Trends in Chemical Contamination, Toxicity and Land Use in California Watersheds:

Stream Pollution Trends (SPoT) Monitoring Program Third Report - Five-Year Trends 2008-2012

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List of Acronyms

- BMI: Benthic Macroinvertebrate
- BOG: Bioassessment Oversight Group that directs the SWAMP bioaccumulation monitoring program
- CDPR: California Department of Pesticide Regulation
- 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
- 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 flameretardants. 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 [\(Macdonald, 2000\)](#page-61-0).
- PSA: Perennial Streams Assessment. The SWAMP statewide program measuring ecological indicators at probabilistically selected sites in California streams.
- RMC: Regional 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

Executive Summary

The Stream Pollution Trends (SPoT) program conducts statewide monitoring to provide information needed 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.

The SPoT program is specifically designed to fill critical information needs for state, regional and local resource management programs, including Clean Water Act §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 also remains adaptive by monitoring 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 tend to integrate contaminants transported from land surfaces throughout the drainage area, and 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.

Toxicity of sediments was assessed using the amphipod *Hyalella azteca*, which represents a genus found throughout California watersheds. The percentage of sediments toxic to amphipods remained relatively consistent among the sampling years represented in this report, and averaged 19%.

Detections and concentrations of currently used pyrethroid pesticides continue to increase in California watersheds, primarily those with the highest percentage of urban land use. While the trend data do not show an increase in the incidence of sediment toxicity when testing is conducted at the standard protocol temperature, the incidence of toxicity greatly increased in a subset of sites when tests were conducted at a temperature that more closely reflects the ambient temperature in California watersheds (~15°C). Higher toxicity at colder temperature is diagnostic of toxicity due to pyrethroid pesticides. 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.

While organochlorine compounds, such as PCBs and the legacy pesticide DDT continued to be detected in many of the state's watersheds, the concentrations have always been below those demonstrated to cause toxicity to *H. azteca*. These chemicals continue to be of concern in California because of their potential to bioaccumulate. While concentrations in fish do not often exceed thresholds of concern [\(Davis et al.,](#page-60-0) [2013\)](#page-60-0), numerous fish consumption advisories have been issued for lakes, rivers, bays, and coastal areas due to these contaminants. PBDEs also are not acutely toxic to *H. azteca*, but have potential to bioaccumulate in the environment, and may affect human health. These chemicals did not exhibit any significant trends at the statewide level, or by land use, and although PDBEs are in the process of being phased out in California, SPoT will continue to measure them to document the potential decreasing trend. Concentrations of metals in sediments were relatively stable, and selected metal concentrations were 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.

In a recent summary of SWAMP surface water toxicity testing conducted between 2001 and 2010, Anderson et al. (2011) showed that approximately 45 to 50% of the sites monitored by State Water Resources Control Board programs demonstrated some water or sediment toxicity. Correlation and toxicity identification evaluation studies showed that the majority of toxicity was associated with pesticides, specifically organophosphate and pyrethroid pesticides. The results of SPoT monitoring corroborate these findings.

Given the evidence that pesticides are associated with ambient toxicity in California waters, certain emerging pesticides were prioritized for inclusion in the SPoT analyte list. The phenylpyrazole insecticide fipronil was measured in urban watersheds in 2013, and the neonicotinoid imidacloprid will likely be added in the coming years. Because SPoT utilizes toxicity testing, in part, to monitor for emerging chemicals of concern, in 2015 the program will test with an additional organism that is more sensitive to fipronil, imidacloprid, and their degradates. In collaboration with California State University Monterey Bay, the program also began statewide monitoring of algal toxins in sediment

in 2013. 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.

An assessment 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 correlation between amphipod survival in laboratory toxicity tests and the Index of Biological Integrity (IBI) calculated from the bioassessments. This analysis also revealed a significant negative correlation with contaminant concentrations, particularly pyrethroid pesticides. The IBI was also negatively correlated with some habitat parameters. As more benthic macroinvertebrate data are incorporated into the databases, a more detailed assessment of these relationships will be possible. These statistical relationships provide a basis for developing hypotheses for assessing causal relationships between in-stream ecological degradation and toxicity and chemical stressors.

Based on SPoT's statewide coverage, the program is positioned to detect changes in toxicity and contamination in California watersheds as management actions are implemented. For example, SPoT is collaborating with the California Department of Pesticide Regulation to determine if use restrictions and outreach to professional pesticide applicators result in a decline in sediment-associated pyrethroids in urban watersheds. SPoT sites and data also are used by several Regional Water Boards to detect and monitor trends in stream contaminant concentrations and effects. The SPoT program will provide data on the effectiveness of urban and agricultural management practices, such as low impact development and vegetated buffer zones, and will track source controls, such as the phase-out of copper in vehicle brake pads.

The data presented in this report describe the baseline condition for the SPoT long-term trends assessment. 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. Analysis of five years of SPoT data has suggested that elements of the program should be adjusted in coming years to accommodate the evolving data needs of water quality managers. Suggested revisions include the strategic addition of contaminants of emerging concern as they are identified, and the concomitant de-emphasis of legacy contaminants that pose less of an environmental threat to California watersheds. The program is also revising the number and frequency of statewide stations monitored to maximize its ability to address key management questions concerning contaminants that pose the greatest risk to California's surface waters.

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 quality 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 a 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. Most 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 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 takes place. It should be noted that SPoT has been discussing the possibility of expanding the program to include water column monitoring. This is intended to address newer classes of pesticides which, based on their high solubility, would not be expected to partition to sediments.

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\)](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 low watershed areas. A targeted approach allows SPoT flexibility to link to established sites and to support collaboration with watershed-based monitoring programs.

Coordination and Collaboration with other Programs

The SPoT network of sites was established through coordination with Regional Board monitoring coordinators 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 \(Bay](#page-59-1) [Area Stormwater Agencies Association\), 2011\)](#page-59-1). 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 (Appendix 2). 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".

SPoT is one of three 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 have different assessment questions from those of SPoT. While all three programs seek to measure aquatic ecosystem health on a statewide level, the PSA uses probabilitybased 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 stressors are related to the biological condition [\(Ode et](#page-62-0) [al., 2011\)](#page-62-0). Other than nutrients, the PSA program does not measure chemical contaminants. The focus of BOG is on fishing as a beneficial use [\(Davis et al., 2013\)](#page-60-0). 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 have been exceeded. SPoT also uses a targeted sampling design to revisit the same sites yearly. This design allows for succinct trend analysis, and allows the program to detect emerging chemicals through consistent use of toxicity testing. BOG focuses on chemicals that bioaccumulate, such as mercury and PCBs.

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 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. SPoT complements the BOG by identifying watershed sources for contaminants measured in fish from downstream waterways. The BOG complements SPoT by providing perspectives on the fate and human health aspects of pollutants in streams, particularly as related to their uptake in fish tissue and risk associated with human consumption. 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.

More recently, SPoT has been working with the California Department of Pesticide Regulation (DPR) to increase monitoring at four sites to capture short-term trends in the reduction of pyrethroids. DPR recently implemented regulations to reduce the quantity of pyrethroids applied by professional applicators on impervious surfaces in urban areas. Funding provided by DPR has enabled SPoT to increase monitoring at two base stations, and add two DPR stations to the program. The four stations are monitored four times per year for sediment toxicity, as well as pyrethroid and fipronil concentrations in sediment. This intensive monitoring began in 2013 and initial results will be discussed in the next report. It is anticipated that additional toxicity testing with the chironomid *Chironomus dilutus* will be included to account for fipronil toxicity at the most urban (Tier II) sites in 2015.

In 2013 SPoT began monitoring cyanotoxins from cyanobacteria to provide statewide baseline data for this class of contaminants in sediment. Cyanobacteria blooms are expected to increase due to nutrient enrichment, warming surface water temperatures and extreme weather associated with climate change. Microcystins are a class of potent cyanotoxins occurring primarily in freshwater environments. California State University Monterey Bay (CSUMB) researchers analyzed SPoT sediments for microcystin-LR. Microcystin-LR, the most toxic and often most common variant of microcystin, was identified in 77% of the 83 samples analyzed. This is the first statewide survey of microcystin presence in California sediments. This monitoring also began in 2013 and initial results will be discussed in the next report.

SPoT was specifically designed to provide data that can inform regulatory programs and conservation initiatives. SPoT data can be 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 409 manually generated lines of evidence from the SPoT data set.

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 five 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. Methods and quality assurance sections cover the 2011 and 2012 sampling seasons. The focus of the current report is on fiveyear trends in toxicity and chemical measurements as they relate to land use, but the combined Results and Discussion sections cover six topics: contaminant trends related to land use, toxicity trends related to land use and contaminants, SPoT indicators in relation to stream ecology, regional trends summarized based on individual Regional Board coverage, statistical relationships among SPoT parameters, and evaluation of the current program design. These data will inform evolution of the next several years of the program.

Methods

Site Selection and Survey Timing

SPoT has surveyed 92 to 100 sites in four of the five years covered in this report. SPoT program funding was greatly reduced in 2009 and only 23 sites were sampled. Full funding was restored in 2010, and 95 stations were surveyed, followed by 100 in both 2011 and 2012 (Figure 1, Appendix 2). In 2009 sites were chosen based on several factors: input from Regional Boards and regional representation, inclusion of reference sites, and some focus on known toxic locations.

A number of factors were considered when selecting SPoT sites [\(Hunt et al., 2012\)](#page-61-1). 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 eight-digit USGS hydrologic unit code watershed in the California Region and four 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 CDPR to survey current-use pesticides, and storm water sites monitored for regional MS4 NPDES monitoring programs.

During sample collection at most SPoT sites, fine sediment particles were found in thin layers throughout the channel. Some sites were dominated by deep deposits of fine sediment. At many sites, however, there were fewer 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.* (2010) mapped fine sediment distributions at 99 transects in three California streams, each designated as agricultural, urban or residential. They estimated that an average of 17% of the stream bed was characterized as "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 metric for evaluating annual trends.

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 (Figure 1). 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. 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.

Figure 1. 2012 SPoT sites (black circles), reference sites (green circles), and land use categories.

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 [\(Hunt et al., 2012\)](#page-61-1). 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;
- 2. Tier I Contaminants Organic Contaminants (organophosphate, organochlorine, pyrethroid pesticides, and polychlorinated biphenyls (PCBs)) and Metal Contaminants - Ag, Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn;
- 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 [\(SPoT, 2010\)](#page-63-0). 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 [\(http://swamp.mpsl.mlml.calstate.edu/\)](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/.](http://www.ceden.org/) Data for the SPoT program can be accessed from the CEDEN query system, [http://www.ceden.us/AdvancedQueryTool.](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](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 2. 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, depicted with different colors in Figure 1). The following NLCD categories were used in the analyses relating land cover to water quality. "Urban" (NLCD 22, 23, 24) included low, medium, and high intensity developed areas. "Agricultural" land cover was represented by cultivated crops (NLCD 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 20% urban cover (NLCD categories 22+23+24) at the 5 km scale. This characterization is in line with studies indicating stream degradation where impervious surface cover exceeds 10% [\(Schueler,](#page-63-1) [1994\)](#page-63-1). Watershed areas were characterized as "agricultural" if they had greater than 20% cultivated crop cover (NLCD 82). Watershed areas were characterized as "open" if they had greater than 50% combined undeveloped space (forest, wetland, shrub, barren and grassland). One site could not be defined by these criteria (603BSP002), but was considered open based on land use in the larger watershed. Thirteen sites were placed in more than one category (Table 1). It was difficult to isolate purely open watersheds at any scale. In 2012, at the 5 km scale, seven watersheds were classified as open combined with agriculture or urban, including one reference site. Six sites were defined as both agriculture and urban.

Table 1. Number of stations sampled in each 5 km land use category.

Toxicity Testing and Statistical Analyses

Toxicity tests with *Hyalella azteca* were conducted following U.S. EPA standard methods [\(U.S. EPA, 2000;](#page-63-2) [SWAMP, 2008\)](#page-63-3), and the toxicity of sediment samples was determined using the U.S. EPA's test of significant toxicity-TST [\(U.S. EPA, 2010;](#page-63-4) [Denton et al., 2011;](#page-60-1) [Diamond et al., 2011\)](#page-60-2). 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 [\(Anderson et al., 2011\)](#page-59-2). 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, [\(Macdonald, 2000\)](#page-61-0). All detected pyrethroids were summed together where indicated, and pyrethroids were also summed as carbon normalized toxic units [\(Amweg et al., 2005\)](#page-59-3). 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 [\(Topping and Kuwabara, 2003;](#page-63-5) [Mahler](#page-62-1) [et al., 2006;](#page-62-1) [Bonifacio et al., 2010\)](#page-60-3).

Multivariate principal components analysis was used for all statistical evaluations of relationships between toxicity, pollutants, and land cover. The analysis was run with a correlation matrix and varimax rotation, and included any factors which accounted for greater than 10% of the total variance. A component loading cutoff value of 0.50 was used in selecting variables for inclusion into factors [\(Tabachnick and Fidell, 1996\)](#page-63-6). Statewide trends within each land use were analyzed using one-way analysis of variance. 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 [\(Gibbs et al., 2010\)](#page-60-4).

Results and Discussion

Physical and Chemical Trends Related to Land Use

The SPoT program is designed to detect long-term changes in watershed contaminants and toxicity as they relate to changes in land use. After five years of monitoring, several clear trends are emerging in California surface waters monitored by SPoT. The following box plots divide toxicity and chemical concentrations among the three primary land uses described above. Analysis of variance was used to determine if concentrations were significantly increasing or decreasing based on the mean concentration and the variability among concentrations within the land use categories. Furthermore, multivariate analysis was used to investigate the relationships among toxicity, sediment chemical concentrations and land use.

Sediment collection for SPoT emphasizes collecting fine-grained depositional sediments, as many contaminants associate with the smaller size fraction (<63 µm), which accumulate in low energy depositional areas. Fine sediment particles 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 microhydrological 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.

While field teams strive to collect the finest-grained material available, a number of samples were composed primarily of grains larger than 63 µm (Figure 3) because finegrained material was not available. There was a significant decrease in the overall amount of fine-grained sediments collected between 2008 and 2012 ($p = 0.036$). This overall trend was driven by a significant decrease in percent fines collected at urban $sites (p = 0.031).$

Field teams also avoid or remove conspicuous debris, including leaves and other large organic material. Total organic carbon (TOC) content cannot be readily determined in the field, and the sampling protocol has no set 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 4).

Figure 3. Percent fines versus land use. Boxes represent first and third quartiles, line represents median, and t-bars 1.5 times the inter-quartile range. Additional points are outside of the inter-quartile range.

Figure 4. Total organic carbon versus land use. Boxes represent first and third quartiles, line represents median, and t-bars 1.5 times the inter-quartile range. Additional points are outside of the inter-quartile range.

Figure 5. Total pyrethroids versus land use. Boxes represent first and third quartiles, line represents median, and t-bars 1.5 times the inter-quartile range. Additional points are outside of the inter-quartile range.

Figure 6. Total PAHs versus land use at Tier II sites. Boxes represent first and third quartiles, line represents median, and t-bars 1.5 times the inter-quartile range. Additional points are outside of the interquartile range.

Figure 7. Total PBDEs versus land use at Tier II sites. Boxes represent first and third quartiles, line represents median, and t-bars 1.5 times the inter-quartile range. Additional points are outside of the interquartile range.

Figure 8. Organochlorine compound trends. Boxes represent first and third quartiles, line represents median, and t-bars 1.5 times the inter-quartile range. Additional points are outside of the inter-quartile range.

Figure 9. Sum of cadmium, copper, lead and zinc versus land use. Boxes represent first and third quartiles, line represents median, and t-bars 1.5 times the inter-quartile range. Additional points are outside of the inter-quartile range.

Pyrethroid pesticides demonstrated a significant increasing trend throughout the state (p = 0.004, Figure 5), likely driven by a significant increasing trend in urban watersheds. (p = 0.004). There were no significant pyrethroid trends in agricultural or open watersheds. Bifenthrin was the most commonly detected pyrethroid and was measured in 69% of the samples collected between 2008 and 2012. The remaining pyrethroids were detected in 19% to 39% of the samples, depending on the specific pyrethroid. There are two possible explanations for the increased detections of bifenthrin in these samples. One is that of all the pyrethroids, bifenthrin is the most stable in aquatic environments. At 20 °C, bifenthrin has an aerobic half-life in sediment ranging from 12 to 16 months. The half-life range is 25-65 months at 4 °C, and anaerobic half lives are much longer [\(Gan et al., 2005\)](#page-60-5). Statewide bifenthrin use reported to the California Department of Pesticide Regulation increased between 2008 and 2012. The total pounds of active ingredients applied went from 120,089 pounds in 2008 to 285,941 pounds in 2012, with a peak of 354,390 pounds in 2010 (www.cdpr.ca.gov/docs/pur/purmain.htm).

PAHs and PBDEs were only measured in SPoT samples from Tier II sites, mostly in urban watersheds, but with some sites in agricultural and open watersheds (Figures 6 and 7). Concentrations of these chemical classes were higher in urban watersheds, but remained consistent throughout the study period with the exception of a significant decrease in PAHs in open watersheds ($p = 0.027$, Figure 6).

The concentrations of the chlorinated compounds (DDTs and PCBs) significantly decreased during the sampling period (Figure 8). Significant downward trends were noted in watersheds from each land use, as well as statewide ($p = 0.000 - 0.017$). It is interesting to note that the concentrations in 2008 and 2009 were much higher than those measured in 2010, 2011 and 2012. Laboratory reporting limits were higher during these years, but the difference in analytical reporting did not account for the downward trend the magnitude of detections significantly decreased over the five years. Because of the sharp decrease in concentrations between 2009 and 2010, additional sampling year data are necessary before these trends can be confirmed.

Trace metals were measured in both whole sediments and sediments sieved to less than 63 µm. Because trace metals bind preferentially to smaller sediment size fractions, particularly clays, it was suggested at the program's initiation that sieving sediments would allow for a better comparison of metal concentrations across watersheds by reducing the effects of grain size differences. Relative differences of metals in sieved and unsieved samples were compared to determine the benefit of this additional analysis to the SPoT program in detecting long term trends. Because of high variability observed in metals concentrations measured among years, and because of the high variability in results between sites, it was determined that sieved metals do not provide additional information beyond the results of the bulk metals analysis [\(Anderson et al.,](#page-59-4) [2012\)](#page-59-4).

There were no significant upward or downward trends in the sums of Cd, Cu, Pb, and Zn from unsieved samples based on statewide analysis or analysis by land use (Figure 9). While these metals are considered to be representative of human, rather than natural inputs, their concentrations are not equally weighted. Zinc concentrations drive the box plots in Figure 9 with concentrations approximately three times greater than copper. Copper concentrations are approximately twice those of lead, whereas cadmium concentrations average less than 0.5 µg/g. Individually, copper did not exhibit a significant statewide trend (data not shown), although continued monitoring of this metal will be important to determine the effectiveness of the reduced use of copper in automobile brake pads. This may be more apparent in urban watersheds so the possibility of this trend will be investigated in subsequent reports. Similarly, the mean concentrations of mercury in sediments were largely unchanged over the sampling period (data not shown). Mercury bioaccumulates in higher trophic level organisms and has been identified as one of the primary contaminants of concern in coastal sport fish tissues monitored by SWAMP's Bioassessment Oversight Group (BOG) [\(http://www.swrcb.ca.gov/water_issues/programs/swamp/coast_study.shtml\)](http://www.swrcb.ca.gov/water_issues/programs/swamp/coast_study.shtml). Mercury in sediment demonstrated high statewide variability, and specific sites in highly urbanized regions had the highest concentrations.

Detections and concentrations of organophosphate pesticides in sediment decreased between 2008 and 2012. Chlorpyrifos was detected in 12% of SPoT sites in 2008 and only 1 out of 23 sites sampled in 2009. No chlorpyrifos was detected in 2010, but one sample from 2011 contained this chemical. Analysis of chlorpyrifos use through the Department of Pesticide Regulation showed an 18% decrease in use of chlorpyrifos between 2008 and 2012 (www.cdpr.ca.gov/docs/pur/purmain.htm). It is likely that reductions in chlorpyrifos detections are related to regulatory controls implemented by the EPA and DPR (e.g., regulatory actions to minimize spray drift).

Summary of Contaminant Trends

The trend data show a statewide decrease in the organochlorine compounds DDT and PCBs, whereas several other chemical classes showed no significant change (Table 2). Some chemicals that showed no change at the statewide level did exhibit significant upward or downward trends at individual sites, including metals, PAHs, and PBDEs. Use of PBDE flame retardants is being restricted in California and changes in sediment concentrations of this class of chemicals will be the subject of continued SPoT monitoring in Tier II watersheds.

Table 2. Summary of trends at a statewide level, trends related to land use, and trends at individual sites.

Detections and concentrations of the pyrethroid pesticides continue to increase in California watersheds. While the data do not show an increase in the incidence of sediment toxicity when testing is conducted at the standard protocol temperature, the incidence of toxicity within years was greatly increased in a subset of sites when tests were conducted at a temperature that more closely reflects the ambient temperature in California watersheds (~15 °C, see below). Higher toxicity at colder temperature is diagnostic of toxicity due to pyrethroid pesticides, and the pattern of increasing detections of pyrethroids coupled with increasing toxicity in SPoT samples when tests are conducted at colder temperature suggests that current monitoring may underestimate the occurrence of pyrethroid-associated toxicity using the standard protocol.

Management Actions and Anticipated Future Trends

California regulatory agencies recognize the role pesticide contamination plays in degradation of state waters and are now implementing plans to address sources of specific current-use pesticides. For example, the DPR implemented use restrictions for pyrethroid pesticides used by pest control businesses in urban settings and is providing outreach to pesticide applicators to instruct proper application techniques on impermeable surfaces. These are intended to reduce the mass of active ingredients applied and to minimize off-site runoff into stormwater systems and adjacent watersheds. DPR also plans on following urban restrictions with regulations to address agricultural use of pyrethroids affecting surface water quality. The U.S. EPA is also requiring label changes for pyrethroid products to reduce their impact on surface water quality [\(http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2008-0331-](http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2008-0331-0021)) [0021\).](http://www.regulations.gov/#!documentDetail;D=EPA-HQ-OPP-2008-0331-0021)) SPoT is collaborating with DPR to monitor additional sites with greater intensity to determine if these regulations result in a decline in sediment-associated pyrethroids in urban watersheds.

In urban areas, municipal stormwater (MS4) NPDES permitting requires numerous management practices to reduce pollutant and sediment discharges. For example, incorporation of Low Impact Development practices on future construction projects is being required throughout the state. Statewide source controls have also been implemented in a few specific cases, e.g., the phase out of copper in vehicle brake pads, and prohibitions on use of lead in wheel weights and brake pads.

In agricultural areas, management actions requiring on-farm practices to reduce pollutants in runoff and in some cases to treat runoff are being incorporated into Water Board irrigated lands programs. For pesticides, in addition to restrictions on pounds of pesticide active ingredients applied per acre and number of applications per crop, growers are receiving recommendations, and in some cases requirements, for vegetated buffer zones and setbacks to limit the potential for off-field transport of pesticides in spray drift, irrigation and stormwater runoff.

Based on SPoT coverage of 62 8-digit hydrologic units, and the intensive sampling efforts conducted in partnership with DPR, the program is positioned to detect changes in pyrethroid contamination in California watersheds as these management actions are implemented. SPoT data provide water resource managers with short and long term readings of how effective use restrictions are in reducing contamination. Addition of emerging contaminants of concern to the SPoT analyte list will allow the program to evolve to address issues related to introduction of new chemicals in California watersheds.

Toxicity Trends Related to Land Use

The incidence of sediment toxicity has remained relatively stable between 2008 and 2012 (Table 3). The percentage of toxic and highly toxic samples increased in 2009, but this likely reflects the reduced sample size during that year and the increased weighting toward urban sites. The majority of toxic and highly toxic sites were located in urban areas (lower survival depicted in Figure 10). Highly toxic samples were collected from fifteen separate sites over the last five years. Eight of these sites were solely urban, and two were classified as urban/agriculture. Four sites were from agricultural watersheds, and one was classified as a combination of agriculture and open space. The locations of these sites were mostly in the southern California regions. There were no significant upward or downward trends in toxicity at urban or agricultural sites, but there was a significant decrease in toxicity at open sites ($p = 0.015$, Figure 3). Sitespecific trends in toxicity are discussed in the regional summaries provided below.

Figure 11 depicts a five-year average of toxicity in the SPoT program. Sixty-six percent of the stations tested to date have not had a single toxic sample, whereas 34% have demonstrated at least some toxicity. The long-term trend can be illustrated by tracking a running average of five years of data.

Table 3. SPoT sediment toxicity trends in tests conducted at 23 °C from 2008-2012. Toxicity was determined based on the Test for Significant Toxicity (TST), and highly toxic sites had percent survival lower than the high toxicity threshold for *Hyalella azteca* (38.6%).

Figure 10. Survival in toxicity tests versus land use. Boxes represent first and third quartiles, line represents median, and t-bars 1.5 times the inter-quartile range. Additional points are outside of the interquartile range.

Mean Magnitude of Toxicity 2008 - 2012

Figure 11. Five-year average of toxicity in the SPoT program.

The Relationship of Toxicity to Chemical Thresholds and Sediment Guideline Values

The relationships between amphipod mortality and sediment chemical concentrations are investigated with multivariate analysis described below. 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 *Hyalella 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 [\(Macdonald, 2000\)](#page-61-0). 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 [\(Macdonald,](#page-61-0) [2000\)](#page-61-0). The PEC provides some predictive ability, but is not derived from direct doseresponse experiments. Forty-nine threshold values for thirty-seven individual chemicals and sums were used to evaluate several chemical classes including pyrethroid pesticides, organochlorine pesticides, organophosphate pesticides, PAHs, PCBs, and metals. Twelve of these chemicals and sums were also evaluated with organic carboncorrected 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 pesticide 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 [\(Phillips et al., 2011\)](#page-62-2). Trace metal concentrations exceeded PECs at many sites, but it is unlikely these concentrations contributed to observed toxicity to *Hyalella 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 μ g/g). This was also true for arsenic (PEC = 33 μ g/g; LC50 = 532 μ g/g), and for nickel (PEC = 48.6 μ g/g; LC50 = 521 μ g/g). Chromium most often exceeded the PEC, but it is unlikely this metal is contributing to toxicity [\(Besser et al., 2004\)](#page-60-6). 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 [\(Bonifacio et al., 2010\)](#page-60-3). 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 collected between 2008 and 2012. Most of the elevated concentrations were for the pyrethroid pesticide 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 the LC50 value. 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 [\(Weston et al., 2005\)](#page-64-0). 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 [\(Maund et al., 2002\)](#page-62-3), and normalizing concentrations to TOC account for the relative effect of this sediment constituent on toxicity. Although there was a significant correlation between organic carbon-corrected TUs and percent survival (p < 0.001, Figure 12), there were five samples with a toxic unit sum greater than 5 that were not toxic or moderately toxic (Figure 12). 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 carbon at these sites has 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 [\(Kukkonen et al., 2005\)](#page-61-2).

Figure 12. 2008-2012 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.

Further Diagnosing the Contribution of Pyrethroids to Toxicity

The standard U.S. EPA protocol for *Hyalella azteca* specifies the test be conducted at 23 °C. It has long been recognized that some pyrethroid pesticides are more toxic at colder temperatures [\(Coats et al., 1989\)](#page-60-7), and this characteristic has been used as a TIE tool to diagnose pyrethroid-associated toxicity [\(Anderson et al., 2008\)](#page-59-5). A similar response to cold temperature was observed with DDT, but to a lesser extent [\(Weston et](#page-63-7) [al., 2009\)](#page-63-7). In a SWAMP statewide study of urban creek toxicity, Holmes et al. used this attribute to help identify pyrethroids as the likely cause of toxicity to *H. azteca* [\(Holmes](#page-61-3) [et al., 2008\)](#page-61-3). Increasing toxicity with decreasing temperature has been demonstrated specifically with *H. azteca* in more recent studies (Weston [et al., 2009\)](#page-63-7), and also with chironomids [\(Harwood et al., 2009\)](#page-61-4). Harwood et al. (2009) showed this is due to slower metabolic breakdown of pyrethroids at lower temperatures and increased nerve sensitivity.

The average statewide surface water temperature was calculated for water samples collected in SPoT hydrologic units as part of various SWAMP surveys. Samples represented daytime temperatures measured at depths less than 0.1 m as part of SWAMP routine monitoring, which was conducted during all months of the year (Cassandra Lamerdin, Moss Landing Marine Laboratories, personal communication). The average temperature for data collected between 2001 and 2010 was 15.8 °C, considerably lower than the standard test temperature (23 °C). Average temperatures ranged from a low of 9.7 °C in Region 6 to a high of 20.7 °C in Region 7. Since 2010, temperature effects were evaluated using a subset of SPoT stations. Tests were

conducted at the standard 23 °C and also at 15 °C, to help diagnose toxicity due to pyrethroids. In addition, the 15 °C test temperature assesses toxicity at a more environmentally relevant temperature for California surface waters [\(Anderson et al.,](#page-59-4) [2012\)](#page-59-4).

Tests of samples from the SPoT base stations demonstrate that significantly more samples were toxic when tested at 15 °C, and the magnitude of toxicity was much greater at the lower test temperature (Table 4). Samples were approximately 2-3 times more likely to be toxic when tested at 15 °C. When the results of the 15 °C tests are plotted against toxic units as in Figure 12, it is apparent that the TU threshold has shifted to a lower value, indicating that less pyrethroid is necessary to create the same toxic response (Figure 13). These results suggest that pyrethroid pesticides likely played a role in the increased incidence of toxicity in these samples. Although DDT can cause a similar response at colder temperatures, the concentrations of DDT in the sediment 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).

Table 4. Comparison of percent survival in samples tested at 23 °C and 15 °C.

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 [\(Ingersoll et al., 2005\)](#page-61-5). Because the more photo stable pyrethroids (e.g., bifenthrin) may persist for over a year, the potential for chronic impacts of these pesticides on California watersheds are also likely underestimated by SPoT results. MPSL 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. Previous studies have shown that growth after 28d exposure in the longer-term protocol is a more sensitive endpoint. It is not clear whether the longer-term protocol is appropriate for future SPoT monitoring.

Figure 13. 2010-2012 toxicity data from 15 °C tests plotted against the sum of pyrethroid toxic units corrected for organic carbon. See text for explanation of toxic units and organic carbon correction.

Chemicals of Concern

In a recent summary of SWAMP surface water toxicity testing conducted between 2001 and 2010, Anderson et al. (2011) showed that approximately 45 to 50% of the sites monitored by SWRCB programs demonstrated some water or sediment toxicity. Correlation and toxicity identification evaluation studies showed that the majority of toxicity was associated with pesticides, specifically organophosphate and pyrethroid pesticides. The current SPoT results corroborate these findings. Previous analysis of SPoT data found that sediment toxicity was highly correlated with pyrethroid concentrations in sediment [\(Anderson et al., 2012;](#page-59-0) [Hunt et al., 2012\)](#page-61-0). There has been a steady decline in organophosphate pesticide concentrations detected in SPoT samples, including a statewide decline in the detections of chlorpyrifos. However, chlorpyrifos continues to be associated with sediment toxicity in certain agriculture regions of the state, such as the central coast [\(Phillips et al., 2012\)](#page-62-0).

Given the evidence that pesticides are associated with ambient toxicity in California waters, certain emerging pesticides were prioritized for inclusion in the SPoT analyte list as monitoring proceeds. For example, recent regional monitoring has suggested an increase in the detection of the phenylpyrazole insecticide fipronil and its degradates in urban watersheds [\(Gan et al., 2005;](#page-60-0) [Holmes et al., 2008\)](#page-61-1). Because of increasing use and the potential for surface water toxicity due to fipronil, this pesticide was measured at Tier II sites in 2013. It should be noted that the current SPoT test organism, *H. azteca*, is approximately 20 times less sensitive to fipronil and its degradates than another commonly used freshwater sediment test organism, *Chironomus dilutus* [\(Weston and](#page-64-0)

[Lydy, 2014\)](#page-64-0). This is an important point to consider for future monitoring. Because SPoT uses toxicity testing, in part, to monitor for emerging chemicals of concern, the program will need to be adaptive in its future choices for test organisms. This will require some re-alignment of funding for existing contaminant monitoring and a revision of program design to free-up resources for additional toxicity testing.

Other important classes of organic chemicals detected in SPoT samples included organochlorine pesticides and PCBs. While pesticides such as DDT continued to be detected in many of the state's watersheds, the concentrations have always been below those demonstrated to cause toxicity to *H. azteca*. PCBs were also detected in many of the watersheds, but concentrations were generally lower than guideline thresholds. Organochlorine chemicals (e.g., DDT and PCBs) continue to be of concern in California because of their potential to bioaccumulate. While concentrations in fish do not often exceed thresholds of concern [\(Davis et al., 2013\)](#page-60-1), some fish consumption advisories have been issued due to these contaminants for lakes, rivers, bays, and coastal areas.

PBDEs are also not acutely toxic to *H. azteca*, but have potential to bioaccumulate in the environment, and affect human health. These chemicals did not exhibit any significant trends at the statewide level, or by land use, but did significantly decrease at one site. Because these chemicals are in the process of being phased out in California, SPoT will continue to measure them to document the potential decreasing trend.

Concentrations of metals in sediments were relatively stable during the last five years, and selected metal concentrations were lower than toxicity thresholds established for *H. azteca* (Cd, Cu and Zn). 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.

SPoT Indicators in Relation to Stream Ecology

SPoT measures sediment toxicity to amphipods and chemical concentrations as indicators of stream water quality. Numerous studies have linked low amphipod survival in laboratory toxicity tests with ecological degradation as indicated by impacted benthic macroinvertebrate (BMI) communities in California watersheds [\(Anderson et al., 2011\)](#page-59-1). The relationship between laboratory sediment toxicity test results, chemical contamination and macroinvertebrate community structure in SPoT watersheds was investigated for the current report to develop connections between the indicators of water quality impairment measured by SPoT and indicators of ecological impairment measured by the various programs conducting bioassessment monitoring in these watersheds.

The main source of these data was the SWAMP Bioassessment Reporting Module. Additional southern California data were provided through the cooperation of the southern California Stormwater Monitoring Council (SMC data compiled by Raphael Mazor, Southern California Coastal Water Research Project). To identify spatially appropriate data, coordinates from SPoT stations and stations from the SWAMP and SMC bioassessment programs were compared to determine which stations were reasonably proximate to the SPoT stations. Eight of the bioassessment sites used in the analysis were collected from the same coordinates as the SPoT stations, and twenty-one of the sixty-six samples analyzed were collected within one km of the SPoT site. The remaining bioassessment samples were collected within 15 km of SPoT stations. Bioassessment data from each year were matched with the toxicity and chemistry data from the appropriate SPoT sampling year. The SWAMP stations represented samples from southern, central and northern California, and the SMC stations were all from southern California. Spearman Rank correlations were conducted between toxicity and chemistry results and individual Index of Biological Integrity (IBI) scores calculated for each sample, as well as several habitat measurements conducted as part of the bioassessments. An IBI is calculated by combining several biological indicators (metrics), into a summary index. IBI scores were calculated using methods that were appropriate to each region, and in the case of these analyses, reflect the ecological complexity of the macroinvertebrate communities. The California Stream Condition Index is a more comprehensive next-generation index that is under development and will likely be used in the next reporting cycle.

Percent amphipod survival in laboratory toxicity tests was significantly positively correlated with the IBI (p<0.01, Figure 14), as were the Ephemeroptera/Plecoptera/Trichoptera index, taxonomic diversity and richness, and fine gravel substrates. The positive correlates are all indicators of healthy insect communities and desirable habitat. The EPT index indicates the relative densities of mayflies, stoneflies, and caddis flies, which represent three insect groups considered to be sensitive indicators of water quality. Pyrethroid pesticides, chlorinated compounds, and the benthic tolerance value were significantly negatively correlated with IBI. In addition, two measures of habitat, embeddedness, and particle sizes smaller than sand, were negatively correlated with the IBI. The data in Figure 14 demonstrate that amphipod survival in 77% of the corresponding SPoT stations were not toxic. IBI scores from the toxic and highly toxic samples ranged from 0.1 to 13.6, but the IBI scores for the non-toxic samples ranged from 0 to 73.3. This suggests that factors other than contaminants are influencing macroinvertebrates at these sites. Most of the IBI scores in this dataset were less than or equal to 30, and therefore represent degraded macroinvertebrate communities.

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 [\(Anderson et al., 2003a;](#page-59-2) [Anderson et al., 2003b;](#page-59-3) [Phillips et al.,](#page-62-1) [2004;](#page-62-1) [Weston et al., 2005;](#page-64-1) [Anderson et al., 2006;](#page-59-4) [Phillips et al., 2006;](#page-62-2) [Larry Walker](#page-61-2) [Associates, 2009\)](#page-61-2). Other studies have shown the importance of physical habitat in structuring BMI communities [\(Hall et al., 2007;](#page-60-2) [Hall et al., 2009;](#page-61-3) [Larry Walker](#page-61-2) [Associates, 2009\)](#page-61-2). In the current analysis the IBI was significantly negatively correlated with contaminants, particularly pyrethroid pesticides. The only habitat metric that had the same relationship with IBI was category of particles smaller than sand.

It is likely that these and other stressors interact to influence macroinvertebrate communities. The current analysis represents a preliminary attempt to determine relationships between the SPoT indicators of watershed degradation and ecological impacts measured by the SWAMP/PSA and SMC bioassessment programs. As SPoT, SWAMP/PSA, and SMC monitoring proceeds, the number of samples available for similar analyses will increase. SPoT staff will continue to coordinate with SWAMP and other regional monitoring groups to build on these datasets. As more BMI data are incorporated into the SWAMP and SMC databases, a more detailed assessment of these relationships will be investigated. These statistical relationships provide a basis for developing hypotheses for assessing causal relationships between in-stream ecological degradation measured in SWAMP and SMC monitoring and toxicity and chemical stressors measured by SPoT.

Figure 14. Relationship between amphipod survival in sediment toxicity tests and benthic macroinvertebrate IBI scores. IBI scores were calculated from field bioassessment data from 66 sites assessed during SWAMP and SMC monitoring conducted between 2008 and 2012, and corresponded to SPoT amphipod sediment toxicity tests conducted at the same or proximate stations during these years. Amphipod survival is presented as a percentage of the respective control sample survival value.

Regional Trends

The following sections summarize SPoT results for the nine Water Quality Board Regions on a site by site basis. Statistically significant trends at individual sites were determined using regression analysis, but non-significant trends are also noted. The power analysis, discussed below, determined that many trends could take greater than five years to emerge, so trend data in these sections should be viewed with this in mind. The toxicity summaries are listed using the same color code as depicted in Figure 11.

Region 1 – North Coast

All of the watersheds in Region 1 were classified as open land use at the 5 km scale (Table 5). Laguna de Santa Rosa (114LGMIR) also had some agricultural influence at the 5 km scale, although the proximity of agricultural operations apparently did not influence the detection of pesticides or the occurrence of toxicity at this site. Five of the eight sites in Region 1 had a single incidence of moderate toxicity in 2010, but all eight sites were not toxic in 2011 and 2012. Samples from the Mad River (109MAD101) and Eel River (111EELFRN and 111SF0933) were also tested at 15 °C in 2011 and 2012, but these samples were not toxic. There were no significant increasing or decreasing trends for the measured chemical classes. 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 5. Summary toxicity and chemistry data for sites sampled in Region 1. Statistically significant trends are noted with arrows. "NT" denotes non-toxicity and "ST" denotes some toxicity.

Region 2 – San Francisco Bay

Eight of the eleven watersheds sampled in Region 2 were classified as urban at the 5 km scale (Table 6). Most of these watersheds are characterized as open at the watershed 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 was an overall trend of decreasing toxicity. Sites such as San Leandro (204SLE030) and San Mateo Creeks (204SMA020) had significant trends of increasing amphipod survival in toxicity tests. Most of the toxicity observed in the region occurred in 2008. There was one highly toxic site in 2010 (Kirker Creek, 207KIR020), and only Walker Creek (207WAL020) was moderately toxic in 2011 and 2012. Many of these sites were also tested at 15 °C. Walker Creek was moderately toxic when tested at 23 °C, but approximately 75% of the sites had significantly greater toxicity at the colder test temperature (data not shown). This suggests that pyrethroids play a large role in sediment toxicity at Region 2 SPoT sites. Despite a statewide increase in pyrethroid pesticides in urban watersheds, a significant reduction of pyrethroids was observed at Laurel Creek. Sediments collected at Lagunitas Creek (201LAG125) had lower pyrethroid concentrations after an initial detection in 2008, but sediments from Coyote Creek (205COY060), Guadalupe Creek (205GUA020), Sonoma Creek and Walker Creek all showed marked, but statistically insignificant increases in pyrethroids. A significant reduction in PBDEs was observed in San Lorenzo Creek, and significant reductions in organochlorine compounds were observed in San Mateo Creek. Other statistically insignificant trends included a reduction of PAHs at Kirker Creek and a reduction of DDT at Coyote Creek.

Table 6. Summary toxicity and chemistry data for sites sampled in Region 2. Statistically significant trends are noted with arrows. "NT" denotes non-toxicity, "ST" denotes some toxicity, and "MT" denotes moderate-toxicity.

Region 3 – Central Coast

At the 5 km scale, five of the Region 3 watersheds are classified as urban (Table 7). Of the thirteen sites tested in 2012, four are classified as open and two were classified as agriculture. The remaining two sites were classified as combinations of agriculture with urban or open land use. Tembladero Slough (309TDW) and the Santa Maria River (312SMA) sites have been consistently toxic over the last five years. These two sites are the most significantly impacted by agriculture. Toxicity of Tembladero Slough sediment has been improving significantly, but the site remains classified as moderately toxic. Santa Maria River is classified as highly toxic, and has had only one moderately toxic response. Santa Maria River was the only site to exhibit significant decreasing trends for PAHs and DDTs. Although DDT seems to be decreasing at this site, past measurements of this chemical have been some of the highest in the state. The Salinas River at Davis Road (309DAV) and Arroyo Grande Creek (310ARG) both had large, but statistically insignificant increases in pyrethroid pesticide concentrations. Arroyo Grande Creek was moderately toxic in 2012, and appears to be trending toward increasing toxicity. The Salinas River at Davis Road, San Antonio Creek (313SAI) and Atascadero Creek (315ATA) were moderately toxic in 2008 or 2009, but have since been non toxic. Several sites were also tested at 15 °C in order to determine the influence of pyrethroid pesticides on the observed toxicity. Of these sites, only Arroyo Grande Creek was toxic in 2011 and 2012, but this site was highly toxic when tested at the colder temperature. Several other sites were also toxic or highly toxic at the colder temperature.

Region 4 – Los Angeles

Five of eight sites in Region 4 are classified as urban, or have urban influence at the 5 km scale (Table 8). No sites are solely agriculture at the 5 km scale, but three sites have agriculture mixed with urban or open land use. Region 4 has the greatest number of toxic sites in the state. Half of the sites were considered highly toxic in 2012, 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. Ballona Creek had a significant increase in pyrethroids, and the Los Angeles River had an increase in pyrethroids that was not statistically significant. San Gabriel River has demonstrated non-significant increases in toxicity and all chemical classes. Bouquet Creek consistently has the highest concentrations of total pyrethroid pesticides in the state, and is consistently rated as highly toxic. 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. The Santa Clara River and Calluegas Creek also had significant decreases in DDT. Six of the eight 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. Toxic concentrations of pyrethroids were measured in all of the samples that were highly toxic at 15 °C.

Table 8. Summary toxicity and chemistry data for sites sampled in Region 4. Statistically significant trends are noted with arrows. "NT" denotes non-toxicity, "MT" denotes moderate-toxicity, and "HT" denotes high toxicity.

Region 5 – Central Valley

Approximately one-third of SPoT sites are in Region 5. At the 5 km scale, these watersheds are mostly characterized as agricultural (Table 9). Three watersheds are characterized primarily as urban, and six as open land use. Three watersheds are agricultural combined with urban or open land use. The majority of the sites in Region 5 have never been toxic and generally have low concentrations of measured chemicals, including pesticides. Only five sites in the region have ever been toxic, and only three were toxic in 2011 or 2012. Marsh Creek (541MERECY) has been highly toxic every time it has been sampled. This site is influenced by urban and agricultural land use and has the highest concentrations of pyrethroids in the region. Orestimba Creek (541STC019) and Del Puerto Creek (541STC516) have also been highly toxic in 2010 and 2011, respectively, but in 2012 Orestimba Creek was not toxic and Del Puerto Creek was moderately toxic. These sites are classified as moderately toxic based on the five-year average. There has been a significant increase in the concentration of total pyrethroids measured at Orestimba Creek since 2008, and a significant decrease in DDT. Prior to 2012, Bear Creek (535MER007) had not been toxic, but high toxicity was observed that year. This watershed is two-thirds agriculture at the 5 km scale, but there were no obvious chemical causes for the observed toxicity based on detected chemicals. A number of significant trends have occurred in the remaining non toxic sites. These include decreases in DDT at Colusa Basin Drain (520CBDKLU) and San Joaquin River at Crows Landing (535STC504), and a decrease in PAHs at Bear Creek. Significant increases in pyrethroids, PAHs and metals were observed at Dry Creek (535STC206), one of the few urban watersheds in the region. Several sites demonstrated increases in pyrethroids that were not considered statistically significant. These include Bear Creek, Harding Drain (535STC501), San Joaquin River at Crows Landing and Marsh Creek. Two sets of ten samples were tested at 15 °C in 2011 and 2012 to determine the contribution of pyrethroid pesticides to the observed toxicity. In

2011 there were no differences between the toxicity responses at the two temperatures, but in 2012 one sample was moderately toxic at 23 °C, whereas four samples were toxic or highly toxic at 15 °C.

Table 9. Summary toxicity and chemistry data for sites sampled in Region 5. Statistically significant trends are noted with arrows. Toxicity color scheme is described in introductory paragraph. "NT" denotes non-toxicity, "MT" denotes moderate-toxicity, and "HT" denotes high toxicity.

Region 6 – Lahontan

Nine of the ten current Region 6 sites have been monitored continuously since the beginning of the program. Seven of these sites were characterized as open land use at the 5 km scale (Table 10). Two additional sites, the Upper Truckee River (634UTRSED) and the Truckee River at Trout Creek (635TROSED), also have urban influence at the 5 km scale. Bishop Creek (603BSP002) was the only Region 6 watershed to be characterized as urban. To date there have been no toxic samples in Region 6. The five-year average survival in all samples was >94%. There have also not been any significant upward or downward trends in chemical concentrations. Even though most of these sites are classified as being in watersheds dominated by open land use, pyrethroids were detected at eight of ten sites. Bifenthrin was detected most often, but a number of samples contained cyhalothrin, cypermethrin, deltamethrin and permethrin. Three Region 6 sites were tested at 15 °C in 2011 and 2012 to determine the potential contribution of pyrethroid pesticides to any observed toxicity. Testing at a colder temperature, one that is more relevant to temperatures measured in the region, did not increase the toxicity of any of the samples.

Table 10. Summary toxicity and chemistry data for sites sampled in Region 6. Statistically significant trends are noted with arrows. Toxicity color scheme is described in introductory paragraph. "NT" denotes non-toxicity."

Region 7 – Colorado River Basin

The three Region 7 sites that are evaluated as part of SPoT are also routinely monitored as part of other Regional Board programs. The Coachella Valley Stormwater Channel Outlet (719CVSCOT) was characterized with open land use at the 5 km scale, whereas the Alamo River Outlet (723ARGRB1) and the New River Outlet (723NROTWM) were both primarily agriculture (Table 11). Coachella Valley has never been toxic, but the southern river outlets have been moderately toxic intermittently. 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 [\(Phillips et al., 2007\)](#page-62-3). Significant decreases in DDT were observed at Coachella Valley and the New River, and a significant decrease in metals was observed at the Alamo River. The New River was also tested in 2011 and 2012 at 15 °C to determine the potential contribution of pyrethroid pesticides to the observed toxicity. Testing at the colder temperature did not affect the organism response in 2011, but increased the sample response from moderately toxic to highly toxic in 2012. The toxicity responses corresponded to higher concentrations of pyrethroids in the 2012 sample.

Table 11. Summary toxicity and chemistry data for sites sampled in Region 7. Statistically significant trends are noted with arrows. Toxicity color scheme is described in introductory paragraph. "NT" denotes non-toxicity and "ST" denotes some-toxicity.

Region 8 – Santa Ana

Three of the four sites in the Santa Ana Region were 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 open land use. 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) have been significantly toxic in every sampling event (Table 12). San Diego Creek has been highly toxic in four of five sampling events, and Chino Creek was highly toxic in one of three events. The only significant trend observed in the chemistry data set was a decrease in DDT at San Diego Creek. There was also a non-significant increase in pyrethroid pesticides at this site. San Diego Creek has lower average concentration of pyrethroids than Chino Creek only because there was a very high detection of total pyrethroids in 2011 at Chino Creek. This detection corresponded to the one incidence of high toxicity at this site. The three urban sites were also tested at 15 °C to evaluate the potential contribution of pyrethroid pesticides to the observed toxicity. Although Chino Creek and San Diego Creek were already toxic or highly toxic, testing at the colder temperature increased the magnitude of toxicity in all cases, and caused the moderately toxic samples to become highly toxic. Santa Ana River also became highly toxic in 2012

when tested at 15 °C. All of the highly toxic samples contained toxic concentration of total pyrethroids.

Table 12. Summary toxicity and chemistry data for sites sampled in Region 8. Statistically significant trends are noted with arrows. Toxicity color scheme is described in introductory paragraph. "NT" denotes non-toxicity, "MT" denotes moderate-toxicity, and "HT" denotes high toxicity.

Region 9 – San Diego

Nine sites were sampled in 2011 and 2012, up from seven in 2010. Eight of these sites had primarily urban land use at the 5 km scale, and the ninth site had a combination of urban and open space land use. Three sites were moderately toxic in 2011 and 2012, including Escondido Creek (904ESCOxx), San Dieguito River (905SDSDQ9), and Sweetwater River (909SWRWSx), but the Tijuana River (911TJHRxx) has been highly toxic since 2008 (Table 13). This site also has the highest average concentration of total pyrethroids, and has consistently been one of the most pyrethroid-contaminated sites in the state, based on SPoT monitoring. Los Penasquitos Creek (906LPLPC6) also had a very high total pyrethroid contamination in 2012, but the site was not toxic. In the three years this site has been sampled it has shown a non-significant increase in pyrethroid pesticides. There were several increasing or decreasing trends in the region, but they were not statistically significant. Concentrations of metals appear to be decreasing at Santa Margarita River (902SSMR07) and Escondido Creek, metal concentrations appear to be increasing at Los Penasquitos Creek, and PCBs are decreasing at San Diego River (907SDRWAR). Four sites were also tested in 2011 and 2012 at 15 °C to determine the contribution of pyrethroids to the observed toxicity. Of the eight samples tested over two years, two were moderately toxic at 23 °C, but four were moderately toxic and three were highly toxic at 15 °C. This suggests pyrethroids were playing a role in the toxicity of these samples. One sample remained non toxic (San Diego River).

Table 13. Summary toxicity and chemistry data for sites sampled in Region 9. Statistically significant trends are noted with arrows. Toxicity color scheme is described in introductory paragraph.

Reference Site Summary

All references samples were nontoxic in all years except for the Smith River (103SMHSAR) tested in 2010. The range of total organic carbon (TOC) and percent fine grained sediments at the reference sites were representative of those in the statewide monitoring sites (Figure 15). Concentrations of pyrethroids were below the median, but the average concentration at Lagunitas Creek (201LAG125) and Sespe Creek (403STCSSP) were clearly influenced by local agriculture and urban land uses. Average reference site concentrations of total DDT and total PCBs were less than 1 ng/g with the exception of Tuolumne River (535STC210) having an average total DDT concentration of 2.31 ng/g. The concentrations of the sum of Cd, Cu, Pb and Zn were representative of the statewide concentrations. Although the reference sites were in watersheds having limited human activity, concentrations of anthropogenic chemicals such as pesticides and metals are still detected to some degree. Although the concentrations of pyrethroid pesticides were below the median, these contaminants are still prevalent in these undeveloped watersheds. The concentrations of metals and organochlorine compounds were mostly between the first and third quartiles depicted in Figure 14.

Figure 15. Average measured parameters from the five reference sites (black circles) plotted upon box plots of the averages from non-reference sites. Boxes represent first and third quartiles, line represents median, and t-bars represent 95% confidence limits. Additional points are outside of the inter-quartile range.

The Relationship among Measured SPoT Parameters

Principal components analysis (PCA) was used to examine significant relationships among the various parameters measured in the program. In addition, average yearly watershed discharge (cubic feet per second) was included to investigate the possible role of variations in yearly rainfall on contaminant concentrations. Two sets of analyses were performed. The first PCA included a complete set of the sites, but only the chemical parameters that were measured at all of the sites. The second PCA was conducted on the Tier II sites, and included the same chemicals as the first PCA, but also chemicals only measured at Tier II sites (PAHs, PBDEs). Urban and row crop land use at all three scales (1km, 5km, and whole watershed), physical characteristics (TOC and percent fines), and average watershed discharge were included for both analyses. A post-PCA regression analysis was performed to determine which PCA factors were most closely related to toxicity. This analysis was conducted by comparing the individual coefficients that were produced within each factor to the percent survival results.

In both analyses the row crop land use at all scales grouped with the average yearly discharge measured in each watershed (Table 14). This is an obvious relationship because SPoT watersheds that included row crop agriculture as the predominant land use were the largest in terms of discharge, so it is likely that average discharge is not the most appropriate measurement for the influence of runoff in a watershed.

Subsequent reports will attempt to include actual rainfall data, particularly at locations proximate to the sampling station.

Urban land use at all scales grouped with two sets of organochlorine compounds in the greater data set, but a different result was observed for the Tier II data set. Only urban land use at the watershed scale grouped with any other components, including pyrethroids, the sum of four metals, and total organic carbon. These sediment constituents, along with percent fines grouped together in the main data set, but not with any land use. Hydrocarbons (PAHs) and PBDEs, which were strictly Tier II chemicals, grouped with PCBs and chlordanes in the Tier II analysis, but not with any land use. It is interesting to note that the pyrethroids, which showed a significant increasing trend in urban watersheds, did not group with urban land use in the main data set, and only grouped with the watershed scale urban land use in the Tier II data set. It is also interesting to note that the Tier II chemicals that were measured in the most urban watersheds did not group with urban land use at any scale.

Principal components regression analysis was performed between the individual coefficients within the PCA factors and percent survival. There were significant negative relationships between factors containing pyrethroid pesticides and percent amphipod survival for both sets of data ($p \le 0.003$). For the larger data set there was also a significant relationship between percent survival and Factor 1, which contained watershed discharge and row crop land use.

Pollutant Associations with Land Cover

Principal components analyses were used to determine relationships among contaminant factors and land use factors. At the statewide scale, PCBs and organochlorine pesticide chlordanes were associated with urban land use at all scales, but the pyrethroids, which have significantly increased in urban watersheds, were associated with metals, TOC and percent fines in this dataset. The highest concentrations of pyrethroids were detected in urban watersheds, but there were enough detections in watersheds dominated by agricultural and open land use to keep pyrethroids from associating solely with urban land use in the statewide PCA. In the Tier II (urban) data set, pyrethroids, metals and TOC were all related to urban land use at the watershed scale. The only factor related to row crop land use was average annual watershed discharge. This was somewhat expected because most of the larger watersheds monitored in the program flow through areas with heavy agricultural development. This result also indicates that average annual discharge might not be the most appropriate measure of watershed hydrography. Future analysis will consider rainfall, or more discrete measurements of discharge.

At the statewide level, principal components regression analysis showed significant relationships between toxicity and two separate factors. The first factor contained pyrethroids, metals, TOC and percent fines, and the second factor contained row crop land use. At the Tier II level, toxicity was significantly related to only the factor containing urban land use, pyrethroids, metals and TOC. None of the measured metals exceeded known toxicity thresholds, and this and all other evidence from SPoT analyses suggest that pyrethroids are driving the majority of observed toxicity.

Evaluation of the Current Program Design

Assessment of Variability

The SPoT program currently assesses one-hundred sites yearly to determine long-term trends in toxicity and chemical contamination. SPoT stations are located near the base of major watersheds, and sampling is conducted once per year after the rainy season. Following recommendations of the SPoT SRC, additional testing was conducted at selected SPoT sites to assess the temporal and spatial variability of toxicity and contamination on a more frequent time scale than once per year. Results of these additional assessments were analyzed to determine the extent to which a once-per-year summer sampling event at single SPoT stations provided adequate spatial and temporal representation of the watershed for the determination of long-term trends in contamination and toxicity.

Three Region 5 sites were selected for the initial phase of this study in 2010, and three additional sites were selected in Regions 4, 5 and 8 for 2011 and 2012. For each of the SPoT sites in this study, two to three additional stations were monitored upstream. These "variability sites" were located within a few kilometers of the base station in order

to provide greater spatial representation. All stations plus the base station were sampled three times per year to represent the summer, fall and winter seasons.

Toxicity was estimated using 10-day amphipod survival tests, and contamination was characterized by measurement of pyrethroid pesticides. Pyrethroids were selected because of their pervasive use in urban and agricultural watersheds and increasing importance in driving sediment toxicity in California watersheds. Toxicity was also tested at two temperatures as described above. The toxicity and chemistry data were analyzed by first conducting a two-factor analysis of variance (ANOVA without replication) on the spatial and temporal data within the sampling season. The three stations in the watershed were the first factor, and the three seasons sampled was the second factor. The results of these analyses determined if there were significant differences among the seasons within the year, or the stations within the watershed, respectively. The results from the three base station samples conducted within each year were then compared to the base station results from other years using an F-Ratio test to determine if seasonal variability was significantly greater than annual variability. Three within-year base station results for Marsh Creek were compared to the three years Marsh Creek has been sampled. Coyote Creek and San Diego Creek had six within-year base station results, which were compared to the five years these sites have been sampled.

If the variability among years is greater than the variability within a year, then it is assumed that yearly sampling is representative of the watershed for any given year. Results of the F-Ratio tests indicate that annual variability was greater than seasonal variability in all cases except for toxicity measured at 15 °C at San Diego Creek and Marsh Creek (Table 15). The cold temperature tests were generally more toxic than the tests at 23 °C, but were also less variable because all of the tests had very low survival. Conclusions regarding the representativeness of the current once per year sampling depend on the spatial and seasonal variability of toxicity and chemistry at these sites. Variability components measured at these sites would likely change during years with heavier rainfall. The current results suggest once per year sampling adequately represent highly variable indicators in particular watersheds, especially for sites with less overall variability.

Table 15. Probability values for statistical comparisons among stations, seasons and years at variability sites. Values with an "S" represent significant differences (p<0.05). NA indicates not analyzed because Coyote Creek was not tested annually at 15 °C.

Power Analysis

Power analyses were conducted on toxicity and chemistry data from the variability sites because these data provided power estimates for yearly sampling to compare to sampling three times per year. Power analyses were also conducted on a subset of base stations to determine the ability of the sampling regimes to measure significant trends. Based on the variability of parameters measured once per year for the last five years, it can take an average of 3 to 4 years to observe a 25% change in toxicity. Parameters that are more variable, such as total pyrethroids, can take anywhere from 5 to 9 years to observe a 25% change. Power analysis conducted on the data from the variability sites demonstrated that trends could be detected more quickly by sampling the sites multiple times per year (Table 16). It is predicted that sampling three times per year at the variability sites could detect trends in toxicity and bifenthrin in an average of two years. More frequent sampling is advantageous for parameters that are expected to change quickly, such as pyrethroids (see discussion below), but trends for parameters that remain fairly constant, such as metals, could likely be detected by sampling on longer time scales. Chemical trends that are likely to change on a longer time scale will be analyzed every other year. These data informed revisions to the program for the 2015 sampling season (see below).

Table 16. Results of power analysis indicating the number of years necessary to observe a 25% change in toxicity or bifenthrin concentration if samples were collected once per year versus three times per year.

Recommendations for SPoT Monitoring in 2015-2017

Most of the recommendations of the last report [\(Anderson et al., 2012\)](#page-59-0) were implemented, including the completion of the base station representativeness study (which was adapted into the DPR collaboration for 2013-2014), addition of fipronil analysis to Tier II sites, and the discontinuation of unsieved metals analysis. The 2013 sampling season followed a similar format to previous years, and includes the monitoring of the same 100 base stations. Because of limited funding in 2014, the total number of base stations was reduced to 85, and the analysis of metals and organochlorine compounds were omitted for this sampling year. The decision to reduce these types of analyses was based on the stable or downward trends in these analytes exhibited in the 2008-2012 data set.

Following input from the Scientific Review Committee, we recommend the following for the 2015-2016 monitoring year:

- 1) Use the first five years of data, along with new data from 2013-2014 to redesign the program. The new design will focus on emerging contaminants and consider changes to the analyte list, as well as the addition of toxicity test organisms that are more sensitive to emerging contaminants. Some possibilities include:
	- o Maintaining a core set of 50 critical sites that are monitored once per year.
	- \circ Monitor the remaining 50 sites every other year; rotating 25 in every year.
	- o Testing a subset of sites (e.g., Tier II) with the midge *Chironomus dilutus* to screen for contaminants that are more toxic to this species, such as fipronil.
- o Reduce the frequency of metals analysis and the analysis of chlorinated compounds.
- o Consider collecting and testing water samples at a subset of sites to determine if more soluble pesticides such as neonicotinoids are present at toxic concentrations. Add water column testing with *Chironomus dilutus* to address toxicity of neonicotinoids and fipronil (likely to occur after 2015 as funding allows).
- o Collaborate with DPR to address emerging pesticides of concern.
- 2) Continue to develop a comprehensive database to explore statistical relationships between SPoT chemical and toxicity indicators and ecological indicators. Develop a collaboration with the Perennial Streams Assessment Program to create or relocate PSA sites to SPoT locations. Consistent bioassessment data at SPoT stations will support the connection between toxicity indicators and ecological indicators. Toxicity and chemistry data will support PSA causal assessments.
- 3) Continue monitoring microcystin-LR in sediments. Consider monitoring microcystin-LR in water samples as funding allows (likely to occur after 2015).

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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:

- I. *Are our aquatic ecosystems healthy?*
- II. *What stressors and processes affect our water quality?*

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

I. *Are beneficial uses impaired?*

Management goal: Determine whether aquatic life beneficial uses in California streams are impaired 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.

II. *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.

III. *What is the magnitude and extent of any problems?*

Management goal: Determine the number of large California watersheds potentially impaired 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.

IV. *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 instream 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.

V. *Are solutions working?*

Management goal: Relate changes in concentrations and toxicity of sedimentassociated 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: SPoT 2008-2012 Station Information

Station codes with a "(T)" indicate 2012 Tier II stations.

CMP – Cooperative Monitoring Program **ILRP** – Irrigated Lands Program **MRP** – Municipal Regional Permit Monitoring **Regional** – Independent Regional Monitoring **Regional Board** – SWAMP monitoring by Regional Board **SMC** – Stormwater Monitoring Coalition **USGS NAWQA** – USGS National Water Quality Assessment Program

List of retired, relocated, and renamed stations.

Appendix 3: Toxicity Threshold Evaluation Concentrations

Appendix 4: Quality Assurance Information

Quality Assurance/Quality Control (QA/QC)

The data discussed below were evaluated in the Stream Pollution Trends (SPoT) report and were used to determine stream pollution trends for California. Thorough objectives for achieving quality data are outlined in the SWAMP Quality Assurance Program Plan (QAPrP). In general, data quality is demonstrated through analysis of the following quality control (QC) samples:

- Laboratory method blanks;
- Surrogate spikes;
- Matrix spikes (MSs) and matrix spike duplicates (MSDs);
- Certified reference materials (CRMs)/laboratory control spikes (LCSs);
- Laboratory duplicates (DUP)

Data for Project IDs SWB_SPoT_2011, SWB_SPoT_Variability_2011,

SWB_SPoT_2012, and SWB_SPoT_Variability_2012 have been verified according to SWAMP Standard Operating Procedures (SOPs) for chemistry and toxicity data verification. The data verification process determines whether the data are compliant with the individual measurement quality objectives (MQOs) specified in the SWAMP QAPrP. The counts in the following sections represent field observations, metals, mercury, total organic carbon, grain size, organochlorine pesticides, organophosphorus pesticides, pyrethroid pesticides, polybrominated diphenyl ethers (PBDEs), polychlorinated biphenyls as congeners (PCBs) and aroclors, polynuclear aromatic hydrocarbons (PAHs), and *Hyalella azteca* toxicity test results from the SPoT program. Data were classified into one of the following classification levels:

Compliant

Data classified as "compliant" meet or exceed all of the MQOs and other data quality requirements specified in the SWAMP QAPrP. These data are considered usable for their intended purpose without additional scrutiny.

Qualified

Data classified as "qualified" do not meet one or more of the MQOs and other data quality requirements specified in the SWAMP QAPrP. These data are considered usable for its intended purpose following an additional assessment to determine the scope and impact of the quality control failure.

Estimated

Data classified as "estimated" are assigned to data batches and sample results that are not considered to be quantifiable. Included in this classification are results qualified with one of the following flags:

J–Estimated value (EPA Flag)

Screening

Data classified as "screening" are considered non-quantitative and marked as screening and may or may not meet the minimum data quality requirements specified in the SWAMP QAPrP. These data may not be usable for its intended purpose and requires additional assessment.

Rejected

Data classified as "rejected" do not meet the minimum data quality requirements specified in the SWAMP QAPrP. These data are not considered usable for its intended purpose.

Not applicable

Data classified as "not applicable" refers to data that were not verified since there were no project MQOs or QC requirements for the specific parameter, or a failure result was reported and could not be verified.

No data have been validated. This section does not attempt to determine whether or not data should be used. Decisions regarding data use can only be made after data validation and comparison to project-specific data quality objectives (DQOs) is performed.

SWAMP criteria for percent recovery (%R) of surrogates, matrix spikes, and Certified Reference Materials and relative percent difference (RPD) for field and laboratory duplicates for sediments are presented in Table A1.

Laboratory Method Blanks

Laboratory method blanks are used to evaluate laboratory contamination during sample preparation and analysis. Blank samples undergo the same analytical procedure as samples with at least one blank analyzed per 20 samples. The required frequency was met for all 191 batches.

Data that met the MQO for method blanks are those with values less than the reporting limit (RL) for that particular analyte within each analytical batch. All 285 laboratory method blanks met the MQO.

Surrogate Spikes

Surrogate spikes are used to assess analyte losses during sample extraction and cleanup procedures, and must be added to every field and quality control sample prior to extraction. Whenever possible, isotopically-labeled analogs of the analytes should be used.

All field samples and QC were spiked with surrogates as required. Surrogates for organophosphorus pesticides analyzed by CSUMB-IIRMES were reported in the associated organochlorine pesticide batches.

All surrogate percent recoveries were within the acceptance criteria listed in Table A1, with the exception of surrogates spiked in sample 205COYSCL in batch WPCL_L-020- 12_BS672_S_PYD, CRM L-019-12-SRM 1944-BS 682 in batch WPCL_L-019- 12 BS682 S OCH, and 000NONPJ in batch WPCL L-259-12 BS705 S PBDE. The associated pyrethroid, organochlorine pesticide, and PBDE analytes in these samples were classified as qualified with regard to the SWAMP QAPrP MQO for surrogates (Table A2).

Matrix Spikes and Matrix Spike Duplicates

A laboratory-fortified sample matrix (matrix spike, or MS) and a laboratory fortified sample matrix duplicate (MSD) are both used to evaluate the effect of the sample matrix on the recovery of the target analyte(s). Individually, these samples are used to assess the bias from an environmental sample matrix plus normal method performance. In addition, these duplicate samples can be used collectively to assess analytical precision.

Aliquots of randomly selected field samples were spiked with known amounts of target analytes. The %R of each spike was calculated as follows:

%R= (MS Result – Sample Result)/ (Expected Value – Sample Result) * 100

The %R acceptance criteria vary according to analyte groups (Appendix X, Table1).

This process was repeated on the same native samples to create a laboratory fortified sample matrix spike duplicate (MSD). MSDs were used to assess laboratory precision and accuracy. MS/MSD RPDs were calculated as:

RPD = (|(Value1-Value2)|/(AVERAGE(Value1+Value2)))*100

where:

Value1 = matrix spike value, and Value2 = matrix spike duplicate value.

According to the SWAMP QAPrP for conventional, organic and inorganic analyses, at least one MS/MSD pair should be performed per 20 samples or one per batch, whichever is more frequent. The required frequency was met for all 191 batches.

Laboratory batches with MS/MSD %R and RPD values outside of acceptance criteria were either classified as compliant or qualified based on number of QC elements outside criteria. These are presented in Table A3. All other MS/MSD %Rs and RPDs were within acceptance criteria.

Certified Reference Materials and Laboratory Control Samples

Certified reference materials (CRMs) and laboratory control samples (LCSs) are analyzed to assess the accuracy of a given analytical method. As required by the SWAMP QAPrP, one CRM or LCS should be analyzed per 20 samples or one per batch, whichever is more frequent. The required frequency was met for all 191 batches.

Laboratory batches with CRM or LCS %R or RPD values outside of acceptance criteria were either classified as compliant or qualified based on number of QC elements outside criteria. These are presented in Table A4. All other CRM and LCS %Rs and RPDs were within acceptance criteria.

Laboratory Duplicates

Laboratory duplicates (DUPs) were analyzed to assess laboratory precision. As required by the SWAMP QAPrP a duplicate of at least one field sample per batch was processed and analyzed. Two percent of the batches (6 out of 285 total batches) did not include DUPs performed at the required frequency. One total organic carbon and five grain size batches were classified as qualified and are presented in Table A5.

The duplicates were compared and an RPD was calculated as described in Section 3.3. RPDs <25% were considered acceptable as specified in the QAPrP. All RPDs >25% were classified as qualified and are presented in Table A6.

Field Duplicates

Field duplicates are analyzed to assess field homogeneity and field sampling procedures. Sediment duplicates were obtained from homogenized field samples. Field duplicates sampled are presented in Table A7.

Field duplicate values were compared to field sample values from each site and RPDs were calculated as described in Section 3.3. RPDs <25% were considered acceptable as specified in the QAPrP. RPDs >25% are presented in Table A8. All other RPDs were acceptable.

Toxicity Tests

All *Hyalella azteca* data were classified as compliant with regard to the SWAMP QAPrP MQO for toxicity tests.

Holding times

Eight percent of the results (4,521 out of 55,284 total results) were outside the SWAMP QAPrP MQOs for holding times. Of the 4,521 results, 745 pyrethroid and PBDE results were classified as estimated since the holding time was exceeded by more than three times and 3,776 metals, mercury, PBDE, PAH, PCB, and pyrethroid results were classified as qualified due holding time exceedances. Sediment metal and mercury samples exceeded the 1-year holding time criteria until analysis. Sediment PBDE, PAH, PCB, and pyrethroid samples exceeded the 40 day holding time criteria from extraction to analysis. Although data were classified as estimated and qualified it was considered usable for the intended purposes for this report. The field samples affected (does not include laboratory QA/QC) are presented in Table A9.

QA/QC Summary

There were 55,284 chemistry results, including; integrated samples, and field duplicates and laboratory QA/QC samples. Of these:

- 47,882 (86.6%) were classified as "compliant"
- 6,510 (11.8%) were classified as "qualified"
- 695 (1.2%) were classified as "estimated"
- 150 (0.27%) were classified as "screening"
- 0 (0%) were classified as "rejected"; and

47 (0.08%) were classified as "NA", since results were not reported by the laboratory due to matrix interferences or results were not reported due to high native concentrations) and could not be verified.

Classification of this dataset is summarized as follows:

- All data presented in Table A2 were classified as qualified due to surrogate recovery exceedances.
- All data presented in Table A5 was classified as qualified due to insufficient QC samples performed.
- All data presented in Tables A3, 4A, A6, and A8 were classified as qualified due to RPD exceedances.
- All data presented in Tables A3 and A4 were classified as either compliant or qualified due to recovery exceedances.
- Results for samples presented in Table A9 were classified as qualified or estimated due to holding time exceedances.
- 150 screening level results (PAH analytes that could not be quantified or PCB aroclors) were classified as qualified.

Data that meet all SWAMP MQOs as specified in the QAPrP are classified as "SWAMPcompliant" and considered usable without further evaluation. Data that fail to meet all program MQOs specified in the SWAMP QAPrP, have analytes not covered in the SWAMP QAPrP, or are insufficiently documented such that supplementary information is required for them to be used in reports are classified as "qualified" non-compliant with the SWAMP QAPrP. No data were classified as rejected for this project during the data quality assessment (DQA) phase of reporting, end users may find qualified data batches meet project data quality objectives. A 100% completeness level was attained which met the 90% project completeness goal specified in the SWAMP QAPrP.

Table A2. Surrogate recoveries that did meet quality control acceptance criteria.

Surrogate	Station Code	Sample Type	Batch ID	$\%$ Recovery	Laboratory
Dibromooctafluorobiphenyl, 4- 4'-(Surrogate); Total; % recovery	205COYSCL	Integrated	WPCL L-020- 12 BS672 S PYD	41.5	DFG-WPCL
PBDE 100-L (Surrogate); Total; % recovery	000NONPJ	Integrated	WPCL L-259- 12 BS705 S PBDE	168	DFG-WPCL
DDD(p,p')(Surrogate); Total; % recovery	LABQA	CRM	WPCL L-019- 12 BS682 S OCH	182	DFG-WPCL

Table A3. Matrix spikes (MS), matrix spike duplicates (MSD), percent recoveries (%R), and relative percent differences (RPD) that did not meet quality control acceptance criteria. Boldface type indicates values that did not meet the quality control objective.

Table A4a. Batches containing certified reference material (CRM that did not meet quality control acceptance criteria.

Note: *%R were outside the MQO but inside the CRM manufacture range

Table A4b. Batches containing laboratory control spike (LCS) that did not meet quality control acceptance criteria.

Analyte	Station Code/LabSampleID	Lab Batch ID	LCS %R	LCSD %R	RPD	Laboratory
Phorate; Total; ng/g dw	7291-BS1	IIRMES TO-03- 138 S OP	47	20	82	CSULB- IIRMES
Phorate; Total; ng/g dw	7479-BS1	IIRMES TO-03- 140 S OP	20		258	CSULB- IIRMES
Cyfluthrin, total; Total; ng/g dw	L-023-13-LCS	WPCL L-023- BS728 S PYD 13	151	129	16	DFG-WPCL
Cypermethrin, Total; Total; ng/g dw	L-023-13-LCS	WPCL_L-023- BS728 S PYD 13.	169	155	8.7	DFG-WPCL

Table A5. Batches for which laboratory duplicates (DUP) were not run.

Analyte	Station Code	Sample Date	Parent Value	Duplicate Value	RPD	Laboratory	Batch ID
Deltamethrin/Tral omethrin; Total; ng/g dw	205COYGA	03-Jan-13	13.2	10.2	26	DFG- WPCL	WPCL L-023- 13 BS728 S PYD
Bifenthrin; Total; ng/g dw	310ARG	16-May-12	15.0	6.51	79	DFG- WPCL	WPCL L-213- 12 BS698 S PYD
Cyfluthrin, total; Total; ng/g dw	310ARG	16-May-12	36.2	21.9	49	DFG- WPCL	WPCL L-213- 12_BS698_S_ PYD
Cyhalothrin, Lambda, Total; Total; ng/g dw	310ARG	16-May-12	3.87	2.43	46	DFG- WPCL	WPCL L-213- 12 BS698 S PYD
Cypermethrin, Total; Total; ng/g dw	310ARG	16-May-12	64.4	42.0	42	DFG- WPCL	WPCL L-213- 12 BS698 S PYD
Esfenvalerate/Fe nvalerate, Total; Total; ng/g dw	310ARG	16-May-12	5.00	3.30	41	DFG- WPCL	WPCL L-213- 12 BS698 S PYD
Permethrin, cis-; Total; ng/g dw	310ARG	16-May-12	12.1	7.72	44	DFG- WPCL	WPCL L-213- 12 BS698 S PYD
PBDE 047; Total; ng/g dw	000NONPJ	14-May-12	17.6	13.6	26	DFG- WPCL	WPCL L-259- 12 BS705 S PBDE
PBDE 049; Total; ng/g dw	000NONPJ	14-May-12	1.88	1.38	30	DFG- WPCL	WPCL L-259- 12 BS705 S PBDE
PBDE 099; Total; ng/g dw	000NONPJ	14-May-12	22.2	16.1	32	DFG- WPCL	WPCL L-259- 12 BS705 S PBDE
PBDE 209; Total; ng/g dw	000NONPJ	14-May-12	284	395	33	DFG- WPCL	WPCL L-259- 12 BS705 S PBDE

Table A7. Field Duplicate Samples

Table A8. Field duplicate samples that did not meet quality control acceptance criteria.

