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

Study 302: Mitigation of pesticide runoff using a bioreactor in Santa Maria Valley

Scott D. Wagner
November 24, 2015

1.0 INTRODUCTION

Pesticides are frequently applied in agricultural settings throughout California (CDPR, 2014; Deng, 2015). The Santa Maria Valley ranks among the top agricultural areas in the state for pesticide use, making it a focus of the pesticide monitoring program at the California Department of Pesticide Regulation (CDPR) (CDPR, 2014). Irrigation water runoff and water release from treated fields in these areas have the potential to contaminate local surface waters and consequently lead to toxicity in sensitive aquatic organisms (Ensminger et al., 2011). In an effort to mitigate contaminated runoff, regulators and stakeholders are currently researching methods to improve runoff water quality.

Denitrifying bioreactors are a technology currently undergoing research and development 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 wood chip 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 rotation 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). 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.

The Coastal San Luis Resource Conservation District (CSLRCD) has constructed a woodchip bioreactor lined with 40 mm heavy duty agricultural liner and fed by water from Little Oso Flaco

Lake in San Luis Obispo County, California. Source water is pumped several hundred yards away from the bioreactor through a PVC pipe and distributed over about half the length of the bioreactor through a gated irrigation pipe (Figures 1–4). After filling, the bioreactor gravity drains over a period of several days back into Little Oso Flaco Lake then refills again. The State Water Resources Control Board (SWRCB) funded the project through the Central Coast Regional Water Quality Control Board (CCRWQCB). The California Department of Recreation (State Parks) is the landowner of the project site (CSLRCD). Bioreactor construction was completed by October 30, 2014, and was monitored for water volume treated, nitrate concentration reduction, and nitrate load reduction. A total of 360,000 gallons were treated, average concentration was reduced by 12 ppm (average inflow of 20 ppm and average outflow of 8 ppm) and 36 pounds of nitrate as nitrogen was removed (SCLRCD). Preliminary data shows that the bioreactor is efficient for nitrate removal. However, pesticide removal efficiency has not been monitored and evaluated. The CDPR Surface Water Protection Program (SWPP) is proposing to monitor for pesticide removal.

2.0 OBJECTIVES

For this mitigation project, the objectives are:

1) Determine the presence and concentrations of selected pesticides at the inlet and outlet to the studied bioreactor;
2) Determine the removal rates of various classes of pesticides and identify which are most effectively removed by the bioreactor;
3) Evaluate the effectiveness of pesticide removal throughout the year;
4) Determine if the bioreactor reduces water toxicity using *Ceriodaphnia dubia*, *Hyalella azteca,* and *Chironomus dilutus* toxicity tests.

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, PhD
- Statistician: Yina Xie, PhD
- Laboratory Liaison: Sue Peoples
- Analytical Chemistry, water: Center for Analytical Chemistry, California Department of Food and Agriculture (CDFA)

- Collaborators: Peter Meertens, Katie McNeill, Karen Worcester (Central Coast Regional Water Quality Control Board); Ronnie Glick (California State Parks); GW Bates (Coastal San Luis Resource Conservation District); Cathy M. Fisher, Santa Barbara County Agricultural Commissioner

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 the surface water monitoring database and monitoring prioritization model. Some of the most commonly detected pesticides in the Oso Flaco Creek watershed are in the pesticide classes of pyrethroids, organophosphates, and neonicotinoids (imidacloprid) (Table 1). 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, bifenthrin, and fenpropathrin), organophosphates (e.g. malathion) or neonicotinoids (e.g. imidacloprid). In an effort to reduce laboratory costs, only 6 pyrethroids will be analyzed rather than all insecticides within the class. These 6 pyrethroids were chosen based on results from the monitoring prioritization model for Oso Flaco Creek (Table 2) and include bifenthrin, fenpropathrin, permethrin, esfenvalerate, lambda-cyhalothrin, and cyfluthrin.

Two preliminary samples will be collected in December 2015 and February 2016 to establish a baseline concentration at the inlet and an upstream site. This upstream site is located at the confluence of Oso Flaco Creek and Little Oso Flaco Creek (Figure 5). Sampling at the upstream site will provide data on the pesticide concentration of the source water for Little Oso Flaco Lake. These preliminary samples will also ensure that there is a detectable pesticide concentration at the inlet sites. If pesticides cannot be detected in any of the preliminary samples, then it is likely the project will be cancelled since it will be impossible to measure the endpoints.

Beginning in July 2016, water samples collected from the inlet and outlet of the bioreactor will be analyzed for the pre-selected suite of pesticides. Three samples, one for each class of analyzed pesticide, will be collected at the inlet and outlet of the bioreactor; thus, six samples will be collected each sampling event. Each sampling event will follow the bioreactor sampling protocol of the CSLRCD. There will be a total of 8 sampling events.

A subset of the water samples will be sent to the UC Davis Aquatic Health Program (AHP) for toxicity testing. Toxicity tests will be conducted following three sampling events (July, November, and June). Each toxicity test will consist of a 96-hour survival test using the water flea *Ceriodaphnia dubia*, the amphipod *Hyalella azteca* and the midge *Chironomus dilutus* (Table 4). One test will be conducted for inlet water and another one for outlet water. Due to concerns about dilution at the inlet source, a third toxicity test sample will be collected at the upstream site (Figure 5).

5.0 CHEMICAL ANALYSIS

A suite of pesticides in each class of organophosphates, pyrethroids, and neonicotinoids (imidacloprid) will be analyzed by CDFA. Classes were chosen based on past detections (Table 1) and the monitoring prioritization model (Table 2). 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 and NO_3-N will also be measured on-site while collecting water samples. A photometric meter (LaMotte Smart2 Colorimeter Kit) will be used to measure both nutrient levels at the inlet and outlet in an effort to continue monitoring for nitrate reduction. These nutrient concentrations will be collected at every sampling event and will be conducted exclusively on-site. Given the low cost of the photometric measurement method, nitrate and ammonia sampling is not included in the budget.

6.0 DATA ANALYSIS

The concentration and mass of each pesticide analyzed as well as the toxicity of water samples 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/toxicity 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 programming language will be used to conduct the statistical analysis.

7.0 TIMETABLE

Field Sampling: July 2016–June 2017

Chemical Analysis: July 2016–September 2017

Summary Report: January 2018

8.0 LABORATORY BUDGET

The total budget for this project is $50,000.00. The cost for the CDFA chemical analyses of water samples is $36,000 (Table 3). The expected cost for toxicity tests is $9,720. Thus, the total cost is $45,720. Money remaining in the budget may cover the cost of blanks and matrix samples

used by the CDFA lab, pending charges. All costs are estimated but do not include field blanks or laboratory QC.

9.0 LITERATURE CITED

CDPR (California Department of Pesticide Regulation) 2014. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. http://calpip.cdpr.ca.gov/

Coastal San Luis Resource Conservation District. Final Report: Oso Flaco On-Farm Water Quality Implementation and Demonstration Project. SWRCB Grant Agreement No: 12-078-130.

Deng, X. 2015. Study 290 Ambient Monitoring Report. California Department of Pesticide Regulation. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/report_290_deng.pdf

Ensminger, M; Bergin, R; Spurlock, F; and Goh, KS. 2011. Pesticide concentrations in water and sediment and associated invertebrate toxicity in Del Puerto and Orestimba Creeks, California, 2007-2008. *Environmental Monitoring and Assessment.* 175: 573-587.

Helsel, D.R. 2011. *Statistics for censored environmental data using Minitab and R* (Vol. 77): John Wiley & Sons.

Leverenz, HL; Haunschild, K; Hopes, G; Tchobanoglous, G; and Darby, JL. 2010. Anoxic treatment wetlands for denitrification. *Ecological Engineering.* 36: 1544-1551.

Pinilla, P; Ruiz, J; Lobo, MC; Martinez-Inigo, MJ. 2007. Degradation of oxadiazon in a bioreactor integrated in the water closed circuit of a plant nursery. *Bioresource Technology.* 99:2177-2181.

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.

Segawa, R. 1995. California Department of Pesticide Regulation SOP QAQCC001.00: Chemistry laboratory quality control. http://www.cdpr.ca.gov/docs/emon/pubs/sops/qaqc001.pdf. Accessed 23 September 2015.

Zheng, Y. and Dunets, S. Bioreactors for contaminant removal. Greenhouse and Nursery Water Treatment Information System. School of Environmental Sciences, University of Guelph.

Table 1. A snapshot of pesticides detected in Oso Flaco Creek from CDPR's Surface Water Database

COUNTY	SITE	CHEMICAL	CONC_PPB	LOQ_PPB	SAMP_DATE	SAMP_TIME	LAT_NAD83	LONGI_NAD83	SITE_CODE	STUDY_CD
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	oxyfluorfen	9.23	0.05	8/14/2013	1443	35.01637	-120.58655	40_13	262
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	malathion	5.1791	0.04	4/20/2010	1510	35.01637	-120.58655	40_13	93
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	bensulide	5.06	0.04	9/4/2013	1338	35.01637	-120.58655	40_13	262
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	glyphosate	3.7	2	3/26/2013	1530	35.01637	-120.58655	40_13	293
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	chlorantraniliprole	1.64	0.1	9/25/2013	1350	35.01637	-120.58655	40_13	461
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	bensulide	1.33	0.04	5/15/2013	1450	35.01637	-120.58655	40_13	262
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	chlorantraniliprole	1.25	0.1	10/16/2013	1415	35.01637	-120.58655	40_13	461
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	malathion	1.124	0.04	6/8/2010	1515	35.01637	-120.58655	40_13	93
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	imidacloprid	1.12	0.05	5/14/2014	1430	35.01637	-120.58655	40_13	460
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	bensulide	1.09	0.04	8/31/2011	1345	35.01637	-120.58655	40_13	94
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	bensulide	0.964	0.04	8/14/2013	1443	35.01637	-120.58655	40_13	262
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	bensulide	0.859	0.04	5/16/2012	1300	35.01637	-120.58655	40_13	95
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	oxyfluorfen	0.84	0.05	6/16/2009	1520	35.01637	-120.58655	40_13	92
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	methomyl	0.78	0.2	9/17/2013	1430	35.01637	-120.58655	40_13	293
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	azoxystrobin	0.745	0.05	5/14/2014	1430	35.01637	-120.58655	40_13	460
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	chlorantraniliprole	0.7	0.1	7/11/2013	1400	35.01637	-120.58655	40_13	461
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	imidacloprid	0.679	0.05	8/20/2014	1415	35.01637	-120.58655	40_13	460
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	bensulide	0.585	0.04	4/20/2010	1510	35.01637	-120.58655	40_13	93
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	chlorantraniliprole	0.585	0.1	8/14/2013	1445	35.01637	-120.58655	40_13	461
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	imidacloprid	0.578	0.05	8/31/2011	1345	35.01637	-120.58655	40_13	94
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	imidacloprid	0.577	0.05	9/17/2014	1423	35.01637	-120.58655	40_13	460
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	malathion	0.556	0.1	6/24/2013	1045	35.01637	-120.58655	40_13	314
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	imidacloprid	0.544	0.05	6/8/2010	1515	35.01637	-120.58655	40_13	93
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	bensulide	0.53	0.04	7/31/2013	1400	35.01637	-120.58655	40_13	262
San Luis Obispo	Oso Flaco Crk at Oso Flaco Lake Rd	imidacloprid	0.495	0.05	7/31/2013	1400	35.01637	-120.58655	40_13	262

Table 2: Monitoring Prioritization Model Result for Oso Flaco Creek Watershed

CHEMNAME	usescore	benchmark	toxscore	finalscore
MALATHION	5	0.295	5	25
OXYFLUORFEN	3	0.29	5	15
PERMETHRIN	2	0.0106	6	12
CHLORPYRIFOS	2	0.05	6	12
BIFENTHRIN	2	0.075	6	12
FENPROPATHRIN	2	0.265	5	10
CYPRODINIL	3	16	3	9
IMIDACLOPRID	3	34.5	3	9
AZOXYSTROBIN	3	49	3	9
PYRACLOSTROBIN	2	1.5	4	8
TRIFLURALIN	2	7.52	4	8
SPIROMESIFEN	2	8.4	4	8
FENHEXAMID	4	670	2	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
PROPICONAZOLE	2	21	3	6
FLUDIOXONIL	2	70	3	6
BENSULIDE	3	290	2	6
BOSCALID	3	533	2	6
DIAZINON	1	0.105	5	5
ABAMECTIN	1	0.17	5	5
CYPERMETHRIN	1	0.195	5	5
PARAQUAT DICHLORIDE	1	0.396	5	5
FENBUTATIN-OXIDE	1	0.57	5	5
CARBARYL	1	0.85	5	5
POTASSIUM N-METHYLDITHIOCARBAMATE	5	27000	1	5
PROMETRYN	1	1.04	4	4
METHOMYL	1	2.5	4	4
CHLORANTRANILIPROLE	1	4.9	4	4
PENDIMETHALIN	1	5.2	4	4
TRIFLOXYSTROBIN	1	7.15	4	4
TRIFLUMIZOLE	2	140	2	4
PENTHIOPYRAD	2	145	2	4
BUPROFEZIN	2	165	2	4
DICLORAN	2	240	2	4

Table 3. Sampling regimen and cost of chemical analysis

Analyte Group*	Dec.	Feb.	Jul.	Aug.	Oct.	Nov.	Jan.	Mar	Apr.	Jun.	Total Number of Samples	Cost per Sample	Total Cost per Analyte Group	Total Cost
IMD	2	2	2	2	2	2	2	2	2	2	20	600	12,000	
OP	2	2	2	2	2	2	2	2	2	2	20	600	12,000	
PY-6	2	2	2	2	2	2	2	2	2	2	20	600	12,000	
														36,000

*IMD=Imidacloprid ; OP=Organophosphates; PY-6=Pyrethroids (six analyte screen)

Table 4. Toxicity testing regimen and budget

Test species	Jul.*	Nov.	Jun.	Total Number of Tests	Cost per Test	Total Cost per Test Group	Total Cost
C. dubia	4	4	4	12	270	3,240	
H. azteca	4	4	4	12	270	3,240	
C. dilutus	4	4	4	12	270	3,240	
							9,720

*Number of tests includes the three sampling sites plus one control for each test type per event

Figure 1. Bioreactor adjacent to Little Oso Flaco Lake.

Figure 2. Bioreactor adjacent to Little Oso Flaco Lake (viewed near inlet).

Figure 3. Bioreactor adjacent to Little Oso Flaco Lake with pump on and water flowing into bioreactor.

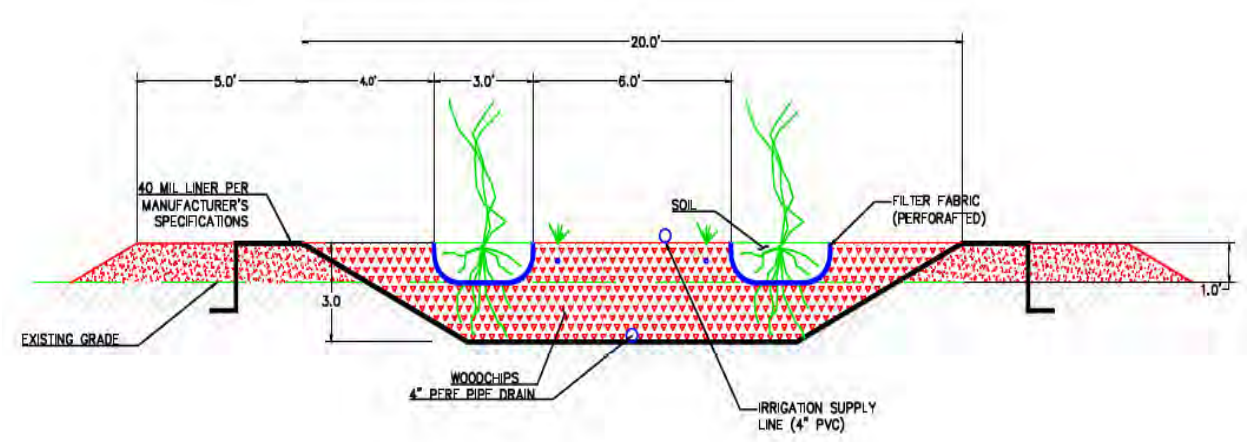


Figure 4. Cross section of bioreactor.

Figure 5. Map of bioreactor and upstream toxicity test sampling site

October 23, 2015

Kean S. Goh, Ph.D.,
Environmental Program Manager I
Department of Pesticide Regulation
Environmental Monitoring Branch
1001 I Street, Sacramento, CA 95812

Sent via Electronic Mail

Dear Dr. Goh:

SUPPORT FOR CDPP STUDY COLLABORATION

We greatly appreciate the efforts of California Department of Pesticide Regulations (DPR) to evaluate the effectiveness of woodchip bioreactor denitrification treatment systems in reducing pesticides in agricultural runoff. We are pleased to collaborate with you and your staff on the DPR project, *Mitigation of Pesticide Runoff Using a Bioreactor in Santa Maria Valley.* The project specifically studies the pesticide removal from a bioreactor in the Oso Flaco watershed. We also appreciate the ongoing monitoring of surface waters in the Central Coast Region by DPR. The annual monitoring of agricultural drainages in the Salinas and Santa Maria watersheds provides valuable information on the pesticides present in surface waters.

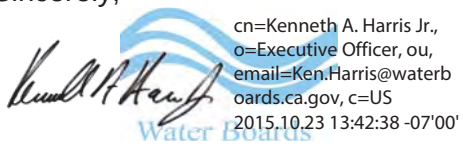
As you know, numerous waterbodies in Santa Maria and Oso Flaco watersheds are polluted with pesticides and have pesticide-related toxicity to aquatic life. These water bodies are identified as impaired on the Clean Water Act section 303(d) list of impaired waters and are addressed in the Total Maximum Daily Loads for Toxicity and Pesticides in the Santa Maria Watershed. The impairments for pesticides and toxicity are based on violations of the Central Coast Regional Water Quality Control Board's (Central Coast Water Board) Basin Plan general narrative objectives for toxicity and pesticides. These water quality impairments are among the Central Coast Water Board's highest priorities.

Woodchip bioreactors are an emerging technology for treating nitrate in farm runoff and watershed drainages and the Central Coast Water Board is providing grant funds for several bioreactor projects in the Santa Maria and Salinas watersheds. In October 2014, the Coastal San Luis Resource Conservation District (CSLRCD) completed construction of the woodchip bioreactor adjacent to Little Oso Flaco Lake. The State Water Resources Control Board funded the project and the Central Coast Water Board managed the contract. The California Department of Parks and Recreation is the landowner of the Oso Flaco bioreactor project site and along with the grower, has provided construction, monitoring, support and access to the project site. The CSLRCD has demonstrated that the bioreactor is effective in reducing nitrate loading to Little Oso Flaco Lake; however, pesticide removal efficiency has not been monitored and evaluated. We are excited that the DPR Surface Water Protection Program (SWPP) is

proposing to monitor for pesticide removal at this and potentially other locations (e.g. Salinas and Santa Maria) in the region.

We have several staff available to coordinate with you on this project. Karen Worcester is the Central Coast Ambient Monitoring Program manager, Peter Meertens is the Central Coast Water Board DPR MAA coordinator, and Katie McNeill is the Grants Program Coordinator. We look forward to working with you and your staff. If you have comments or questions, please contact Peter Meertens at (805) 549-3869 (Peter.Meertens@waterboards.ca.gov), Karen Worcester at (805) 549-3333 (Karen.Worcester@waterboards.ca.gov), or Katie McNeill at (805) 549-3336 (Katie.Mcneill@waterboards.ca.gov).

Sincerely,



Kenneth A. Harris Jr.
Executive Officer

cc:
David Duncan, DPR, Environmental Monitoring Branch Chief, david.duncan@cdpr.ca.gov
Scott Wagner, DPR, Environmental Scientist. Scott.Wagner@cdpr.ca.gov
G.W. Bates, District Engineer, SLCRCD, gbates@coastalrcd.org
Ronnie Glick, State Parks, Senior Environmental Scientist, Ronnie.Glick@parks.ca.gov
Mike Mills, Oso Flaco Grower, millsfarmsllc@aol.com

\\ca.epa.local\RB3\Shared\NPS\Pesticides\DPR_Protocol Studies and Reports\A - Bioreactor Study\DPR_osoflaco_pesticide_study_ltr_101515.docx