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Study 259. Effectiveness of a Constructed Treatment Wetland at Reducing Pesticide Concentrations in Agricultural Runoff

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I. INTRODUCTION

In California, a wide variety of pesticide active ingredients (AIs) are applied throughout the year. In 2007, for example, over 300 pesticide AIs were applied in agricultural areas of the state (DPR 2009a). Much of this pesticide use is adjacent to rivers and streams, and pesticide contamination of surface waters has been reported throughout the state (DPR 2009b); many of these contaminants are toxic to aquatic organisms (US EPA 2009, Starner 2008, Starner 2007).

A variety of strategies to minimize off-site movement of pesticides into surrounding surface waters have been developed by researchers worldwide (Reichenberger, *et al.* 2007). One such strategy is the reduction of pesticide concentrations in surface water through the use of constructed treatment wetlands. Natural wetlands generally contain shallow water or saturated conditions, unique wetland soils, and vegetation adapted to wet conditions (Mitsch and Gosselink 2000). Due to this combination of characteristics, wetlands have a very high rate of biological activity and as such can transform, moderate, or remove many common water contaminants. Constructed treatment wetlands are man-made versions of natural wetlands, designed to emphasize specific characteristics of wetlands to improve treatment capacity. These are biologically complex systems which are potentially capable of achieving high levels of treatment (Kadlec and Wallace 2009). Recent research indicates that wetlands of various designs can be used to treat natural waters contaminated with chemical pesticides (Moore *et al.* 2009, Budd *et al.* 2009, Imfeld *et al.* 2009, Gregoire *et al.* 2009, Moore *et al.* 2007, Moore *et al.* 2006, Rose *et al.* 2006, Blankenberg *et al.* 2006, Sherrard *et al.* 2004, Schulz *et al.* 2003a, Schulz *et al.* 2003b, Braskerud and Haarstad 2003, Moore *et al.* 2002, Schulz and Peall 2001, Moore *et al.* 2001, Moore *et al.* 2000). The purpose of this project is to determine the effectiveness of a constructed treatment wetland located in Monterey County at reducing pesticide concentrations in surface water contaminated with agricultural runoff.

II. OBJECTIVE

The objective of this study is to determine the reduction in mass of selected pesticides in agricultural runoff due to flow through a constructed treatment wetland.

Results will be used to guide future mitigation research efforts and may be used to aid in the development of surface water mitigation programs.

III. PERSONNEL

This is a cooperative study between the Department of Pesticide Regulation (DPR) and The Watershed Institute / California State University Monterey Bay (CSUMB).

DPR personnel are from the Environmental Monitoring Branch, Surface Water Protection Program, under the general direction of Kean S. Goh, Ph.D., Program Manager (Supervisor) I. Key DPR personnel are listed below:

Project Leader:	Keith Starner
Field Coordinator:	Kevin Kelley
Senior Scientist:	Frank Spurlock, Ph.D.
Laboratory Liaison:	Sue Peoples
Chemists:	California Department of Food and Agriculture, Center for Analytical Chemistry Staff Chemists

Collaborator: Fred Watson, Ph.D. Co-Director, The Watershed Institute, CSUMB.

Questions concerning this project should be directed to Keith Starner at (916) 324-4167 or by email at kstarner@cdpr.ca.gov.

IV. STUDY PLAN

Beginning in 2005, an active offline treatment wetland was designed and constructed by researchers from California State University, Monterey Bay (CSUMB), Moss Landing Marine Laboratory (MLML), and Resource Conservation District of Monterey County (Figures 1 -3). The wetland, referred to as the Molera Wetland, is situated on a 1.2 hectare parcel of public land located between the confluence of Tembladero Slough and the Old Salinas River Channel in the northwest; and the intersection of Molera Road and Monterey Dunes Way in the southeast. The wetland was designed to ensure that all water entering the wetland would pass through most of the wetland before being released and to avoid the possibility that any part of the inflow could flow through the system in a shorter period of time than the remaining water. The wetland has a high length-to-width ratio (42:1) and a long sinuous snake-shaped channel with earthen berms separating the reaches of the channel (Figures 1 through 3). A system of pumps was developed to allow water from Tembladero Slough to be pumped directly into the treatment wetland. This system can be operated as a pulsed-inflow/continuous outflow system, with water from Tembladero Slough pumped into the wetland for a specified number of hours per day and allowed to discharge continuously at a controlled rate. Residence times can be varied by varying rate of inflow and outflow. Previous work has shown that, under specific operational parameters, the Molera wetland can reduce concentrations of diazinon in treated surface water (Hunt *et al.* 2007; Watson *et al.* in preparation). The current project aims to expand the understanding of the Molera wetland's treatment effectiveness by the inclusion of a variety of additional current-use insecticides and herbicides in addition to diazinon. Tembladero Slough receives agricultural inputs from the surrounding area, including from numerous 303d-listed water bodies. Surface water sampling results from DPR and others (Kozlowski *et al.* 2004, DPR 2009b) have shown frequent detections of a variety of current-use pesticides in Tembladero Slough, especially during the peak pesticide-use period (late spring to late summer). As such, the input into the wetland will consist of surface water with field-incurred pesticide contamination.

The study will be conducted in two phases.

Phase 1: Characterization of Wetland Input Concentrations (Summer 2009)

Water samples for pesticide analysis will be collected at the input of the wetland on several different dates in order to determine appropriate target analytes and sample timing. Sampling will occur during the peak pesticide application period during the irrigation season in the area (summer, approximately July-August).

Sampling will be conducted on eight to twelve sample dates/times (sample events), with ca. six analyses per sample event. Samples will be analyzed for organophosphate insecticides (primary OP screen, acephate, bensulide), carbamate insecticides, pyrethroid insecticides, and dinitroaniline herbicides). Total samples: ca. 50-70.

Phase 2: Determination of Wetland Effectiveness (Summer 2010)

Study design for Phase 2 will depend on results from Phase 1. Results from Phase 1 will be used to determine the most appropriate target analytes and sample timing for Phase 2. Physiochemical properties of the target analytes will be considered when determining appropriate target residence times for Phase 2. Over the course of Phase 2, a maximum of 25 sets of samples will be collected, representing 25 different sampling dates/times (sample events). For each of the sample events, multiple water samples (each for a separate chemical analysis) will be collected at each of a minimum of three locations in the wetland (near the input, near the output, and at one intermediate point). Sampling for each sampling event will be shifted in time in order to track each parcel of water as it moves from input to outlet of the wetland. Alternatively, samples for each sample event may be collected synchronously if needed and if results from Phase 1 indicate minimal variation of inflow concentrations. Sampling logistics would vary considerably for the two potential scenarios, and will be determined once the results from Phase 1 are available for review. For the maximum of 25 sample events and three sample locations, a total maximum of 75 samples would be collected for each pesticide chemical analysis to be conducted. The number of separate chemical analyses to be conducted, and thus the overall total number of samples to be collected, will be determined by the results of Phase 1.

During each sample event, flow into the wetland (instantaneous flow and daily total in gallons) will be measured and recorded regularly using a permanently installed McCrometer Propeller flow meter. Instantaneous flow at the outlet will be quantified regularly using volumetric discharge methods, such as a calibrated bin or a timed surface float.

If appropriate based on the chemical and physical properties of the selected analytes, sediment samples for pesticide analysis and additional water samples for total suspended solids (TSS) analysis may also be collected. Additional water quality parameters (pH, salinity, etc.) will be measured as appropriate.

The mass of pesticides entering and exiting the wetland will be estimated by measuring pesticide concentrations and inflow and outflow volumes. Water losses due to evaporation and leakage to shallow ground water will be estimated using results from a loss estimation experiment conducted previously at the wetland (Watson *et al.* in preparation) and appropriate weather data.

V. SAMPLING METHODS/ CHEMICAL ANALYTICAL METHODS

Surface water samples for chemical analysis will be collected directly into 1-liter amber glass bottles either by hand or using an extendable grab pole. Amber bottles will be sealed with Teflon-lined lids and samples will be transported and stored on wet ice or refrigerated at 4^{o}C until extraction for analysis.

Chemical analysis will be performed by the California Department of Food and Agriculture's Center for Analytical Chemistry. Analytical method details are provided in Table 1. Additional information regarding analytical methods is available (DPR 2009c). Quality control will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa, 1995).

VI. DATA ANALYSIS

For selected pesticides, the mass entering and exiting the wetland will be estimated and compared in order to determine the effectiveness of the treatment wetland. These estimations will be derived from pesticide concentration and water balance measurements. Standard statistical tests (t-test, etc.) will be used in the analysis. Specific statistical methods used and analyses conducted will be documented in the final report.

Concentrations of pesticides in water will be reported as micrograms per liter (µg/L) / parts per billion (ppb) or nanograms per liter (ng/L) / parts per trillion (ppt).

VII. TIMETABLE

Phase 1: Characterization of Wetland Input Concentrations

Sample Collection:	Summer 2009
Chemical Analysis:	Summer to fall 2009

Phase 2: Determination of Wetland Effectiveness

Samples Collection:	Summer 2010
Chemical Analysis:	Summer to fall 2010
Draft Report:	Fall 2011

IX. BUDGET

Phase 1: Characterization sampling will consist of eight to twelve sampling events, with approximately six separate chemical analyses per event. Samples will be analyzed for organophosphate insecticides (primary OP screen, acephate, bensulide), carbamate insecticides, pyrethroid insecticides, and dinitroaniline herbicides).

Estimated total Phase 1 water samples for chemical analysis: ca. 50-70 samples.

Phase 2: Effectiveness determination sampling will consist of ca. 25 sample events, with samples collected from a minimum of three locations within the wetland. This will result in a total of 75 samples for each chemical analysis over the course of the project. It is estimated that samples will be collected for between two and three separate chemical analyses, resulting in a maximum total of approximately 225 samples.

Estimated total Phase 2 water samples for chemical analysis: maximum total of 225 samples.

X. REFERENCES

Blankenberg, A.B., Braskerud, B., and Haardstad, K. 2006. Pesticide retention in two small constructed wetlands: treating non-point source pollution from agricultural runoff. *Intern. J. Environ. Anal. Chem*. 86 (3-4) 225-231.

Braskerud, B.C., Haardstad. K. 2003. Screening the retention of thirteen pesticides in a small constructed wetland. *Water Sci. Technol*. 48:267-274.

Budd, R., O'Geen, A., Goh., K.S. 2009. Efficacy of constructed wetlands in pesticide removal from tailwaters in the Central Valley, California. *Environ. Sci. Technol*. 43 2925-2930.

DPR 2009a. California Department of Pesticide Regulation: Pesticide Information Portal, Pesticide Use Report (PUR) data.
http://calpip.cdpr.ca.gov/cfdocs/calpip/prod/main.cfm

DPR 2009b. California Department of Pesticide Regulation: Surface Water Database. http://www.cdpr.ca.gov/docs/sw/surfdata.htm

DPR 2009c. California Department of Pesticide Regulation: Analytical Methods. http://www.cdpr.ca.gov/docs/emon/pubs/em_methd_main.htm

Gregoire, C., Elsaesser, D., Huguenot, D., Lange, J., Lebeau, T., Merli, A., Mose, R., Passeport, E., Payraudeau, S., Schütz, T., Schulz, R., Tapia-Padilla, G., Tournebize, J., Trevisan, M., Wanko, A. 2009. Mitigation of agricultural nonpoint-source pesticide pollution in artificial wetland ecosystems. Environ. Chem. Lett. 7 205-231.

Imfeld, G., Braeckevelt, M., Kuschk, P., Richow, H.H. 2009. Monitoring and assessing processes of organic chemicals removal in constructed wetlands. *Chemosphere* 74 349-362.

Kadlec, R.H. and Wallace, S.D. 2009. Treatment Wetlands. 2nd Edition. CRC Press, Boca Raton, USA, 1016 pages.

Kozlowski, D., Watson, F., Angelo, M. and Larson, J. 2004. Monitoring chlorpyrifos and diazinon in Impaired Surface Waters of the Lower Salinas Region. Technical Memorandum, The Watershed Institute. http://www.cdpr.ca.gov/docs/emon/surfwtr/contracts/ccows_frpt.pdf

Harris, K., Watson, F., Karminder, B., Burton, R., Carmichael, S., Casagrande, J. M., Casagrande, J.R., Daniels, M., Earnshaw, S., Frank, D., Hanson, E., Lienk, L.L., Martin, P., Travers, B., Watson, J., Wiskind, A. 2007. Agricultural Management Practices and Treatment Wetlands for Water Quality Improvement in Southern Monterey Bay Watersheds: Final Report. Watershed Institute, California State University Monterey Bay.

Hunt, J.W., Anderson, B.S., Phillips, B.M., Largay, B., Watson, F., Harris, K., Hanson, E., Beretti, M., Schager, R., Brown, K., and Bern, A.L. 2007. Effectiveness of agricultural management practices in reducing concentrations of pesticides associated with toxicity to aquatic organisms. Data Summary and Final Report. Central Coast Regional Water Quality Control Board, San Luis Obispo, CA.

Mitsch, J. M. and Gosselink, J.G. 2000. Wetlands. 3rd Edition. John Wiley and Sons, Inc., New York, USA, 920 pages.

Moore, M.T., Cooper, C.M., Smith, Jr., S., Cullum, R.F., Knight, S.S., Locke, M.A., Bennett, E.R. 2009. Mitigation of two pyrethroid insecticides in a Mississippi Delta constructed wetland. *Env. Poll.* 157 250-256.

Moore, M.T., Cooper, C.M., Smith Jr., S., Cullum, R.F., Knight S.M., Locke M.A., Bennett E.R. 2007. Diazinon mitigation in constructed wetlands: influence of vegetation. *Water, Air, and Soil Pollution* 184 313-321.

Moore, M.T., Bennett, E.R., Cooper, C.M., Smith Jr., S., Farris, J.L. Drouillard, K.G., Schulz, R. 2006. Influence of vegetation in mitigation of methyl parathion runoff. *Env. Pollut*. 142 288-294.

Moore M.T., Rodgers J.H., Smith Jr., S., Cooper C.M. 2001. Mitigation of metolachlor-associated agricultural runoff using constructed wetlands in Mississippi USA. *Agric. Ecosyst. Environ.* 84 169-176.

Moore, M.T., Schultz R., Cooper C.M., Smith Jr., S., Rodgers Jr J.H. 2002. Mitigation of chlorpyrifos runoff using constructed wetlands. *Chemosphere* 46 827-835.

Moore, M.T., Rodgers, J.H., JR., Cooper, C.M., Smith Jr, S. 2000. Constructed wetland for mitigation of atrazine-associated agricultural runoff. *Env. Pollut.* 110 393-399.

Reichenberger, S., Bach, M., Skitschak, A., Frede, H. 2007. Mitigation strategies to reduce pesticide inputs into ground- and surface water and their effectiveness; A review. *Sci. Total Env.* 384 1-35.

Rose M.T., Sanchez-Bayo F., Crossan A.N., Kennedy L.R. 2006. Pesticide removal from cotton farm tailwater by a pilot-scale ponded wetland. *Chemosphere* 63 1849-1858.

Segawa, R. 1995. Chemistry Laboratory Quality Control. Environmental Hazards Assessment Program QAQC001.00. Department of Pesticide Regulation, Sacramento, CA.

Sherrard, R.M., Bearr J.S., Murray-Gulde, C.L., Rodgers, J.H. Jr., Shah, Y.T. 2004. Feasibility of constructed wetlands for removing chlorothalonil and chlorpyrifos from aqueous mixtures. *Environ. Pollut.* 127 385-394.

Schulz, R. and Peall, S.K.C. 2001. Effectiveness of a constructed wetland for retention of nonpoint-source pesticide pollution in the Lourens River Catchment, South Africa. *Environ. Sci Technol.* 35 422-426.

Schulz, R., Hahn, C., Bennett, E.R., Dabrowski, J.M., Thiere, G., Peall, S.K. 2003a. Fate and effects of azinphos-methyl in a flow-through wetland in South Africa. *Environ. Sci Technol.*37 2139-2144.

Schulz, R., Moore, M.T., Bennett, E.R., Farris, J.L., Smith, Jr., S., Cooper, C.M. 2003b. Methyl parathion toxicity in vegetated and nonvegetated wetland mesocosms. *Env.Tox. Chem*.22 1262-1268.

Starner, K. 2007. Assessment of acute aquatic toxicity of current-use pesticides in California, with Monitoring Recommendations. Technical Memorandum, California Department of Pesticide Regulation, Environmental Monitoring.
http://www.cdpr.ca.gov/docs/emon/surfwtr/policies/starner_sw01.pdf

Starner, K. 2008. Review of US EPA Aquatic Life Benchmarks, with Monitoring Recommendations. Technical Memorandum, California Department of Pesticide Regulation, Environmental Monitoring.
http://www.cdpr.ca.gov/docs/emon/surfwtr/policies/starner_benchmarks.pdf

US EPA 2009. US EPA Office of Pesticide Program's Aquatic Life Benchmarks. Web page. Benchmarks updated April 2009.
http://www.epa.gov/oppefed1/ecorisk_ders/aquatic_life_benchmark.htm

Harris, K., Watson, F., Brown, K., Burton, R., Carmichael, S., Casagrande, J.M., Casagrande, J.R., Daniels, M., Earnshaw, S., Frank, D., Hanson, E., Lienk, L.L., Martin, P., Travers, B., Watson, J., Wiskind, A. 2007. Agricultural Management Practices and Treatment Wetlands for Water Quality Improvement in Southern Monterey Bay Watersheds: Final Report. Report to California State Water Resources Control Board. The Watershed Institute, California State Monterey Bay, Publication No. WI-2007-01, 162 pp.

Watson, F.G.R., Harris, K., Daniels, M., Martin, P., Wiskind, A. In preparation. Effectiveness of an active offline treatment wetland for removal of nutrients and pesticides from a waterway.

Photo: Google Earth

Figure 1. Constructed treatment wetland near the confluence of Tembladero Slough and Old Salinas River, Monterey County, California.

Flow diagram after Hunt *et al.* 2007

Figure 2. Wetland detail with direction of water flow indicated.

Photo: Miles Daniels

Figure 3. View of wetland showing vegetation.

Table 1. Department of Food and Agriculture, Center for Analytical Chemistry analytical method details.

Determination of Organophosphate Pesticides in Surface Water using Gas Chromatography (Insecticide Method 289)

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Azinphos methyl	0.0099	0.05
Chlorpyrifos	0.0008	0.01
Diazinon	0.0012	0.01
Dichlorvos	0.0098	0.05
Dimethoate	0.0079	0.04
Disulfoton	0.0093	0.04
Ethoprop	0.0098	0.05
Fenamiphos	0.0125	0.05
Fonofos	0.008	0.04
Malathion	0.0117	0.04
Methidathion	0.0111	0.05
Methyl Parathion	0.008	0.03
Phorate	0.0083	0.05
Profenofos	0.0114	0.05
Tribufos	0.0142	0.05

Carbamate (CB) Insecticides in Surface Water

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Aldicarb SO	0.0277	0.05
Aldicarb SO2	0.0214	0.05
Oxamyl	0.0255	0.05
Methomyl	0.0265	0.05
Mesurol SO	0.0264	0.05
3 OH-Carbofuran	0.0232	0.05
Mesuol SO2	0.0299	0.05
Aldicarb	0.0196	0.05
Carbofuran	0.0244	0.05
Carbaryl	0.0136	0.05
Mesurol	0.0270	0.05

Pyrethroids (PY) in Surface Water

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Bifenthrin	0.00176	0.005
Fenpropathrin	0.00152	0.015
Lambda-cyhalothrin epimer	0.00109	0.015
Lambda-cyhalothrin	0.00115	0.015
Permethrin (cis)	0.00352	0.015
Permethrin (trans)	0.00768	0.015
Cyfluthrin	0.00173	0.015
Cypermethrin	0.00175	0.015
Fenvalerate/esfenvalerate	0.00175	0.015
Deltamethrin	0.00186	0.015
Resmethrin	0.00382	0.015

Table 1 (cont). Dept. of Food and Agriculture, Center for Analytical Chemistry analytical method details.

Determination of Acephate and Methamidophos in Surface Water by LC-MS (Method 313)

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Acephate	0.0370	0.25
Methamidaphos	0.126	0.25

Determination of Ethalfluralin, Trifluralin, Benfluralin, Prodiamine, Pendimethalin, Oxyfluorfen, and Oryzalin in Surface Water (Herbicide Method 310)

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Oryzalin	0.01	0.05
Ethalfluralin	0.01	0.05
Trifluralin	0.01	0.05
Benfluralin	0.01	0.05
Prodiamine	0.01	0.05
Pendamethalin	0.01	0.05
Oxyfluorfen	0.01	0.05

Determination of Bensulide in Surface Water

Compound	***Method Detection Limit (µg/L)***	***Reporting Limit (µg/L)***
Bensulide	0.014	0.05