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Environmental Monitoring Branch
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**STUDY #264. URBAN PESTICIDE MONITORING IN NORTHERN
CALIFORNIA**

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I. INTRODUCTION

Urban pesticide uses include structural pest control, landscape maintenance, rights-of-way applications, public health protection, and residential applications. In California, the Department of Pesticide Regulation (CDPR) maintains pesticide use records for urban pesticide use made by licensed applicators. Yearly, applicators generally report over 12 million pounds active ingredient (a.i.) of urban pesticide use in California (CDPR, 2009a). However, urban pesticide use by individual homeowners is not reported, so that total use is greater than reported use. Based on pesticide sales records, the total use of all urban pesticide products likely exceeds 300 million pounds. It has been estimated that urban pesticide use accounts for over 70% of the total pesticide use in California (UP3 Project, 2007).

With this high volume of urban pesticide use there is a potential for pesticide runoff into urban creeks and rivers via storm drains. Numerous urban creeks are listed on the 2006 Federal Clean Water Act Section 303(d) list due to the presence of organophosphorous (OP) pesticides (Cal/EPA, 2009), likely contributed by this urban runoff. Additionally, recent monitoring has shown that urban waterways are frequently contaminated with pyrethroids, OPs, fipronil; many of these detections are at concentrations that exceed the acute toxicity to sensitive aquatic organisms (Oki and Haver, 2009; Weston *et al.*, 2005; Weston *et al.*, 2008). In 2008 CDPR initiated a statewide urban monitoring project to address the problems of pesticides in urban waterways (CDPR, 2009b). In addition to finding the above mentioned pesticides, CDPR also detected degradates of fipronil, carbaryl, diuron, simazine, prometon, pendimethalin, oryzalin, prodiamine, triclopyr, dicamba, 2,4-D, and MCPA (He *et al.*, 2009).

Due to the numerous detections in CDPR's 2008 study, additional urban monitoring is warranted to assess urban pesticide water quality trends. With new surface water regulations being proposed in California, long term monitoring at selected urban sites will help determine the effectiveness of any new regulations (CDPR, 2009c). This project will continue to monitor storm drains and urban waterways at selected monitoring sites from CDPR's 2008 study as well as at monitoring stations established by the University

of California (Oki and Haver 2009). Potentially, mitigation measures or public outreach could be future goals of the long term urban monitoring projects.

II. OBJECTIVE

The objectives of this study are two-fold:

- 1) Determine the presence and concentrations of selected pesticides in urban storm drains and creeks;
- 2) Assess whether selected pesticides are present in concentrations that could be toxic to aquatic organisms.

III. PERSONNEL

The study will be conducted by staff from the CDPR's Environmental Monitoring Branch under the general direction of Sheryl Gill, Senior Environmental Scientist. Key personnel are listed below:

- Project Leader: Michael Ensminger
- Field Coordinator: Kevin Kelley
- Senior Scientist: Frank Spurlock
- Laboratory Liaison: Sue Peoples
- Analytical Chemistry: Center for Analytical Chemistry, Department of Food and Agriculture (CDFA)
- Collaborator: Lorence Oki, University of California at Davis, CE Assistant Specialist, Landscape Horticulture, Department of Environmental Horticulture, Phone: (530) 754-4135, Email: lroki@ucdavis.edu

Please direct questions regarding this study to Michael Ensminger, Environmental Scientist, at (916) 324-4186 or mensminger@cdpr.ca.gov.

IV. STUDY PLAN

4.1 Monitoring Sites

Water quality monitoring will be conducted at 13 sites in Northern California (Table 1). Generally sites were selected to fit the model from CDPR's 2008 study; consisting of two to three storm drains and one receiving water body per watershed area (CDPR, 2009b). However, both the Antelope and Natomas sites consist solely of a single storm drain outflow. Automated sampling equipment has been installed at these sites by the University of California (Oki and Haver, 2009); we will evaluate these sites for potential long-term monitoring in collaboration with the University of California.

The storm drain monitoring sites in the Sacramento Area consist exclusively of single family dwellings (the Roseville sites also include two parks and an elementary school). The Dublin site consists of single family dwellings, multiple family dwellings, light commercial buildings, parks, and schools.

4.2 Sampling

Water sampling. There will be two baseflow and two storm sampling events. Baseflow sampling will occur in August and October. We will conduct storm sampling with the first major storm (rain) event of the 2010 water year (water runs from October 2009 through September 2010) and with a major storm in the winter or early spring of 2010 (Table 2).

CDPR staff will collect water samples for chemical analysis and for determining total suspended solids (TSS) and total organic carbon (TOC). During creek sampling, CDPR will collect samples from the center channel using an extendable pole directly into 1-L amber glass bottles. When collecting water samples from storm drains, samples will be collected by hand directly into 1-L bottles. Water samples may also be collected by automated samplers where set up by the University of California (Oki and Haver, 2009). All bottles will be sealed with Teflon® lined lids following CDPR SOP FSWA002.00 (Bennett, 1997). Samples will be stored and transported on wet ice or refrigerated at 4°C until analyzed.

Sediment sampling. Sediment samples will be collected once, prior to the first major storm event of the 2010 water year (Table 2). Sediment samples will be collected following CDPR SOP FSWA016.00 (Mamola, 2005). Sediments will be analyzed for pyrethroids, chorpyrifos, and for TOC.

Sample Transport. CDPR staff will transport samples following the procedures outlined in CDPR SOP QAQC004.01 (Jones, 1999b). A chain-of-custody record will be completed and accompany each sample.

Table 1. Urban monitoring sites in Northern California. For additional information, see Appendix.

| Area | City/ Community | Stormdrain Outfalls Sites | Receiving Water Sites | Total Sites |
|--------------------|--------------------|------------------------------|--------------------------|-------------|
| Bay Area | Dublin | 3 | 1 | 4 |
| Sacramento Area | Roseville | 3 | 1 | 4 |
| | Folsom | 2 | 1 | 3 |
| | Antelope | 1 | 0 | 1 |
| | Natomas | 1 | 0 | 1 |
| Total | | 10 | 3 | 13 |

4.3 Field Measurements

Physiochemical properties of water will be determined using a YSI 6920 V2-2 multiparameter sonde according to the methods describe by Doo and He (2008). At each site, water parameters measured *in situ* will include pH, temperature, conductivity,

turbidity, and dissolved oxygen. Salinity and total dissolved solids will be estimated from conductivity.

Stormdrain discharge or stream flow rates will be measured to characterize the flow regime and to estimate the total loading of target pesticides. Where possible, flow will be calculated using a Global portable velocity flow probe (Goehring, 2008).

Table 2. Sampling schedule for urban pesticide monitoring in Northern California.

| Sample Type | August | October | Oct - Nov | Jan - Mar | Total |
|-------------------|-----------------|----------|-----------------|------------|-------|
| Event | Baseflow | Baseflow | Stormwater | Stormwater | |
| Water Samples | | | | | |
| Number of sites | 15 ¹ | 13 | 12 ² | 13 | |
| Number of samples | 96 | 78 | 72 | 78 | 324 |
| Sediment Samples | | | | | |
| Number of samples | 0 | 10 | 0 | 0 | 10 |

¹Some original sites from the 2008 – 2009 FY study (CDPR Study 249) were included at this sampling date, and the Folsom receiving water site was not collected during this event.

²A sample at the Natomas site could not be collected during this event.

4.4 Quality Assurance/Quality Control

Quality Assurance/Quality Control (QA/QC) will be conducted in accordance with Standard Operating Procedure QAQC001.00 (Segawa, 1995). Ten percent of the total number of samples will be submitted as field blanks, blind spikes, or field duplicates. In addition, QA/QC procedures developed by US EPA (2002) and for the Surface Water Ambient Monitoring Program (SWAMP) by California’s State Water Resources Control Board (SWAMP, 2008) will be consulted where applicable.

V. LABORATORY ANALYSIS

The Center for Analytical Chemistry, California Department of Food and Agriculture, Sacramento, CA (CDFA) will conduct the pesticide analysis for the study. They will analyze six different analyte groups which will include up to 57 chemical compounds for analysis (Table 3). Beginning in 2010, short screens for OPs and photosynthetic inhibitor herbicides will be used, reducing the total number to 40 chemical compounds.

CDPR will analyze TSS in the water samples and will analyze TOC in both water samples and sediment samples. TSS samples will be analyzed following US EPA method 160.2 (US EPA, 1971) and as described in Kelley and Starner in CDPR Study Memo 219

(2004). TOC will be analyzed with a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan).

Table 3. Chemical analysis of pesticides in the Northern California urban monitoring study.

| Analyte Group | Analytical Method | Method Detection Limit ($\mu\text{g L}^{-1}$) | Reporting Limit ($\mu\text{g L}^{-1}$) |
|-------------------------------------|-------------------|---|--|
| Carbamate Insecticides | HPLC | 0.01 – 0.02 | 0.05 |
| Fipronil & Degradates | GC-MSD (SIM) | 0.003 – 0.005 | 0.05 |
| Organophosphorous Insecticides | GC-FPD | 0.008 – 0.0142 | 0.05 |
| | GC-MS | 0.0008 – 0.00142 | 0.01 |
| Auxin Inhibitor Herbicides | GC-MS | 0.064 | 0.1 |
| Pyrethroid Insecticides | GC-ECD | 1.09 – 7.68 (ng L^{-1}) | 5 – 15 (ng L^{-1}) |
| Photosynthetic Inhibitor Herbicides | LC-MS/MS | 0.01 – 0.031 | 0.05 |

VI. DATA ANALYSIS

All data generated by this project will be entered to a central database that holds all data including weather and field information, field measurements, and laboratory analytical data. All data will be shared between CDPR and Lorence Oki, University of California. We will use various nonparametric and parametric statistical methods to analyze the data. The data collected from this project may be used to develop or calibrate an urban pesticide runoff model.

VII. LABORATORY BUDGET

The total cost for the CDFA chemical analyses is \$244,660. This cost includes QC sample analysis (Table 4).

Table 4. Analytical cost estimates for urban samples collected in Northern California.

| Sample Type | Sampling Sites | | Sampling Event | | Number of Samples* | Chemical Analyses | | | | | | | | | Price per sample | Cost |
|-------------|----------------|-----------------|----------------|-------------|--------------------|-------------------|----------|-------------------|--------------|--------------|-------------|----------------------------|-------------------------------------|--------------|------------------|-----------|
| | Bay Area | Sacramento Area | Baseflow | Storm event | | Carbamates | Fipronil | Organophosphorous | | Chlorpyrifos | Pyrethroids | Auxin Inhibitor Herbicides | Photosynthetic Inhibitor Herbicides | | | |
| | | | | | | | | long screen | short screen | | | | long screen | short screen | | |
| Water | 4 | 9 | 2 | 1 | 43 | \$800 | \$500 | \$650 | | | \$800 | \$575 | \$720 | -- | \$4045 | \$173,935 |
| Water** | 4 | 9 | 0 | 1 | 15 | \$800 | \$500 | -- | \$500 | | \$800 | \$575 | -- | \$450 | \$3625 | \$54,375 |
| Sediment | 4 | 6 | 1 | 0 | 11 | -- | -- | -- | | \$300 | \$800 | | | | \$1100 | \$12,100 |
| Total | 4 | 9 | 2 | 2 | 70 | | | | | | | | | | | \$240,410 |

*includes QC samples.

**includes short screens in place of long screens.

VIII. LITERATURE CITED

Bennett, K. 1997. California Department of Pesticide Regulation SOP FSWA002.00: Conducting surface water monitoring for pesticides. Accessed at <http://www.cdpr.ca.gov/docs/empm/pubs/sops/fswa002.pdf> on December 10, 2009.

Cal/EPA. 2009. Central Valley Regional Water Quality Control Board. Accessed at http://www.swrcb.ca.gov/centralvalley/water_issues/tmdl/impaired_waters_list/index.shtml on December 8, 2009.

CDPR. 2009a. California Department of Pesticide Regulation's Pesticide Information Portal, Pesticide Use Report (PUR) data. Accessed at <http://www.cdpr.ca.gov/docs/pur/purmain.htm> on December 8, 2009.

CDPR. 2000b. Surface water protocols: Study 249a and 249b. Accessed at <http://www.cdpr.ca.gov/docs/emon/surfwtr/protocol.htm> December 8, 2009.

CDPR. 2000c. Surface water regulations. Accessed at <http://www.cdpr.ca.gov/docs/emon/surfwtr/regulatory.htm> December 8, 2009.

Doo, S. and L-M. He. 2008. California Department of Pesticide Regulation SOP EQWA010.00: Calibration, field measurement, cleaning, and storage of the YSI 6920 V2-2 multiparameter sonde. Accessed at <http://www.cdpr.ca.gov/docs/emon/pubs/sopequip.htm> on December 9, 2009.

Goehring, M. 2008. California Department of Pesticide Regulation SOP FSWA014.00: Instructions for the use of the Global FP101 and FP201 flow probe for estimating velocity in wadable streams. Accessed at <http://www.cdpr.ca.gov/docs/emon/pubs/sopfield.htm> on December 9, 2009.

Oki, L. and D. Haver. 2009. Monitoring pesticides in runoff in Northern and Southern California neighborhoods. Accessed at <http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations.htm> on December 8, 2009.

He, L-M., M. Ensminger, K. Kelley, F. Spurlock, and K. Goh. Monitoring pesticides in urban stormdrain and surface waters in four metropolitan areas of California. Accessed at <http://www.cdpr.ca.gov/docs/emon/surfwtr/presentations.htm> December 8, 2009.

Jones, D. 1999. California Department of Pesticide Regulation SOP QAQC004.01: Transporting, packaging and shipping samples from the field to the warehouse or laboratory. Accessed at <http://www.cdpr.ca.gov/docs/empm/pubs/sops/qaqc0401.pdf> on December 10, 2009.

Kelley, K. and K. Starner. 2004. Preliminary results for Study 219: Monitoring surface waters and sediments of the Salinas and San Joaquin River Basins for organophosphate and pyrethroid pesticides. Accessed at <http://www.cdpr.ca.gov/docs/emon/surfwttr/swmemos.htm> on December 10, 2009.

Mamola, M. 2005. California Department of Pesticide Regulation SOP FSWA016.00: Method procedure for collecting sediment for pesticide analysis [Online]. Accessed at <http://www.cdpr.ca.gov/docs/empm/pubs/sops/FSWA016.pdf> on December 10, 2009.

Segawa, R. 1995. California Department of Pesticide Regulation SOP QAQC001.00: Chemistry Laboratory Quality Control. Accessed at <http://www.cdpr.ca.gov/docs/emon/pubs/sop.htm> on December 9, 2009.

SWAMP. 2008. Quality assurance management plan for the state of California's surface water ambient monitoring program. Accessed at <http://swamp.mpsl.mlml.calstate.edu/resources-and-downloads/quality-assurance/quality-assurance-program-plan> on April 12, 2010.

UP3 Project. 2007. Pesticide Sales and Use Information. Pesticides in urban surface water: Urban pesticide use trends report 2007. Accessed at http://www.up3project.org/up3_use.shtml on December 9, 2009.

USEPA. 1971. National Exposure Research Laboratory (NERL), Microbiological and Chemical Exposure Assessment Research Division (MCEARD). Method 160.2, Residue, Non-Filterable (Gravimetric, Dried at 103 – 105° C). Accessed at http://www.caslab.com/EPA-Method-160_2/ on December 10, 2009.

USEPA. 2002. Guidance for quality assurance project plans (QA/G-5), EPA/240/R-02/009. Accessed at <http://www.epa.gov/quality/qs-docs/g5-final.pdf> on December 10, 2009.

Weston, D.P., R.L. Holmes, J. You, and M.J. Lydy. 2005. Aquatic toxicity due to residential use of Pyrethroid Insecticides. *Environ. Sci. Technol.* 39, 9778-9784.

Weston, D.P., R.L. Holmes, and M.J. Lydy. 2009. Residential runoff as a source of Pyrethroid pesticides to urban creeks. *Environmental Pollution* 157:287-294

Appendix. Detailed Sampling Site Information

| Site ID | Site Address/Location | GPS Coordinates (NAD83) | Site type | Stormdrain Area (approximate) |
|--|---|--------------------------------|------------------|--------------------------------------|
| Pleasant Grove Creek, Roseville (Placer County) | | | | |
| PGC010 | 1432 Diamond Woods Circle at Dr. Paul J. Dugan Park | 38.80477 -121.32733 | Stormdrain | 50 acres |
| PGC020 | Intersection of Opal Drive and Northpark Drive | 38.80232 -121.33855 | Stormdrain | 150 acres |
| PGC030 | Pleasant Grove Creek at Crocker Ranch Road | 38.79908 -121.34698 | Stormdrain | 85 acres |
| PGC040 | Pleasant Grove Creek at Veterans Memorial Park | 38.79857 -121.34802 | Receiving Water | |
| Martin Canyon/Koopman Canyon Creek, Dublin (Alameda County) | | | | |
| MCC010 | Near 7494 Donohue Drive at Fire Station | 37.70922 -121.93335 | Stormdrain | 500 acres |
| MCC020 | Millbrook Ave at end of cul-de-sac | 37.71668 -121.93524 | Stormdrain | 225 acres |
| MCC030 | I-680 between Dublin Boulevard and Amador Valley Road | 37.70686 -121.92711 | Stormdrain | 290 acres |
| MCC040 | I-680 between Dublin Boulevard and Amador Valley Road | 37.70593 -121.92658 | Receiving Water | |
| Sacramento Area Sites (Sacramento County) | | | | |
| ANT001 | Story Ridge Way and Redwater Dr., Sacramento | 38.72617 -121.3735 | Stormdrain | 25 acres |
| NAT001 | Babcock Way and Brookmere Way | 38.66745 -121.52411 | Stormdrain | 15 acres |
| FOL001 | Marsh Hawk Dr. near Widgeon Ct., Folsom | 38.65567 -121.144 | Stormdrain | 20 acres |
| FOL002 | Brock Circle, Folsom | 38.6503 -121.14494 | Stormdrain | 30 acres |
| FOL100 | Iron Point Rd., near Buckingham Way, Folsom | 38.64559 -121.14442 | Receiving Water | |