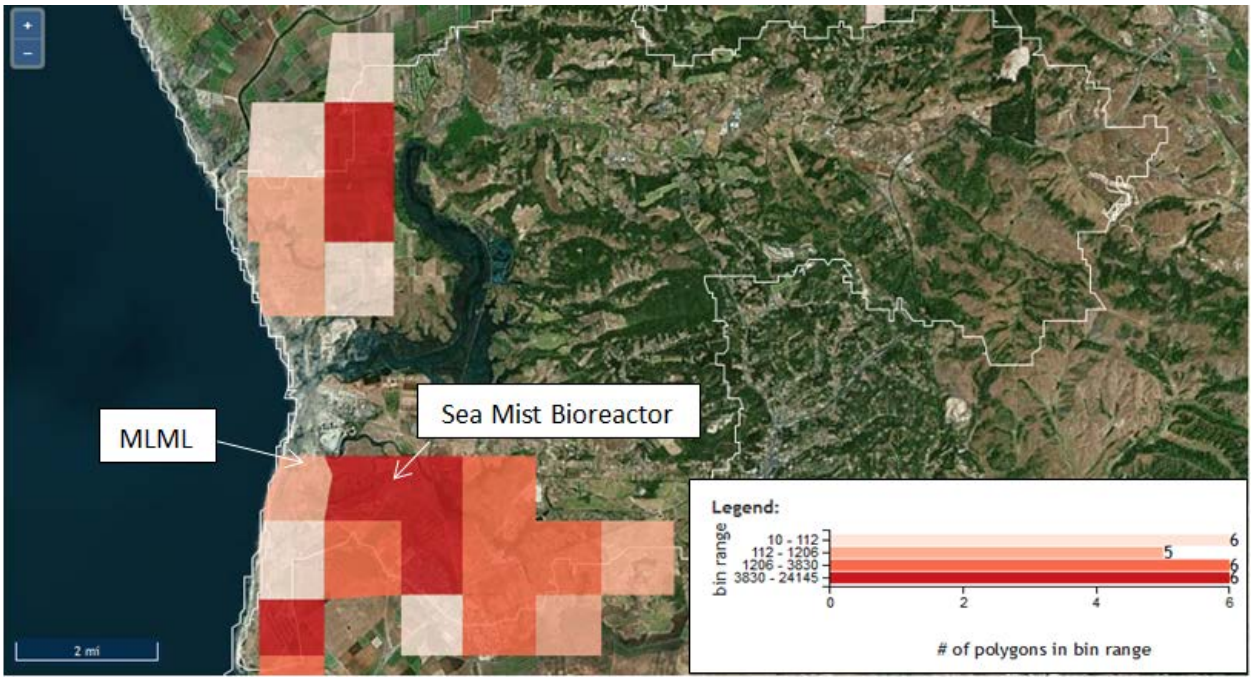

Fig. 3. Elkhorn Slough PUR query area for combined Brussels Sprout and Globe Artichoke PUR 2013-2014 query. Darker red colors indicate areas where PUR is higher. Bin range is in pounds of pesticide reportedly applied.

Table 2. Monitoring Prioritization Model for Elkhorn Slough Watershed, using PUR data from 2013-2014

CHEMNAME	usescore	benchmark	toxscore	finalscore
MALATHION	5	0.295	5	25
NALED	4	0.07	6	24
PERMETHRIN	3	0.0106	6	18
BIFENTHRIN	3	0.075	6	18
PARAQUAT DICHLORIDE	3	0.396	5	15
CAPTAN	5	13.1	3	15
DIFLUBENZURON	2	0.0014	7	14
CHLORPYRIFOS	2	0.05	6	12
PYRACLOSTROBIN	3	1.5	4	12
CHLOROTHALONIL	3	1.8	4	12
DIURON	3	2.4	4	12
MANCOZEB	4	47	3	12
FENPROPATHRIN	2	0.265	5	10
OXYFLUORFEN	2	0.29	5	10
CYPRODINIL	3	16	3	9
FLUDIOXONIL	3	70	3	9
METHIDATHION	2	1.1	4	8
METHOMYL	2	2.5	4	8
PENDIMETHALIN	2	5.2	4	8
LAMBDA-CYHALOTHRIN	1	0.0035	7	7
CYFLUTHRIN	1	0.0125	6	6
ESFENVALERATE	1	0.025	6	6
NOVALURON	1	0.075	6	6
DIMETHOATE	2	21.5	3	6
IMIDACLOPRID	2	34.5	3	6
SPINETORAM	2	77.9	3	6
OXYDEMETON-METHYL	2	95	3	6
BENSULIDE	3	290	2	6
BOSCALID	3	533	2	6
FENHEXAMID	3	670	2	6
THIOPHANATE-METHYL	3	930	2	6

DIAZINON	**1**	**0.105**	**5**	**5**
ABAMECTIN	**1**	**0.17**	**5**	**5**
TAU-FLUVALINATE	**1**	**0.175**	**5**	**5**
CYPERMETHRIN	**1**	**0.195**	**5**	**5**

Table 3. Sampling schedule and cost of chemical analysis.

Analyte Group*	September	May	July	September	Total Number of Samples	Cost per sample	Total Cost Per Analyte Group	Total Cost
DN/OXY	2	2	2	2	8	840	6,720	
IMD	2	2	2	2	8	600	4,800	
OP	2	2	2	2	8	600	4,800	
PY-6	2	2	2	2	8	600	4,800	
								21,120

*DN/OXY=Dinitroanilines/Oxyfluorfen; IMD=Imidacloprid; OP=Organophosphates; PY-6=Pyrethroids (six analyte screen)