Spatial and Temporal Trends in Toxicity and Chemical Contamination Relative to Land Use in California Watersheds:

Stream Pollution Trends (SPoT) Monitoring Program

Fourth Report - Seven-Year Trends 2008-2014

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List of Acronyms

BMI:	Benthic Macroinvertebrate
BOG:	Bioassessment Oversight Group that directs the SWAMP bioaccumulation monitoring program
CEDEN:	California Environmental Data Exchange Network
DDT:	Dichlorodiphenyltrichloroethane, synthetic organochlorine pesticide known for its persistent toxicity and banned in the United States in 1972
DFW:	California Department of Fish and Wildlife
DPR:	California Department of Pesticide Regulation
EPT:	Ephemeroptera/Plecoptera/Trichoptera Index
GIC:	The Geographic Information Center at California State University, Chico
IBI:	Index of Biological Integrity
LC50:	Median Lethal Concentration
MPSL:	Marine Pollution Studies Laboratory, consisting of the toxicology laboratory at Granite Canyon, and the logistics, data management, and trace metal analytical laboratory at Moss Landing
NAWQA:	National Water Quality Assessment, a program of the US Geological Survey
NLCD:	National Land Cover Dataset
PAH:	Polycyclic aromatic hydrocarbons, a suite of organic pollutants produced through combustion of fossil fuels
PBDE:	Polybrominated diphenyl ethers, which are widely employed as flame-retardants. In 2006 the State of California began prohibiting the manufacture, distribution, and processing of pentaBDE and octaBDE products.
PCB:	Polychlorinated biphenyls, a group of industrial compounds widely used for their insulating properties. PCB production was banned in the United States in 1979.
PEC:	Probable Effect Concentration. An empirically derived sediment quality objective that sets a concentration above which toxicity is expected to occur (Macdonald, 2000).
PSA:	Perennial Streams Assessment. The SWAMP statewide program measuring ecological indicators at probabilistically selected sites in California streams.
RMC:	Regional Monitoring Coalition
SMC:	Stormwater Monitoring Coalition
SRC:	Scientific Review Committee
SPoT:	Stream Pollution Trends Monitoring Program
SQO:	Sediment Quality Objectives

SWAMP: Surface Water Ambient Monitoring Program

TMDL: Total Maximum Daily Load

TOC: Total Organic Carbon

TU: Toxic Unit

WPCL: California Department of Fish and Wildlife's Water Pollution Control Lab

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Executive Summary

The Stream Pollution Trends (SPoT) program conducts statewide monitoring to provide information on the health of California waterways with respect to sediment toxicity and contamination. SPoT data is used by the California Water Boards to assess the levels to which aquatic life beneficial uses are supported in California streams and rivers. As part of the Surface Water Ambient Monitoring Program (SWAMP), SPoT was initiated in 2008 with three primary goals:

1. Determine long-term, statewide trends in stream contaminant concentrations and effects.

2. Relate key water quality indicators to land-use characteristics and management efforts.

3. Establish a network of sites throughout the state to serve as a backbone for collaboration with local, regional, and federal monitoring programs and management agencies.

The SPoT program is specifically designed to fill critical information needs for state, regional and local resource management programs, including Clean Water Act (CWA) §303d impaired waters listing, CWA §305b condition assessment, total maximum daily load (TMDL) assessment and allocation, non-point source program water quality assessment, stormwater and agricultural runoff management, pesticide regulation, and local land use planning. The program continues to evolve to address contaminants of emerging concern through collaborations with the California Department of Pesticide Regulation, various federal and state agencies, university research groups, and others.

Watersheds described in this report represent approximately one half of California's major watersheds. Sediments deposited at the base of these watersheds integrate contaminants transported from land surfaces throughout the drainage area. Chemical analyses of sediment combined with sediment toxicity testing allow an assessment of water quality trends in these watersheds and throughout the state. When combined with land-use characterizations, SPoT data provide water quality managers with essential information about how land use affects water quality.

SPoT Findings (2008-2014)

- 19% of samples, on average, are toxic to the amphipod *Hyalella azteca*.
- Increasing Trends: pyrethroid insecticides, metals and PBDE flame retardants in urban watersheds.
- Decreasing Trends: DDTs and PCBs.

- Emerging insecticide fipronil increased in second year of monitoring.
- 29% of sediment samples contained the algal toxin microcystin.
- There are significant statistical relationships among laboratory toxicity, benthic macroinvertebrate communities, sediment concentrations of pyrethroid pesticides.

Pyrethroids are found at more sites and at higher concentrations than before

Detections and concentrations of currently used pyrethroid insecticides continue to increase in California watersheds, primarily those with the highest percentage of urban land use. The increase in pyrethroid concentrations did not coincide with an increase in toxicity at the standard test temperature of 23°C, however, a cold-temperature modification greatly increased toxicity in a subset of sites. Higher toxicity at colder temperature is diagnostic of toxicity due to pyrethroid pesticides, and the colder temperature (15°C) more closely reflects the ambient temperature in California watersheds. The pattern of increasing detections of pyrethroids coupled with the increase of cold temperature toxicity suggests that current monitoring using the standard protocol may under-estimate the occurrence of pyrethroid-associated toxicity. Toxicity of sediments was assessed using the amphipod *Hyalella azteca*, which represents a genus found throughout California watersheds.

Urban Watersheds: significant increases in PBDEs and metals and significant decreases in organochlorine compounds

While organochlorine compounds, such as PCBs and the legacy insecticide DDT, continued to be detected in many of the state's watersheds, the concentrations are a fraction of those demonstrated to cause toxicity to *H. azteca*. PBDEs exhibited a significant increase at the statewide level, driven by a significant increase in urban watersheds. PBDEs also are not acutely toxic to *H. azteca*, but may affect human health. Despite low concentrations, organochlorines and PBDEs continue to be of concern in California because of their potential to bioaccumulate, although concentrations of organochlorines in fish do not often exceed thresholds of concern and fish consumption advisories have not been necessary (Davis et al., 2013). PDBEs are being phased out in California, but they are still present in many commercial products. SPoT will continue to measure these chemicals and document their anticipated decline. Concentrations of selected metals in sediments also showed a significant increase, largely within urban watersheds, but metal concentrations were nonetheless lower than toxicity thresholds established for *H. azteca*. Because of differences in sensitivity between *H. azteca* and other resident taxa, and the potential for particular metals to either be toxic to resident macroinvertebrates (Cd, Cu, and Zn) and stream algae, or to bioaccumulate (Hg), metals will continue to be important indicators of watershed contamination as SPoT proceeds.

Toxicity and chemical analysis provide insight into ecological condition

An investigation of the relationship between water quality indicators measured by SPoT and watershed ecological indicators measured by SWAMP and other benthic macroinvertebrate bioassessment programs showed a significant positive correlation between amphipod survival in laboratory toxicity tests and the California Stream Condition Index (CSCI) calculated from bioassessment data. Thus, low laboratory toxicity coincides with healthy stream ecosystems. Both the CSCI and amphipod survival in the laboratory were negatively correlated with sediment pyrethroid concentrations. These statistical relationships suggest pyrethroids are impacting stream biota and demonstrate how toxicity and chemistry data generated by programs such as SPoT can provide a basis for developing hypotheses for assessing causal relationships between in-stream ecological degradation and toxicity and chemical stressors.

Evaluating the effectiveness of regulatory programs

Based on SPoT's statewide coverage, the program is assessing whether toxicity and contamination are reduced in California watersheds as regulatory policies are implemented. SPoT continues to collaborate with the California Department of Pesticide Regulation (DPR) to determine if use restrictions and outreach to professional pesticide applicators result in a decline in sediment-associated pyrethroids in urban watersheds. To date, there are no significant downward trends at four SPoT sites selected to monitor effectiveness of 2012 label restrictions. Data from regional SPoT sites are also used by several Regional Water Boards to detect and monitor trends in stream contaminant concentrations and effects. The SPoT program continues to provide data on the effectiveness of urban and agricultural management practices, such as low impact development and vegetated buffer zones, and tracks source controls, such as the phase-out of copper in vehicle brake pads.

Adapting to future needs

Given the evidence that pesticides are associated with most ambient toxicity detected in California waters (Anderson et al., 2011a), emerging pesticides were prioritized for inclusion in the SPoT analyte list. The phenylpyrazole insecticide fipronil has been measured in urban watersheds since 2013, and is already showing an increase in concentrations and detections at SPoT sites. SPoT uses toxicity testing, in part, to monitor emerging chemicals of concern. The program began testing sediment with the midge *Chironomus dilutus*, which is more sensitive to fipronil and its degradates. This species is also sensitive to the neonicotinoid insecticide imidacloprid. Water column monitoring for this chemical will take place in 2018 as part of a continuing collaboration with DPR.

Algal toxins produced by benthic and other cyanobacteria are a class of contaminants expected to impact California watersheds as global temperatures rise. In collaboration with California State University Monterey Bay, the program began monitoring microcystin in sediments in 2013. Microcystin was detected in 29% of SPoT samples in 2014. Recent laboratory studies have demonstrated that microcystin bioaccumulates in benthic macroinvertebrate tissues. These toxins represent an emerging threat to human and ecological health in California, and the SPoT data will complement those of other state and regional programs to assess this threat.

The data presented in this report depict changing conditions in contamination and toxicity in California watersheds. They also demonstrate a significant relationship between land use and stream pollution, and provide data directly relevant to a number of agency water quality protection programs. The SPoT program is managed to adapt to changing conditions, and the revised program design in 2015 was based on trends from the first five years of data. Changes included the addition of contaminants of emerging concern, such as fipronil, addition of toxicity species/protocols sensitive to new contaminants, and the reduced emphasis on legacy contaminants that pose less of an environmental threat to California watersheds. The program also revised the number and frequency of stations monitored to maximize its ability to address key management questions concerning contaminants that pose the greatest risk to California’s surface waters. Moving forward, the program is planning to expand the collaboration with DPR to create a water column monitoring component that will include toxicity tests and chemical analyses that focus on pesticides of emerging concern (e.g., neonicotinoids). This collaboration will also address the goals of the State Water Board’s Strategy to Optimize Resource Management of Storm Water (Storm Water Strategy, STORMS).

Section 1 – Introduction

SPoT in the SWAMP Assessment Framework

The Stream Pollution Trends program (SPoT) is a core component of the Surface Water Ambient Monitoring Program (SWAMP) and monitors changes in water quality and land use in major California watersheds throughout the state. SPoT provides water quality information to regional and statewide water resource managers responsible for evaluating the effectiveness of regulatory programs and conservation efforts at a watershed scale. SPoT is a long-term statewide trends assessment program, and the data collected are being used to detect changes in contamination and associated biological effects in large watersheds at temporal and spatial scales appropriate for management decision making. A complete discussion of assessment questions and links to various water quality programs is included in Appendix 1.

The three specific program goals are to:

1. Determine long-term trends in stream contaminant concentrations and effects statewide.

2. Relate water quality indicators to land-use characteristics and management effort.

3. Establish a network of sites throughout the state to serve as a backbone for collaboration with local, regional, and federal monitoring.

Monitoring Objectives and Design

The methods of the program were selected to meet the following monitoring objectives:

1. Determine concentrations of a relevant suite of current-use and legacy contaminants in depositional sediment collected near the base of large California watersheds;

2. Determine whether these depositional sediments are toxic to representative species;

3. Quantify land cover data available from the National Land Cover Dataset and other public sources;

4. Analyze data to evaluate relationships between contaminant concentrations, toxicity, and land cover metrics;

5. Conduct trends analyses to detect the direction, magnitude, and significance of change in the above parameters over time.

The SPoT indicators are measured in stream sediment because this environmental compartment integrates chemical contamination over time. Many trace metal and organic pollutants that enter streams adhere to suspended sediment particles and organic matter, and this sediment-associated phase is the major pathway for contaminant loading in streams and downstream waterways. In addition, river benthic environments are ecologically important because they provide habitat to key elements of aquatic macroinvertebrate and algal communities. Sediment measurements are appropriate for long-term trend monitoring because pollutants that accumulate in depositional sediment on the stream bed are much more stable over time (~months to years) than dissolved or suspended pollutants that move downstream in pulses that are highly variable over short time scales (~hours). SPoT surveys are timed to collect sediment in summer after the high water season when most sediment and pollutant transport and deposition takes place. Expanding SPoT to include water column monitoring has been considered to address newer classes of pesticides which, based on their high solubility, would not partition to sediments. This possibility is discussed in the Future Work section (below).

The monitoring design was based on the US Geological Survey's National Water Quality Assessment (USGS – NAWQA: http://water.usgs.gov/nawqa/). The NAWQA program is designed to increase understanding of water-quality conditions, of whether conditions are getting better or worse over time, and how natural features and human activities affect those conditions. The NAWQA integrator site concept provided the basis for the SPoT monitoring design. NAWQA integrator sites are established near the base (discharge point) of larger, relatively heterogeneous drainage basins with complex combinations of environmental settings. Sediments collected from depositional areas at integrator sites provide a composite record of pollutants mobilized from throughout the watershed. While many hydrologic, engineering, and environmental variables affect the ability of this record to adequately characterize all pollutant-related activities, sediment samples collected from such areas are considered to be a relatively good and logistically feasible means of assessing large watersheds for long-term trends (e.g., Horowitz and Stephens, 2008; see, http://pubs.usgs.gov/circ/circ1112/sediment_tissue.html).

SPoT employs a targeted monitoring design to enable trend detection on a site-specific basis. To serve their purpose as integrator sites, SPoT sites are located at the base of large watersheds containing a variety of land uses. Because depositional sediment is needed for sample collection, sites are targeted in locations with slow water flow and appropriate micro-morphology, to allow deposition and accumulation. SPoT and NAWQA use integrator sites because both programs focus on understanding causes and sources of water quality impairment. The connection with land use is a major part of the assessment, and targeted sites allow greater discretion to adjust to significant land cover variation in lower watershed areas. A targeted approach allows SPoT flexibility to link to established sites and to support collaboration with other watershed-based and regional monitoring programs.

Coordination and Collaboration with other Programs

The SPoT network of sites was established through coordination with Regional Board monitoring programs and stormwater agencies, under the guidance of the SPoT Scientific Review Committee (SRC). The Southern California Stormwater Monitoring Coalition participated in site selection for the southern California SPoT sites. A representative from the Bay Area Stormwater Management Agencies Association served on the SWAMP committee that designed the program, and all SPoT sites in the San Francisco Bay Region are aligned with the Regional Monitoring Coalition monitoring sites for the Municipal Regional Stormwater NPDES Permit (BASMAA (Bay Area Stormwater Agencies Association), 2011)(Table 1). SPoT sites in the Central Coast and Central Valley Regions are shared by the Cooperative Monitoring Program for agriculture and Irrigated Lands Regulatory Program, respectively. The Delta Regional Monitoring Program (Delta RMP) assessments will include data from five SPoT sites within the Sacramento-San Joaquin River Delta. In most cases, the SPoT assessments of sediment toxicity and chemistry complement water column measurements made by cooperating programs. SPoT data have also been included in a series of California Regional Water Quality Control Board reports that are in the series "Toxicity in California Waters" (Anderson et al., 2011a).

Table 1. SPoT collaborations and programs SPoT monitoring data supports.

	Collaboration	Objective
Stream Pollution Trends Program	Intensive Site Study with the Department of Pesticide Regulation	Determine the effectiveness of new pyrethroid pesticide label regulations (effective 2012)
	Agricultural Surface Water Monitoring with the Department of Pesticide Regulation	Collaboration with Regions 3 and 7 to determine toxicity to alternate species and presence of emerging pesticides
	Cyanobacteria CEC Monitoring with CSUMB	Determine presence and potential effects of the cyanotoxin microcystin
	Collaboration with Bioassessment Monitoring Programs	Linking SPoT toxicity and chemistry data with bioassessment data to support causal assessments
	State and Regional Water Board 303(d) Listings through the Integrated Reporting Process	Water Boards assess water quality monitoring data for California's surface waters to determine if they contain pollutants at levels that exceed protective water quality standards
	Agricultural Monitoring for the Region 3	Provide data for conditional waiver of waste

	Cooperative Monitoring Program	discharger requirements
	Agricultural Monitoring for the Region 5 Irrigated Lands Regulatory Program	Provide data for the monitoring of agricultural runoff in the Central Valley
	Stormwater Monitoring for Region 2 Stormwater Permits	Provide long-term trends data for San Francisco Bay Area municipal stormwater permits
	Regions 4, 8 and 9 Stormwater Monitoring Coalition Site Overlap	SPoT sites overlap with several SMC monitoring locations and provide additional data

In addition to co-locating sites with other monitoring efforts, and creating collaborations with other agencies and programs, the core SPoT program was designed to provide data that can inform regulatory programs and conservation initiatives. SPoT data is incorporated directly into the Clean Water Act § 303[d] listing of impaired waters, as well as into the statewide status assessments required by § 305[b]. SPoT data are included in the Integrated Report process and incorporated into the lines of evidence process used to evaluate sites for inclusion in regional 303(d) lists of degraded water bodies. Statewide, there are 1766 manually generated lines of evidence based on SPoT data for the 2014 Integrated Report currently under development.

The SPoT focus on causes and sources of pollutants in watersheds feeds directly into Total Maximum Daily Load program efforts to quantify pollutant loadings and understand sources and activities that contribute to those loadings. By coordinating with local and regional programs, SPoT provides statewide context for local results, and provides information useful for local management and land use planning activities. SPoT is also specifically designed to assist with the watershed-scale effectiveness evaluation of management actions implemented to improve water quality, such as pesticide reduction or irrigation management on farms, and installation of stormwater treatment devices or low impact development in urban areas. Use of SPoT data for watershed scale evaluations of management practice effectiveness is currently limited by the lack of a comprehensive and standardized reporting system for practice implementation. This is the subject of on-going efforts at DPR, County Agriculture Commissioner Offices, and the Regional Boards.

Report Outline

The SPoT reporting schedule is intended to summarize program findings biennially. This report summarizes results of seven years of SPoT monitoring from sites representing approximately one half of California's major watersheds, and presents data in support of the primary program goals discussed above. All technical methods are summarized in Appendix 2. The focus of the current report is on trends in toxicity and chemical measurements as they relate to land use, but the combined Results and Discussion sections cover topics related to the project's assessment questions. Level 1 assessment questions are the highest level, as adopted by SWAMP and the California Water Quality Monitoring Council (Bernstein, 2010). The Level 2 assessment questions apply to each of the two Level 1 questions (Appendix 1).

Level 1 Assessment Questions

A) Are our aquatic ecosystems healthy?
B) What stressors and processes affect our water quality?

Level 2 Assessment Questions

1) Are beneficial uses impacted?
2) Are conditions getting better or worse?
3) What are the magnitude and extent of any problems?
4) What's causing the problem?
5) Are solutions working?

Section 2 – Toxicity Results

1) *Are beneficial uses impacted?*

Yes. Significant toxicity is consistently observed indicating beneficial uses are not fully protected.

2) *Are conditions getting better or worse?*

Maybe. The percentage of toxic samples has remained consistent, but there are an increasing number of sites with “some toxicity” or “high toxicity”.

Toxicity Trends

Toxicity testing involves the exposure of organisms to environmental samples in a controlled laboratory setting. Measuring contaminant concentrations alone does not always provide enough information to adequately evaluate potential adverse effects that arise from chemical interactions. Therefore, exposure of the amphipod *Hyalella azteca* to field-collected sediments evaluates the potential for sediment-bound contaminants to adversely affect the resident biota, and therefore, beneficial uses.

Significant toxicity to *H. azteca* was determined using the Test for Significant Toxicity (TST (U.S. EPA, 2010)), and samples were highly toxic if the percent survival was lower than the high toxicity threshold of 38.6% survival (Anderson et al., 2011a). The results of the *H. azteca* sediment toxicity tests have been consistent over the last seven years. Toxic and highly toxic samples account for an average of 18.6% of the samples tested, and there are no significant trends in toxicity either statewide or by land use (Figure 1).

The majority of toxic and highly toxic sites were located in urban areas. Highly toxic samples were collected from 19 separate sites over the last seven years, an increase of four in the last two years. Ten of these sites were solely urban, and two were classified as urban/agriculture. Five sites were from agricultural watersheds, and two were classified as other. Approximately half of these sites were in the southern California regions.

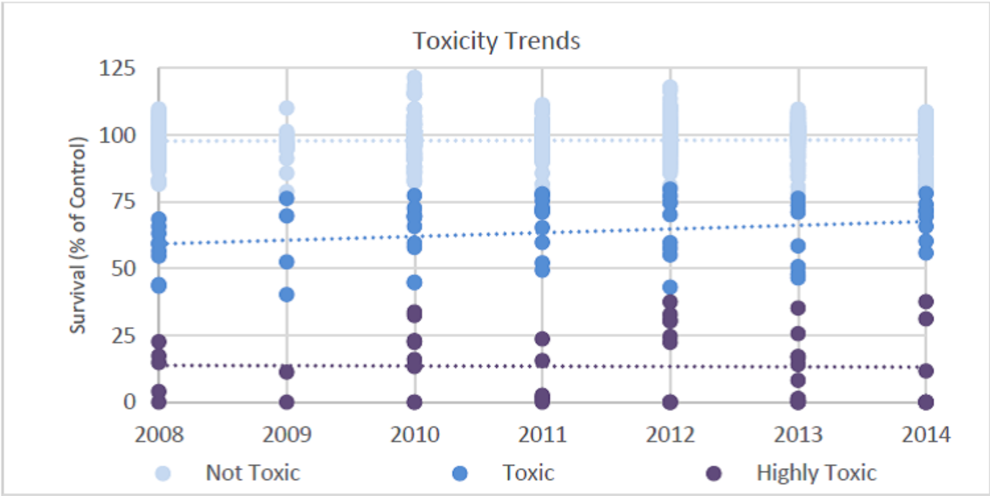

Figure 1. Statewide toxicity trends.

The previous report calculated the average toxicity of each site for the first five years of the program (2008-2012). A new five-year average was calculated for the current report (2010-2014) to illustrate trends in the rolling averages. Although there are only two periods to evaluate, there are three results of note. There was a greater number of sites classified as having no toxicity in the second period (Figure 2). There is also a greater number of sites classified as moderately toxic (having had one highly toxic sample in five years), or highly toxic (having an average survival less than the high toxicity threshold of 38.6%).

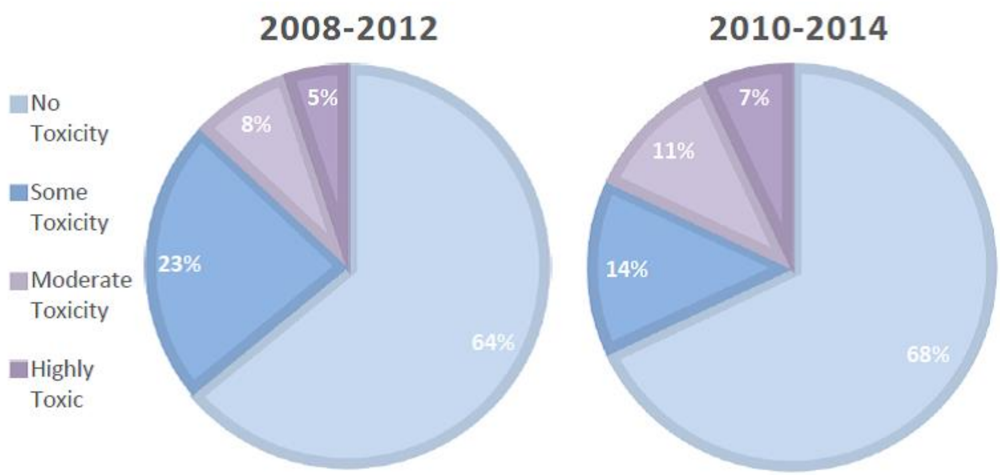

Figure 2. Percentage of samples in each toxicity category for two assessment time frames.

Section 3 – Contaminant Results and Results of Physical Parameters

2) *Are conditions getting better or worse?*

Yes and No. Average concentrations of pyrethroids, metals and PBDEs are significantly increasing. DDTs and PCBs are significantly decreasing. Fipronil use is increasing, as are the number of detections and average concentrations.

3) *What are the magnitude and extent of any problems?*

Significant contaminant increases were observed in urban watersheds. Between 2010 and 2013, average concentrations of pyrethroids have doubled. The cyanotoxin microcystin was detected in 29% of sediment samples in 2014.

Why Fine-Grained Sediments?

SPoT emphasizes collecting fine-grained depositional sediments, because contaminants associate with smaller size fractions. Fine sediment particles accumulate in low energy depositional areas, and can be found throughout the channel at many sites in thin layers covering other dominant substrate, including sand, cobble, boulders, concrete, and woody debris. Fine sediments form deeper layers in pockets and larger depressions where micro-hydrological and geomorphic conditions favor deposition. These deeper depositional areas were targeted for sample collection because they allowed the most effective collection of fine material. In some sampling areas, fine sediments formed large and deep deposits across the channel, but many other sites have few locations where fine sediment accumulated in layers thick enough to allow efficient sample collection (>2 cm). To put the availability of depositional areas into context, consider that Hall et al. (2012) mapped fine sediment distributions at 99 transects in three California streams, each designated as agricultural, urban or residential. Two of these creeks contain SPoT sites, and range from 13-16% “depositional”. SPoT results should not be construed as a characterization of the entire stream in which study sites were located. Rather they are intended as relative indicators of the annual pollutant mobilization and transport within target watersheds, which is a useful measurement for evaluating annual trends.

Contaminant Trends

SPoT data capture trends at three different scales: statewide, by land use, and at individual sites. Trend data from individual sites are discussed in the Regional Summaries in Section 8. Watersheds were defined as urban, agricultural or other depending on the dominant land uses within 5 km of the sampling location. Clear trends emerged after five years, and included significant increases in pyrethroid concentrations, as well as significant decreases in the organochlorine compounds PCBs and DDTs (Phillips et al., 2014). Two additional years of data confirm these trends (Table 2) and demonstrate additional significant increases in metals and PBDE both statewide and in urban watersheds, as well as increases in fine-grained sediment and total organic carbon (statewide only). The number and variety of trends observed at individual sites was unchanged (discussed in Section 8).

Table 2. Summary of trends at three scales: statewide, by land use, and at individual sites.

Variable	Statewide	Urban	Agriculture	Other	Individual Sites
Pyrethroids	↑	↑	=	=	1↑
Bifenthrin	↑	↑	↑	=	1↑
Cd, Cu Pb, Zn	↑	↑	=	=	3↑ 1↓
Copper	=	=	=	=	4↑ 1↓
PBDE	↑	↑	=	=	2↑
PAH	=	=	=	=	1↑ 1↓
DDT	↓	↓	=	=	4↓
PCB	↓	=	=	=	1↓
Fine Grain Size	↑	↑	=	↑	3↑ 3↓
Total Organic Carbon	↑	=	=	=	6↑ 2↓

Toxic Units

A toxic unit is calculated by dividing the measured concentration of a chemical in sediment by the organism-specific median lethal concentration (LC50).

For example, if 120 ng/g of bifenthrin were measured in the sample, the toxic units of bifenthrin would be calculated by dividing 120 ng/L by the bifenthrin LC50 for *H. azteca* (12.9 ng/g). 120/12.9 = 9.3 toxic units.

Approximately 50% mortality would be expected at one toxic unit.

Statewide Trends and Trends by Land Use

Although the maximum pyrethroid pesticide concentration was much lower in 2014 than in 2013 (1124 ng/g vs. 4254 ng/g, respectively), concentrations of this chemical class continue to significantly increase. This trend was driven by the concentrations of pyrethroids detected in urban watersheds (Figure 3A), primarily by bifenthrin (Figure 3B), the most frequently detected pyrethroid. Bifenthrin is the most stable pyrethroid for many pathways, and therefore, the most persistent (Spurlock and Lee, 2008). In 2008 pyrethroids were detected in 54% of SPoT samples, whereas in 2014, pyrethroids were detected in 88% of SPoT samples. To date, bifenthrin has been detected in 73% of SPoT samples, and was detected at greater than one toxic unit in 11% of SPoT samples (see sidebar). Cyhalothrin is the next most detected pyrethroid (45% of samples), but cypermethrin is the next most detected compound at concentrations greater than one toxic unit (4% of samples). Pyrethroid concentrations in general, and bifenthrin concentrations in particular, remain lower and much more consistent in the agricultural and other watersheds, but bifenthrin did show a small significant increase in agricultural watersheds. The role of pyrethroids in toxicity is discussed further below.

The sum of four metals (Cd, Cu, Pb and Zn), used as an indicator of metal contamination commonly released into the environment by human activity, demonstrated a significant increase statewide. As with the pyrethroids, the increasing trend was driven by an increase of these four metals in urban watersheds (Figure 3C). There was not a large difference among metal concentration in the three lands uses, but there is a clear increase in the urban watersheds in 2013. Copper concentrations were plotted as a representative metal (Figure 3D), but also to examine whether or not copper concentrations have been decreasing due to reduced use in automobile brake pads. This trend would likely be most apparent in urban watersheds, but data through 2013 show an increase in urban copper concentrations, although this increase was not statistically significant. Measurable reductions of copper due to brake pad manufacturing content reductions are not expected until the early 2020s (Moran, 2016). The highest concentrations of zinc were detected in 2012 and 2013 at a single urban site, but this metal did not show a significant increase statewide. The role of metals in the cause of toxicity is discussed below.

PBDEs and PAHs were measured in the most urban watersheds, since they originate from urban sources. Sites from these watersheds are referred to as Tier II sites in SPoT. The list of Tier II sites underwent changes early in the program as some sites were dropped and others were added. The list has also changed based on current land use data. Because of these changes, there are several of PAH and PBDE measurements at non-Tier II sites. These sites are represented in the average concentrations from the agricultural and other watersheds shown in Figures 3E and F. Concentrations of PBDEs significantly increased statewide with urban PBDE concentrations driving the trend (Figure 3E). PBDE 209 is the dominant congener in sediments because it is the primary component of the commercial mixture DecaBDE, and recent elevated detections of this congener are likely driving the increasing trend. Although PBDE use is getting phased out nationwide as of 2013, it will likely take some time to see a significant downward trend in SPoT sediments. Monitoring data from San Francisco Bay also show a lack of a downward trend (Sutton et al., 2015). PAHs did not exhibit any significant trends, although urban concentrations were more than five times higher than concentrations from agricultural or open watersheds (Figure 3F).

Concentrations of organochlorine compounds decreased significantly between 2008 and 2012. These compounds were not measured in 2014, and despite showing a marked increase in 2013, the trend analysis indicates both PCBs and DDTS are significantly decreasing since the beginning of the project (Figures 3G and H).

While field teams strive to collect the finest-grained material available, a number of samples were composed primarily of size fractions larger than 63 µm because fine-grained material was not available. There was a significant increase in the overall amount of fine-grained sediments collected between 2008 and 2014, a trend that was driven by a significant increase in percent fines collected at urban sites (Figure 3I). Field teams also avoid or remove conspicuous debris, including leaves and other large organic material, which would influence the organic carbon content of samples. Total organic carbon (TOC) content cannot be determined in the field, and because of this, the sampling protocol has no criterion for TOC concentration. Samples from urban sites generally had higher TOC content than agricultural or open space samples, but there were no significant upward or downward trends for TOC, indicating that the samples had consistent carbon content among sample years (Figure 3J).

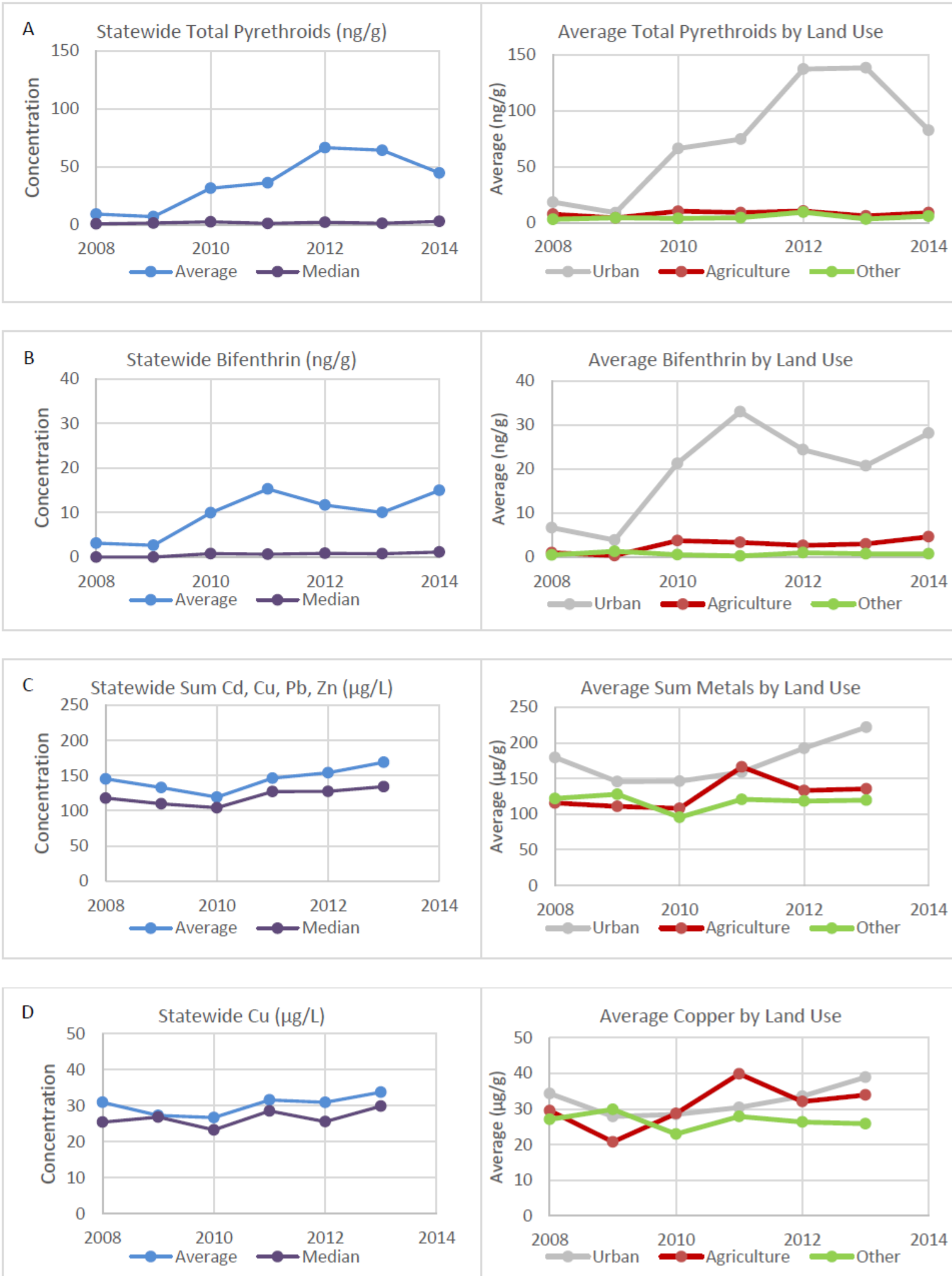

Figure 3A-D. Maximum and average statewide concentrations, and average concentrations by land use.

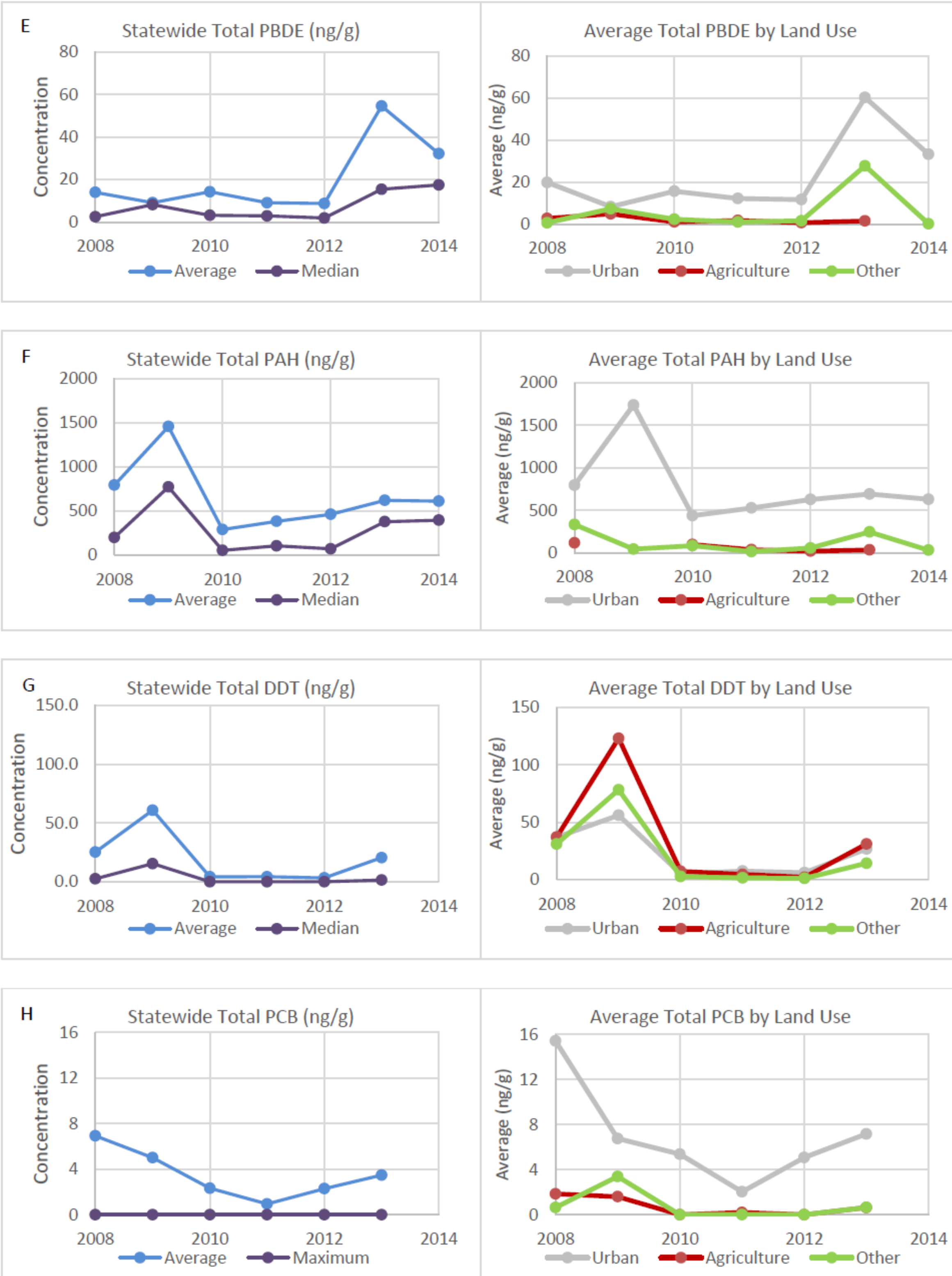

Figure 3E-H. Maximum and average statewide concentrations, and average concentrations by land **use.**

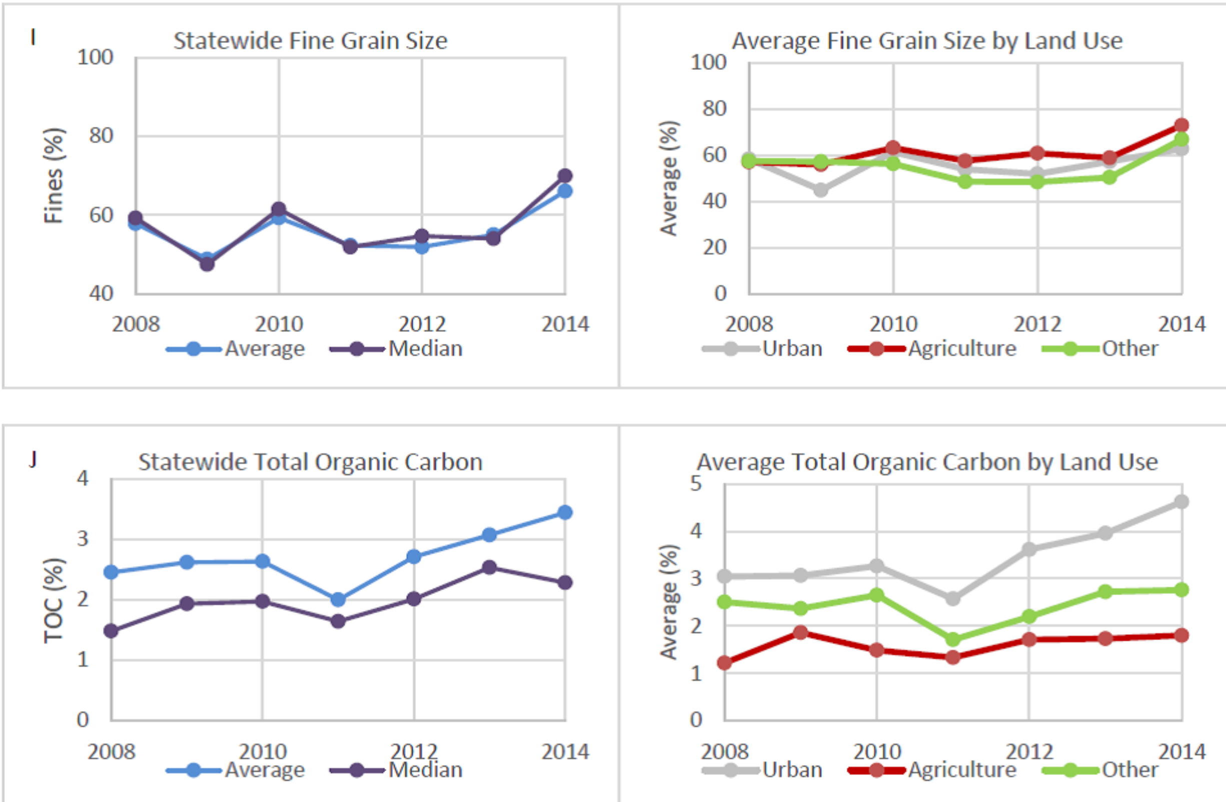

Figure 3I-J. Maximum and average statewide concentrations, and average concentrations by land use.

Contaminants of Emerging Concern – Fipronil

Use of the phenylpyrazole insecticide fipronil has been steadily increasing since its introduction in 1993 (Simon-Delso et al., 2015). This pesticide and its degradates are of ecological concern in California watersheds because of toxicity to stream insects, particularly chironomids (Weston and Lydy, 2014). SPoT began measuring fipronil in sediments in 2013. Because fipronil is not registered for use in agriculture applications, SPoT monitoring for this insecticide emphasizes Tier II sites in urban watersheds. The primary use for fipronil is structural pest control which includes outdoor spraying and underground injection for termites. Fipronil is applied under and inside structures and includes application as a dust injected into building wood. The reported use data compiled by the California Department of Pesticide Regulation (Figure 4) could be considered a good indicator of increased outdoor use of fipronil in California. These data are not necessarily an accurate depiction of outdoor use because some of the insecticide is used for underground injection (for termite control) and indoor applications (e.g., for pet treatment). In addition, DPR compilations of the sales data for this pesticide do not equate with the reported use data. Despite these discrepancies, the DPR data suggest an increasing trend for use of this insecticide in California. Increasing use of fipronil combined with its relative persistence and toxicity to stream invertebrates suggest fipronil and its degradates are potentially important emerging threats to California's aquatic ecosystems.

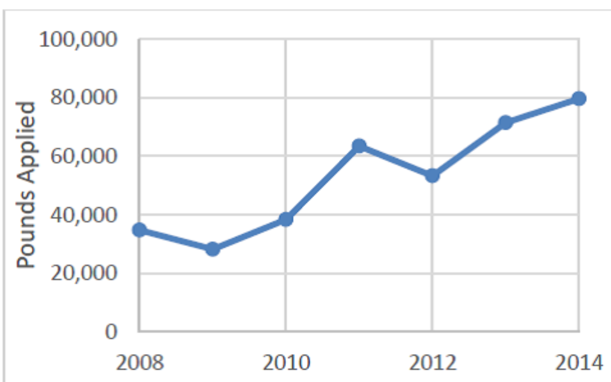

Figure 4. Fipronil use (in pounds) compiled by the California Department of Pesticide Regulation. Note uncertainties regarding the accuracy of pesticide use data in the DPR database are discussed in the text.

Sediment concentrations of fipronil were measured at the SPoT Tier II urban sites in 2013 and 2014. The goal of these measurements was to determine the presence and magnitude of this urban-use insecticide and its degradates. The data show a relatively high incidence of fipronil detection in urban sediments, particularly of the fipronil sulfide and sulfone degradates, which are more toxic than the parent compound (Weston and Lydy, 2014). Both the percent detections and the average and maximum concentrations of all fipronil compounds increased in SPoT Tier II sediments from 2013 to 2014 (Table 3).

Table 3. Concentrations (ng/g) of fipronil and its degradates in 2013 and 2014.

Metric	Year	Fipronil	Fipronil Sulfide	Fipronil Sulfone	Fipronil Desulfinyl
Percent Detection	2013	18	41	62	33
	2014	30	47	77	43
Average (Standard Deviation) Concentration	2013	0.550 (2.27)	0.445 (1.14)	2.88 (8.49)	1.32 (5.63)
	2014	1.27 (5.08)	0.641 (1.64)	3.55 (10.7)	3.07 (12.9)
Maximum Concentration	2013	13.1	6.42	51.0	35.1
	2014	27.4	8.83	58.5	70.7

In addition to testing with *H. azteca*, SPoT began assessing toxicity of Tier II sediments with midge larvae in 2015 (*Chironomus dilutus*). Chironomids are particularly sensitive to fipronil, and with *H. azteca*, provide complementary data regarding risk of pesticide mixtures in urban sediments. Both tests assess survival and growth after 10 days. As a preliminary assessment, the sediment concentrations of fipronil and its degradates were compared to sediment LC50 values for *C. dilutus*. Based on published toxicity values, twenty of the forty-two Tier II stations exceeded toxicity thresholds for either fipronil or its degradates in 2013-2014 monitoring years. *Hyalella azteca* is less sensitive to fipronil than *C. dilutus*, but more sensitive to pyrethroid pesticides.

Cyanotoxins

Freshwater cyanobacterial harmful algal blooms (CHABs) are an emerging threat to drinking water resources and aquatic habitat through the production of potent cyanotoxins. Hepatotoxic microcystins, a potent class of cyanotoxins produced by several cyanobacterial taxa, have increasingly been identified in freshwater habitats worldwide. Microcystins are stable cyclic heptapeptides and may persist in the environment for weeks to months in water and sediments. Cyanobacteria blooms are expected to increase due to nutrient enrichment, warming surface water temperatures, and extreme weather associated with climate change. Previous research has shown that microcystin binds to carbonaceous monitoring substrates suspended in water, such as the Solid Phase Adsorption Toxin Tracking (SPATT) resins employed by Kudela et al. (2011). Their sorptive characteristics suggest microcystin should also sorb to sediments.

In 2013 SPoT began a collaboration with Erin Stanfield and others at California State University Monterey Bay (CSUMB) to develop and implement a method to analyze microcystin in sediment extracts. This represents the first statewide survey of microcystin in California stream benthos and provides baseline data for this CEC in California watersheds.

The 2013 results showed detections of microcystins in 77% of 83 sediment samples, but there was concern that some of the low detections were due to ELISA false positives from matrix interference of humic material and other particles in the sediment extracts. In 2014, the method was revised to include solid-phase extraction as an additional clean up step. Microcystins were detected in 29% of 99 sediment samples in 2014 using the revised method. Microcystins were detected in eight of the nine Water Quality Control Board Regions, and in watersheds with diverse habitat types and land uses. Concentrations ranged from 0.103 to 7.740 ng/g microcystin equivalents. The percentage of samples with detections was similar to those reported by Fetscher et al. (2015) for microcystins in Southern California wadeable streams.

Ten samples were re-extracted and analyzed by King County Environmental Laboratory (Washington) for quality assurance and method validation. Samples were chosen based on a range of concentrations measured by CSUMB, and were re-analyzed using both ELISA and LC/MS. The ELISA method has a lower detection limit (0.16 ug/L in extract) than for LC/MS (1 ug/L in extract), therefore some samples with low concentrations were not detected by LC/MS. Relative percent differences for the ELISA measurements ranged from 1 to 74% with neither lab producing consistently higher results (Table 4). Most concentrations were below 5 ng/g microcystin equivalents.

ELISA results are reported as microcystin equivalents, as there are numerous microcystin variants, or congeners, determined by amino acid components. Although the ELISA test is designed to assess microcystin LR, the most toxic and often most common variant of microcystin, there is potential for cross reactivity with other variants, suggesting that reported values may include other variants. LC/MS results are reported as microcystin variants. King County used standards for six microcystin variants (LR,RR,YR,LA,LW,LF), with reported values for each of the variants. This allowed for quantification of microcystin LR specifically. However, without standards for all the other variants, the total microcystin value may be underreported. Given these caveats, ELISA is the preferred method for an initial screening test to assess presence or absence of microcystins. If more detailed analyses is needed, such as concentrations of specific variants, LC/MS provides more specificity.

Table 4. Microcystin interlaboratory results from 2014 survey. Concentrations are reported in ng/g microcystin equivalents (see text).

Site	CSUMB ELISA	King County ELISA	King County LC/MS	RPD Between ELISA Measurements	RPD Between CSUMB ELISA and LC/MS
204SLE030	0.293	0.610	0.4	70	31
312SMA	0.266	0.270	ND	1	NA
504SACHMN	4.48	2.73	1.90	49	81
520SACLSA	5.13	4.34	2.50	17	69
535MER546	0.325	0.150	ND	74	NA
535STC504	0.424	0.600	ND	34	NA
535STC504 DUP	0.959	1.31	ND	31	NA
541MER542	0.465	0.790	ND	52	NA
541STC019	0.670	1.02	ND	41	NA
544SAC002	54.5	63.9	81.2	16	39

Microcystins in the water column have had a number of effects on fish populations, and occasionally have caused harm to mammals (Malbrouk and Kestemont, 2006; Miller et al., 2010; Backer et al., 2013), but the ecological relevance of sediment-bound microcystins is relatively unknown. Initial research has begun on the potential for microcystins to bioaccumulate in freshwater benthic organisms, and the potential for these contaminants to affect resident benthic macroinvertebrates. Dose-response studies are planned using the midge *Chironomus dilutus.*

Monitoring microcystins bound to stream sediments may be an indicator of harmful algal blooms upstream or in-stream toxin production. Future research includes analysis of spatial and temporal patterns in toxicity and evaluating whether *in situ* or upstream processes are responsible for sediment-bound microcystins.

Section 4 - The Relationship among Measured SPoT Parameters

3) *What are the magnitude and extent of any problems?*

Chemical contamination and toxicity are most severe in urban watersheds.

4) *What's causing the problem?*

Urban watersheds have the highest contaminant concentrations, and toxicity has the strongest correlations with urban insecticides.

Spearman rank correlations were used to examine significant statistical relationships among the various parameters measured in the program to determine possible causes of sediment toxicity. Correlations included percent urban or agricultural land use at a 5 km radius, Tier I and Tier II chemicals and physical measurements, and toxicity measured as percent survival. The first set of comparisons were between summed chemical classes and percent land uses to determine significant relationships. Comparisons were then made between percent survival and the various chemical and physical parameters.

Percent land use in urban watersheds had moderate and strong positive correlations with pyrethroids , sum PCBs, sum PAHs and sum PBDEs (Table 5). A significant correlation with pyrethroids was somewhat expected because of the significant increase in average pyrethroid concentration observed in urban watersheds. PAHs and PBDEs were mostly measured in urban watersheds, and showed expected increases with percent urban land use. Percent agricultural land use did not have any strong positive correlations with chemicals, but had moderate negative correlations with fipronil, PAHs and PBDEs, chemical classes that are primarily used and detected in urban watersheds.

Toxicity measured as percent survival had a very weak positive correlation with agricultural land use and a weak negative correlation with urban land use. Percent survival had moderate and strong correlations with pyrethroids and fipronil, respectively, and weak correlations with all other chemical classes. The results of correlation analysis only imply causes of toxicity. Specific causes of toxicity are discussed in the next section.

Table 5. Results of multiple Spearman rank correlation analyses for all data. All relationships presented were statistically significant at $p < 0.0001$. Values with "MR" indicate moderate relationships and values with "SR" indicate strong relationships.

	Urban Watershed		Agricultural Watershed		Percent Survival	
Variable	**Coefficient**	**N**	**Coefficient**	**N**	**Coefficient**	**N**
Urban Watershed	NA	NA	NA	NA	-0.313	584
Agricultural Watershed	NA	NA	NA	NA	0.157	584
Sum Pyrethroids	0.543 MR	585 MR	NS	NS	-0.458 MR	584 MR
Sum Fipronil	0.393	70	-0.453 MR	70 MR	-0.628 SR	70 SR
Sum Metals	0.335	500	NS	NS	-0.310	499
Sum DDT	0.331	500	NS	NS	-0.326	499
Sum PCB	0.407 MR	500 MR	-0.258	500	-0.251	499
Sum PAH	0.691 SR	223 SR	-0.564 MR	223 MR	-0.311	222
Sum PBDE	0.618 SR	207 SR	-0.426 MR	207 MR	-0.280	207
% Fines	NS	NS	0.168	584	-0.223	583
% Total Organic Carbon	0.339	585	-0.334	585	-0.369	584

Section 5 - The Relationship between Toxicity and Chemical Concentrations

4) *What's causing the problem?*

Toxicity thresholds for pesticides were exceeded in 19% of the samples. Most of the exceeded thresholds were for pyrethroids.

Significantly more samples were toxic, and the magnitude of toxicity was much greater when samples were tested at a more environmentally relevant test temperature.

Comparing Survival to Toxicity Thresholds and Sediment Quality Guidelines

The relationships between amphipod mortality and sediment chemical concentrations are investigated with multivariate analysis described above. To further investigate the toxicological relevance of these relationships, amphipod survival was compared to individual chemical threshold values to determine which chemical occurred at toxic concentrations. Concentrations used are summarized in Appendix 3. Where possible, median lethal concentrations (LC50s) derived from spiked sediment toxicity studies using *H. azteca* were used to evaluate chemistry data. Median lethal concentrations are preferable because they are derived from exposure experiments with single chemicals. The probable effects concentration (PEC) sediment quality guidelines were used when spiked-sediment LC50s were not available (Macdonald, 2000). Probable effects concentrations are consensus based guidelines that were developed from other empirically-derived sediment quality guideline values. The PEC is a concentration that if exceeded, harmful effects are likely to be observed (Macdonald, 2000). The PEC provides some predictive ability, but is not derived from direct dose-response experiments. Fifty-five threshold values for 40 individual chemicals and sums were used to evaluate several chemical classes including pyrethroid pesticides, organochlorine pesticides, organophosphate pesticides, PAHs, PCBs, and metals. Twenty of these chemicals and sums were evaluated with organic carbon-corrected threshold values.

Of the chemical thresholds evaluated, guideline values were exceeded for total chlordane and several metals, and LC50 values were exceeded for most pyrethroids and the organophosphate insecticide chlorpyrifos. Although the total chlordane probable effects concentration (PEC) was exceeded in approximately 6% of the samples, the samples with the highest concentrations were not consistently toxic. It should be noted that the PEC for chlordane may not be a reliable indicator of the potential for acute toxicity to amphipods. Recent dose-response experiments have shown that chlordane is essentially not toxic to the marine amphipod *Eohaustorius* *estuarius* at concentrations found in surficial sediments (Phillips et al., 2011). Trace metal concentrations exceeded PECs at many sites, but it is unlikely these concentrations contributed to observed toxicity to *H. azteca* because the concentrations did not exceed published LC50s derived from laboratory dose-response experiments. For example, copper sometimes exceeded the PEC (149 µg/g), but concentrations were always well below the LC50s for this metal to *H. azteca* (LC50 = 260 µg/g). This was also true for arsenic (PEC = 33 µg/g; LC50 = 532 µg/g), and for nickel (PEC = 48.6 µg/g; LC50 = 521 µg/g). Chromium most often exceeded the PEC, but it is unlikely this metal is contributing to toxicity (Besser et al., 2004). As laboratory dose response data become available for more contaminants, these will be used as the primary values for assessing the potential for toxicity to *H. azteca*. Both nickel and chromium are geologically abundant, particularly in areas of serpentine soils, such as those common in the Franciscan formation of the central and northern coast ranges (Bonifacio et al., 2010). Both are also used in various industrial applications, so natural sources cannot be assumed for all elevated samples. It should be noted that the comparison of sediment metal concentrations to published guideline values and other effect thresholds emphasize toxicity to invertebrates. In the case of laboratory dose-response experiments, these usually involve standard test species. These comparisons do not consider possible effects on other stream communities, such as algal communities. These may be more sensitive to sediment metal concentrations.

Pesticide LC50s were exceeded in 19% of the samples. Most of the elevated concentrations were for the pyrethroid insecticide bifenthrin. To better evaluate the contribution of pyrethroids to observed toxicity, concentrations were converted to toxic units (TUs). Toxic units are calculated by dividing the measured concentration of an individual pyrethroid by its median lethal concentration (LC50). Because pyrethroids in a mixture can work additively, the TUs are summed. Approximately 50% mortality would be expected at one TU, and previous research has demonstrated that significant toxicity is observed when the sum of the TUs is greater than one (Weston et al., 2005). This analysis is made more accurate by calculating the TU values based on LC50s that have been corrected for the concentration of organic carbon in the sediment. Elevated concentrations of organic carbon can reduce the bioavailability of organic chemicals such as pesticides (Maund et al., 2002), and normalizing concentrations to TOC account for the relative effect of this sediment constituent on toxicity. Although there was a significant relationship between organic carbon-corrected TUs and percent survival (Figure 5), there were five samples with a toxic unit sum greater than 5 that were not toxic or moderately toxic. Considering the three non-toxic samples with TU values greater than 5, all of these samples have demonstrated increasing total pyrethroid concentrations over the last five years with only moderate toxicity in one sample. The organic carbon concentrations at these sites have remained less than 5%, and were generally variable. The TOC measurement utilized by SPoT does not differentiate among the various types of organic carbon that might be present. It is possible that the type of carbon at these sites varies and may have a greater binding capacity. Black carbon, which is derived from fossil fuels, can reduce the bioavailability of organic compounds beyond that of plant-derived organic carbon (Kukkonen et al., 2005).

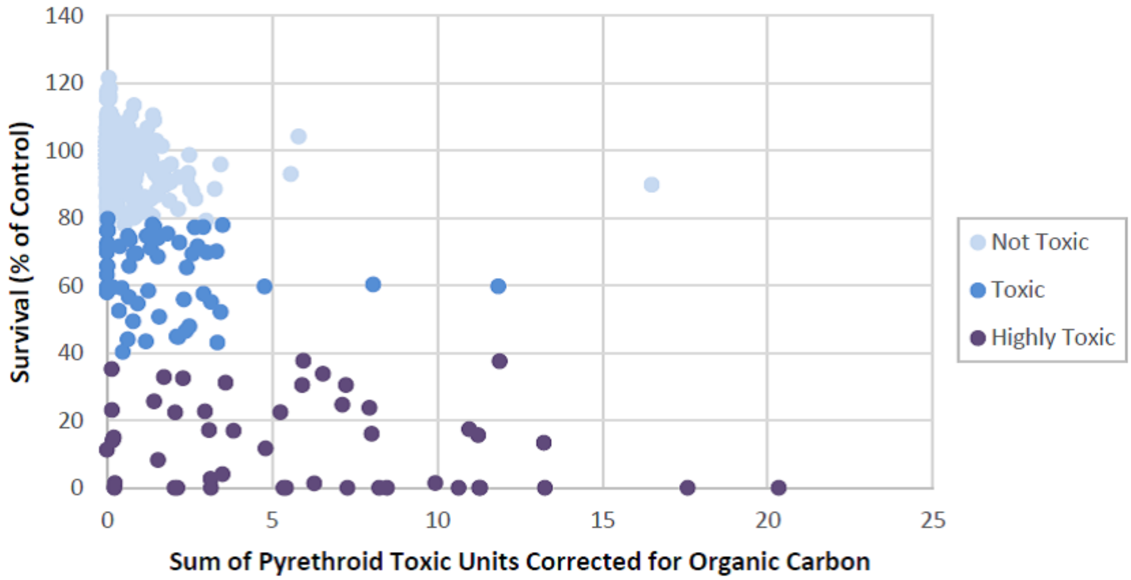

Figure 5. 2008-2014 toxicity data plotted against the sum of pyrethroid toxic units corrected for organic carbon. See text for explanation of toxic units and organic carbon correction.

Potential Impacts at an Environmentally Relevant Temperature

Since 2010, subsamples of *H. azteca* toxicity tests, which are normally conducted at 23°C, were also conducted at a colder temperature of 15°C. This lower temperature better represents the average temperature for surface waters at SWAMP water analysis sites between 2001 and 2010, which was 15.8°C. Tests were conducted at two temperatures to determine toxicity at a more environmentally relevant temperature (Anderson et al., 2012), but also to diagnose the contributions of pyrethroids to observed toxicity. Some pyrethroids are more toxic at colder temperatures (Coats et al., 1989), and this characteristic has been used as an investigative tool to diagnose pyrethroid-associated toxicity (Anderson et al., 2008). Increasing toxicity with decreasing temperature has been demonstrated specifically with *H. azteca* in more recent studies (Weston et al., 2009), and also with chironomids (Harwood et al., 2009). Harwood et al. (2009) showed this is due to slower metabolic breakdown of pyrethroids at lower temperatures and increased nerve sensitivity.

Between 2010 and 2014 27% of SPoT sites were tested at 15°C (159 of 584 samples). Samples were selected based on previous toxicity results and had to have had pyrethroids detected in the low to moderate toxic unit range. A candidate sample typically had low to moderate toxicity and pyrethroids ranging from one to five toxic units.

Significantly more samples were toxic when tested at 15°C, and the magnitude of toxicity was much greater at the lower test temperature (Figure 6). Samples were almost three times more likely to be toxic when tested at 15°C. These results suggest that pyrethroids likely played a role in the increased incidence of toxicity in these samples. These data also suggest that the potential for surface water toxicity is likely underestimated in SPoT watersheds based on assessing toxicity at the standard protocol temperature (23°C). The toxicity results in approximately half of the samples tested at 15°C did not change, but there were no samples having significantly higher survival at the colder temperature.

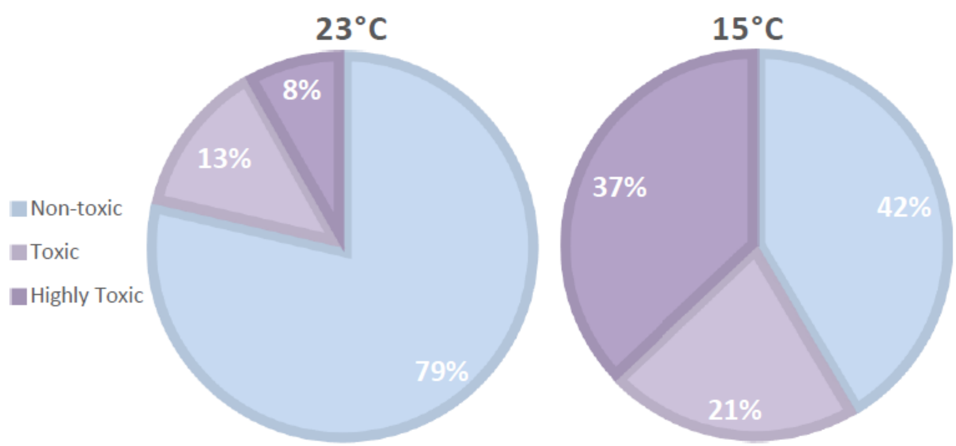

Figure 6. Percentage of samples in each *H. azteca* toxicity category for a subset of samples tested at two temperatures between 2010 and 2014.

The samples that appear to be most vulnerable to increased pyrethroid toxicity when tested at a lower temperature are those that contain less than five toxic units of total pyrethroids. The majority of samples tested at 23°C contain less than five toxic units and are generally not toxic or moderately toxic (Figure 5). These are the samples targeted for 15°C tests because lowering the test temperature shifts the toxic unit threshold to a lower value, indicating that less pyrethroid is necessary to cause a toxic response (Figure 7). Although DDT can cause a similar response at colder temperatures, the concentrations of DDT in these sediments were well below toxicity thresholds for *H. azteca*. These data also suggest that the potential for surface water toxicity is likely underestimated in SPoT watersheds based on assessing toxicity at the standard protocol temperature (23 °C).

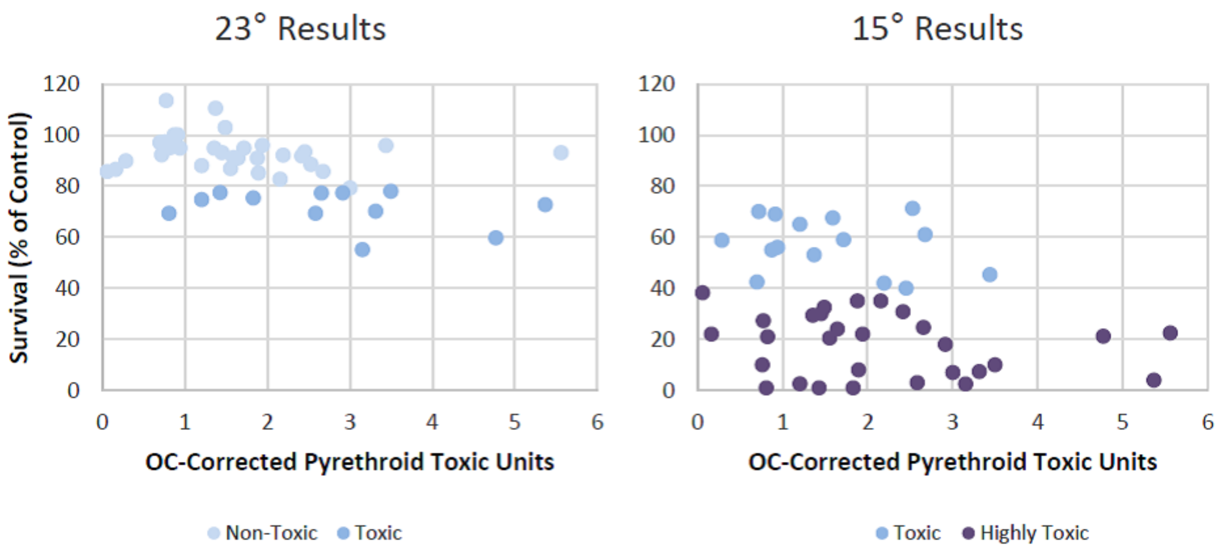

Figure 7. Percent survival of samples with 0 – 6 sum pyrethroid toxic units tested at two different temperatures.

Utility of *Hyalella azteca* for Pyrethroid Monitoring in Sediments

Hyalella azteca have been used extensively for sediment toxicity assessment in a variety of monitoring programs in California (e.g., SWAMP, SPoT and SMC). These amphipods rank as one of the most sensitive standard test organisms to pyrethroids, and their use in SPoT has clearly identified pyrethroids as a contaminant of concern.

It should also be noted that the 10-day test protocol with *H. azteca* represents an acute exposure to sediment contaminants. Previous data have shown the 28-day protocol with this species is more sensitive than the 10-day growth and survival test because it incorporates growth over four weeks (Ingersoll et al., 2005). Because the more photo stable pyrethroids (e.g., bifenthrin) may persist from 277 to 1950 days, depending on sediment conditions (Gan et al., 2005; Budd et al., 2011), the potential for chronic impacts of these pesticides on California watersheds are also likely underestimated by SPoT results. Anderson et al. (2015) compared the relative sensitivities of the 10-day and 28-day *H. azteca* protocols as part of a project by the Central Valley Regional Water Quality Control Board to develop sediment quality criteria for bifenthrin. The results of these experiments determined that the shorter-term protocol was appropriate for the measurement of survival because there was little difference in survival LC50s between 10-day and 28-day exposures (LC50s = 9.1 and 9.6 ng/g bifenthrin for 10-day and 28-day tests, respectively). The LC50 values for tests conducted at 15°C were 5.1

and 3.4 ng/g for the 10-day and 28-day tests, respectively. This study also showed that the lowest toxicity threshold measured for bifenthrin toxicity to *H. azteca* (growth IC20 = 0.61 ng/g) occurred in the 28-day exposure conducted at 15°C. Although there were not large differences in the statistical endpoints between the 10-day and 28-day tests, conducting these tests at 15°C, particularly the 28-day test, demonstrated the greatest sensitivity.

Section 6 - Management Actions and Anticipated Future Trends

5) *Are solutions working?*

It is too soon to tell if more stringent rules for the urban application of pyrethroid pesticides will result in reduced load to urban watersheds, or if the reduction of copper in automobile brake pads will result in a corresponding reduction of copper in SPoT sediments.

Intensive Site Study

California regulatory agencies recognize the role pesticide contamination plays in degradation of state waters and have implemented plans to address sources of specific current-use pesticides. In 2012 DPR implemented use restrictions (California Code of Regulations Title 3: Food and Agriculture, Sections 6970 and 6972) for pyrethroid pesticides used by pest control businesses in urban settings and has provided outreach to pesticide applicators to instruct proper application techniques on impermeable surfaces (http://www.cdpr.ca.gov/docs/pressrls/2012/120718.htm). This project is intended to reduce the mass of active ingredients applied and to minimize off-site runoff into stormwater systems and adjacent watersheds. The U.S. EPA is also requiring label changes for pyrethroid products to reduce their impact on surface water quality (EPA-HQ-OPP-2008-0331-0021). In 2013 SPoT began a collaboration with DPR to monitor additional sites with greater intensity to determine if these regulations result in a decline in sediment-associated pyrethroids in selected urban watersheds.

Four sites were chosen, two existing DPR urban monitoring stations (Salt Creek and Pleasant Grove Creek), and two existing SPoT stations (Bouquet Canyon Creek and Kirker Creek). All stations previously demonstrated significant toxicity and elevated concentrations of pyrethroids (Weston et al., 2005; Ensminger et al., 2013; Phillips et al., 2014). The four sites were sampled four times per year (2013-2014), and the sediment was analyzed for toxicity to *H. azteca*, as well as pyrethroid pesticides and fipronil and its degradates. Previous toxicity and total pyrethroid data were available for Kirker Creek and Bouquet Canyon Creek sites where sampling was initiated in 2008 and 2010, respectively. Water samples from the DPR sites were also sampled and analyzed for pesticides.

There were no significant reductions in the sum of pyrethroids or fipronil in sediments either during the eight sampling periods in 2013-2014, or when previous data were considered in the analysis (Table 6). The four intensive study sites contain a broad range of pyrethroid concentrations from low ng/g to low µg/g. Pyrethroid concentrations at Pleasant Grove Creek were on the low end of the range, and toxicity was not observed until the last sampling event of 2014. Kirker Creek has had consistently moderate concentrations of pyrethroids since 2008, and aside from one incidence in 2010, where total pyrethroids exceeded 90 ng/g, the site was not significantly toxic until the end of 2014. Neither of these toxic samples could be attributed to pyrethroids alone. Salt Creek and Bouquet Canyon Creek were both significantly toxic in every event, and in most cases the samples were designated highly toxic. Concentrations of pyrethroids at Bouquet Canyon Creek were the highest measured in the SPoT program. It was interesting to note that the final sample from 2014 was not highly toxic, and the concentration of pyrethroids was greatly reduced. This sampling event coincided with a large rain event in southern California, and it was clear from the grain size observed at the sampling site that the system had been flushed. Initial observations from 2015 show this site has returned to similarly toxic conditions as depositional sediment accumulate at the site.

Table 6. Percent survival and concentrations of total pyrethroid (ng/g - Sum PYR) and total fipronil (ng/g - Sum FIP) at intensive study sites. Previous data are presented for Kirker Creek and Bouquet Canyon Creek. Values with "NT" indicate "non-toxic" samples, "ST" indicates "some toxicity," and "HT" indicates "highly toxic" samples.

Year	Kirker Creek			Bouquet Canyon Creek			Pleasant Grove Creek			Salt Creek		
	% Surv.	Sum PYR	Sum FIP	% Surv.	Sum PYR	Sum FIP	% Surv.	Sum PYR	Sum FIP	% Surv.	Sum PYR	Sum FIP
2008	93 NT	4.45	NA	NA	NA	NA	NA	NA	NA	NA	NA	NA
2010	34 HT	91.3	NA	0 HT	1043	NA	NA	NA	NA	NA	NA	NA
2011	86 NT	32.1	NA	0 HT	1571	NA	NA	NA	NA	NA	NA	NA
2012	86 NT	2.04	NA	0 HT	1115	NA	NA	NA	NA	NA	NA	NA
2013 A	86 NT	19.8	1.30	0 HT	4254	106	95 NT	1.88	2.76	16 HT	218	34.7
2013 B	92 NT	7.92	3.94	0 HT	733	124	96 NT	0.450	2.70	28 HT	99.0	19.7
2013 C	100 NT	17.8	4.52	0 HT	2404	140	101NT	1.18	2.60	26 HT	188	16.2
2013 D	89 NT	29.9	5.94	4 HT	1327	54.1	91 NT	0.147	0.180	26 HT	245	18.4
2014 A	101 NT	22.5	2.17	0 HT	1124	167	110 NT	0.290	0.700	22 HT	196	25.3
2014 B	82 NT	13.4	3.24	0 HT	1053	288	108 NT	2.57	2.56	31 HT	304	21.4
2014 C	91 NT	23.6	4.37	0 HT	970	171	103 NT	1.64	2.00	52 ST	122	22.2
2014 D	59 ST	16.7	3.87	51 T	26.6	7.48	64 ST	4.16	2.04	0 HT	264	39.8

Water samples were also measured during this period as part of DPR's ambient monitoring program (Budd, 2015; Ensminger, 2015). Five samples were collected at Pleasant Grove Creek from 2013 to 2014, and eight samples were collected at Salt Creek during the same period. Only bifenthrin was detected in two of five water samples from Pleasant Grove Creek. Salt Creek had multiple of detections of bifenthrin, cyfluthrin and permethrin. Half of the samples were collected during storm events, and these samples contained the highest concentrations. No significant trend could be determined at either site. The Salt Creek site was included in a USGS statewide pesticide monitoring program starting in 2015 and water pesticide, herbicide and fungicide data from this monitoring will be included in a future SPoT report.

Furthering the Collaboration with DPR

Intensive sediment and water monitoring at these sites continued in 2015, and is scheduled to continue in 2016. In 2014 and 2015 there was an additional collaboration with DPR integrating Regional SWAMP monitoring for water column toxicity at DPR's agricultural surface water monitoring sites. Regional Water Quality Boards 3 and 7 funded toxicity testing using *H. azteca* and *C. dilutus* at 17 sites. Significant toxicity was observed at sites that were minimally toxic to U.S. EPA 3-species tests (Anderson et al., in preparation). Chemical analysis by DPR detected a number of current-use and emerging pesticides, and toxicity testing results indicated these chemicals have the potential to impact the receiving systems. In addition to monitoring organophosphate and pyrethroids in water, this monitoring is specifically targeting water concentrations of the neonicotinoid insecticide imidacloprid. Neonicotinoids are not expected to partition to sediments due to their high solubility. These data informed a recent SWAMP memo on changing patterns in toxicity, and provided recommendations for choosing toxicity test species for pesticide-related projects (www.waterboards.ca.gov/water_issues/programs/swamp/docs/workplans/tox_recs_tech_memo.pdf). This project has led to an ongoing collaboration between SPoT and DPR that will conduct toxicity testing on DPR Surface Water Monitoring samples collected from urban and agricultural watersheds throughout the state. Water column toxicity testing with *C. dilutus* and *H. azteca* coupled with DPR analysis of current use pesticides in water is intended to provide up-to-date information on risk of emerging contaminants to California watersheds. These data can then be used to more proactively manage pesticides before they impact receiving waters.

Estimations of Copper Reduction due to Reduced Copper in Automobile Brake Pads

California law enacted in 2010, requires automobile brake pads sold in the state to contain no more than 5% copper by weight by 2021 and no more than 0.5% copper by weight by 2025 (California Senate Bill 346, 2010). There have already been significant reductions in the copper contents of brake pads, and pad manufactured in 2021 are expected to contain 81 to 99% less copper (Moran 2016). Urban runoff copper reductions lag behind copper content reductions in manufactured brake pads because brake pads are only changed on average every three to five years, wholesaler and retailer inventories take an average of two years to turn over, and urban watersheds do not immediately clear pollutants when discharges cease. Consequently, it is unlikely that we will see appreciable reduction in sediment copper concentrations before the 2020s (Moran 2016). The SPoT program will be able to track these reductions through routine monitoring and the addition of copper to the analyte list for the intensive stations monitored as part of the collaboration with DPR.

Section 7 - SPoT Indicators in Relation to Stream Ecology

A) *Are our aquatic ecosystems healthy?*

Not all of our watersheds are healthy. When data from SPoT are combined with data from other programs, it is clear that anthropogenic stressors are affecting ecosystem health.

B) *What stressors and processes affect our water quality?*

Data from SPoT indicate that pesticides are the most significant environmental stressor.

SPoT is one of several statewide monitoring programs conducted under the SWAMP framework. The Perennial Streams Assessment program (PSA) and the Bioaccumulation Oversight Group (BOG) also conduct statewide surveys, but address different assessment questions. The PSA uses probability-based assessments of macroinvertebrate and algal communities to determine stream condition. This program examines the relationship between the stream condition and land use, and determines which of the stressors measured are likely related to the biological condition (Ode et al., 2011). Other than nutrients, the PSA program does not measure chemical contaminants. The focus of BOG is on fishing as a beneficial use (Davis et al., 2013). BOG uses a targeted design to sample sport fish from popular fishing areas in rivers and streams. Selected contaminants are analyzed in fish tissue to determine if established concentrations of concern for human health have been exceeded. BOG focuses on chemicals that bioaccumulate, such as mercury and PCBs. SPoT also uses a targeted sampling design, but unlike the other two programs, revisits the same sites annually. This design allows for succinct trend analysis, and allows the program to detect emerging chemicals through consistent use of toxicity testing. PSA, BOG, and SPoT together provide freshwater data similar to those used in other programs to develop sediment quality objectives (SQOs) in marine and estuarine habitats. Co-location of sites or addition of specific indicators across the PSA, BOG, and SPoT programs could allow for development of freshwater SQOs for California.

SPoT complements the PSA by focusing on the magnitude of pollution in streams, using toxicological endpoints to establish causal connections between these chemicals and biological impacts, and by analyzing land cover as part of a watershed-scale evaluation of the sources of pollutants affecting aquatic life. The PSA helps address SPoT goals by assessing the overall ecological health of wadeable perennial streams, and by testing assumptions about the status of reaches upstream of the intensive land uses that are associated with pollutants measured by SPoT. Data from SPoT sites have already been integrated with bioassessment data from SMC monitoring in southern

California, and there are plans for further collaborations between SPoT and existing bioassessment programs.

Although there have not yet been synoptic assessments of benthic macroinvertebrates at SPoT sites, the previous SPoT report compared bioassessment data collected at proximate sites to toxicity and chemistry data measured at SPoT sites. Statistical comparisons were made for sixty-six sites and significant relationships were detected between toxicity and measures of an index of biological integrity (IBI). Pyrethroid pesticides, chlorinated compounds, and the benthic tolerance value were significantly negatively correlated with IBI, indicating a relationship between field chemistry and biological data with laboratory toxicity test results.

Previous California studies have demonstrated significant correlations between sediment and water toxicity in laboratory tests and degraded macroinvertebrate communities. These studies have indicated that toxicity observed in urban and agricultural water bodies is linked to declines in a number of BMI metrics and are also correlated with chemical contamination, particularly with pesticide concentrations in water and sediment (Anderson et al., 2003a; Anderson et al., 2003b; Phillips et al., 2004; Weston et al., 2005; Anderson et al., 2006; Phillips et al., 2006; Larry Walker Associates, 2009). Other studies have shown the importance of physical habitat in structuring BMI communities (Hall et al., 2007; Hall et al., 2009; Larry Walker Associates, 2009).

Additional data analyses were conducted for the current reporting cycle using the California Stream Condition Index (CSCI). The CSCI was recently developed as a statewide scoring tool that summarizes benthic macroinvertebrate data into a single index of stream health (Rehn et al., 2015; Mazor et al., In review). The CSCI is calculated from a multi-metric index that measures ecological structure and function, and an observed-to-expected index that measures taxonomic completeness. The new analyses compared data from SPoT, the southern California Stormwater Monitoring Coalition, and other programs that utilized measures of sediment toxicity and chemistry, to CSCI values calculated from bioassessment data sets. Bioassessment data came from the same sites as the toxicity and chemistry samples, or from sites within 500 meters.

The CSCI had a significant positive relationship with toxicity measured as percent amphipod survival, and a significant negative relationship with pyrethroids measured as toxic units (Figure 8). Samples with low percent survival and elevated concentrations of pyrethroids tend to be from sites with lower CSCI scores (i.e., impacted sites). It should be noted that these figures represent wedge-shaped scatter plots, sites with low CSCI scores do not always have low laboratory survival or contain elevated concentrations of pyrethroids. This is because other factors can contribute to degraded benthic assemblages, such as degraded habitat or extreme conventional water quality characteristics.

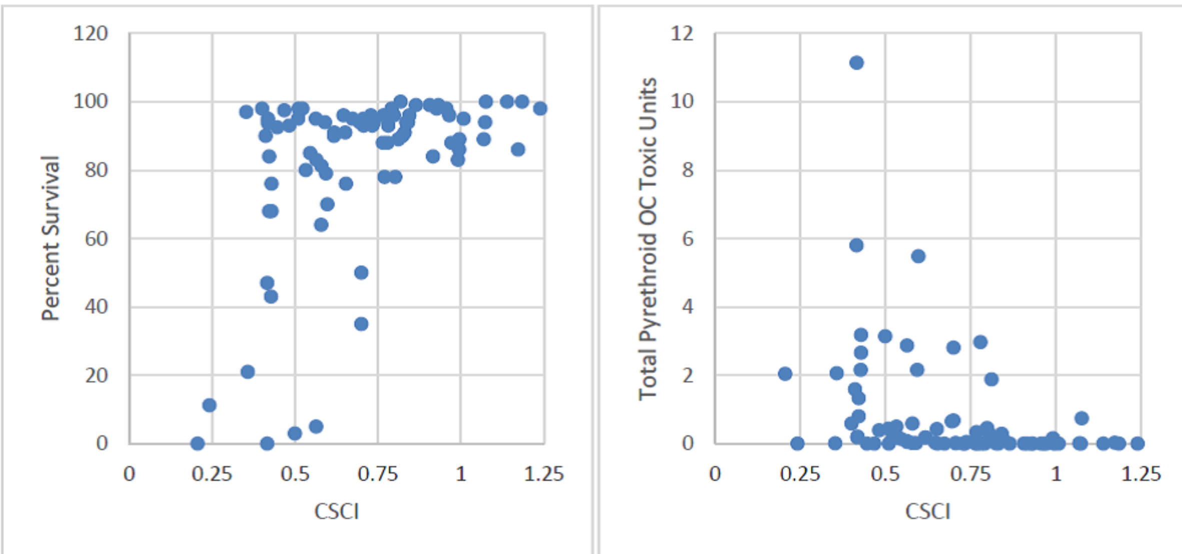

Figure 8. Left - Relationship between the percent survival of amphipods in laboratory sediment toxicity tests compared to measures of California Stream Condition Index at sites at or within 500 meters of sediment collection. Right – Relationship between the sediment concentrations of pyrethroids measured as organic carbon-corrected toxic units compared to CSCI.

To date, SPoT data have demonstrated links between laboratory toxicity and elevated concentrations of pyrethroid pesticides in sediments. Significant relationships between toxicity, chemistry and CSCI scores in SPoT data, and data from other programs, indicate a further connection with ecosystem response. There have been significant losses in insect populations worldwide (Dirzo et al., 2014), and pesticides are likely contributing significantly to these losses particularly pyrethroid insecticides and the newer classes of systemic insecticides that include fipronil and the neonicotinoid imidacloprid (Morrissey et al., 2015; van Lexmond et al., 2015). SPoT began monitoring fipronil in 2013, and the program has already noted a significant increase in concentrations of this compound and its degradates, reflecting increased use throughout the state (Weston and Lydy, 2014). Like all neonicotinoids, imidacloprid is highly soluble, and is unlikely to be at appreciable concentrations in sediment. SPoT has proposed to conduct water column toxicity tests at agriculture and urban stations currently monitored by DPR for a suite of current use pesticides, including neonicotinoids. SPoT's network of sites and its ongoing collaboration with DPR uniquely positions both programs to provide timely ecological risk data to be more proactive in managing emerging pesticides in urban and agriculture runoff.

Section 8 – Trends at Individual Sites and Regional Summaries

All of the tables in this section are similarly configured. Statistically significant trends are noted with arrows. The toxicity abbreviations denote the following.

Region 1 – North Coast

All but one of the watersheds in Region 1 are classified as "other" land use at the 5 km scale. Smith River (103SM1009) has sufficient cover of developed open space to place it in the urban land use category. Laguna de Santa Rosa (114LAGWOH) also has some agricultural influence at the 5 km scale, and was moderately toxic in 2013. Five of the eight sites in Region 1 had a single incidence of moderate toxicity in 2010, but these sites have not been toxic since with the exception of the Navarro River (113NA3269) which was moderately toxic in 2013 and 2014. No Region 1 samples were tested at 15°C in 2013 or 2014, but previous tests of Region 1 samples at the colder temperature did not increase toxicity. There were no significant increasing or decreasing trends for the measured chemical classes except for TOC, which showed a significant decrease in the South Fork of the Eel River (111SF0933). Chlorinated compounds were rarely detected, and metal concentrations remained unchanged. Samples from the Russian River (114RRDSDM) had the highest average pyrethroid concentrations of any SPoT site in Region 1.

Table 7. Region 1 sampling station trends from 2008 – 2014.

	Primary			Mean %	Mean Total Concentration (ng/g)							
Station Code	5km Land Use	Years Sampled		Survival 2010-2014	Pyrethroid	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
103SM1009	Urban	2008	2013	92 ST	0.024	120	1.81		0	0	41.2	2.28
105KLAMKK	Other	2008	2014	97 NT	0	125			0	0	42.5	1.34
109MAD101	Other	2008	2013	90 ST	0.028	93.8			0	0	34.6	1.18
111EELFRN	Other	2008	2013	91 ST	0.086	81.2			0	0	51.0	2.56
111SF0933	Other	2008	2013	90 ST	0	80.6		178	0	0	26.3	0.68 ↓
113NA3269	Other	2010	2014	74 ST	0	64.7			0	0	31.3	0.96
114LAGWOH	Other	2008	2014	91 ST	0.693	94.4			2.67	0	62.5	2.75
114RRDSDM	Other	2008	2014	101 NT↑	3.48	111		61.8	0.731	0.282	57.9	2.16

Region 2 – San Francisco Bay

Eight of the eleven watersheds sampled in Region 2 are classified as urban at the 5 km scale. Only Sonoma Creek (206SON010) was influenced by agriculture based on the NLCD, and only on the 1 km and 5 km scales. Although most of the sites in the region have urban influences, there continues to be a trend of decreasing toxicity to amphipods. San Leandro (204SLE030), Coyote (205COY060), and Laurel Creeks

(207LAU020) had significant trends of increasing amphipod survival in toxicity tests. There was one highly toxic site in 2010 (Kirker Creek, 207KIR020), and Walnut Creek (207WAL020) was moderately toxic most often. Most Region 2 sites have been tested at 15 °C. The most significant reductions of survival at the colder temperature occurred between 2010 and 2012, with only moderate reductions of survival in cold temperatures in 2013 and 2014. Despite a statewide increase in pyrethroid pesticides in urban watersheds, there were no significant increases of pyrethroids at individual Region 2 sites. Fipronil increased at seven of the eight stations it was measured between 2013 and 2014. Significant increases in PBDEs were observed in San Mateo Creek (204SMA020) and Guadalupe River (205GUA020). These were the only increases of PBDEs in the state.

Table 8. Region 2 sampling station trends from 2008 – 2014.

	Primary			Mean %	Mean Total Concentration (ng/g)								
Station Code	5km Land Use	Years Sampled		Survival 2010-2014	Pyrethroid	Fipronil	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
201LAG125	Other	2008	2013	99 NT	1.05		82.0			0	0.052	41. 6	2.09
201WLK160	Other	2008	2014	92 ST	0.315		70.5			0	0.099	51.9	2.72
204ALA020	Urban	2008	2014	97 NT	6.78	0.767	122	19.2	161	5.12	1.54	68.6	2.08
204SLE030	Urban	2008	2014	94 NT↑	33.0	0.568	438	65.7	2057	49.1	38.2	66.4	7.76
204SMA020	Urban	2008	2014	91 NT	36.7	2.58	236	23.7 ↑	1577	60.8	14.0	52.3	4.96
205COY060	Urban	2008	2014	96 NT↑	121	1.30	250	58.2	1269	17.7	19.0	68.1	3.67
205GUA020	Urban	2008	2014	91 ST	54.3	0.580	334	60.2 ↑	1891	29.0	72.8	66.8	4.37
206SON010	Other	2010	2013	96 NT	15.8		118		23.4	0.088	0.433	68.2 ↑	2.84
207KIR020	Urban	2008	2014	78 MT	28.7	1.73	221	11.9	168	0.44 ↓	1.55	62.1 ↓	2.33
207LAU020	Urban	2008	2014	101 NT↑	13.0	0.275	131	5.68	88.8	0.256	0.334	60.6	2.26
207WAL020	Urban	2008	2014	80 ST	35.5	0.533	203	16.7	1229	4.83	8.36	59.3	2.86

Stations 205COY060 and 205GUA020 will be included in DPR surface water collaboration.

Region 3 – Central Coast

At the 5 km scale, six of the Region 3 watersheds are classified as urban. Of the remaining sites tested, five are classified as other and two are classified as urban/agriculture. Tembladero Slough (309TDW) and the Santa Maria River (312SMA) sites have been consistently toxic during the first five years of SPoT, but Santa Maria River has shown a significant increase in survival in 2013 and 2014 with back-to-back non-toxic samples. Field observations have shown the Santa Maria River channel upstream of this site has filled in with the emergent macrophyte pennywort (*Hydrocotyle* sp.) due to lack of large flood events over the past few years. This plant is effective at sorbing pesticides and its increased growth in the river channel has likely reduced loading of pesticides from upstream agriculture sources (Anderson et al., 2011b).

Table 9. Region 3 sampling station trends from 2008 – 2014.

Station Code	Primary 5km Land Use	Years Sampled		Mean % Survival 2010-2014	Mean Total Concentration (ng/g)								
					Pyrethroid	Fipronil	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
304SLRWAT	Urban	2011	2014	100 NT	0.214	0	48.2	0.280	24.8	0.093	0	34.4	1.24
304SOK	Urban	2008	2014	98 NT	1.47	0.200	75.4	6.02	272	0.377	0	33.4	0.98
305THU	Ag/Urb	2008	2014	100 NT	10.3		126	1.91	108	134	0.097	72.9	3.59
307CML	Urban	2008	2013	97 NT	11.7		128	6.23	195	0.191	0.086	44.8	5.25
309DAV	Other	2008	2014	97 NT	47.4		162	5.89	427	70.6	6.00	62.0	3.60
309TDW	Ag/Urb	2008	2014	28 HT	73.2		177		51.9	117	9.69	84.0	2.51
310ARG	Urban	2008	2014	84 ST	33.7	0.153	130	15.2	262	78.0	0.156	52.6	4.53
310SLB	Other	2008	2014	100 NT	3.61		109		251	0.267	1.61	36.2	2.82
312SMA	Other	2008	2014	57 MT↑	33.4		123	0.598	10.0	175	0.177	84.1	2.48
313SAI	Other	2008	2014	101 NT	4.92		64.1		8.30	6.49	0	68.3	2.99
314SYN	Other	2011	2014	96 NT	7.26		106			2.17	0	38.6	2.36
315ATA	Urban	2008	2014	102 NT	16.6	0.452	93.0	5.21	368	7.99	6.10	48.2	3.46
315MIS	Urban	2008	2014	101 NT	10.9	0.799	119	12.1	716	3.27	1.09	37.4	3.67

309DAV will be included in the DPR surface water collaboration.

Although these two watersheds are not classified as agricultural at the 5 km scale, they are some of the most significantly impacted by agriculture. There were no other significant trends measured in Region 3 for toxicity or any of the chemical parameters measured, but fipronil had higher concentrations in 2014 at four of the five sites where it is measured. Several sites were also tested at 15 °C in order to determine the influence of pyrethroid pesticides on the observed toxicity. Repeat sites included Arroyo Grande Creek (310ARG) and Salinas River at Davis Road (309DAV). Both of these sites exhibited less toxicity at the colder temperature in 2013 and 2014 than in previous years.

Region 4 – Los Angeles

Seven of the eight sites in Region 4 are classified as urban at the 5 km scale. No sites are solely agriculture at the 5 km scale, but two sites have agriculture mixed with urban or open land use (Sespe Creek 403STSSSP and Calluegas Creek 408CGCS06). Region 4 continues to have the greatest number of toxic sites in the state. Half of the sites have five-year averages that categorize them as moderately toxic or highly toxic, including three major Los Angeles basin watersheds (Los Angeles River 412LARWxx, Ballona Creek 404BLNAxx, and San Gabriel River 405SGRA2x), as well as Bouquet Canyon Creek (403STCBQT) in northern Los Angeles County. Only the Los Angeles River had a significant increase in any of the chemical categories (metals). Fipronil increased between 2013 and 2014 at two of the four stations where it was measured for both years. Three sites have never been toxic: Ventura River (402VRBOxx), Santa Clara River Estuary (403STCEST), and Sespe Creek (403STCSSP), the latter being one of the five SPoT reference sites. Seven of eight of the Region 4 sites were also tested at 15°C to determine the contribution of pyrethroid pesticides to the observed toxicity. All but one site, the Santa Clara River Estuary, had significantly greater toxicity when tested at the colder temperature, suggesting toxicity was due to pyrethroids.

Table 10. Region 4 sampling station trends from 2008 – 2014.

Station Code	Primary 5km Land Use	Years Sampled		Mean % Survival 2010-2014	Mean Total Concentration (ng/g)								
					Pyrethroid	Fipronil	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
402VRB0xx	Urban	2008	2014	98 NT	7.14	8.14	114	72.0	344	0.501	8.67	68.8	3.68
403STCBQT	Urban	2010	2014	0 HT	1821	136	386	248	710	1.23	8.68	73.9	11.4
403STCEST	Urban	2008	2014	98 NT	1.99		81.3			7.41	0.311	65.7	1.59
403STCSSP	Other	2008	2014	99 NT	8.73	4.60	132	105	455	1.60	0.542	67.5	2.11
404BLNAxx	Urban	2008	2014	35 HT	349	25.7	419	61.2	1306	30.5	29.0	57.6	10.6
405SGRA2x	Urban	2008	2014	45 MT↓	169	6.81	259	71.9	1058	6.95	8.61	62.7	4.07
408CGCS06	Urban	2008	2014	97 NT	9.66	1.26	100	3.90	75.6	56.4 ↓	5.47	56.3	1.85
412LARWxx	Urban	2010	2014	79 MT	115	6.63	262 ↑	44.0	539	4.86	9.30	69.0	8.39

403STCBQT, 404BLNAxx, 405SGRA2x, and 412LARWxx will be included in the DPR surface water collaboration.

Region 5 – Central Valley

Approximately one-third of SPoT sites are in Region 5, and at the 5 km scale, 19 of 34 watersheds are characterized as agricultural and one is characterized as urban/agricultural. Five watersheds are characterized primarily as urban, and the remainder are other. The majority of the sites in Region 5 have never been toxic and generally have low concentrations of measured chemicals, including pesticides. Only seven sites in the region have ever been toxic, but two sites are consistently highly toxic (Marsh Creek 541MERECY and Del Puerto Creek 541STC516). Marsh Creek is influenced by urban and agricultural land use and continues to have the highest concentrations of pyrethroids in the region, as well as the highest concentration of fipronil. Seven sites were sampled for fipronil, and there were detections at three sites. The only significant contaminant trend was a reduction of PAHs at Bear Creek (535MER007). Significant increases in percent fines and TOC were observed at Bear River (519BERBRY) and Merced River (535MER546), respectively. Twelve Region 5 samples have been tested at 15°C since 2010 to determine the contribution of pyrethroid pesticides to the observed toxicity. Four of these sites had significantly greater toxicity at the colder temperature.

Table 11. Region 5 sampling station trends from 2008 – 2014.

Station Code	Primary 5km Land Use	Years Sampled		Mean % Survival 2010-2014	Mean Total Concentration (ng/g) Pyrethroid	Fipronil	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
504BCHROS	Urban	2008	2014	104 NT	2.87	0.262	124	8.29	1035	37.0	0.418	53.4	3.03
504SACHMN	Agri.	2008	2014	104 NT	0.219		149			0	0	39.1	0.743
508SACBLF	Other	2008	2014	100 NT	2.01		273	1.30	97.2	0	0	52.3	1.66
510LSAC08	Agri.	2008	2013	103 NT	0.731		152	2.84	42.0	1.51	0	42.3	0.700
511CAC113	Agri.	2008	2014	100 NT	0.793		102			0.586	0	58.0	1.56
515SACKNK	Agri.	2008	2014	98 NT	2.61		168			8.47	0	74.9	1.88
515YBAMVL	Urban	2008	2014	100 NT	1.06	0	107	6.14	57.7	0.235	0	40.3	1.16
519AMNDVY	Urban	2008	2014	100 NT	1.25	0	107	0.512	57.3	0.385	0	42.6	0.766
519BERBRY	Agri.	2008	2014	101 NT	0.712		130			0	0	55 ↑	1.42
519FTRNCS	Agri.	2008	2014	103 NT	0.462		121			0.309	0	51.7	1.11
520BUTPAS	Agri.	2008	2014	99 NT	1.72		155			1.46	0	72.0	1.76
520CBDKLU	Agri.	2008	2014	97 NT	5.52	0	171	0.419	49.1	9.64	0	83.5	2.70
520SACLSA	Other	2008	2014	103 NT	0.425	0	163	0.134	24.0	0.736	0	45.0	1.04
526PRFALR	Other	2010	2013	105 NT	0.111		79.2			0	0	17.9	0.608
531SAC001	Other	2008	2014	100 NT	0.681		150	0.567	17.2	0.203	0	83.6	1.89
532AMA002	Other	2010	2014	101 NT	4.92		108			0	0	47.7	3.27
535MER007	Agri.	2008	2014	77 MT	2.84		100	1.16	40 ↓	1.03	0	69.8	1.58
535MER546	Agri.	2008	2014	103 NT	0.600		84.2			0.552	0	40.2	1.14↑
535STC206	Urban	2008	2014	89 ST	46.8	0.264	146	27.7	391	1.99	1.29	60.7	2.64
535STC210	Other	2008	2014	94 NT	0.176		140			3.03	0	37.1	2.33
535STC501	Agri.	2009	2013	101 NT	2.51		82.2		385	0.528	0	39.0	1.34
535STC504	Agri.	2008	2014	107 NT	2.23		186			3.86	0	68.6	1.59
541MER522	Other	2008	2014	106 NT	0.399		162			0.800	0	51.8	1.17
541MER542	Other	2008	2014	100 NT	0.132		58.9		0	0.130	0	50.5	1.08
541MERECY	Urban	2010	2014	20 MT	92.3	0.948	233	16.5	220	22.7	0	48.3	2.30
541SJC501	Agri.	2008	2014	103 NT	1.31		163	0.918	36.1	3.10	0	47.9	0.867
541STC019	Agri.	2008	2014	73 MT	13.9		122		0	74.2	0	86.9	1.39
541STC516	Agri.	2010	2014	27 HT	36.6		153		1.70	20.3	0	83.2	1.75
544SAC002	Agri.	2010	2014	100 NT	0.888		155			0.657	0	38.2	0.760
551LKI040	Agri.	2008	2014	101 NT	1.19		86.5		29.8	1.88	0.416	50.2	1.45
554SKR010	Other	2008	2013	104 NT	0		104			0	0.037	33.0	1.37
558CCR010	Agri.	2008	2014	97 NT	0.82		118		6.20	0.542	0.979	50.6	0.870
558PKC005	Ag/Urb	2008	2014	93 NT	16.4		146		513	14.3	1.04	56.9	1.63
558TUR090	Agri.	2008	2014	80 MT	1.20		97.3		18.2	1.57	0.049	64.1	1.26

Big Chico Creek (504BCHROS) had a significant spike of PAHs in 2013. Concentrations of total PAHs had previously been as high as 449 ng/g but increased to 5148 ng/g. Concentrations returned to 178 ng/g in 2014. Elevated concentrations did not affect survival in the toxicity tests. Tule River (558TUR090) had never been toxic until 2013 when one percent survival was observed in the sample. This low survival corresponded to a pulse of almost four toxic units of chlorpyrifos. Organophosphate pesticides were not measured in 2014.

Region 6 – Lahontan

Three of the ten Region 6 sites are characterized as urban at the 5 km scale, and the remainder are characterized as other. The Upper Truckee River (634UTRSED), Trout Creek (635TROSED), and Bishop Creek (603BSP002) have enough surrounding developed open space to be characterized as urban. To date there have been no toxic samples in Region 6, and the current five-year average survival in all samples is >94%. There have also not been any significant upward or downward trends in chemical concentrations, but there have been some small significant shifts in the amount of fines collected at two sites. Even though most of these sites are classified as being in watersheds dominated by other land use, pyrethroids were detected at nine of ten sites. The average pyrethroid concentrations are lower than those previously reported. Several Region 6 sites have been tested at 15°C to determine if toxicity would be observed in these samples at a more environmentally relevant temperature, but no samples showed increased toxicity. Fipronil samples were collected at three sites, but there were no detections.

Table 12. Region 6 sampling station trends from 2008 – 2014.

Station Code	Primary 5km Land Use	Years Sampled		Mean % Survival 2010-2014	Mean Total Concentration (ng/g)							
					Pyrethroid	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
603BSP002	Urban	2008	2014	98 NT	3.44	110	1.37	163	0.726	0	56.7	3.31
603LOWSED	Other	2008	2013	99 NT	0.510	64.4			0	0	42.6 ↓	6.48
628DEPSED	Other	2010	2013	100 NT	0.629	106			0	0	62.6	5.38
631WWKLAR	Other	2008	2014	95 NT	0	147			0	0	62.1	2.10
633WCRSED	Other	2008	2014	98 NT	0.895	122			0	0	50.7	4.25
634UTRSED	Urban	2008	2014	97 NT	0.038	131	0.268	60.0	0	0	48.8	2.86
635MARSED	Other	2008	2014	96 NT	1.13	130			0	0	68.5 ↑	4.45
635TRKSED	Other	2008	2013	98 NT	3.65	115			0	0.089	58.2	3.65
635TROSED	Urban	2008	2014	99 NT	1.95	104	0.363	40.3	0	0	44.5	3.31
637SUS001	Other	2008	2014	103 NT	0.310	113	0	44.5	0	0.070	78.6	2.21

Region 7 – Colorado River Basin

The three Region 7 sites that are evaluated for SPoT are also routinely monitored as part of other Regional Board programs. The Coachella Valley Stormwater Channel Outlet (719CVSCOT) and the Alamo River Outlet (723ARGRB1) are characterized as other at the 5 km scale, whereas and the New River Outlet (723NROTWM) is characterized as an agricultural watershed. Although Alamo River is not characterized as an agricultural watershed, there is a significant amount of agriculture in the larger watershed. Coachella Valley has never been toxic, but the southern river outlets have been moderately toxic intermittently, and both sites were highly toxic in 2013. Two sediment toxicity identification evaluations (TIEs) were recently conducted on sediment collected from the Alamo River site as part of routine SWAMP monitoring. The toxicity and chemistry results suggest that pyrethroid pesticides were contributing to the observed toxicity. Pyrethroid concentrations have generally been higher at the New River site, and a previous study identified cypermethrin as the cause of water column toxicity at this site (Phillips et al., 2007). Pyrethroids had a significant increase statewide, but only significantly increased at two individual sites. Both of these sites were located in Region 7. The Alamo River Outlet had a significant increase in total pyrethroids and the Coachella Valley Drain had a significant increase in bifenthrin. Significant decreases in DDT were observed at the New River, and a significant decrease in metals was observed at the Alamo River. The New River and Alamo River were both non-toxic in 2014, but exhibited high toxicity when tested at 15°C.

A recent collaboration between DPR and SWAMP showed that many of the agriculture sites in Region 7 are contaminated by mixtures of pyrethroid pesticides and toxic concentrations of chlorpyrifos. Samples from these sites were highly toxic to *H. 51ilute* in water exposures, and some were toxic to *C. 51ilutes*. Toxicity was driven by mixtures of chlorpyrifos and pyrethroids (Anderson et al. in preparation). All of the sites had detections of the neonicotinoid pesticide imidacloprid, in water. Two of these sites have been selected for continued water chemistry and toxicity monitoring as part of a collaboration between SPoT and DPR.

Table 13. Region 7 sampling station trends from 2008 – 2014.

Station Code	Primary 5km Land Use	Years Sampled		Mean % Survival 2010-2014	Mean Total Concentration (ng/g)							
					Pyrethroid	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
719CVSCOT	Other	2008	2014	97 NT	4.37	169	2.16	158	12.5	0	59.5	1.90
723ARGRB1	Other	2008	2014	68 MT	7.77 ↑	96.6 ↓	0.070	16.8	25.3	0	69.4 ↓	2.63
723NROTWM	Agri.	2008	2014	67 MT	17.4	96.8	1.84	19.5	27.2 ↓	0	73.9	1.62

723ARGRB1 and 723NROTWM will be included in DPR surface water collaboration.

Region 8 – Santa Ana

Three of the four sites in the Santa Ana Region are classified as urban at the 5 km scale. The fourth site, San Jacinto Creek (802SJCREF), is one of the five SPoT reference sites, and was classified as other. No toxicity has been observed at San Jacinto Creek or at the Santa Ana River at Prado Basin (801SARVRx), but Chino Creek (801CCPT12) and San Diego Creek (801SDCxxx) continue to be significantly toxic in every sampling event. San Diego Creek has been highly toxic in five of seven sampling events, and Chino Creek was highly toxic in one of five events. The only significant trend observed in the chemistry data set was a decrease in PCB at the Santa Ana River. San Diego Creek and Chino Creek have some of the higher average total pyrethroid concentrations in the state. Non-toxic and moderately toxic sites are consistently toxic or highly toxic when tested at 15°C. Fipronil was measured at two sites and significantly increased at San Diego Creek (801SDCxxx).

Table 14. Region 8 sampling station trends from 2008 – 2014.

Station Code	Primary 5km Land Use	Years Sampled		Mean % Survival 2010-2014	Mean Total Concentration (ng/g)								
					Pyrethroid	Fipronil	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
801CCPT12	Urban	2010	2014	54 MT	105	0.839	228	23.5	410	2.37	0	51.0	3.47
801SARVRx	Urban	2008	2014	95 NT	11.9		138	16.8	450	5.05	4.7 ↓	43.9	1.44
801SDCxxx	Urban	2008	2014	37 HT	115	7.87	130	10.9	292	18.2	1.75	63.6	2.36
802SJCREF	Other	2008	2013	102 NT	0.454		104	0.586	145	0.281	2.55	50.6	1.40

Region 9 – San Diego

All Region 9 sites are characterized as urban at the 5 km scale. Mostly moderate toxicity has been observed at San Juan Creek (901SJSJC9), Escondido Creek (904ESCOxx), San Dieguito River (905SDSDQ9), and Sweetwater River (909SWRWSx). San Juan Creek is also exhibiting a significant decrease in survival., The Tijuana River (911TJHRxx) has been highly toxic since 2008. This site also has the highest average concentration of total pyrethroids in the region, and has consistently been one of the most pyrethroid-contaminated sites in the state, based on SPoT monitoring. There were several increasing or decreasing trends in the region including increases in metals at San Diego River (907SDRWAR) and Sweetwater River, increasing PAHs at San Diego River, and a decrease in DDT at Santa Margarita River (902SSMR07). Fipronil concentrations tended to decrease between 2013 and 2014. Testing at 15°C consistently demonstrates significantly increased toxicity, indicating the contributing role of pyrethroids.

Table 15. Region 9 sampling station trends from 2008 – 2014.

Station Code	Primary 5km Land Use	Years Sampled		Mean % Survival 2010-2014	Mean Total Concentration (ng/g)								
					Pyrethroid	Fipronil	4 Metals (µg/g)	PBDE	PAH	DDT	PCB	% Fines	% TOC
901SJSJC9	Urban	2008	2014	76 ST↓	32.5	3.44	121	12.4	327	7.23	0.985	71.0	2.11
902SSMR07	Urban	2008	2014	103 NT	4.20		90.0	0.265	20.3	8.94 ↓	0.450	53.4	3.88
903SLRRBB	Urban	2011	2014	99 NT	0.542		101			6.19	1.28	39.9	1.11
904ESCOxx	Urban	2008	2014	83 ST	17.9	1.17	177	5.08	386	1.54	1.16	55.0	2.85
905SDSDQ9	Urban	2010	2014	80 MT	0.466	0.126	109	0.610	54.2	0.278	0	54.7	1.57
906LPLPC6	Urban	2010	2014	90 NT	172	7.46	257	27.8	392	0.122	1.02	69.5	3.11
907SDRWAR	Urban	2009	2014	91 NT	81.1	13.6	401 ↑	38.2	2010 ↑	14.1	19.7	59.0	7.04
909SWRWSx	Urban	2011	2014	73 ST	43.9	2.17	167 ↑	15.4	423	4.11	0	34.3	3.06
911TJHRxx	Urban	2008	2014	11 HT	385	1.22	348	116	213	3.28	13.7	84.7	5.65

907SDRWAR will be included in DPR surface water collaboration.

Recommendations for SPoT Monitoring in 2017-2019

SPoT is detecting trends in toxicity and current-use chemicals, particularly pesticides, thus meeting the general goals of the project. As the project has matured it has broadened its collaborations with other agencies and programs, and increased its focus on contaminants of emerging concern, such as fipronil and microcystin. Data from SPoT are increasingly important to making the link between contaminants, toxicity and impacts to the benthic macroinvertebrate community.

Following input from the SPoT Scientific Review Committee, as well as the SWAMP Round Table Strategic Planning Committee, we recommend the following items for the next reporting cycle:

- Be at the forefront of emerging pesticide trends. There is currently a gap in statewide pesticide monitoring due to the lack of a comprehensive statewide ambient water column monitoring program. The following recommendations will keep California ahead of emerging trends.
  - This includes additional sediment toxicity tests and analytical methods for early detection of emerging compounds, and should include water column toxicity monitoring to detect the effects of more soluble pesticides such as imidacloprid and other neonicotinoids.
  - A SPoT water column monitoring component will be implemented as further collaboration with the Department of Pesticide Regulation’s urban and agricultural monitoring programs.
  - Continue to strengthen communication with agencies working on this issue (U.S. EPA, DPR), as well as work groups that are addressing CECs (SCCWRP, SFEI).
  - SPoT data should be integrated into the SWRCB’s STORMS stormwater program as this program is implemented.

- Create further links between SPoT measures of toxicity and chemistry, and assessments of benthic macroinvertebrate communities.
  - SPoT is continuing to work with the Bioassessment Programs under SWAMP, the southern California Stormwater Monitoring Coalition, and initiating a collaboration with USGS for its 2017 CWQA to have synoptic bioassessment data collected at SPoT stations.

Appendix 1: Assessment Questions and Links to Water Quality Programs

The following is a summary of SPoT program elements in the context of the SWAMP Assessment Framework (Bernstein, 2010), with linkages to regulatory and resource management programs that can incorporate SPoT data. The SWAMP Assessment Framework provides guidance and context for developing question-driven monitoring to provide water quality information directly useful for resource management. The beneficial use that is assessed is aquatic life protections and the water body types that are assessed are streams that range from ephemeral creeks to large rivers. This summary states the assessment questions SPoT addresses, and lists the resource management programs to which SPoT provides essential information. Level 1 assessment questions are the highest level, as adopted by SWAMP and the California Water Quality Monitoring Council (Bernstein, 2010; page 8 and Figure 2). The Level 2 assessment questions apply to each of the two Level 1 questions.

Level 1 Assessment Questions:

A) Are our aquatic ecosystems healthy?
B) What stressors and processes affect our water quality?

Level 2 Assessment Questions for both of the Level 1 questions stated above:

1) Are beneficial uses impacted?

Management goal: Determine whether aquatic life beneficial uses in California streams are impacted by sediment-associated chemical pollutants.

Supports: 303(d) listing and 305(b) reporting

Monitoring strategy: Analyze pollutant concentrations and toxicity in sediments collected from targeted depositional areas in 100 large watersheds statewide. Compare toxicity results to narrative standards; compare chemical concentrations to available sediment quality guidelines and threshold effects values.

Certainty/precision: Analytical precision for chemical and toxicological measurements is high. Level of representativeness for all possible sites in the watersheds at all times of the year is moderate and being evaluated through integrated special studies.

Reference conditions: Five reference sites in large watersheds across the state.

Spatial scale: State of California. Results are interpreted on a statewide basis to allow perspective for local and regional analyses by partner programs.

Temporal scale: Surveys on an annual basis over an extended period (> 10 years) to evaluate long-term trends.

2) Are conditions getting better or worse?

Management goal: Determine the magnitude and direction of change in concentrations of sediment-associated chemical pollutants and toxicity.

Supports: Basin Planning, implementation of urban and agricultural management practices, permit reissuance, EPA Measure W.

Monitoring strategy: Survey stream sites in up to 100 large watersheds statewide annually for an extended period (> 10 years). Evaluate temporal trends at each site.

Certainty/Precision: Precision is evaluated through integrated special studies that survey three to four additional sites in each of a rotating subset of selected watersheds during three seasons within each year.

Reference conditions: as described above.

Spatial and Temporal Scale: as described above.

3) What is the magnitude and extent of any problems?

Management goal: Determine the number of large California watersheds potentially impacted by sediment-associated chemical pollutants and toxicity, and the magnitude of observed impairment.

Supports: 303(d), TMDL, stormwater permit monitoring, agricultural permit/waiver monitoring

Monitoring strategy: Survey stream sites in 100 large watersheds statewide; provide statewide perspective for local and regional permit and Basin Plan monitoring. Collaborate with statewide and local programs to determine upstream extent of observed impairment.

Certainty / precision: as described above.

Reference conditions: as described above.

Spatial and Temporal Scale: as described above.

4) What's causing the problem?

Management goal: Determine relationships between stream pollution and watershed land cover. Compare chemical concentrations to observed toxicity, known toxicity thresholds and guideline values.

Supports: 305(b), TMDL, Basin Planning, County land use planning, pesticide surface water regulations and DPR pesticide registration (especially for pyrethroids).

Monitoring strategy: Analyze geospatial and statistical correlations between in-stream pollutant concentrations/toxicity and land cover data extracted for the watersheds draining to the stream sites. Evaluate statistical relationships between measured chemicals and observed toxicity.

Certainty/precision: high (n = 92 for year 2008 correlation analyses).

Reference conditions: Data from reference sites included in correlation gradients.

Spatial and Temporal Scale: as described above.

5) Are solutions working?

Management goal: Relate changes in concentrations and toxicity of sediment-associated pollutants with implementation of water quality management programs and practices.

Supports: TMDL, management practice implementation programs, EPA Measure W, urban and agricultural regulatory programs.

Monitoring strategy: Compare changes in in-stream chemical concentrations and implementation of management strategies and practices.

Certainty / precision: Currently low, due to the limited amount and standardization of quantitative information on implementation of management practices statewide. Efforts are underway to support and standardize reporting of practices implemented, land area affected, volume of water treated, and effectiveness of treatment. It is anticipated that improvements in this area will improve precision of analyses to determine whether implemented solutions are effective.

Reference conditions: Reference sites provide data for watersheds in which solutions are less necessary and fewer new management practices will be implemented.

Spatial and Temporal Scale: as described above.

Appendix 2: Methods

Site Selection and Survey Timing

A number of factors were considered when selecting SPoT sites (Hunt et al., 2012). The most important factors included location in a large watershed with heterogeneous land cover; location at or near the base of a watershed, defined as the confluence with either an ocean, lake, or another stream of equal or greater stream order; and location where site-specific conditions are appropriate for the indicators selected (e.g., depositional areas, sufficient flow, appropriate channel morphology, substrate). The current 100 SPoT sites represent 58 8-digit USGS hydrologic unit code watershed in the California Region and 4 in the Great Basin Region. Availability of previous data on sediment contaminant concentrations, biological impacts, or other relevant water quality data was also an important consideration, particularly if sites could be co-located with key sites from cooperative programs. Two examples of co-location are the intensive monitoring sites currently monitored by DPR to survey current-use pesticides, and storm water sites monitored for regional MS4 NPDES monitoring programs.

The SPoT reference sites provide information on temporal trends in contamination and toxicity in the absence of any obvious sources of contaminants based on land use. Five large watersheds with relatively low levels of human activity were selected, representing the north coast, San Francisco Bay Area, Sierra foothills, coast range, and southern California inland areas. Sites in these watersheds were selected based on the criteria outlined above. Two reference sites are USGS NAWQA sites in the San Joaquin and Santa Ana River study units: Tuolumne River at Old La Grange bridge 535STC210 (San Joaquin) and San Jacinto River Reference Site 802SJCREF (Santa Ana).

SPoT surveys are timed so that sediment is collected from recent stream bed deposits during base flow periods after the high flow season, when most sediment and pollutant transport and loading take place. Fine grained sediments are targeted for sample collection. Fine sediment particles can be found in thin layers throughout the channel, or in specific areas were dominated by deep deposits of fine sediment.

In general, surveys began in coastal southern California in late spring, ran through coastal central California in early summer, the Central Valley in mid-summer, the eastern Sierra in late summer, and ended at the North Coast and Colorado River Basins in the fall. This timing has been consistent among sampling years to minimize intra-annual variation as a factor affecting long term trends.

Indicators and Parameters Measured

SPoT indicators were selected to measure contaminants previously demonstrated to be of concern in California streams, as well as assess toxicity to a benthic crustacean representing a resident genus. Indicators were chosen based on criteria outlined in the SPoT 2008 Report (Hunt et al., 2012). Based on these criteria, the following sediment indicators were selected:

1. Toxicity – 10-day growth and survival test with the representative freshwater amphipod *Hyalella azteca*, to estimate biological effects of contaminants. A 10-day growth and survival test with *Chironomus dilutus* was added to the Tier II list for the 2015 season.

2. Tier I Contaminants (measured at all sites) - Organic Contaminants (organophosphate, organochlorine, pyrethroid pesticides, and polychlorinated biphenyls (PCBs)) and Metal Contaminants - Ag, Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn. Metals, OPs, OCs and PCBs are measured bi-annually.

3. Tier II Contaminants – a subset of sediments from the most urban watersheds was also measured for polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs). Fipronil was added to the Tier II list in 2013.

4. Total organic carbon (TOC) and sediment grain size.

5. Algal Toxins - the cyanotoxin microcystin-LR was added to all sites in 2013.

Participating Laboratories and Data Storage and Management

All 2011-2012 chemical analyses and toxicity tests were performed by SWAMP laboratories: the California Department of Fish and Wildlife (DFW) Water Pollution Control Laboratory (trace organics), the Marine Pollution Studies Laboratory at Moss Landing (MPSL, trace metals), and the UC Davis MPSL at Granite Canyon (toxicity). Microcystin-LR was analyzed by Cal State University Monterey Bay (CSUMB- starting in 2013). All methods and quality assurance/quality control (QA/QC) requirements are listed in the SPoT Quality Assurance Project Plan (SPoT, 2010). The results of QA/QC measurements for the 2011-2012 surveys are provided in Appendix 3.

All data collected for this study are maintained in the SWAMP database, which is managed by the data management team at Moss Landing Marine Laboratories (http://swamp.mpsl.mlml.calstate.edu/). The complete dataset includes QA data (quality control samples and blind duplicates) and additional ancillary information (specific location information, and site and collection descriptions). The complete dataset from this study is also available on the web at http://www.ceden.org/. Data for the SPoT program can be accessed from the CEDEN query system, http://www.ceden.us/AdvancedQueryTool.

Geographic Information System Analyses

Anthropogenic contaminant concentrations in streams are influenced by the mobilization of pollutants in their watersheds. The analyses described here evaluate the strength of relationships between human activity in watersheds, as indicated by land cover, and pollutant concentrations in recently deposited stream sediment. Watershed delineations and land cover data extractions were conducted by the Geographic Information Center (GIC) at California State University, Chico (http://www.gic.csuchico.edu/index.html). The entire drainage area specific to each SPoT site was delineated using automated scripts based on digital elevation models. Each delineation file was reviewed by GIC and SPoT program staff for accuracy. Reviews included comparisons to National Hydrologic Dataset catchments, and Google Earth® images of drainage areas as kml files. Drainage areas near the site were delineated with 1 km and 5 km radius buffers to create the 1K and 5K drainage areas for analysis (along with analyses of the entire watershed area draining to each site; Figure 2). Semi-circular buffers were used because engineered drainage structures and other low-watershed features made more precise delineation impossible within the scope of this analysis.

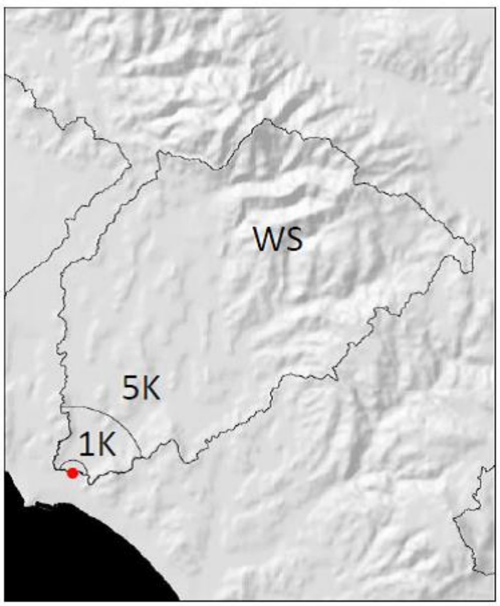

Figure 4. A depiction of watershed delineation. The red dot designates the site at the bottom of the watershed (WS, larger polygon). The semi-circular smaller areas are watershed areas 1 km (1K) and 5 km (5K) from the site.

Drainage area shape files were used to extract land cover grids from the National Land Cover Dataset (NLCD). Land use categorization followed the same criteria as the Perennial Streams Assessment (Ode et al., 2011). The following NLCD categories were used in the analyses relating land cover to water quality. “Urban” included developed open space and low, medium, and high intensity developed areas (NLCD 21, 22, 23, 24). “Agricultural” land cover was represented by pasture/hay and cultivated crops (NLCD 81 and 82). For the purposes of trend analyses by land use, pollutant concentrations were compared to continuous percent land cover data as percent urban, percent agricultural, and percent open. For analyses based on comparisons among watershed types, watershed areas were characterized as “urban” if they had greater than 25% urban cover at the 5 km scale. This characterization is in line with studies indicating stream degradation where impervious surface cover exceeds 10% (Schueler, 1994). Watershed areas were characterized as “agricultural” if they had greater than 50% cultivated crop cover. The remaining watershed areas were characterized as “other”. Three sites were categorized as both urban and agricultural (305THU, 309TDW and 558PKC005).

Toxicity Testing and Statistical Analyses

Toxicity tests with *Hyalella azteca* were conducted following U.S. EPA standard methods (U.S. EPA, 2000; SWAMP, 2008), and the toxicity of sediment samples was determined using the U.S. EPA’s test of significant toxicity-TST (U.S. EPA, 2010; Denton et al., 2011; Diamond et al., 2011). For any given year, sites that were not toxic were coded light blue, sites that were significantly toxic were coded dark blue, and sites that were highly toxic (had percent survival lower than the high toxicity threshold for *Hyalella azteca,* 38.6%) were coded dark purple (Anderson et al., 2011a). Toxicity results from multiple years were summarized using the following criteria: sites with no toxic samples were coded light blue for non-toxic, sites with at least one toxic samples was coded dark blue for some toxicity, sites with at least one sample below the high toxicity threshold were coded light purple for moderate toxicity, and sites with an average survival less than the high toxicity threshold were coded dark purple for high toxicity (see Figure 11).

Because of the large number of sites and analytes, chemicals were grouped into classes for most statistical analyses. DDTs, PCBs, PBDEs, and PAHs were summed, where appropriate, in each analyte class, in accordance with previous studies evaluating sediment quality guidelines, (Macdonald, 2000). All detected pyrethroids were summed together where indicated, and pyrethroids were also summed as carbon normalized toxic units (Amweg et al., 2005). For statistical analyses, the sum of four metals (Cd, Cu, Pb and Zn) was used as an indicator of metal contamination commonly released into the environment by human activity. These metals are less likely to be influenced by geologic abundance in California (Topping and Kuwabara, 2003; Mahler et al., 2006; Bonifacio et al., 2010).

All analyses were done using IBM SPSS Statistics Package (IBM Corporation, 2011) or Q1 Macros for Excel (KnowWare International, Inc.). Power analysis was conducted using Program MONITOR (Gibbs and Ene, 2010).

Analysis of Microcystin

Analysis of the algal toxin microcystin began in 2013 using methods developed by California State University, Monterey Bay, and adopted from Chen et al. (2006). Broadly, extraction methods included sediment homogenization and gravimetric soil moisture determination using a sediment-water slurry. Percent moisture was determined by drying sediments overnight at 100°C, and were immediately weighed following removal from oven. Dried sediment samples were then ground and homogenized with a metal spatula. Approximately 10g (exact mass recorded) from each sample was placed into amber glass bottles with 20 mL of extraction solvent (0.1M EDTA-$Na_4P_2O_7$) at pH 4. Bottles with sediment and extraction solvent were placed in an orbital shaker at 200 rpm and 22°C for 24 hours, followed by sonication for 30 seconds using a sonic dismembrator with an ultrasonic converter (Fisher Scientific). Samples were decanted into glass centrifuge tubes and centrifuged at 13,000 rpm for two minutes to settle residual particulate matter. Samples were then analyzed with competitive enzyme-linked immunosorbent assay (ELISA, Envirologix). In 2014, the methods were further adapted to include solid phase extraction columns (Waters Sep-Pak) on the supernatant as an additional clean up step.

Appendix 3: Toxicity Threshold Evaluation Concentrations

Chemical	Type	Unit	Concentration	Reference
Pyrethroid Pesticides				
Bifenthrin	LC50	ng/g	12.9	(Amweg et al., 2005)
Bifenthrin OC	LC50	µg/g OC	0.52	(Amweg et al., 2005)
Cyfluthrin	LC50	ng/g	13.7	(Amweg et al., 2005)
Cyfluthrin OC	LC50	µg/g OC	1.08	(Amweg et al., 2005)
Cyhalothrin, Lambda	LC50	ng/g	5.6	(Amweg et al., 2005)
Cyhalothrin, Lambda OC	LC50	µg/g OC	0.45	(Amweg et al., 2005)
Cypermethrin	LC50	ng/g	14.9	(Maund et al., 2002)
Cypermethrin OC	LC50	µg/g OC	0.38	(Maund et al., 2002)
Deltamethrin/Tralomethrin	LC50	ng/g	9.9	(Amweg et al., 2005)
Deltamethrin/Tralomethrin OC	LC50	µg/g OC	0.79	(Amweg et al., 2005)
Esfenvalerate/Fenvalerate	LC50	ng/g	41.8	(Amweg et al., 2005)
Esfenvalerate/Fenvalerate OC	LC50	µg/g OC	1.54	(Amweg et al., 2005)
Fenpropathrin	LC50	ng/g	177	(Ding et al., 2011)
Fenpropathrin OC	LC50	µg/g OC	8.9	(Ding et al., 2011)
Permethrin	LC50	ng/g	201	(Amweg et al., 2005)
Permethrin OC	LC50	µg/g OC	10.9	(Amweg et al., 2005)
Fipronil Pesticides				
Fipronil	LC50	ng/g	306	(Ma, 2006)
Fipronil OC	LC50	µg/g OC	9.3	(Ma, 2006)
Fipronil Sulfide	LC50	ng/g	435	(Ma, 2006)
Fipronil Sulfide OC	LC50	µg/g OC	14	(Ma, 2006)
Fipronil Sulfone	LC50	ng/g	158	(Ma, 2006)
Fipronil Sulfone OC	LC50	µg/g OC	4.7	(Ma, 2006)
Organophosphate Pesticides				
Chlorpyrifos	LC50	ng/g	399	(Brown et al., 1997)
Chlorpyrifos OC	LC50	µg/g OC	1.77	(Amweg and Weston, 2007)
Diazinon	LC50	ng/g	1085	(Ding et al., 2011)
Diazinon OC	LC50	µg/g OC	54.6	(Ding et al., 2011)
Organochlorine Pesticides				
Sum DDT	LC50	ng/g	11000	(Nebeker et al., 1989)
Sum DDT OC	LC50	µg/g OC	367	(Nebeker et al., 1989)
Sum Chlordane	PEC	ng/g	17.6	(Macdonald, 2000)

Chemical	Type	Unit	Concentration	Reference
DDD (o,p') OC	LC50	µg/g OC	1300	(Weston et al., 2004)
DDE (o,p') OC	LC50	µg/g OC	8300	(Weston et al., 2004)
Dieldrin OC	LC50	µg/g OC	2000	(U.S. EPA, 2003)
Endrin	LC50	ng/g	4400	(Nebeker et al., 1989)
Endrin OC	LC50	µg/g OC	147	(Nebeker et al., 1989)
Heptachlor Epoxide	PEC	ng/g	16	(Macdonald, 2000)
Methoxychlor OC	LC50	µg/g OC	85.8	(Weston et al., 2004)
PAHs				
Sum PAH OC	LC50	µg/g OC	1800	(Swartz, 1999)
Anthracene	PEC	ng/g	845	(Macdonald, 2000)
Benz(a)anthracene	PEC	ng/g	1050	(Macdonald, 2000)
Benzo(a)pyrene	PEC	ng/g	1450	(Macdonald, 2000)
Chrysene	PEC	ng/g	1290	(Macdonald, 2000)
Fluoranthene OC	LC50	µg/g OC	1077	(Suedel et al., 1993)
Fluorene	PEC		536	(Macdonald, 2000)
Naphthalene	PEC		561	(Macdonald, 2000)
Phenanthrene	PEC		1170	(Macdonald, 2000)
Pyrene	PEC		1520	(Macdonald, 2000)
PCBs				
Sum PCB	LC50		400	(Macdonald et al., 2000)
Metals				
Arsenic	LC50		532	(Liber et al., 2011)
Cadmium	LC50		170	Chen et al Unpublished Data
Chromium	PEC		111	(Macdonald, 2000)
Copper	LC50		260	MPSL Unpublished Data
Lead	PEC		128	(Macdonald, 2000)
Mercury	PEC		1.06	(Macdonald, 2000)
Nickel	LC50		521	(Liber et al., 2011)
Zinc	PEC		459	(Macdonald, 2000)

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