Monitoring Urban Pesticide Runoff in Northern California, 2009 - 2010

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ABSTRACT

The California Department of Pesticide Regulation (CDPR) continued an urban surface water monitoring program in northern California in 2009 - 2010. At 13 sites either at storm drain outfalls or in urban creeks, water and sediment samples were collected in the Sacramento and San Francisco Bay areas. Ninety-five percent of the water samples contained at least one pesticide but multiple detections were common. For example, 75% of the samples contained at least two pesticides, 50% of the samples had four or more pesticides and 25% had six or more pesticides. Bifenthrin, malathion, carbaryl, and fipronil were commonly detected insecticides in surface waters. In addition, fipronil sulfone, diazinon, desulfinyl fipronil, and aldicarb were also detected, and there were trace detections of DDVP (dichlorvos). The herbicides 2,4-D, dicamba, triclopyr, diuron, MCPA, and prometon were also detected above their reporting limits. Rain increased pesticide runoff; dependent on pesticide, detection frequencies were between 17% - 69% higher with rain. Generally, more pesticides were detected during an October first flush rainstorm than an October dryflow (dryflow defined as sampling during California's dry season) sampling event immediately preceding the first flush or during spring rainstorms. Triclopyr, 2,4-D, dicamba, and bifenthrin were detected more frequently in stormdrain outfalls whereas prometon was more commonly detected in receiving waters. There was little difference among other pesticides. Sediment samples were only collected during dryflow and analyzed for pyrethroids and chlorpyrifos. The most common pyrethroids in sediments were bifenthrin, cyfluthrin, permethrin, deltamethrin, λ-cyhalothrin, and cypermethrin. Half of the sediments contained six or more pyrethroids and chlorpyrifos was detected in 20% of the sediments. Of all the pesticides detected, bifenthrin had the most potential to be toxic to sensitive aquatic organisms. On occasion, diuron, fipronil, permethrin, malathion, and diazinon also were detected at concentrations that potentially could be toxic to aquatic life.

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I. INTRODUCTION

Urban pesticide use includes structural pest control, landscape maintenance, rights-of-way and public health pest protection applications, as well as applications to commercial, institutional, and industrial areas, and residential home-and-garden applications. The California Department of Pesticide Regulation (CDPR) compiles pesticide use records for urban pesticide applications made by licensed applicators. Annually, professional applicators apply over 4 million kg active ingredient (ai) of pesticides for urban (non-agriculture) pest control (CDPR 2010). However, homeowners do not report their individual use, so that total urban pesticide use in California is greater than reported use. Based on pesticide products sold in home improvement stores, high homeowner pesticide use is anticipated (Flint 2003; Moran 2005; Osienski et al. 2010). And, although it is difficult to estimate this homeowner use (Zhang and Spurlock 2010), the US EPA has estimated that non-agricultural pesticide use accounts for approximately 20% of all total pesticide use in the United States. Most of these uses are in urban areas (Grube et al. 2011). With over 68 million kg ai of reported pesticide use in California in 2009 (CDPR 2010), 20% urban use would suggest that large amounts of pesticides are applied yearly in California urban areas.

Due to the high volume of urban pesticide use and perhaps lack of consumer awareness, urban pesticide runoff may exceed agricultural runoff (Wittmer et al. 2011). Pesticide runoff into urban creeks and rivers can occur via stormdrains during dryflow or with stormwater runoff leading to concentrations that may be toxic to aquatic organisms (Hoffman et al. 2000; Revitt et al. 2001; Schiff and Sutula 2004; Budd et al. 2007; Sprague and Nowell 2008; Weston et al. 2009; Oki and Haver, 2009). Recent monitoring in California shows that urban waterways are frequently contaminated with pyrethroids, diazinon and chlorpyrifos, and fipronil (Oki and Haver, 2009; Weston et al. 2009; Weston and Lydy 2010; Lao et al. 2010). CDPR initiated its own urban monitoring program in 2008 and found that in addition to the above mentioned pesticides, bifenthrin, carbaryl, malathion, diuron, pendimethalin, 2,4-D, triclopyr, dicamba, and MCPA frequently contaminate urban waterways (Ensminger and Kelley 2011). However, additional monitoring is warranted to more fully understand the extent of pesticide contamination in urban waterways. Thus, CDPR's urban sampling project was expanded in northern California to include additional monitoring sites in the Sacramento area. Specific objectives of this study were fourfold: 1) determine what pesticides, at what concentrations, are present in urban runoff; 2) evaluate the magnitude of measured concentrations relative to water quality or aquatic toxicity benchmarks; 3) assess the effect of waterbody type (e.g., stormwater drain vs. creek); and 4) assess the effect of season (dryflow vs. rainstorm).

II. MATERIALS AND METHODS

Study Area. Monitoring was conducted at 13 sites in northern California, in the San Francisco Bay Area and in the Sacramento area (Figure 1). The sampling sites in the San Francisco Bay area (Dublin) and one of the sampling areas in the Sacramento area (Roseville) were established sampling sites from CDPR's initial urban study in northern California (http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/study249site.pdf). Five additional new sites were added in the Sacramento area. Four of these sites were identical to the northern California sites used by Haver and Oki (2009). For each main sampling area (one in the San Francisco Bay area and two in the Sacramento area), there were two or three stormdrain outfalls for each receiving water site (Figure 2). Two of the five new sites added in the Sacramento area did not fit this model and consisted solely of stormdrain outfalls. Detailed information about the sampling sites can be found in Appendix I, Table A1.

Field Sampling. We will use the term dryflow to indicate sampling when surface waters receive no input from rain storms during California's dry season. This is generally from late April or early May through September or October. Between October 2009 and June 2010, one dryflow and two rainstorm sampling events were completed. The first flush rainstorm of the 2010 water year[1] and one of the two last major spring rainstorms were sampled. In the spring of 2010, we were not able to sample all of the sites together during one rainstorm but had to collect samples during two year-end rainstorms to do so. These will be considered one water year-end rainstorm. Sediments were only collected once, prior to the first rainstorm of the 2010 water year. In addition, a preliminary dryflow monitoring event was conducted in August 2009 at the four Haver and Oki Sacramento area sites.

Water samples from receiving waters were collected from stream banks close to midstream as feasible directly into 1-L glass amber bottles using an extendable pole and sealed with Teflon®-lined lids. Stormdrain outfalls, generally with less flow, were collected by hand directly into 1-L amber bottles. However, dependent on flow and water depth, occasionally water samples from stormdrain outfalls were collected into a stainless steel container and aliquots were poured into 1-L glass bottles. Sediment (up to a 2 cm depth) was collected using a stainless steel trowel or shovel, composited in a stainless steel container, and individual samples were placed into clear glass Mason® jars for later chemical analysis. Sediments could not be collected at all sites. Immediately after sampling, water and sediment samples were stored on wet ice for transport. Upon arrival at the laboratory, water samples were refrigerated (4°C) whereas sediments samples were frozen (–20°C) until chemical analysis.

Total Suspended Solids and Total Organic Carbon. We analyzed total suspended solids (TSS) in water samples and total organic carbon (TOC) in both water and sediment samples. TSS was analyzed following US EPA method 160.2 (US EPA, 1971). Briefly, waters samples were filtered under vacuum through a Buchner funnel lined with a glass fiber filter, dried overnight at 103-105°C, and weighed. TOC was analyzed using a TOC-V CSH/CNS analyzer (Shimadzu Corporation, Kyoto, Japan).

Field Measurements. Water physiochemical properties (dissolved oxygen [DO], electrical conductivity [EC], pH, turbidity, and temperature) were measured *in situ* with a

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[1] A water year is a 12-month period beginning with October 1 for any given year through September 30 of the following year; e.g., water year 2010 is from October 1, 2009 through September 30, 2010 (http://water.usgs.gov/nwc/explain_data.html).

YSI 6920 V2 meter (YSI Incorporated, Yellow Springs, OH). The meter was calibrated prior to field use (Doo and Lee 2008).
To get an estimate over overall pesticide load, flow data measurements were collected using a Global Flow Probe Flow Meter (Global Water, Gold River, CA). Flow could not be taken at all sites at all sampling dates, due to low or no flow or, in some cases, due to rapid flow in larger creeks. In specific cases, flow was estimated using the float method (timing the movement of an object on the surface) or by measuring volume over time (Table A8, Appendix I).

Analytical Chemistry. The California Department of Food and Agriculture (CDFA), Center for Analytical Chemistry, analyzed for a total of 41 different pesticides, or pesticide degradates, in this study. Most of the analyses were from the following pesticide groups: pyrethroids, carbamates, organophosphorus (OP) insecticides, fipronil (FP) and FP degradates, synthetic auxin herbicides, and photosynthesis inhibitor herbicides (triazine, trizinone, urea, and uracil chemistry) (Table 1). Although some of the pesticides included in the chemical analysis are not urban use pesticides, they were analyzed and reported by the laboratory from the same analytical method.

We report the results as: 1) nd, not detected, concentrations below the minimum detection limit; 2) tr, trace detection, where in the chemist's best professional judgment the analyte does exist between the reporting limit and the minimum detection limit; 3) a numerical concentration in ng L^{-1} (pyrethroid water samples), µg L^{-1} (all other water samples), or µg kg $^{-1}$ (dry weight; sediment samples).

QA/QC for Water and Sediment Samples. Quality control for this study followed the CDPR SOP guidelines on Chemistry Laboratory Quality Control (Segawa, 1995). Quality control consisted of blind spikes, laboratory matrix spikes, method blanks, field duplicates, and field blanks. Propazine was also used as a surrogate spike in the photosynthesis inhibitor herbicide analytical screen. Fifteen percent of the field samples were field duplicates, field blanks, or blind spikes.

Statistics. Statistical analyses was conducted using the non-parametric Mann-Whitley mean comparison test, significance at the 0.05 level, with Minitab® Statistical Software (Release 15).

III. RESULTS AND DISCUSSION

Pesticides detected in surface waters

Of the 41 pesticides analyzed, we detected 14 different pesticides (including degradates) above their analytical reporting limit: eight insecticides and six herbicides. In all, we collected 42 water samples for the four sampling timings; 40 samples (95%) contained at least one pesticide. Frequently, more than one pesticide was detected in the water at one site. For example, 75% of the samples contained two or more pesticides, 50% of the samples contained four or more, and 25% of the samples contained six or more pesticides (Figure 3). The new sites in the Sacramento area had approximately the same number of pesticides per sample as the established sites.

The most frequently detected insecticides in surface waters were, in decreasing order, bifenthrin, malathion, carbaryl, fipronil (FP), FP sulfone, diazinon, desulfinyl FP, and trans-permethrin (Figure 4). Bifenthrin was the most frequently detected pesticide in the study, with a 76% detection frequency. The high detection frequency was attributed to a 100% detection frequency during rain runoff. Bifenthrin was detected with about equal frequency in the five new Sacramento sites (72% detection frequency) as was observed in the established sites (79%). Bifenthrin was also the highest detected insecticide in CDPR's initial urban study (Ensminger and Kelley 2011) and has been frequently detected elsewhere (Oki and Haver 2009; Weston et al. 2009). It is apparent that in urban surface waters, bifenthrin is a major contaminant. Only one other pyrethroid was detected, permethrin, during a spring rain event at one of the new Sacramento sites.

Two OPs were detected above their reporting limits, malathion and diazinon. Of these, malathion was most frequently detected. Twenty-six percent of the samples contained malathion (58% including trace detections). Of the new Sacramento sites, the detection of malathion was similar (21%) to the detections in established sites (29%). The OP diazinon was detected in 5% of the samples. Another OP, dichlorvos (DDVP), had trace detections in 20% of the samples. This OP had not previously been detected in CDPR's earlier urban work (Ensminger and Kelley 2011).

Carbaryl was detected almost as frequently as malathion, with a 24% detection frequency (40% with trace detections). Both the new sites and established sites had about the same detection frequency (21% and 25%, respectively). Another carbamate insecticide, aldicarb, was detected in stormdrain outfalls in two of the new sites in the northern section of Sacramento in August 2009. Aldicarb is a restricted use insecticide with no registered urban uses (agricultural use only); 96% of its use is on cotton. In 2009, there were no reported uses of aldicarb in the PUR database in Sacramento County for 2009, or in nearby counties (CDPR 2010). The source of this aldicarb detection would be difficult to locate.

Fipronil was detected in 21% of the samples (with trace detections, 84%). Most of these detections were at the sampling sites in Roseville (50% detections frequency); with minor detections in the San Francisco Bay Area (Dublin; 8%) sites and the new Sacramento area sites (7% detection frequency). Roseville may be a high fipronil use area; in CDPR's initial urban study, in northern California this city had a much higher detection frequency (31%) than did Dublin (7%).

Similar to CDPR's previous urban study, fipronil had a high frequency of trace detections (Ensminger and Kelley 2011). This was also the case with the fipronil (FP) degradates (percentage of detections above reporting limit, detections including trace detections):

- FP sulfone (8%, 76%);
- Desulfinyl FP (3%, 87%);
- FP amide (no detections, 50%);
- FP sulfide (no detections, 40%);
- Desulfinyl FP amide (no detections, 24%).

The detection frequencies between the established and the new sites were about the same for the fipronil degradates.

The most frequently detected herbicides were 2,4-D, dicamba, triclopyr, diuron, MCPA, and prometon (Figure 4). 2,4-D was the second most frequently detected pesticide in this study and as a group, the synthetic auxin herbicides (2,4-D, triclopyr, dicamba, and MCPA) were frequently detected. For urban use, these four herbicides have similar uses and application timings. Frequency of detection ranged from 21% (MCPA) to 74% (2,4-D); detection frequency increased to 32% - 82% if trace detections are considered. Detections of synthetic auxin herbicides in the new sites were comparable to detections in the established sites. Based on results from this study and CDPR's initial urban study, synthetic auxin herbicides are widespread in urban surface waters in northern California.

Diuron was also frequently detected (37% detection frequency, with trace detections, 50%). The new sites had only a slightly higher detection frequency (43%) than did the established sites (33%). Prometon was frequently detected (24%; with trace detections, 40%). Prometon is not applied by professional applicators (nor used in agriculture) therefore its use must come strictly from homeowners (CDPR 2010). Interestingly, in a recent survey of pesticide products sold in large retail stores, prometon was only listed for sale in southern California (Osienski 2010) but in previous surveys it had been found in one product in northern California (Moran 2005). Its moderate detection frequency is likely due to its use and timing (often, to bare ground just prior to the rainy season).

Pesticides detected in sediments

Sediments were collected during the dryflow sampling event; a total of 10 sediment samples were collected from the sampling sites. Two of the sediment samples contained chlorpyrifos and all sediments contained bifenthrin and cyfluthrin. In addition, nine of the samples contained permethrin and half of the sediments contained cypermethrin, deltamethrin, and λ-cyhalothrin. Including chlorpyrifos, there was an average of six pesticides per sediment sample.

Appendix I contains the complete analytical results (for both water and sediment) for the study (Tables A2-A4).

The effect of waterbody type (stormdrain outfall vs. creek receiving water) on pesticide concentrations in urban surface waters.

In the study, there were no significant differences in the median number of pesticides detected per sample in stormdrain outfalls and receiving waters (median 4.0 and 3.0, respectively; p=0.487). This seems to be consistent for the insecticides, as there were little differences between detection frequencies between storm drain outfalls and receiving waters (Figure 5). Bifenthrin had the largest difference, with more detections (12.5%) in stormdrain outfalls than in receiving waters. Although with the small samples size this might not be significant, this is consistent with previous observations (Ensminger and Kelley 2011). Several of the herbicides had larger differences between the waterbody types. The synthetic auxins (except for MCPA) all had higher detection frequencies in stormdrain outfalls than in receiving waters, whereas prometon was more commonly found in receiving waters. For these herbicides, there was 20% or more differences between the two waterbodies. Perhaps these herbicides were applied near the time we collected our samples and were therefore more concentrated in specific locations. More likely this difference is due to the small sample size for receiving waters (n=9).

The effect of season (dryflow vs. rainstorm) on pesticide concentrations in urban surface waters.

The median number of pesticides detected per sample during rainstorm events was significantly greater than during dryflow (median 5.0 and 1.0, respectively; p=0.000). In addition, there were significant differences in pesticide detections between the different rainstorm events. The first flush rainfall in October had significantly more detections (median, 7) than did the October dryflow sampling event immediately preceding the first flush (median, 1; p=0.0002) or the spring rainstorm (median 4, p=0.012; Figure 6). The number of pesticides detected during the October dryflow and the spring rainstorm sampling event were also were significantly different (p=0.001).

Of each individual pesticide, detection frequencies were between 17%-67% higher during the first flush rainfall of the 2010 water year than during the October dryflow sampling event (Figure 7). Generally, the first flush rain event had between 10%-60% higher detection frequencies than the spring rainstorm. However, bifenthrin and dicamba had the same detection frequencies during both rain events and 2,4-D had a higher detection frequency during the spring rain event. Bifenthrin has higher reported use in the late summer through early fall than during the spring, but use is common through most of the year (CDPR 2010; Figure 1A, Appendix 1). Bifenthrin also is known to tightly bind to soil particles; it is likely that we are seeing equal detections at both rain events because of higher sediments in the rain runoff waters. During rain events we had significantly higher TSS and turbidity than during dryflow (Table A6, Appendix I). Between the two rain events there were no significant differences between these variables. Dicamba has very low reported use for the sampling areas and detections likely represent homeowner use. 2,4-D had about twice as much reported use in the spring as the fall, and may account for its higher detection frequency in the spring; homeowner use would likely contribute to the spring load. But because we generally detected more pesticides during the first flush rainfall, this suggests that pesticides accumulate over California’s dry season (May – October) and that dryflow runoff only appears to remove a small percentage of pesticides. However, these pesticides could have been applied prior the impending rainstorm by homeowners or licensed pesticide professionals.

All sites except MCC030, PGC010, and PGC040 had higher detection frequencies with the first flush rainstorm (Figure 8). MCC030 and PGC040 had approximately the same detection frequencies during both rain events; however PGC010 was unusual in that the October dryflow sampling event had highest detection frequency. Including trace detections, however, the October first flush rainstorm had the most detections of all three of these sampling events.

Comparison of Pesticide Concentrations to Aquatic Toxicity Guidelines

Established aquatic toxicity benchmarks can be used to interpret monitoring data and prioritize sites and pesticides for further investigation (US EPA 2011). For this analysis, we used benchmarks available from US EPA Office of Pesticide Programs and Office of Water. But for pyrethroids we also used established *Hyalella azteca* LC_{50}s (where available) due to the sensitivity of this organism to pyrethroids (Anderson et al. 2006; Weston and Jackson 2009). Additionally, recently developed water quality criteria (WQC) by the University of California at Davis (UCD-WQC) was also used to interpret the results (CVRWQCB 2011).

In water samples, we detected seven pesticides above their aquatic toxicity guideline values (Table 2; values in this table below reporting limits are not discussed). In all, 38% of the total samples and 62% of the sites had at least one pesticide above these toxicity values. This high percentage was due to the high number of bifenthrin detections with the potential to be toxic to sensitive aquatic organisms. Pyrethroids are highly hydrophobic and associate with the dissolved organic carbon and suspended sediment in water samples which may limit their bioavailability. Considering these factors with the equation by Spurlock et al. (2005) and using the K_{oc} value of 240000 (NPIC 2011), 34% - 56% of the bifenthrin detections would be bioavailable and have the potential to be toxic to sensitive species (Table 2). However, K_{oc} values are dependent on many factors. For bifenthrin, Laskowski (2002) lists a range of K_{oc} values from 116000 – 888000 ml g^{-1}. With this range of K_{oc}, between 15 – 63% of all bifenthrin's detections would have been bioavailable. It is likely that some of the bifenthrin would have been available for uptake and toxicity to sensitive aquatic species in these waterways.

None of the other detected pesticides approached the level of potential toxicity of bifenthrin. Diuron and fipronil had two detections above their respective benchmarks (5.3%) and permethrin, diazinon, and malathion had one detection (2.6%) above their respective aquatic benchmarks (Table 2). Malathion has a lower WQC than benchmark (0.17 μL^{-1} compared to its benchmark of 0.3 μL^{-1}); in addition, the US EPA Office of Water gives chronic continuous concentration value of 0.1 μL^{-1} (US EPA 2011). Using these values, the percentage of malathion detections above toxicity guideline values would range from 2.6 – 13% (Table 2).

Water Quality

Temperature, pH, EC, turbidity, DO, TSS, and TOC were measured in this study. DO, pH, and EC have specific water quality objectives. EC did not exceed water quality objectives, but pH and DO did (5% and 13% of the time, respectively). Median concentrations of turbidity, TSS, and TOC were 24.7 NTU, 18.3 ppm, and 5.9 ppm, respectively. There were no significant differences in water quality between stormdrain outfalls and receiving waters but there were some differences between dryflow and rain runoff. Water quality data can be found in the Appendix I, Tables A5 – A8.

Quality Control

Quality control was acceptable for the study. CDFA recovered 97% of all matrix, blind, and propazine spikes within acceptable levels with no detections in the lab blanks. Appendix II has more detailed information about quality control.

IV. CONCLUSIONS

The main conclusions from the study are listed below.

1. Ninety-five percent of the water samples contained at least one pesticide. The main insecticides detected in water samples were bifenthrin, malathion, carbaryl, and fipronil. The main herbicides were 2,4-D, dicamba, triclopyr, diuron, MCPA, and prometon.
2. Two additional pesticides were detected in this study which were not observed in CDPR's initial study. The cotton insecticide aldicarb was detected in two of the new Sacramento area sites. The OP insecticide DDVP (dichlorvos) had a 20% trace detection frequency.
3. Urban water bodies contain numerous pesticides at any given time. Seventy-five percent of the sampled waters contained at least two pesticides, 50% contained four or more pesticides and 25% had six or more pesticides.
4. The new sites in the Sacramento area (NAT001, ANT001, FOL001, FOL002, FOL100; see Appendix 1) had approximately the same detection frequency as the established sampling sites.
5. Roseville had a higher detection frequency of fipronil than either the San Francisco Bay Area or new Sacramento area sites.
6. Sediments are contaminated with chlorpyrifos and pyrethroids. Bifenthrin and cyfluthrin were detected in all sediments; permethrin in 90% of sediments. Half of the sediment samples also contained cypermethrin, deltamethrin, and λ-cyhalothrin.
7. Rainstorms drive most pesticides into urban surface waters. Generally, more pesticides are detected in a first flush rainstorm than during late irrigation season dryflow or a late spring rainstorm. More pesticides were detected in spring rainstorms than during dryflow.
8. Some pesticides were more commonly detected in stormdrain outfalls (2,4-D, dicamba, triclopyr), some more frequently detected in receiving waters (prometon), and others were detected with about equal frequency (diuron, bifenthrin, carbaryl, fipronil, malathion, MCPA).
9. Bifenthrin frequently was detected at concentrations that could be toxic to aquatic life. Infrequently, permethrin, fipronil, malathion, diazinon, and diuron were detected at concentrations that potentially could be toxic to aquatic organisms.

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Table 1. Pesticides analyzed by the California Department of Food and Agriculture in water or sediment, with their method detection and reporting limits, and holding times. Specific methods can be found at http://www.cdpr.ca.gov/docs/emon/pubs/em_methd_main.htm.

Analyte Group (method)		Method Detection Limit (μg L^{-1})	Reporting Limit (μg L^{-1})	Holding time (days)
Carbamate Insecticides (HPLC; method EMON-SM 11.3)				
Analytes: aldicarb, aldicarb sufoxide, aldicarb sulfone, methomyl, carbofuran, 3-OH carbofuran, carbaryl, oxamyl, methiocarb		0.01 – 0.02	0.05	28 (acidified)
Fipronil Insecticides (GC/MSD in SIM mode; method EMON-SM 05-013)				
Analytes: fipronil (FP), desulfinyl FP, desulfinyl FP amide, FP sulfide, FP sulfone, FP amide		0.003 – 0.005	0.05	14
Organophosphorus Insecticides in Water (method EMON-SM 46-0)				
Analytes by GC/FPD: dichlorvos[1], dimethoate, malathion, methidathion		0.008 – 0.0142	0.03 – 0.05	7
Analytes by GC/MS: chlorpyrifos, diazinon		0.0008 – 0.0012	0.01	7
Pyrethroid Insecticides (GC-ECD; water method, EMON-SM 05-003; sediment method EMON-SM 52.9)				
Analytes: bifenthrin, cyfluthrin, cypermethrin, deltamethrin/tralomethrin, esfenvalerate/fenvalerate, fenpropathrin, λ-cyhalothrin, permethrin (cis, trans), resmethrin	Water	0.001 – 0.008	0.005 – 0.015	4
	Sediment (μg kg^{-1})	0.107 – 0.183	1.0	183
Photosynthesis Inhibitor Herbicides (triazine, trizinone, urea, and uracil chemistry; (LC/MC/MC; method EMON-SM 62.9)				
Analytes: bromacil, DACT (diamino chlorotriazine), diuron, hexazinone, prometon[1], simazine		0.01 – 0.04	0.05	14
Synthetic Auxin Herbicides (GC/MS; method EMON-SM 05-012)				
Analytes: 2,4-D, dicamba, MCPA, triclopyr		0.064	0.1	12

[1] dichlorvos and prometon only analyzed October 2009

Table 2. US EPA aquatic life benchmarks, water quality criteria, or commonly accepted LC_{50} values of pesticides detected above these toxicity guideline values (in µg L^{-1} except for pyrethroids [ng L^{-1}]). Detection frequencies (DF) greater than the toxicity value are given in parenthesis below the individual toxicity value.

Pesticide	DF for Study	US EPA OPP*								UCD WQC§		$LC_{50}{}^A$
		Aquatic Benchmark						Office of Water				
		AI	CI	AF	CF	ANV	AV	CMC	CCC	AWQC	CWQC	
Diazinon	5.3%	0.11 (2.6%)	0.17 (2.6%)	45	<0.55	3700	--	0.17 (2.6%)	--	0.2	0.07 (2.6%)	--
Diuron	37%	80	200	200	26	2.4 (5.3%)	15	--	--	170	1.3 (7.9%)	--
Fipronil	21%	0.11 (5.3%)	0.011^B (21%)	41.5	6.6	--	--	--	--	--	--	--
Fipronil sulfone	7.9%	0.36	0.037^B (7.9%)	12.5	0.67	140	>100	--	--	--	--	--
Malathion	26%	0.3 (2.6%)	0.035^B (26%)	16.4	8.6	--	--	--	0.1 (13%)	0.17 (7.9%)	0.028^B (26%)	--
Bifenthrin^C	76%	800	1.3^B (76%)	75	40	--	--	--	--	4 (56%)	0.6^B (76%)	7.7 (34%)
trans-Permethrin^C	2.6%	10 (2.6%)	1.4^B (2.6%)	395	51.5	--	--	--	--	10 (2.6%)	--	--

*AI = acute invertebrate; CI = chronic invertebrate; AF = acute fish; CF = chronic fish; ANV = acute nonvascular plant; AV = acute vascular plant; CMC = chronic maximum concentration; CCC = chronic continuous concentration (US EPA 2011).

§AWQC = acute water quality criteria; CWQC = chronic water quality criteria (CVRWQCB 2011).

[A] *Hyalella azteca* LC_{50} (Weston and Jackson 2009)

[B] Below the reporting limits of the chemical analysis.

[C] DF above estimated bioavailable concentration using equation from Spurlock et al. (2005) and K_{oc} values from PPDB (2011) and NPIC (2011).

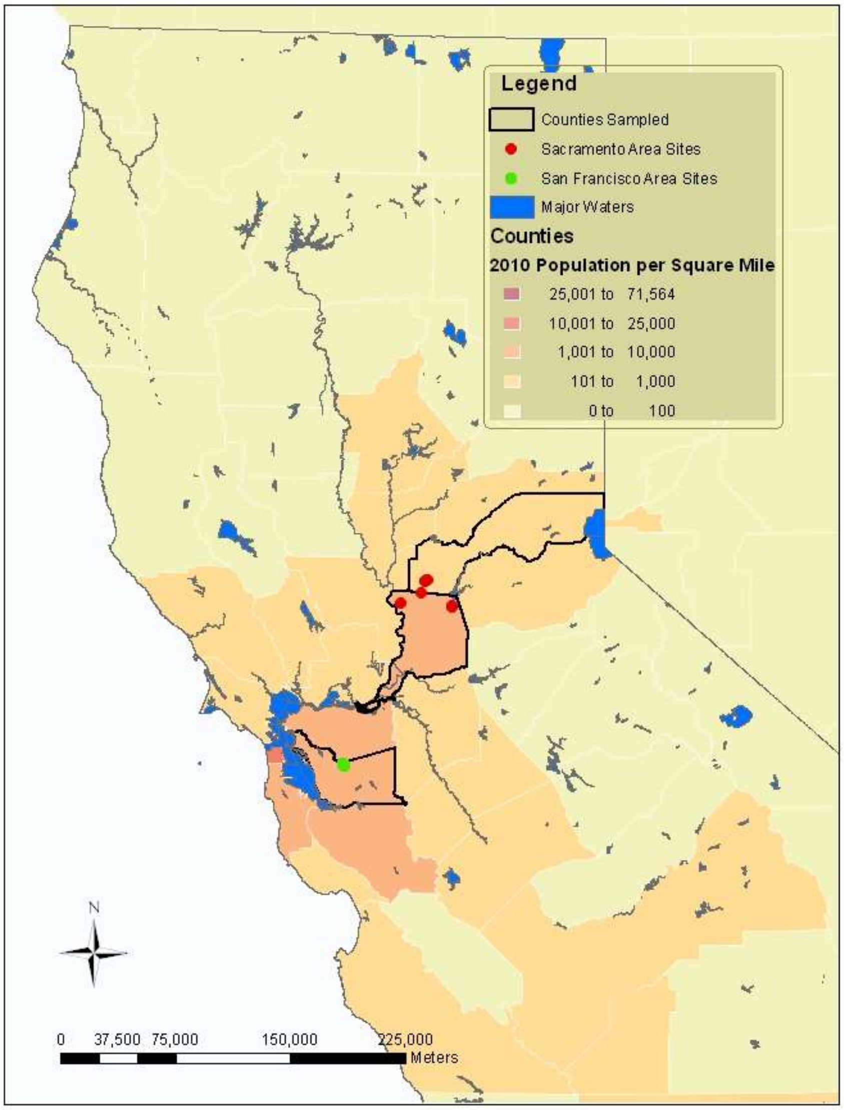

Figure 1. Sampling sites for CDPR's northern California urban monitoring project in the Sacramento and San Francisco Bay areas, California.

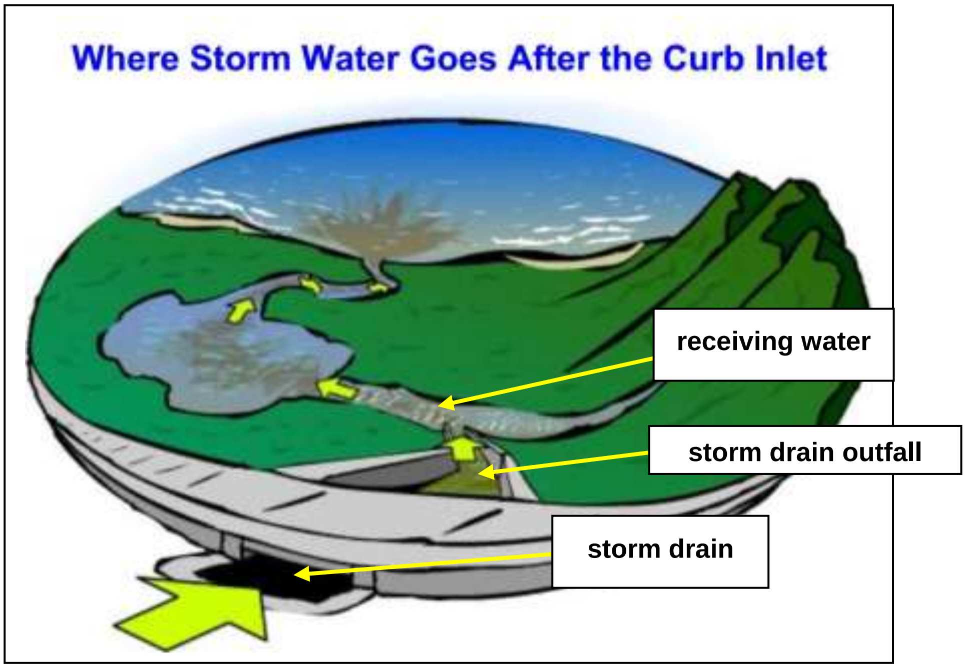

Figure 2. Cartoon depicting a storm drain outfall and receiving water (*from* http://www.stormwater.co.trumbull.oh.us/).

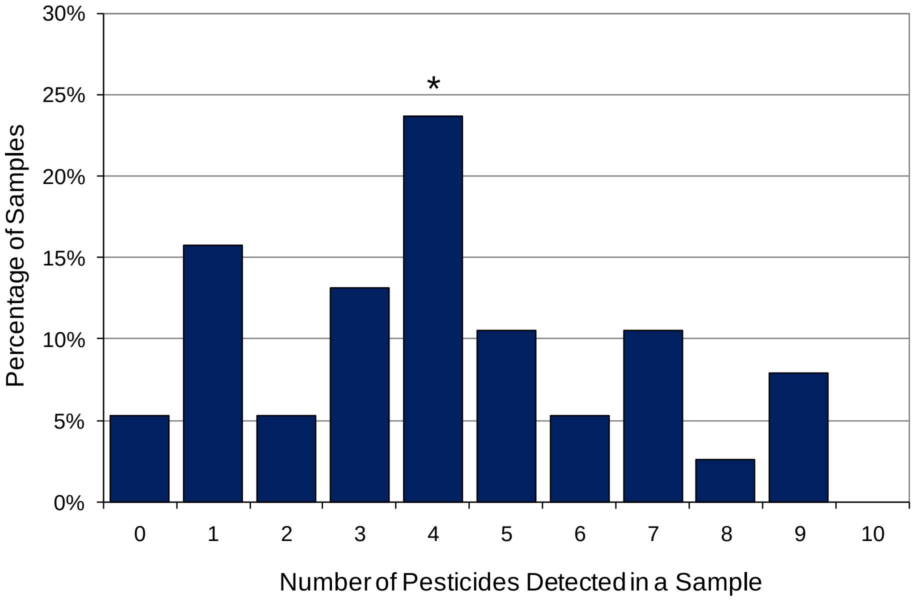

Figure 3. Number of pesticides detected in water samples collected from urban creeks and storm drain outfalls in northern California, USA. All detections were above the analytical reporting limit; * indicates the median number of pesticides detected per water sample.

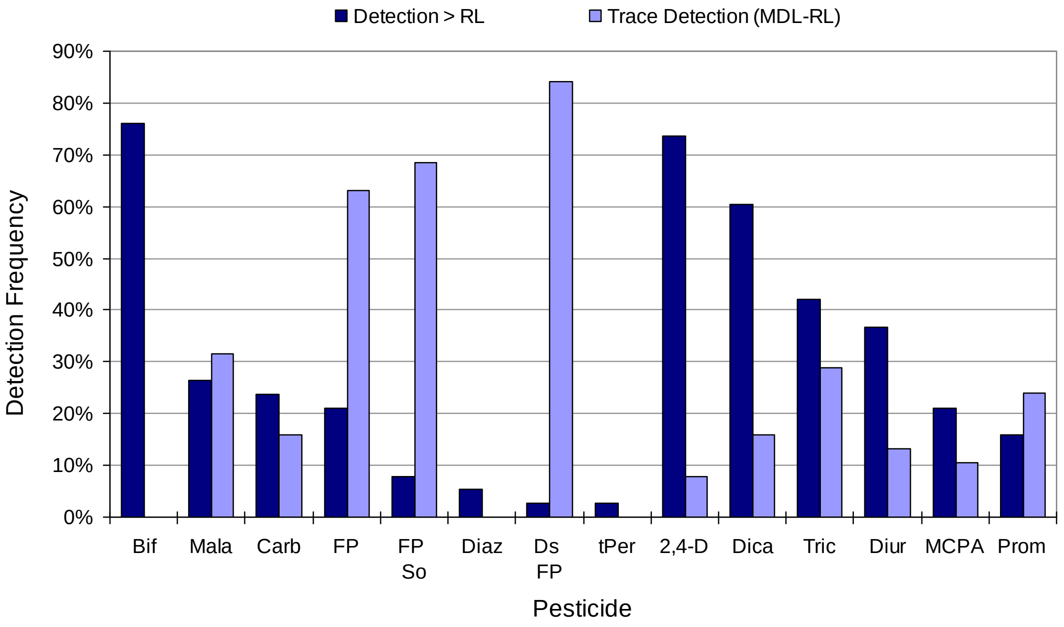

Figure 4. Detection frequency of pesticides (above the reporting limit) between October 2009 and June 2010. Bif, bifenthrin; Mala, malathion; Carb, carbaryl; FP, fipronil; FP So, FP sulfone; Diaz, diazinon; Ds FP, desulfinyl FP; tPer, trans-permethrin; Dica, dicamba; Tric, triclopyr; Diur, diuron; Prom, prometon. There were also trace detections of FP amide (50%), FP sulfide (40%), desulfinyl FP amide (24%), and dichlorvos (20%). DDVP (dichlorvos) was detected in two of the four preliminary samples taken in August 2009 at the new Sacramento sites.

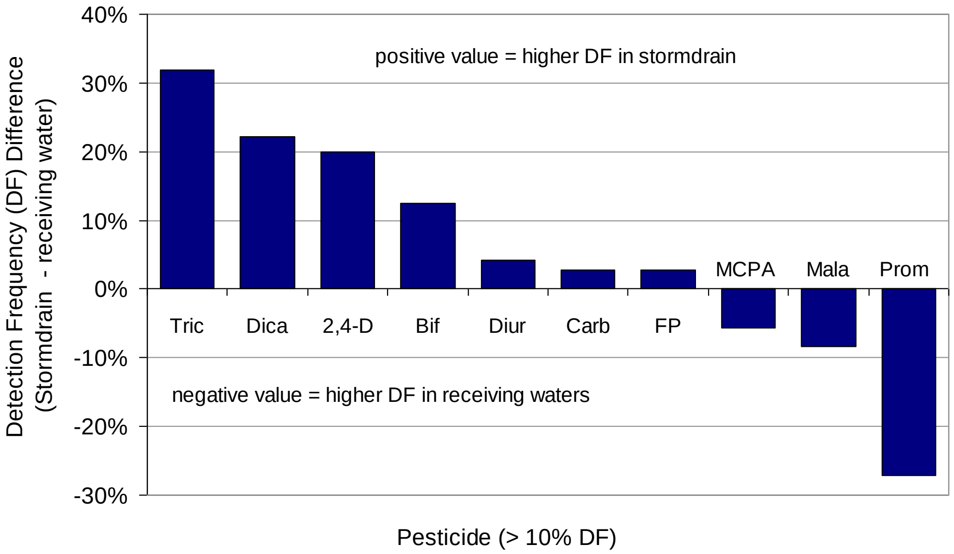

Figure 5. The influence of waterbody on frequency of pesticide detections. Detection frequency (DF) differences were determined by subtracting the detection frequency of stormdrain outfall samples from the detection frequency of receiving water (DF receiving water – DF stormdrain outfall). Tric, triclopyr; Dica, dicamba; Bif, bifenthrin; Diur, diuron; Carb; carbaryl; FP, fipronil; Mala, malathion; Prom, prometon. Only pesticides detected with a greater 10% detection frequency during the entire study are included in the figure.

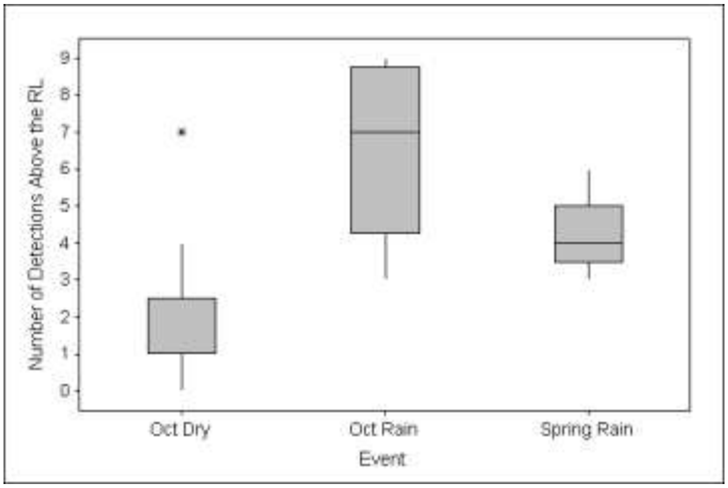

Figure 6. Number of pesticides detected during the different sampling events.

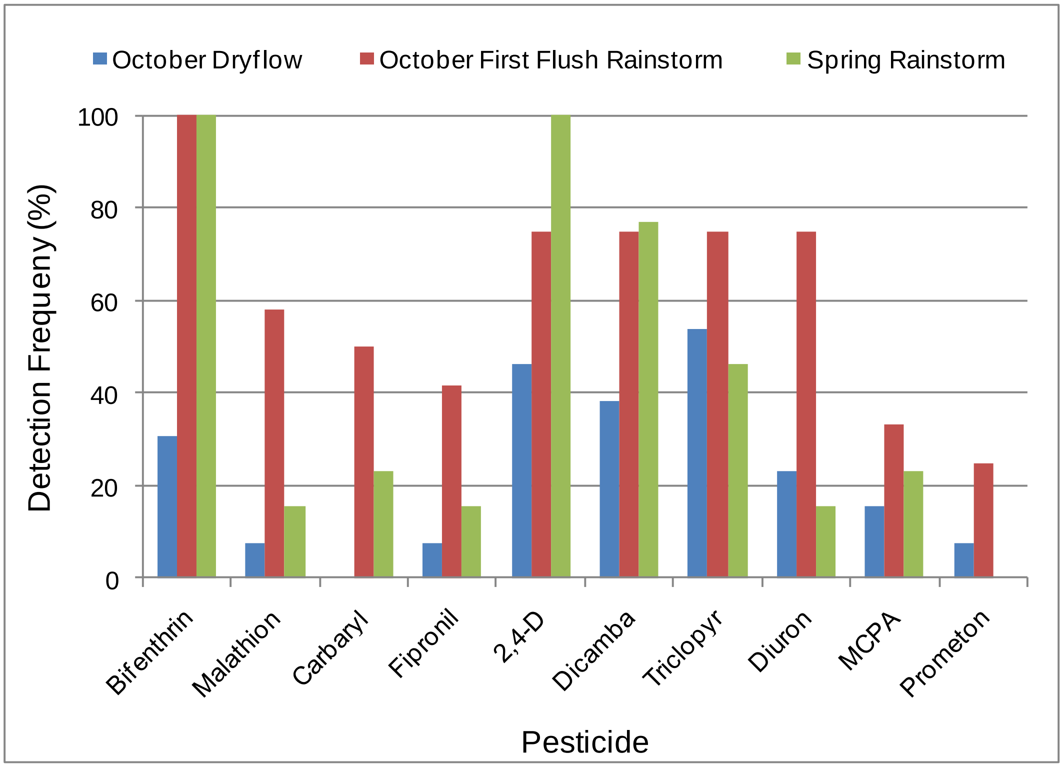

Figure 7. A. Detection frequency of samples collected during an October dryflow sampling event (October 11 or 12, 2009) which was immediately prior to a first flush rain event (October 13, 2009), and samples collected during spring rainstorms (April 4 and May 25, 2010). There was no analytical data for prometon at the spring rainstorm event. Only pesticides detected with a greater 10% detection frequency during the entire study are included in the figure.

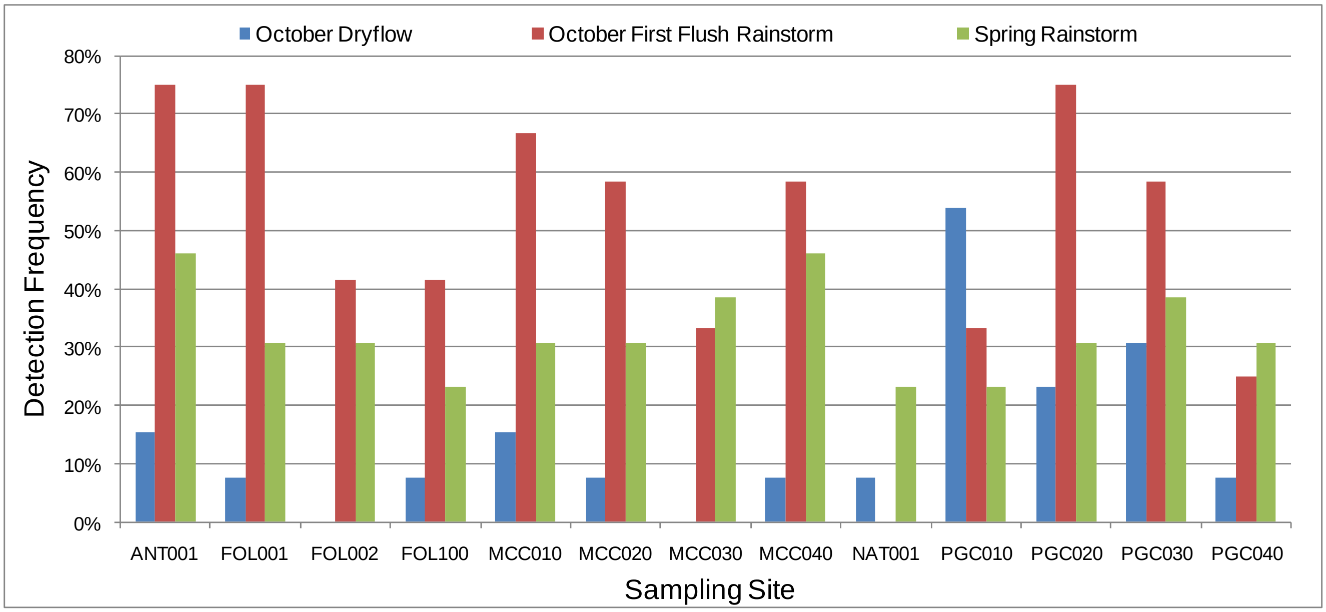

Figure 8. Detection frequency of pesticides detected at the different sampling sites with each sampling event (NAT001 was not sampled in October first flush rainstorm).

VI. APPENDIX I. DATA for Study 264

Appendix I contains data for the urban study, August 2009 – May 2010. Abbreviations commonly used in the Appendix tables:

Abbreviation	Definition
FP	fipronil
SAC	Sacramento Area
SFB	San Francisco Bay Area
mv	missing value, not data available or site not sampled
nd	not detected, below the reporting limit
ppm	parts per million (mg L^{-1})
RW	receiving water
StDr	storm drain outfall
tr	trace detection (below the reporting limit but above the minimum detection limit).
nf	water was not flowing
fl	water was flowing, either too slow or too dangerous to measure

Table A1. Characteristics of the sampling sites in Study 264.

Watershed	Site Location	Site ID	Site Type	Urban Land Use	Approx-imate Area (Acres)	Approximate Residence Number	Datum: WGS84 (Decimal degrees)		City	County
							Latitude	Longitude		
Martin Canyon/ Koopman Canyon Creek	Donohue Drive at Fire Station (established site)	MCC010	Storm Drain	Mostly residential	500	1300	37.70922	-121.93335	Dublin	Alameda
Martin Canyon/ Koopman Canyon Creek	End of Millbrook Avenue (established site)	MCC020	Storm Drain	Mostly residential	225	650	37.71668	-121.93524	Dublin	Alameda
Martin Canyon/ Koopman Canyon Creek	Dublin Blvd by Safeway and I-680 (established site)	MCC030	Storm Drain	Mixed residential and commercial	290	450	37.70686	-121.92711	Dublin	Alameda
Martin Canyon/ Koopman Canyon Creek	Dublin Blvd by Safeway and I-680 (established site)	MCC040	Receiving Water	Mixed residential and commercial			37.706412	-121.92669	Dublin	Alameda
Pleasant Grove Creek	Dr. Paul J. Dugan Park on Diamond Woods Circle (established site)	PGC010	Storm Drain	Mostly residential	50	250	38.80477	-121.32733	Roseville	Placer
Pleasant Grove Creek	Opal and Parkside Way, right-hand side of stream (established site)	PGC020	Storm Drain	Mostly residential	150	450	38.80232	-121.33855	Roseville	Placer
Pleasant Grove Creek	At Crocker Ranch Road (established site)	PGC030	Storm Drain	Mostly residential	85	300	38.79908	-121.34698	Roseville	Placer

Table A1 continued.

Watershed	Site Location	Site ID	Site Type	Urban Land Use	Approximate Area (Acres)	Approximate Residence Number	Datum: WGS84 (Decimal degrees)		City	County
Pleasant Grove Creek	At Veteran's Memorial Park (established site)	PGC040	Receiving Water	Mostly residential			38.79857	-121.34802	Roseville	Placer
Dry Creek	Story Ridge Way and Redwater Drive near influx to Dry Creek (new site)	ANT001*	Storm Drain	Mostly residential	75	400	38.726232	-121.37336	Sacramento	
Sacramento River	Babcock Way and Brookmere Way (new site)	NAT001*	Storm Drain	Mostly residential	50	300	38.66745	-121.52411	Sacramento	
Alder/ Willow Creek	Marsh Hawk Dr. near Widgeon Ct. (new site)	FOL001*	Storm Drain	Mostly residential	60	250	38.655646	-121.14375	Folsom	Sacramento
	At Brock Circle (new site)	FOL002*	Storm Drain	Mostly residential	70	250	38.6503	-121.14494	Folsom	
	Iron Point Rd., near Buckingham Way (new site)	FOL100*	Receiving Water	Mostly residential			38.64559	-121.14442	Folsom	

*ANT001, NAT001, FOL001, FOL002, and FOL100 were new sites to the study.

Table A2. Detections of insecticides in water (concentrations in µg L^{-1} unless specified). Insecticides included in the analyses (Table 1) that were not detected in any event are not included in the table.

Area	Sample Date	Site ID	Site Type	Sampling Event	Aldicarb	Carbaryl	Desulfinyl fipronil	Desulfinyl FP amide	Fipronil	Fipronil amide	Fipronil sulfide	Fipronil sulfone	Diazinon	Dichlorvos	Malathion	Bifenthrin (ng L^{-1})	Permethrin trans (ng L^{-1})
SAC	8/28/2009	ANT001	StDr	Dryflow	0.086	nd	nd	nd	nd	nd	nd	tr	nd	nd	nd	11.3	nd
SAC	8/28/2009	FOL001	StDr	Dryflow	nd	nd	nd	nd	nd	tr	nd	tr	nd	nd	nd	nd	nd
SAC	8/28/2009	FOL002	StDr	Dryflow	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	16.8	nd
SAC	8/28/2009	NAT001	StDr	Dryflow	0.084	nd	tr	nd	tr	tr	nd	tr	nd	tr	nd	nd	nd
SAC	10/12/2009	ANT001	StDr	Dryflow	nd	nd	tr	nd	nd	nd	nd	tr	nd	nd	nd	11.1	nd
SAC	10/12/2009	FOL001	StDr	Dryflow	nd	nd	tr	nd	tr	tr	nd	tr	nd	nd	nd	nd	nd
SAC	10/12/2009	FOL002	StDr	Dryflow	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SAC	10/12/2009	FOL100	RW	Dryflow	nd	nd	tr	nd	nd	nd	tr	tr	nd	nd	nd	nd	nd
SFB	10/11/2009	MCC010	StDr	Dryflow	nd	nd	nd	nd	tr	tr	nd	nd	nd	nd	nd	nd	nd
SFB	10/11/2009	MCC020	StDr	Dryflow	nd	nd	tr	nd	tr	nd	tr	nd	nd	nd	nd	nd	nd
SFB	10/11/2009	MCC030	StDr	Dryflow	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SFB	10/11/2009	MCC040	RW	Dryflow	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
SAC	10/12/2009	NAT001	StDr	Dryflow	nd	nd	nd	nd	nd	nd	nd	tr	nd	nd	nd	nd	nd
SAC	10/12/2009	PGC010	StDr	Dryflow	nd	nd	0.088	tr	0.244	tr	tr	0.066	nd	nd	0.332	14.1	nd
SAC	10/12/2009	PGC020	StDr	Dryflow	nd	nd	tr	nd	tr	nd	tr	nd	nd	nd	nd	7.43	nd
SAC	10/12/2009	PGC030	StDr	Dryflow	nd	nd	tr	nd	tr	nd	tr	tr	nd	nd	nd	49.1	nd
SAC	10/12/2009	PGC040	RW	Dryflow	nd	nd	tr	nd	tr	nd	tr	tr	nd	nd	nd	nd	nd
SAC	10/13/2009	ANT001	StDr	Rainstorm	nd	0.057	tr	tr	tr	tr	tr	tr	nd	tr	0.093	26.2	nd
SAC	10/13/2009	FOL001	StDr	Rainstorm	nd	0.073	tr	tr	0.087	tr	tr	0.062	0.025	nd	nd	26.5	nd
SAC	10/13/2009	FOL002	StDr	Rainstorm	nd	nd	tr	tr	tr	tr	tr	tr	nd	nd	0.043	22.1	nd
SAC	10/13/2009	FOL100	RW	Rainstorm	nd	nd	tr	nd	tr	tr	tr	tr	nd	nd	0.148	15.5	nd
SFB	10/13/2009	MCC010	StDr	Rainstorm	nd	0.05	tr	nd	tr	tr	nd	tr	nd	nd	0.046	18.9	nd
SFB	10/13/2009	MCC020	StDr	Rainstorm	nd	tr	tr	nd	tr	tr	tr	tr	nd	nd	0.186	34.8	nd
SFB	10/13/2009	MCC030	StDr	Rainstorm	nd	tr	tr	nd	tr	nd	nd	tr	nd	nd	tr	16.9	nd
SFB	10/13/2009	MCC040	RW	Rainstorm	nd	0.061	tr	nd	tr	tr	nd	tr	nd	nd	0.134	14.2	nd
SAC	10/13/2009	PGC010	StDr	Rainstorm	nd	nd	tr	tr	0.077	tr	tr	tr	nd	tr	0.098	33.2	nd
SAC	10/13/2009	PGC020	StDr	Rainstorm	nd	0.399	tr	tr	0.203	tr	tr	0.051	0.132	tr	tr	51.3	nd
SAC	10/13/2009	PGC030	StDr	Rainstorm	nd	0.087	tr	tr	0.081	tr	tr	tr	nd	tr	tr	33.3	nd
SAC	10/13/2009	PGC040	RW	Rainstorm	nd	tr	tr	tr	0.053	tr	tr	tr	nd	tr	tr	19.5	nd

Table A2 continued.

Area	Sample Date	Site ID	Site Type	Sampling Event	Aldicarb	Carbaryl	Desulfinyl fipronil	Desulfinyl FP amide	Fipronil	Fipronil amide	Fipronil sulfide	Fipronil sulfone	Diazinon	Dichlorvos	Malathion	Bifenthrin (ng L^{-1})	Permethrin trans (ng L^{-1})
SAC	4/4/2010	ANT001	StDr	Rainstorm	nd	nd	tr	nd	tr	nd	nd	tr	nd	mv	tr	17.1	20
SAC	4/4/2010	FOL001	StDr	Rainstorm	nd	nd	tr	nd	tr	tr	nd	tr	nd	mv	nd	31.1	nd
SAC	4/4/2010	FOL002	StDr	Rainstorm	nd	tr	tr	nd	tr	tr	nd	tr	nd	mv	tr	39.4	nd
SAC	4/4/2010	FOL100	RW	Rainstorm	nd	0.15	tr	nd	tr	nd	nd	tr	nd	mv	nd	8.23	nd
SAC	4/4/2010	NAT001	StDr	Rainstorm	nd	nd	tr	nd	tr	tr	nd	tr	nd	mv	nd	5.37	nd
SAC	4/4/2010	PGC010	StDr	Rainstorm	nd	nd	tr	nd	0.056	nd	nd	tr	nd	mv	tr	40.5	nd
SAC	4/4/2010	PGC020	StDr	Rainstorm	nd	nd	tr	nd	tr	tr	nd	tr	nd	mv	tr	38.8	nd
SAC	4/4/2010	PGC030	StDr	Rainstorm	nd	0.059	tr	nd	tr	tr	nd	tr	nd	mv	0.178	40.6	nd
SAC	4/4/2010	PGC040	RW	Rainstorm	nd	nd	tr	nd	tr	nd	nd	tr	nd	mv	0.064	11.4	nd
SFB	5/25/2010	MCC010	StDr	Rainstorm	nd	tr	tr	nd	tr	nd	nd	nd	nd	mv	tr	14.8	nd
SFB	5/25/2010	MCC020	StDr	Rainstorm	nd	nd	tr	tr	tr	nd	nd	tr	nd	mv	tr	13.8	nd
SFB	5/25/2010	MCC030	StDr	Rainstorm	nd	0.106	tr	nd	tr	nd	nd	nd	nd	mv	tr	8.92	nd
SFB	5/25/2010	MCC040	RW	Rainstorm	nd	tr	tr	nd	0.06	nd	nd	nd	nd	mv	tr	6.84	nd

Table A3. Detections of chlorpyrifos and pyrethroids in sediments (units, µg kg^{-1} dry wt.). All sediments were collected during dryflow.

Site Area	Sample Date	Site ID	Site Type	Chlorpyrifos	Bifenthrin	Cyfluthrin	Cypermethrin	Deltamethrin	Fenvalerate/ esfenvalerate	Lambda-cyhalothrin	Permethrin cis	Permethrin trans	Resmethrin	Fenopropathrin
SFB	10/11/2009	MCC010	StDr	nd	3.26	1.69	nd	nd	nd	nd	2.14	1.79	nd	nd
SFB	10/11/2009	MCC020	StDr	nd	10.14	2.52	nd	nd	nd	nd	1.69	1.71	nd	nd
SFB	10/11/2009	MCC030	StDr	4.74	53.13	29.52	nd	nd	nd	6.20	14.46	11.14	nd	nd
SFB	10/11/2009	MCC040	RW	nd	15.89	3.98	nd	nd	nd	nd	3.96	1.93	nd	nd
SAC	10/12/2009	PGC010	StDr	nd	123.32	18.78	6.38	2.54	nd	3.55	14.59	4.90	nd	nd
SAC	10/12/2009	PGC020	StDr	nd	105.87	10.99	5.83	nd	nd	1.99	8.53	6.56	nd	nd
SAC	10/12/2009	FOL100	RW	nd	106.15	15.79	nd	4.30	nd	nd	nd	nd	nd	nd
SAC	10/12/2009	FOL002	StDr	3.14	138.14	70.74	9.37	9.39	nd	5.29	23.13	8.05	nd	nd
SAC	10/12/2009	FOL001	StDr	nd	120.14	22.88	6.46	7.51	nd	5.52	7.68	7.47	nd	nd
SAC	10/12/2009	ANT001	StDr	nd	96.63	10.71	36.41	3.11	nd	nd	19.88	10.37	nd	nd

Table A4. Detections of herbicides in water samples (concentrations in µg L^{-1}). Herbicides included in the analyses (Table 1) that were not detected in any event are not included in the table.

Site Area	Sample Date	Site ID	Site Type	Sampling Event	2,4-D	Dicamba	MCPA	Triclopyr	Diiuron	Prometon
SAC	8/28/2009	ANT001	StDr	Dryflow	0.428	0.164	nd	0.132	nd	nd
SAC	8/28/2009	FOL001	StDr	Dryflow	0.123	nd	nd	nd	nd	nd
SAC	8/28/2009	FOL002	StDr	Dryflow	nd	nd	nd	nd	nd	nd
SAC	8/28/2009	NAT001	StDr	Dryflow	0.177	0.086	nd	0.123	nd	nd
SAC	10/12/2009	ANT001	StDr	Dryflow	0.197	tr	tr	nd	nd	nd
SAC	10/12/2009	FOL001	StDr	Dryflow	0.094	nd	nd	nd	nd	nd
SAC	10/12/2009	FOL002	StDr	Dryflow	nd	nd	nd	nd	nd	nd
SAC	10/12/2009	FOL100	RW	Dryflow	nd	nd	nd	tr	nd	0.341
SFB	10/11/2009	MCC010	StDr	Dryflow	nd	nd	0.056	tr	0.187	nd
SFB	10/11/2009	MCC020	StDr	Dryflow	nd	nd	nd	tr	1.64	tr
SFB	10/11/2009	MCC030	StDr	Dryflow	nd	nd	nd	nd	nd	nd
SFB	10/11/2009	MCC040	RW	Dryflow	nd	nd	nd	nd	0.73	nd
SAC	10/12/2009	NAT001	StDr	Dryflow	0.056	nd	nd	tr	nd	nd
SAC	10/12/2009	PGC010	StDr	Dryflow	1.69	0.616	nd	nd	nd	nd
SAC	10/12/2009	PGC020	StDr	Dryflow	0.07	0.224	nd	tr	nd	nd
SAC	10/12/2009	PGC030	StDr	Dryflow	0.065	0.117	nd	0.201	nd	nd
SAC	10/12/2009	PGC040	RW	Dryflow	nd	0.123	nd	tr	nd	nd
SAC	10/13/2009	ANT001	StDr	Rainstorm	1.55	0.119	0.068	0.655	0.096	0.064
SAC	10/13/2009	FOL001	StDr	Rainstorm	1.18	0.077	tr	0.164	0.102	tr
SAC	10/13/2009	FOL002	StDr	Rainstorm	tr	0.061	nd	0.094	0.187	tr
SAC	10/13/2009	FOL100	RW	Rainstorm	0.608	tr	tr	tr	0.053	0.123
SFB	10/13/2009	MCC010	StDr	Rainstorm	0.358	0.076	0.185	0.39	0.214	nd
SFB	10/13/2009	MCC020	StDr	Rainstorm	1.07	0.062	tr	0.246	2.53	0.061
SFB	10/13/2009	MCC030	StDr	Rainstorm	0.109	nd	nd	0.081	0.114	nd
SFB	10/13/2009	MCC040	RW	Rainstorm	0.441	tr	0.087	0.179	2.5	tr
SAC	10/13/2009	PGC010	StDr	Rainstorm	tr	0.249	nd	nd	tr	nd
SAC	10/13/2009	PGC020	StDr	Rainstorm	0.097	0.172	nd	0.05	0.355	tr
SAC	10/13/2009	PGC030	StDr	Rainstorm	0.14	0.139	0.064	0.055	tr	nd
SAC	10/13/2009	PGC040	RW	Rainstorm	tr	0.122	nd	tr	tr	tr
SAC	4/4/2010	ANT001	StDr	Rainstorm	1.19	0.195	0.062	tr	0.101	mv
SAC	4/4/2010	FOL001	StDr	Rainstorm	0.7	0.114	0.09	tr	nd	mv
SAC	4/4/2010	FOL002	StDr	Rainstorm	1.36	tr	nd	0.238	0.057	mv
SAC	4/4/2010	FOL100	RW	Rainstorm	0.325	tr	nd	tr	nd	mv
SAC	4/4/2010	NAT001	StDr	Rainstorm	1.53	0.084	nd	nd	tr	mv
SAC	4/4/2010	PGC010	StDr	Rainstorm	0.146	tr	nd	nd	nd	mv
SAC	4/4/2010	PGC020	StDr	Rainstorm	0.544	0.065	nd	0.05	tr	mv
SAC	4/4/2010	PGC030	StDr	Rainstorm	2.73	0.171	nd	nd	nd	mv
SAC	4/4/2010	PGC040	RW	Rainstorm	0.501	0.086	nd	nd	nd	mv
SFB	5/25/2010	MCC010	StDr	Rainstorm	0.372	0.062	nd	0.146	nd	mv
SFB	5/25/2010	MCC020	StDr	Rainstorm	0.237	0.06	nd	0.11	nd	mv
SFB	5/25/2010	MCC030	StDr	Rainstorm	0.19	0.07	nd	0.155	nd	mv
SFB	5/25/2010	MCC040	RW	Rainstorm	0.161	0.064	0.096	0.244	nd	mv

Figure A1.Reported pesticide use compared to the detection frequency at the October dryflow, October rainstorm first flush, and a spring rainstorm event. There was no prometon data for the spring. Two dates in October reflect the two different sampling dates; use data is the same for the two different sampling dates in October. Pesticide use is the total PUR non-agriculture reported use for Alameda, Placer and Sacramento Counties (counties of the sampling sites).

Table A5. Summary of the water quality parameters for the entire study.

	pH	EC (mS cm^{-1})	DO (mg L^{-1})	Temperature (°C)	Turbidity (NTU)	TSS (mg L^{-1})	TOC (mg L^{-1})
Median	7.6	0.1	9.6	15.3	24.7	18.3	5.9
Range	6.7 – 8.6	0.0 – 2.4	1.6 – 14.3	10.4 – 21	0 – 195	0.1 – 1055	0 – 15.9
Criteria for water quality[1]	6.5 – 8.5	> 3.0 (severe)	< 5.0	15.6 – 23.9 (seasonal), or not 2.8°C above natural levels	> 1 NTU or 20% based on natural levels[2]	Shall not cause a nuisance or adversely affect beneficial uses.	--
Percent outside criteria	5%	0%	13%	--	Background natural levels unknown	unknown	

[1] Criteria from Central Valley Regional Water Quality Board, Water Quality Control Plan for the Sacramento and San Joaquin River Basins, http://www.waterboards.ca.gov/centralvalley/water_issues/basin_plans/; The San Diego Regional Water Quality Board, San Diego Region Basin Plan, http://www.waterboards.ca.gov/sandiego/water_issues/programs/basin_plan/; San Francisco Bay Area Regional Water Quality Control Board, basin plan, http://www.swrcb.ca.gov/rwqcb2/basin_planning.shtml

[2] Determined based on medians of sampling sites. If NTUs medians were between 1 – 5, and increase of 1 NTU over the median was an exceedance. If the medians were between 5 – 50 NTUs, an increase of 20% or more was an exceedance. Most exceedances (70%) were during rainstorm sampling and in stormdrain outfalls (67%).

Water Quality Parameters by Category

There were no significant differences in water quality parameters between stormdrain outfalls and receiving waters (Table A6). Rainfall was the biggest factor influencing differences between water quality parameters. During dryflow conditions EC and temperature values were significantly higher than those observed during rainstorm events (p=0.0004-0.0008), whereas during rain events, DO, turbidity, and TSS were significantly higher than during dryflow (p=0.000-0.026; Table A7).

Table A6.Water quality median concentrations between stormdrain outfalls and receiving waters.

	pH	EC (mS cm^{-1})	DO (mg L^{-1})	Temper-ature (°C)	Turbidity (NTU)	TSS (mg L^{-1})	TOC (mg L^{-1})
Stormdrain outfalls	7.6	0.1	9.7	15.5	19.9	17.8	5.7
Receiving waters	7.6	0.3	8.7	15.0	24.7	19.9	6.5
Significant p values	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.	n.s.

Table A7. Water quality median concentrations between dryflow and rainstorm sampling.

	pH	EC (mS cm^{-1})	DO (mg L^{-1})	Temper-ature (°C)	Turbidity (NTU)	TSS (mg L^{-1})	TOC (mg L^{-1})
Dryflow	7.8	0.32	6.1	18.6	4.8	2.9	4.7
Rainstorm	7.4	0.10	9.7	14.9	24.7	31.6	6.1
Significant p values.	n.s.	0.0008	0.026	0.0004	0.024	0.000	n.s.

Table A8. Water quality parameters at the individual sampling sites of the urban study.

Area	Sample Date	Site ID	Site Type	Sample Event	Flow (cfs)	pH	EC (mS cm^{-1})	DO (mg L^{-1})	Temp (°C)	Turb (NTU)	TSS (ppm)	TOC (ppm)
SAC	28-Aug-09	NAT001	StDr	Dryflow	fl	mv	mv	mv	mv	mv	2.12	5.38
SAC	28-Aug-09	ANT001	StDr	Dryflow	0.02	7.99	0.493	7.24	24.46	2.8	2.62	20.45
SAC	28-Aug-09	FOL001	StDr	Dryflow	0.02	6.61	0.201	6.69	21.46	0.3	0.71	5.698
SAC	28-Aug-09	FOL002	StDr	Dryflow	fl	8.03	0.28	8.19	20.55	0	28.48	1.77
SFB	11-Oct-09	MCC010	StDr	Dryflow	0.12	8.58	2.393	14.32	15.7	0	7.20	3.762
SFB	11-Oct-09	MCC020	StDr	Dryflow	0.26	8.52	1.941	13.97	14.03	1.4	21.27	8.957
SFB	11-Oct-09	MCC030	StDr	Dryflow	1.31	8.25	1.125	8.64	18.62	0	1.00	1.957
SFB	11-Oct-09	MCC040	RW	Dryflow	fl	8.07	1.711	13.12	16.79	0	0.20	3.502
SAC	12-Oct-09	ANT001	StDr	Dryflow	0.0002	7.85	0.4886	3.4	19.4	mv	19.80	6.326
SAC	12-Oct-09	FOL001	StDr	Dryflow	0.004	7.06	0.159	5.28	21	mv	1.60	2.265
SAC	12-Oct-09	FOL002	StDr	Dryflow	0.0004	7.86	0.2139	6.1	19.9	mv	1.10	1.511
SAC	12-Oct-09	FOL100	RW	Dryflow	0.22	7.62	0.3245	6.99	15	mv	0.10	4.678
SAC	12-Oct-09	NAT001	StDr	Dryflow	fl	7.8	0.1207	2.58	18.9	mv	1.41	4.374
SAC	12-Oct-09	PGC010	StDr	Dryflow	nf	6.83	0.137	1.62	20.14	8.2	2.90	7.55
SAC	12-Oct-09	PGC020	StDr	Dryflow	fl	6.68	0.143	1.89	16.23	50.2	7.90	8.643
SAC	12-Oct-09	PGC030	StDr	Dryflow	fl	7.66	0.142	1.56	19.07	54.7	3.43	8.91
SAC	12-Oct-09	PGC040	RW	Dryflow	nf	7.56	0.417	10.29	14.07	25	8.89	13.26
SAC	13-Oct-09	ANT001	StDr	Rain	1.86	7.34	0.12	9.61	15.3	13.3	18.78	15.86
SAC	13-Oct-09	FOL001	StDr	Rain	1.62	7.24	0.096	9.78	15.32	28.3	40.00	0
SAC	13-Oct-09	FOL002	StDr	Rain	3.47	7.22	0.076	9.91	14.86	10.9	27.00	6.38
SAC	13-Oct-09	FOL100	RW	Rain	2.73	7.16	0.098	8.52	15.1	33.8	55.34	9.117
SFB	13-Oct-09	MCC010	StDr	Rain	123.98	7.58	1.22	9.66	15.65	63	111.72	mv
SFB	13-Oct-09	MCC020	StDr	Rain	80.56	7.74	0.203	9.4	15.45	195.1	155.65	9.19
SFB	13-Oct-09	MCC030	StDr	Rain	37.76	7.21	0.064	9.65	15.83	96.4	25.80	5.136
SFB	13-Oct-09	MCC040	RW	Rain	35.60	7.56	0.121	9.45	15.83	98.4	87.76	6.513
SAC	13-Oct-09	PGC010	StDr	Rain	fl	7.62	0.074	9.82	14.82	18.5	32.37	5.57
SAC	13-Oct-09	PGC020	StDr	Rain	fl	7.34	0.071	9.79	14.81	30.4	58.48	7.024
SAC	13-Oct-09	PGC030	StDr	Rain	fl	7.56	0.14	9.91	14.98	11.8	17.04	11.07
SAC	13-Oct-09	PGC040	RW	Rain	fl	7.31	0.257	8.09	14.68	24.7	41.98	13.39
SAC	04-Apr-10	ANT001	StDr	Rain	1.56	7.22	0.1	9.54	12.1	38.1	31.63	3.07
SAC	04-Apr-10	FOL001	StDr	Rain	0.33	7.17	0.107	9.91	13.15	11.2	13.14	5.87
SAC	04-Apr-10	FOL002	StDr	Rain	2.42	7.33	0.067	10.7	11.84	21.2	17.59	3.33
SAC	04-Apr-10	FOL100	RW	Rain	0.43	7.35	0.136	8.64	11.08	9	19.90	3.495
SAC	04-Apr-10	NAT001	StDr	Rain	3.60	7.71	0.05	10.9	10.9	7.7	17.76	5.47

Table A8 continued.

Area	Sample Date	Site ID	Site Type	Sample Event	Flow (cfs)	pH	EC (mS cm^{-1})	DO (mg L^{-1})	Temp (°C)	Turb (NTU)	TSS (ppm)	TOC (ppm)
SAC	04-Apr-10	PGC010	StDr	Rain	fl	7.59	0.057	10.29	11.3	mv	11.72	2.28
SAC	04-Apr-10	PGC020	StDr	Rain	23.22	7.43	0.051	10.16	10.81	mv	15.42	2.77
SAC	04-Apr-10	PGC030	StDr	Rain	14.93	7.58	0.012	10.64	10.4	mv	13.52	2.74
SAC	04-Apr-10	PGC040	RW	Rain	fl	7.76	0.25	9.85	11.1	mv	13.22	5.7
SFB	25-May-10	MCC010	StDr	Rain	18.15	8.03	0.34	9.22	16.5	60.4	1054.50	13.15
SFB	25-May-10	MCC020	StDr	Rain	22.90	8.1	0.844	9.31	15.92	58.2	1009.50	15.68
SFB	25-May-10	MCC030	StDr	Rain	7.47	7.22	0.081	9.17	17.63	7.2	543.09	6.7
SFB	25-May-10	MCC040	RW	Rain	26.25	7.82	0.262	8.73	16.89	24.7	541.53	9.33

VII. APPENDIX II. QUALITY CONTROL

1. Holding times. Holding times are the length of time from when the sample is collected to when it is extracted prior to analysis, and vary for the different analyte screens (Table 1). All analyses met there holding times, except for two synthetic auxin analyses and one pyrethroid analysis. The pyrethroid analysis that failed to meet the holding time probably did not affect results. This analysis yielded the same detection percentage as the other rain event (100%) and had a higher median concentration. The holding time exceedances for the synthetic auxin herbicides were quite high, exceeding the 12 day holding time by 112 and 136 days for two different analyses. This has been observed before with this analysis (Ensminger and Kelley 2011); previously a lab duplicate showed that the holding time exceedance of 50 days did not decrease the analysis quality. However in this case, no lab duplicate was run, but based on this previous work and the high overall detection frequency for synthetic auxins, it is likely that the delay in the analyses did not affect lab quality.

2. Lab Blanks. There were no detections in any of the 249 lab blanks.

3. Matrix and propazine surrogate spikes. With analytical batch, control water or sediment is spiked with known concentrations of the pesticides in that particular analytical screen. For the study there were 239 matrix spike analyses; 96% of these were recovered within acceptable limits. Nine pyrethroids (in water) were reported above control limits, but deemed acceptable to the chemist due to the low control levels, thus giving 100% acceptable recovery. All but one of the 49 propazine surrogates (a triazine surrogate) were recovered with laboratory acceptable limits.

4. Blind spikes, Field Blanks, and Field Duplicates. Blind spikes, field blanks, or field duplicates comprised 15% of the water and sediment samples. There were no detections in the field blank and all blind spikes were recovered within acceptable limits. Of field duplicates (water samples), 99% had good reproducibility (less than 25% difference) between the original field sample and the field duplicate. Sediment samples had more variation, with only 73% of the samples having good reproducibility. The sediment matrix may be interfering the analysis and causing some variation in the data or the smaller sample size may be confounding the results.