Spatial and Temporal Trends in Toxicity and Chemical Contamination Relative to Land Use in California Watersheds: Stream Pollution Trends (SPoT) Monitoring Program Fifth Report

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Executive Summary

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

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

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

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

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

This report summarizes and analyzes toxicity and pollutant chemistry data generated by the SPoT Monitoring Program between 2008 and 2017. SPoT has collected and tested over 800 sediment samples from 100 diverse California watersheds, and completed over 900 toxicity tests with sensitive indicator organisms. Analysis has included the measurement of metals, polycyclic aromatic hydrocarbons, polychlorinated biphenyls, legacy pesticides, current use pesticides, and emerging contaminants such as fipronil and polybrominated diphenyl ethers (PBDEs) in watershed sediments. This extensive data set has been analyzed in the context of watershed land use to understand the nature of identified water pollution and its trends.

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

Use of multiple toxicity test species and endpoints

Multiple species and endpoints capture a more complete picture of toxicity in SPoT watersheds. In 2015 SPoT added toxicity testing with the midge *Chironomus dilutus* at a subset of sites to augment amphipod (*Hyalella azteca*) testing in urban watersheds. The midge has different chemical sensitivities to those of the amphipod and responded accordingly.

Of all the samples tested with both species between 2015 and 2017, 29% were significantly toxic to amphipod survival or growth. An additional 17% of samples were toxic to the midge, revealing the importance of adding the midge testing and confirming that multiple species and endpoints capture a more complete picture of toxicity in SPoT watersheds. Based solely on survival, an average of 18% of all the samples tested in the 10-year program were toxic to amphipods. There were no significant trends in amphipod toxicity except for a marginal decrease in toxic response observed in watersheds with minimal agricultural or urban land use.

Significant relationships among toxicity, pyrethroid pesticide concentrations, and urban land use.

Between 2008 and 2017, concentrations of many individual pyrethroid insecticides increased in urban land use watersheds, and the number of detections of many pyrethroids increased in all land uses. Pyrethroids contribute to much of the observed amphipod toxicity, as is evidenced by toxic unit analysis and diagnostic testing at colder temperatures, and both toxicity and pyrethroids concentrations are significantly related to urban land use.

Few other chemical classes are showing significant increasing or decreasing trends. From 2013 to 2017, incidents of detection and detected concentrations of the urban-use insecticide fipronil are stable, and there were no significant trends for individual polycyclic aromatic hydrocarbons (PAHs) or the sum of PAHs. Total polybrominated diphenyl ethers (PBDEs) are significantly increasing. Of the chlorinated compounds, dichlorodiphenyltrichloroethanes (DDTs) are significantly decreasing in open watersheds, but polychlorinated biphenyls (PCBs) show no trend. Trends in copper and zinc concentrations were analyzed as representative metals. Copper concentrations are not showing any trends, but zinc concentrations are significantly increasing statewide.

Collaborative studies with SPoT

Three collaborative studies are in progress between the State Water Resource Control Board's SPoT Program and CDPR and the California Department of Toxic Substance Control (DTSC), and one intra-agency collaboration is underway between SPoT and Water Board researchers studying constituents of emerging concern (CECs). Studies of this type fulfill the program's third goal and demonstrate how agencies and programs can leverage monitoring efforts for greater outcomes. For example, two collaborations with CDPR are providing additional data for tracking trends related to 2012 pyrethroid insecticide regulations and new fipronil label requirements, as well as additional data on the toxicity of surface waters that are generally only monitored with chemical analysis.

Other collaborations include a partnership with California State University Monterey Bay to measure the cyanotoxin microcystin in SPoT sediments, as well as ongoing coordination with current regional monitoring programs, and participation in the development of the Urban Pesticide Cooperative Monitoring Program.

SPoT's evolving monitoring parameters

As SPoT continues to adapt to characterize new classes of chemicals and potential causes of biological impacts, new monitoring tools are needed. Traditional environmental monitoring programs have focused on the targeted analysis of hydrophobic contaminants, but recent advances in chemical analysis have demonstrated the presence of a wide range of polar chemicals in sediments. Many of these chemicals could be contributing to the type of whole organism toxicity that is monitored by SPoT, but could also be contributing to a number of sub-lethal impacts on biota. Use of non-targeted analyses, which can significantly expand the analyte list, may allow for the identification of new contaminants of concern (Ferguson et al. 2019), and allow for regulators and the SPoT Monitoring Program to focus resources on the emerging compounds identified. Potential risk to biota could be determined with coupled effects-based tools, such as bioanalytical monitoring, analysis of adverse outcome pathways, or behavioral endpoints in traditional toxicity testing (Connon et al. 2019). These more nuanced analyses of contaminant effects on organisms can highlight the ecological impacts of impaired water quality.

Future contaminant monitoring should be planned in conjunction with programs prioritizing contaminants of emerging concern (CECs). The monitoring priorities of agencies such as DTSC and CDPR can provide direction for targeted analyses, and the San Francisco Estuary Institute is exploring chemical prioritization based on various forms of predictive toxicology (computational and in vitro), as well as determining contaminants that have widespread outdoor use. Many CEC prioritization lists include polyfluoroalkyl substances (PFAS). Based on statewide prioritization across multiple regulatory programs, persistence, and the potential for presence in sediments, it is likely these compounds will be added to the SPoT analyte list.

Embracing new tools for environmental monitoring, including non-targeted analyses and effects-based biological measurements, will allow SPoT to be at the forefront of emerging chemical trends and their effects on resident biota, and provide better information for water quality management in California.

Section 1 – Introduction

SPoT in the SWAMP Assessment Framework

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

The three specific program goals are to:

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

2. Relate 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, state and federal monitoring.

Monitoring Objectives and Design

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

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

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

3. Quantify land cover data available from the National Land Cover Database;

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

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

The SPoT indicators are measured in stream sediment because this environmental compartment integrates chemical contamination over time. Many trace metal and organic pollutants that enter streams adhere to suspended sediment particles and organic matter, and this sediment-associated phase is the major pathway for contaminant loading in streams and downstream waterways. In addition, river benthic environments are ecologically important because they provide habitat to key elements of aquatic macroinvertebrate and algal communities. Sediment measurements are appropriate for long-term trend monitoring because pollutants that accumulate in depositional sediment on the stream bed are much more stable over time (~months to years) than dissolved or suspended pollutants that move downstream in pulses that are highly variable over short time scales (~hours). SPoT surveys are timed to collect sediment in summer after the high water season when most sediment and pollutant transport and deposition takes place.

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

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

SPoT Watersheds and Sampling History

The program originally targeted 100 sites for sample collection in 2008. Over time, the list of watersheds and the ability to collect samples yearly has varied (Table 1). Ninety-two sites were sampled in 2008, but six of these sites were never revisited because they did not satisfy SPoT objectives , and five were later relocated far enough away to warrant renaming them and creating different site codes. Only twenty-three sites were sampled in 2009 because of budget restrictions, but the number of locations was increased to 95 in 2010. One-hundred sites were sampled between 2011 and 2013, but the list was reduced to 85 in 2014. One-hundred sites were on the list between 2015 and 2017, but only 75 were sampled every year. As of 2018, ninety sites were chosen for yearly sampling (Figure 1). Ten sites were removed permanently because they did not meet SPoT's data quality objectives (depositional sediment that represents loading from the watershed). A reduction in the number of base sites allowed SPoT to sample every site yearly, and maintain a statistically sound design for trend analyses. Of the remaining 90 sites, 64 are in independent watersheds, and 26 are in sub-watersheds. Some northern and southern watersheds cross state and national borders.

Table 1. Timeline of parameters measured as part of SPoT.

	2008	**2009**	**2010**	**2011**	**2012**	**2013**	**2014**	**2015**	**2016**	**2017**	**2018**
Number of Sites	92	23	95	100	100	100	85	75	75	75	90
H. azteca Toxicity	X	X	X	X	X	X	X	X	X	X	X
C. dilutus Toxicity								X	X	X	X
Pyrethroids	X	X	X	X	X	X	X	X	X	X	X
Fipronil (Urban)						X	X	X	X	X	X
Organophosphates	X	X	X	X	X	X		X	X		
Organochlorines	X	X	X	X	X	X		X		X	
PCBs	X	X	X	X	X	X		X		X	
PAHs (Urban)	X	X	X	X	X	X	X	X	X	X	X
PBDEs (Urban)	X	X	X	X	X	X	X	X	X	X	X
Metals/Mercury	X	X	X	X	X	X		X	X	X	X
Microcystin						X	X	X	X	X	X

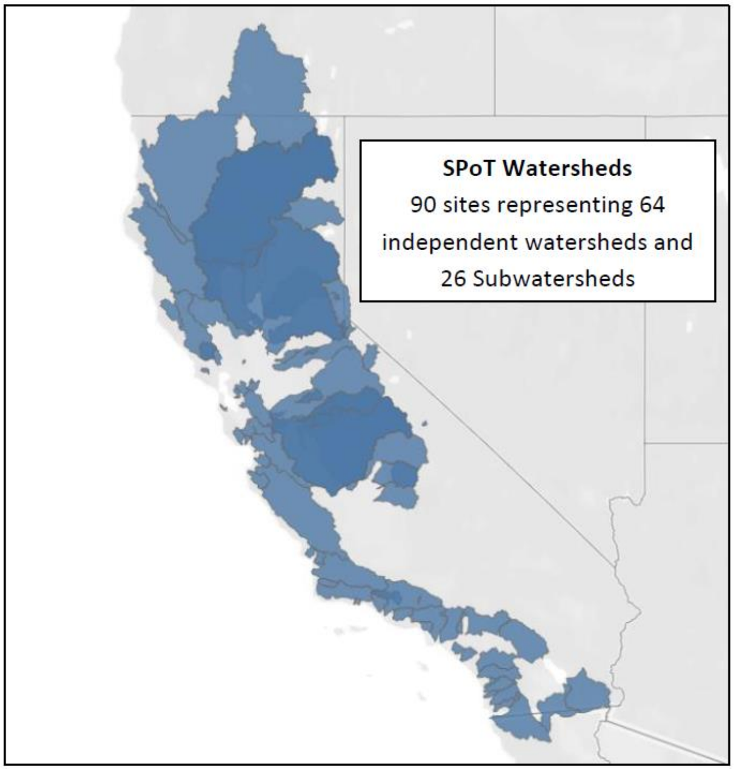


Figure 1. Stream Pollution Trends Project watersheds and subwatersheds. Darker colors indicate subwatersheds within larger watersheds.

Methods for watershed delineation and land use analyses are described in Appendix 2. Measured sediment parameters and land use are compared based on the percentages of urban, agricultural, and open land uses at a 5 km radius from the sampling site. Percentage land use in various National Land Cover Database (NLCD) categories at the 5 km radius is also used to roughly bin watersheds into *urban*, *agricultural*, or *open* categories. The SPoT site list has always been comprised of approximately 40% urban, 25% agriculture, and 35% open sites. Four sites have changed categories with the release of the 2016 NCLD data set. Two stations went from being categorized as both urban and agricultural to only agricultural, one site changed from open to agricultural, and one site changed from urban to open. According to the NLCD, at the 5 km scale, urban land use in watersheds represented by SPoT sites decreased by approximately 1% between 2006 and 2016, and agricultural land uses also decreased by approximately 1.5% during the same period. These results only reflect SPoT watersheds at the 5 km scale, whereas nationally, urban land use increased by 3.6% and agriculture decreased by 0.25% (Homer et al. 2020).

Coordination and Collaboration with other Programs

The SPoT network of sites was established through coordination with Regional Water Board monitoring programs and stormwater agencies, under the guidance of the SPoT Scientific Review Committee (SRC). The Southern California Stormwater Monitoring Coalition participated in site selection for the southern California SPoT sites. A representative from the Bay Area Stormwater Management Agencies Association served on the SWAMP committee that designed the program, and all SPoT sites in the San Francisco Bay Region are aligned with the Regional Monitoring Coalition's monitoring sites for the Municipal Regional Stormwater NPDES Permit (BASMAA 2011)(Table 2). SPoT sites in the Central Coast and Central Valley Regions are shared by the Cooperative Monitoring Program for agriculture and Irrigated Lands Regulatory Program, respectively. The Delta Regional Monitoring Program (Delta RMP) assessments include data from five SPoT sites within the Sacramento-San Joaquin River Delta. In most cases, the SPoT assessments of sediment toxicity and chemistry complement water column measurements made by cooperating programs. SPoT data have also been included in California Regional Water Quality Control Board reports that are in the series "Toxicity in California Waters" (Anderson et al. 2011).

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

The SPoT focus on causes and sources of pollutants in watersheds feeds directly into TMDL 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, legislative and regulatory actions addressing pollutants in products (e.g., restrictions on use of copper in vehicle brake pads and phasing out of various PBDEs), and installation of stormwater treatment devices or low impact development in urban areas. Although stormwater permittees are required to report on green infrastructure and low impact development measures that have been installed locally, use of SPoT data for watershed scale evaluations of regional or local management practice effectiveness is currently limited by the lack of a comprehensive and standardized reporting system for practice implementation.

Table 2. SPoT collaborations and programs currently supported by SPoT monitoring data.

	Collaboration	**Objective**
Stream Pollution Trends Program	Intensive Site Study with the California Department of Pesticide Regulation (CDPR)	Determine environmental response to CDPR's 2012 pyrethroid pesticide regulations and evaluate presence of fipronil and its degradates
	Agricultural Surface Water Monitoring with CDPR	Determine toxicity to alternate test species and presence of emerging pesticides
	Surface Water Contaminant Screening with the Department of Toxic Substance Control	Provide data for the Safer Consumer Products Program
	Urban Pesticide Coordinated Monitoring Program (UPCMP)	Assist with development of monitoring design to coordinate with SPoT
	Cyanobacteria CEC Monitoring with California State University Monterey Bay	Determine presence and potential effects of the cyanotoxin microcystin
	Collaboration with Bioassessment Monitoring Programs	Linking SPoT toxicity and chemistry data with bioassessment data to support causal assessments
	State and Regional Water Board 303(d) Listings through the Integrated Reporting Process	Water Boards assess water quality monitoring data for California's surface waters to determine if they contain pollutants at levels that exceed protective water quality standards
	Agricultural Monitoring for the Region 3 Cooperative Monitoring Program	Provide data for conditional waiver of waste discharger requirements
	Agricultural Monitoring for the Region 5 Irrigated Lands Regulatory Program	Provide data for the monitoring of agricultural runoff in the Central Valley
	Stormwater Monitoring for Region 2 Stormwater Permits	Provide long-term trends data for San Francisco Bay Area municipal stormwater permits
	Regions 4, 8 and 9 Stormwater Monitoring Coalition Site Overlap	SPoT sites overlap with several Stormwater Monitoring Coalition monitoring locations and provide additional data

Section 2 – Urban Land Use, Toxicity and Pyrethroid Insecticides

Section Highlights

Toxicity: Inclusion of multiple species and endpoints show a greater rate of toxicity than when using one species. There is a trend of decreasing toxicity in open watersheds, but no other trends.

Pyrethroids: Concentrations of many individual pyrethroid compounds are increasing, most notably in urban land uses. Number of pyrethroid detections are increasing in all land uses.

Pyrethroids contribute to much of the observed toxicity, and both toxicity and pyrethroid concentrations are significantly related to urban land use.

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

Hyalella azteca is an epibenthic amphipod that is native to California streams. Wild populations have been known to become resistant to anthropogenic chemicals such as pesticides (Weston et al. 2013), but laboratory cultured populations are sensitive indicators of contaminants. The amphipod toxicity test consists of a ten-day sediment exposure with two endpoints, an acute measurement of survival and a chronic measurement of growth. In 2015, SPoT added the midge *Chironomus dilutus* toxicity test at sites in watersheds with greater urban land use. This midge is also native to California streams and builds tubes from sediment particles. The midge exposure and endpoints are similar to those of *H. azteca*, but *Chironomus* has differing sensitivities to various chemicals. Use of both organisms in tandem provides additional information on sample toxicity (Anderson et al. 2018).

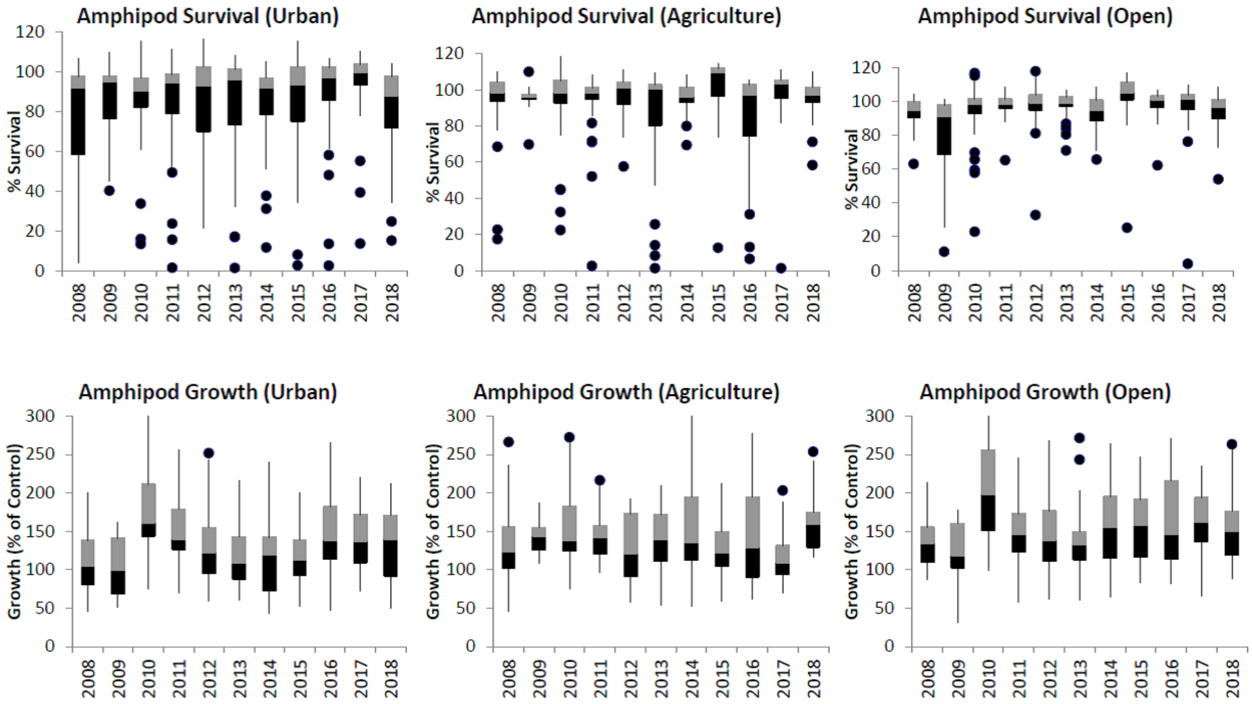


Figure 2. Box plots for *H. azteca* survival and growth (urban, agriculture and open). Box represents the 25th and 75th percentiles; line represents median; whiskers extend to 1.5 the interquartile range; and circles represent measured values outside the above ranges. All further box plots use this scheme.

The results of the *H. azteca* sediment toxicity tests have been consistent during the last eleven years (2018 data are included for toxicity). Based on amphipod survival, toxic and highly toxic (<38.6% survival) samples account for an average of 18% of the samples tested. There were no significant trends in toxicity either statewide or in urban and agricultural watersheds (Figure 2), but there was a significant increase in survival in open watersheds, indicating a reduction of toxicity. Chronic endpoints, such as growth, are generally considered more sensitive than the acute survival endpoint, but toxicity to the *H. azteca* growth endpoint occurs less frequently and can occur in samples that do not have acute toxicity. There were no significant trends in growth toxicity, but inclusion of this endpoint increased the number of toxic samples by an average of 4% throughout the program. Considering both endpoints, the lowest incidence of toxicity was observed in samples from open sites, followed by samples from agricultural sites and samples from urban sites.

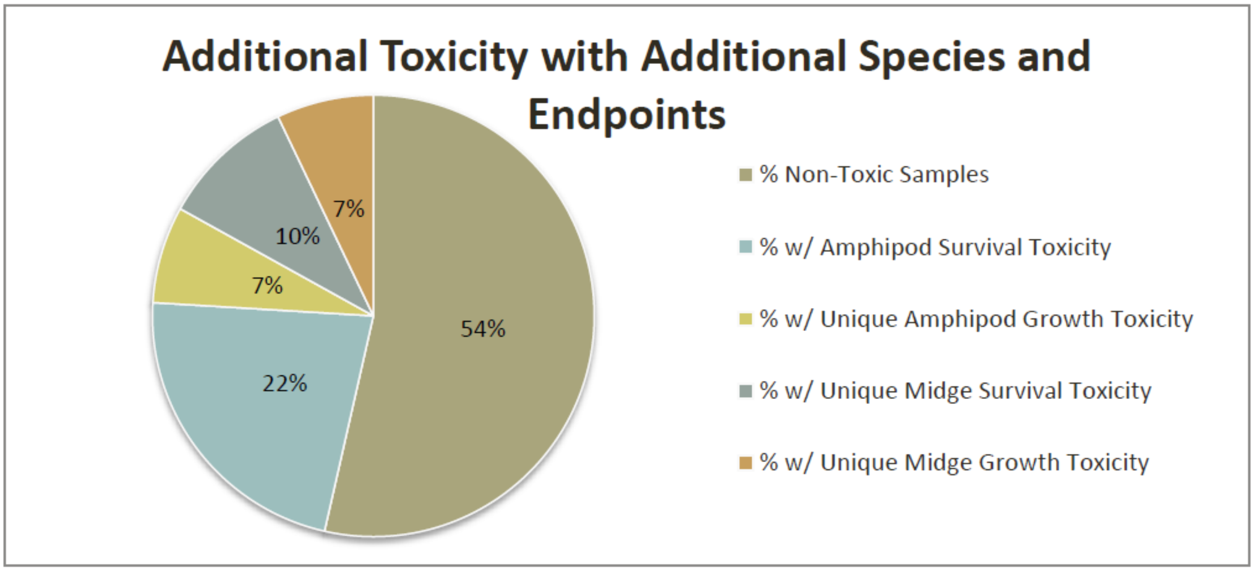


Figure 3. Significant toxicity based on various endpoints in a subset of SPoT samples tested with both *H. azteca* and *C. dilutus* (n=183, 2015-2017).

Toxicity testing with *C. dilutus* was added primarily to detect potential toxicity caused by emerging pesticides, such as fipronil. The midge was used for testing only in urban watersheds because fipronil is solely an urban use insecticide in California. Although this organism identified many of the same toxic samples as the amphipod, inclusion of acute and chronic endpoints identified toxicity at 31 unique sites, or 17% of samples tested during the four years both tests were conducted. Because only four years of midge toxicity data are available, no significant trends have been noted for either the survival or growth endpoints. When the results of paired tests with both *H. azteca* and *C. dilutus* are compared, it is clear the inclusion of multiple species and endpoints captures a more complete picture of toxicity in SPoT watersheds (Figure 3).

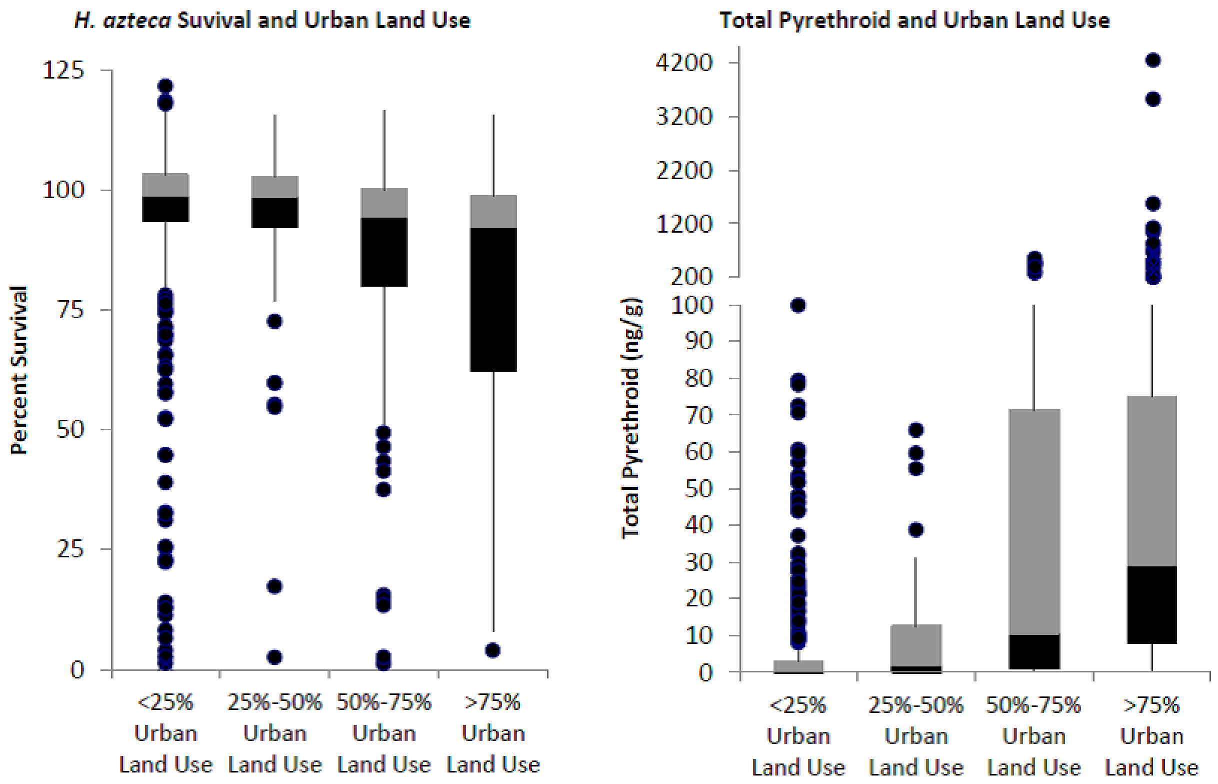


Figure 4. *Hyalella azteca* survival as percent of control (left), and total pyrethroid concentrations in categories of increasing urban land use (right).

Considering both species and endpoints, the most consistent and highest magnitude of toxicity is observed at the bases of urban watersheds, and the *H. azteca* survival response was significantly correlated with percent urban land use (Figure 4A). Highly toxic samples were collected from 30 separate sites over the last eleven years. Nineteen of these sites were solely urban, and one was classified as urban/agriculture. Seven sites were from agricultural watersheds, and three were classified as open. Approximately two-thirds of these sites were in the southern California regions. The number of detections and magnitude of concentrations of pyrethroid insecticides are also significantly related to urban watersheds (Figure 4B).

Pyrethroid Trends by Land Use

Use of pyrethroids in both urban and agricultural settings has increased during the last decade. As such, detection of increasing trends in individual pyrethroid compounds would be expected in certain land use settings in California. Median concentrations are not significantly increasing at SPoT sites in open watersheds, but concentrations of bifenthrin and lambda-cyhalothrin are significantly increasing at SPoT sites in agricultural watersheds. Significant increases in concentrations were also noted at urban SPoT sites for lambda-cyhalothrin, cypermethrin, deltamethrin and esfenvalerate (Table 3). The number of detections of these four pyrethroids (and fenpropathrin) are also significantly increasing at sites in almost every watershed type. Bifenthrin is the most stable and persistent pyrethroid for many pathways (Spurlock and Lee 2008), and it accounts for the majority of pyrethroid detections at SPoT sites. In 2017, bifenthrin was detected in 93% of samples from agricultural watersheds and 90% of samples from urban watersheds. Cyhalothrin and esfenvalerate were also detected in more than 90% of agricultural sites.

Table 3. Significant trends in median concentration and number of detections at SPoT sites from different land use designations (2008-2017).

Analyte	**Trend in Median Concentration**			**Trend in Number of Detections**		
	Agriculture	**Open**	**Urban**	**Agriculture**	**Open**	**Urban**
Bifenthrin	Increase	Stable	Stable	Stable	Stable	Stable
Cyfluthrin	Stable	Stable	Stable	Decrease	Stable	Stable
lambda-Cyhalothrin	Increase	Stable	Increase	Increase	Increase	Increase
Cypermethrin	Stable	Stable	Increase	Increase	Increase	Increase
Deltamethrin	Stable	Stable	Increase	Stable	Increase	Increase
Esfenvalerate	Stable	Stable	Increase	Increase	Increase	Increase
Fenpropathrin	Stable	Stable	Stable	Increase	Increase	Increase
Permethrin	Stable	Stable	Stable	Stable	Stable	Stable

The increasing concentration trends and increasing detection trends in urban watersheds are related to the increasing use of some pyrethroids in urban settings. Professional applicators, who must report their pesticide use to CDPR, apply most of the pyrethroids used in urban landscapes (Budd et al. 2020). Between 2008 and 2017, reported use of deltamethrin, esfenvalerate and lambda-cyhalothrin significantly increased in non-agricultural settings (see California Pesticide Information Portal: calpip.cdpr.ca.gov), whereas reported non-agricultural use of cyfluthrin, cypermethrin and permethrin decreased. It is not clear why non-agricultural cypermethrin use is decreasing while detections are still increasing. Fenpropathrin detections are increasing, but this pyrethroid is not approved for use in urban areas in California, therefore it is increased detections in open and urban areas could be due to agricultural use within the watersheds.

Comparing Organism Survival to Pyrethroid Toxicity Thresholds

The relationships between toxicity and sediment pyrethroid concentrations were investigated by comparing organism survival to individual and combined pyrethroid threshold values. In the case of pyrethroids, median lethal concentrations (LC50s) were used to evaluate the contribution of pyrethroids to observed toxicity. These threshold concentrations were derived from spiked sediment toxicity studies using *H. azteca* and *C. dilutus*, and are preferable to sediment quality guideline values because they are derived from exposure experiments with single chemicals. There are published *H. azteca* LC50 values and organic carbon-normalized LC50 values for all eight pyrethroids measured, but there are currently only five pyrethroid LC50 values for *C. dilutus* (Appendix 4).

To better evaluate the contribution of pyrethroids to observed toxicity, concentrations were converted to toxic units (TUs). Toxic units are calculated by dividing the measured concentration of an individual pyrethroid by its LC50. Because pyrethroids in a mixture can work additively, the TUs are summed. Approximately 50% mortality would be expected at one TU, and previous research has demonstrated that significant toxicity is observed when the sum of the TUs is greater than one (Weston et al. 2005). Data from early SPoT surveys demonstrate significant toxicity does not always occur unless the TU value is greater than five (Phillips et al. 2017). This analysis is made more accurate by calculating the TU values based on LC50s that have been corrected for the concentration of total organic carbon (TOC) in the sediment. Elevated concentrations of TOC can reduce the bioavailability of organic chemicals such as pesticides (Maund et al. 2002), and normalizing concentrations to TOC account for the relative effect of this sediment constituent on toxicity.

Eighty-eight percent of sediment samples with organic carbon-normalized pyrethroid TUs greater than five were significantly toxic to *H. azteca*, and measured concentrations of pyrethroids explained approximately 25% of the observed *H. azteca* toxicity in the last decade. Pyrethroid TU values between 1 and 5 were present in approximately half of the remaining toxic samples, and likely contributed to the observed toxicity. The midge is much less sensitive to pyrethroids, and only one sample had organic carbon-normalized *C. dilutus* TUs greater than one. This sample contained over 4 TUs and was significantly toxic to *C. dilutus*.

Although there was a significant relationship between organic carbon-normalized TUs and percent survival for *H. azteca*, a number of samples with toxic unit sums greater than one were not significantly toxic. Correcting for organic carbon accounts for some portion of pyrethroid bioavailability but cannot account for all of it. The TOC measurement utilized by SPoT does not differentiate among the various types of organic carbon that might be present. It is possible that the type of carbon at these sites varies and may have a greater binding capacity. Black carbon, which is derived from fossil fuels, can reduce the bioavailability of organic compounds beyond that of plant-derived organic carbon (Kukkonen et al. 2005).

Summing pyrethroid toxic units is a way to examine the potential of these insecticides to contribute to toxicity, particularly to *H. azteca*. Concentrations of individual pyrethroids at sites representing various land uses are either demonstrating no trend or significantly increasing, but when statewide pyrethroid trends are examined as the sum of TUs, it is clear there is a significant upward trend (Figure 5). These data demonstrate the increasing potential of pyrethroids to cause toxicity in receiving systems.

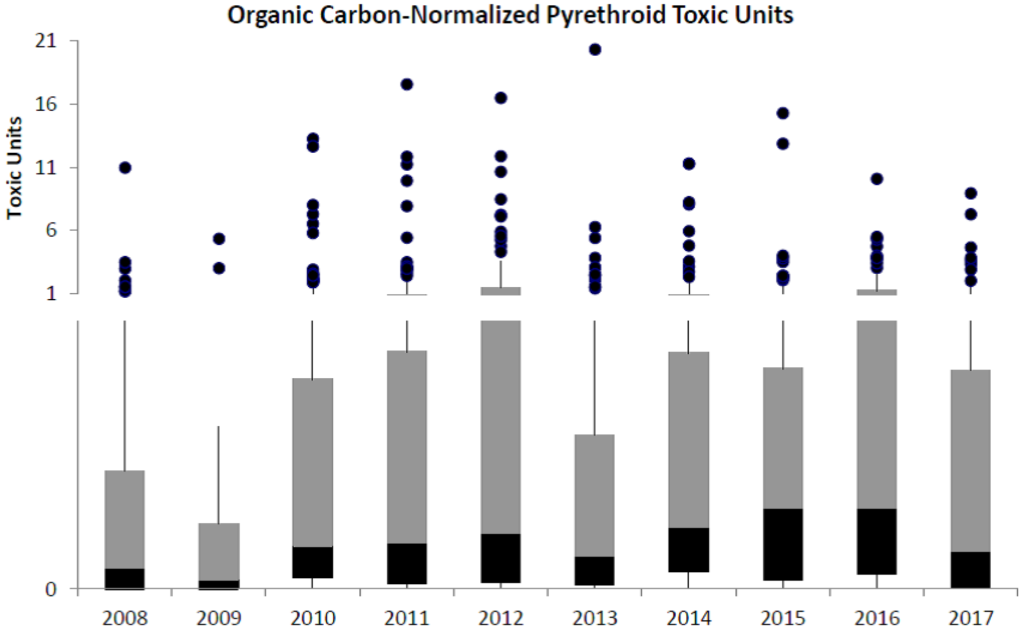


Figure 5. Yearly range of organic carbon-normalized pyrethroid toxic units (2008-2017). Expressed as the potential for a pyrethroid pesticide to cause toxicity to *H. azteca*, concentrations of these compounds continue to significantly increase. (Note: To better illustrate overall trend, a single outlier was omitted from this figure.)

Amphipod test organisms have varying sensitivities to the different pyrethroid compounds. For example, the *H. azteca* LC50 for bifenthrin is 12.9 ng/g, and the LC50 for permethrin is 201 ng/g (Amweg et al. 2005). Because of its low LC50, concentrations of bifenthrin can contribute a high proportion of the measured TUs (Figure 6), and account for approximately half of the TUs in any given year. Permethrin is often measured in higher concentrations but does not contribute as many TUs. Cypermethrin contributes the second most TUs, and deltamethrin has been increasing since 2010.

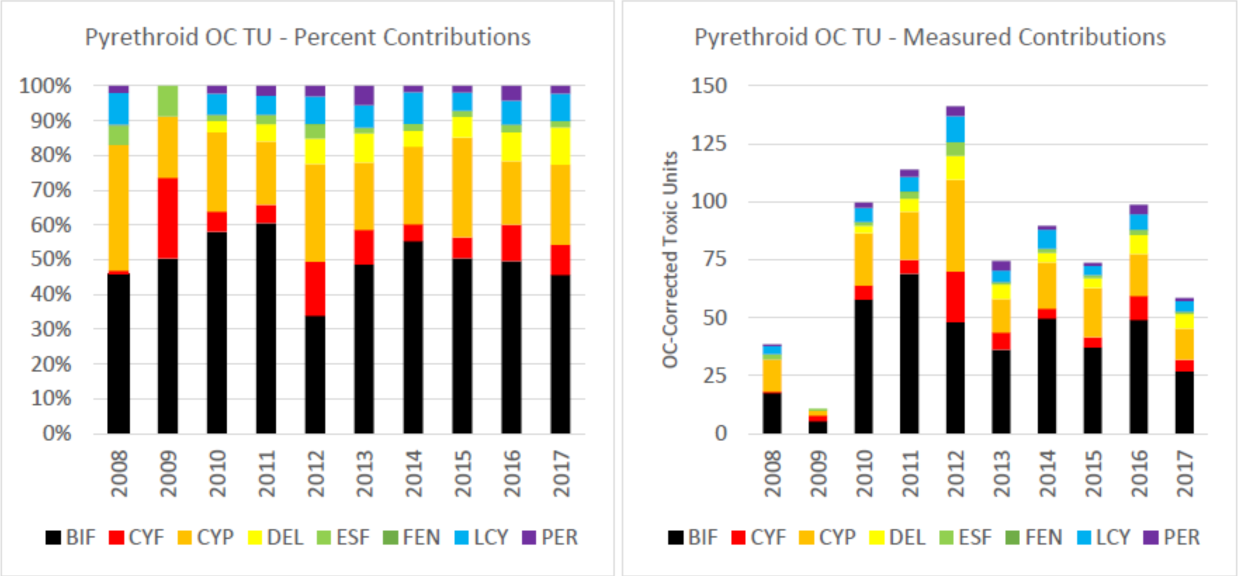


Figure 6. Contributions of organic carbon-normalized toxic units in terms of overall percentage and actual measured contributions. (Note: To better illustrate overall trend, a single outlier was omitted from this figure.)

Potential Impacts at an Environmentally Relevant Temperature

Between 2010 and 2016, 194 subsamples from 57 sites were tested with *H. azteca* toxicity tests at a more environmentally-relevant temperature of 15°C in addition to the standard test temperature of 23°C. This lower temperature better represents the average temperature for surface waters at SWAMP water analysis sites between 2001 and 2010, which was 15.8°C. Some pyrethroids are more toxic at colder temperatures (Coats et al. 1989), and this characteristic has been used as an investigative tool to diagnose pyrethroid-associated toxicity (Anderson et al. 2008). Increasing toxicity with decreasing temperature has been demonstrated specifically with *H. azteca* in more recent studies (Weston et al. 2009), and also with chironomids (Harwood et al. 2009). Harwood et al. (2009) showed this is due to slower metabolic breakdown of pyrethroids at lower temperatures and increased nerve sensitivity. As such, tests were conducted at two temperatures to diagnose the contributions of pyrethroids to observed toxicity. Samples were selected based on previous toxicity results and had pyrethroids detected in the low to moderate TU range. A candidate sample typically had low to moderate toxicity and pyrethroids ranging from one to five TUs.

Significantly more samples were toxic when tested at 15°C, and the magnitude of toxicity was much greater at the lower test temperature (Figure 7). Samples were almost three times more likely to be toxic when tested at 15°C. These results suggest that pyrethroids likely played a role in the increased incidence of toxicity in these samples. These data also suggest that the potential for surface water toxicity is likely underestimated in SPoT watersheds based on assessing toxicity at the standard protocol temperature (23°C). The toxicity results in approximately half of the samples tested at 15°C did not change, but there were no samples having significantly higher survival at the colder temperature.

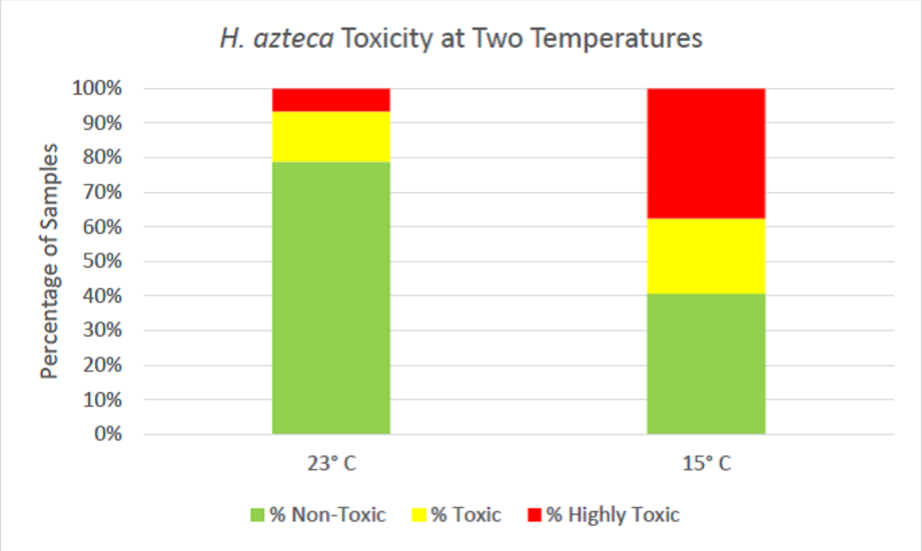


Figure 7. Percentage of samples in each toxicity category tested using *H. azteca* at two temperatures between 2010 and 2016.

The samples that appear to be most vulnerable to increased pyrethroid toxicity when tested at a lower temperature are those that contain less than five toxic units of total pyrethroids. The majority of samples tested at 23°C contain less than five toxic units and are generally not toxic or moderately toxic. These are the samples targeted for 15°C tests because lowering the test temperature shifts the TU threshold to a lower value, indicating that less pyrethroid is necessary to cause a toxic response (Figure 8). Although DDT can cause a similar response at colder temperatures, the concentrations of DDT in these sediments were well below toxicity thresholds for *H. azteca*. These data also suggest that the potential for surface water toxicity is likely underestimated in SPoT watersheds based on assessing toxicity at the standard protocol temperature (23 °C). Testing at two temperatures ended in 2016.

The SWAMP Toxicity Workgroup provided guidance for using data generated from tests at non-standard temperatures (Phillips et al. 2016). The cold temperature treatment provides supporting evidence for the cause of toxicity in tests conducted at standard temperatures. Therefore, data from these tests should be interpreted as additional lines of evidence for regulatory decisions in tests where the data can be compared to data from tests conducted at the standard temperature. Whenever possible, toxicity data should be used in combination with pyrethroid concentration data to determine the potential for pyrethroid impairment of sediment in a water segment.

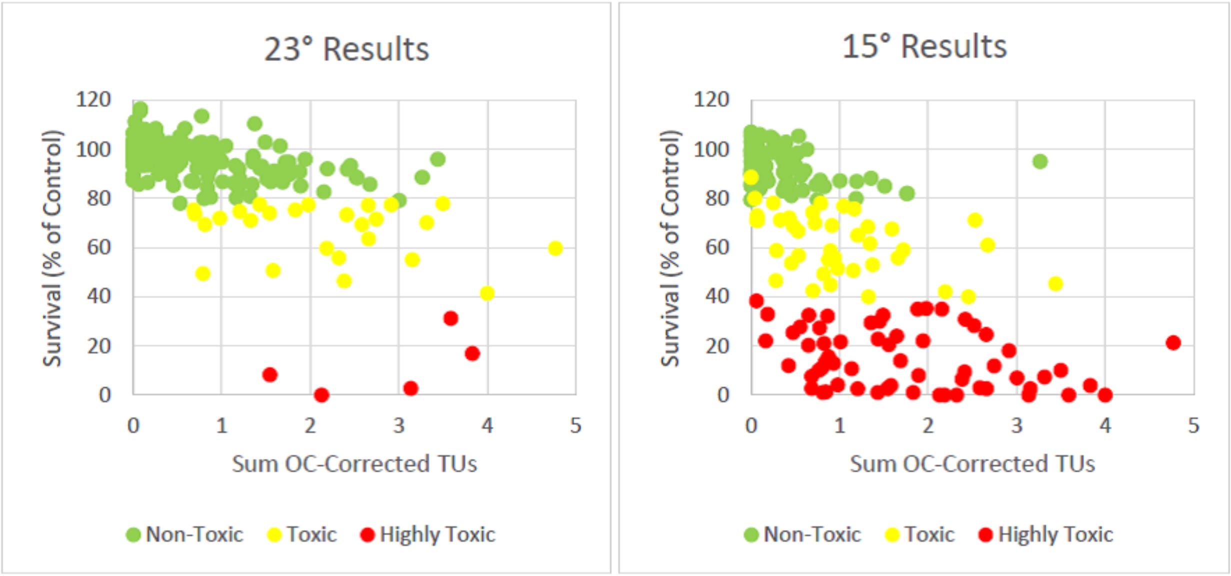


Figure 8. Percent survival of samples with 0 – 5 sum pyrethroid toxic units tested at two different temperatures.

Section 3 – Trends in Other Contaminant Classes

Section Highlights

Urban Contaminants: Frequency of detection and detected concentrations of fipronil and two degradates did not significantly increase. There were no significant trends for individual PAHs or the sum of PAHs. Total PBDEs are significantly increasing.

Chlorinated Compounds: DDTs are significantly decreasing in open watersheds, but PCBs show no trend.

Metals: Copper concentrations are not showing any trends, but zinc concentrations are significantly increasing statewide.

Urban Contaminant Classes

Several contaminant classes are only measured at representative urban sites (Tier II, see Appendix 2). These forty sites underwent changes early in the program as some monitoring sites were dropped and others were added based on whether or not the sites met SPoT objectives. The list has also changed based on current land use data. Because of these changes, there were fewer Tier II sites in the early years of the program, but the current list of forty sites has been consistent since 2015. Contaminant classes measured at only Tier II sites include the urban-use insecticide fipronil, PAHs and PBDEs.

Fipronil

The phenylpyrazole fipronil is a current-use insecticide that was registered in the U.S. in 1996. In California, fipronil is only approved for urban use. The primary outdoor use for fipronil is structural pest control which includes outdoor spraying around buildings to control nuisance insects like ants. Other structural pest control applications, primarily for termite control, include underground injection (into soil around foundations) and indoors in non-occupied foundation spaces (e.g., a dust injected into building wood). Fipronil is also well-known as the active ingredient in anti-flea and tick topical pet applications. Use of the phenylpyrazole insecticide fipronil has been steadily increasing since its introduction (Simon-Delso et al. 2015). This pesticide and its degradates are of ecological concern in California watersheds because of toxicity to stream insects, particularly chironomids (Weston and Lydy 2014).

SPoT began measuring fipronil and its degradates in sediments in 2013. Because fipronil is not registered for use in agriculture applications, SPoT monitoring for this insecticide only occurs at Tier II sites in urban watersheds. Besides the parent compound, there are five major degradates of fipronil, but there are currently only sediment toxicity threshold concentrations available for the parent compound and three of the degradates. The goal of these measurements was to determine the presence and magnitude of this urban-use insecticide and its degradates. The data show a relatively high incidence of fipronil detection in urban sediments, particularly of the fipronil sulfide and sulfone degradates, which are more toxic than the parent compound (Weston and Lydy, 2014).

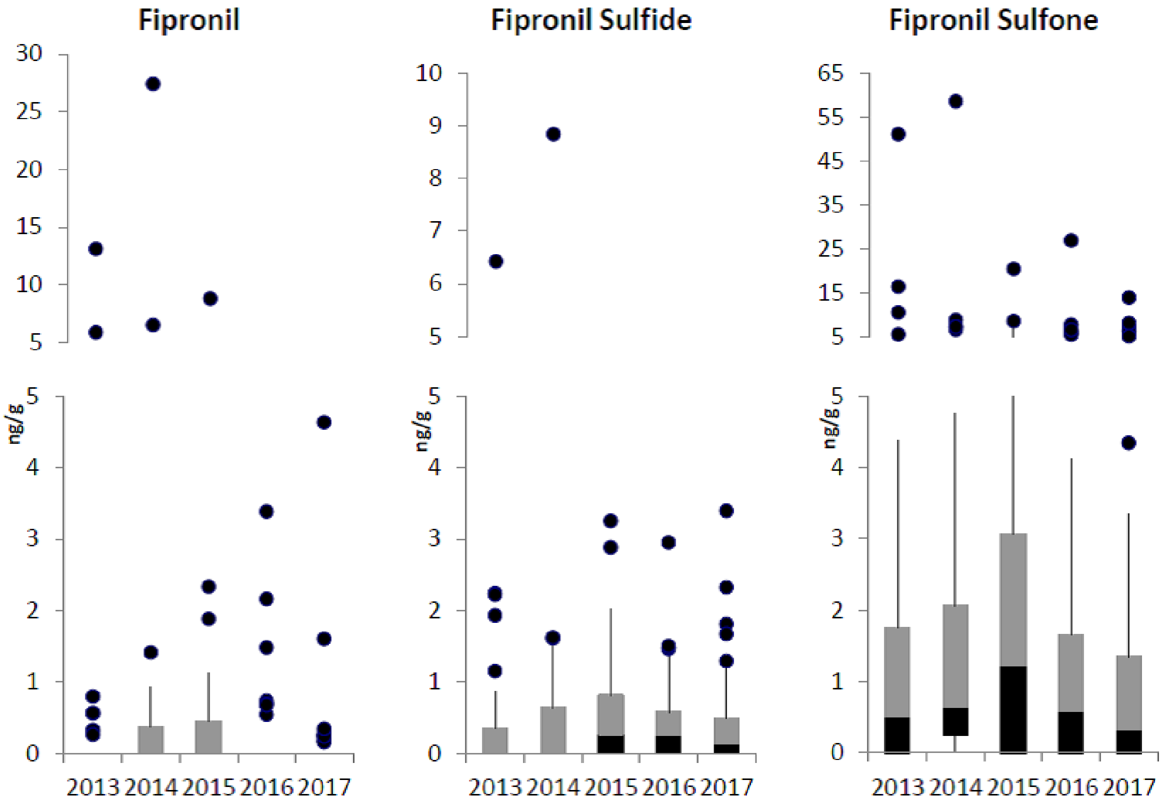


Figure 9. Concentrations of fipronil and two of its degradates, fipronil sulfide and fipronil sulfone at SPoT Tier II sites.

Trends in fipronil concentrations and detections were analyzed for the parent compound (fipronil), as well as fipronil sulfide and fipronil sulfone. Incidents of detection and detected concentrations of these compounds did not significantly increase during the five years they were measured. The fipronil parent compound was detected in approximately 24% of samples, whereas fipronil sulfide and fipronil sulfone were detected in an average of 54% and 71% of samples, respectively. These degradate have comparable sensitivity to the parent compound. Fipronil and its degradates were not suspected of contributing to *H. azteca* toxicity because concentrations of these compounds were well below the individual and summed amphipod toxicity thresholds. Some concentrations of the fipronil compounds were above the individual and summed *C. dilutus* toxicity thresholds, but there was no significant relationship between these elevated concentrations and midge toxicity.

Polycyclic Aromatic Hydrocarbons

Polycyclic aromatic hydrocarbons (PAHs) are ubiquitous in the environment, with one of the major sources being the petroleum industry. PAHs are often concentrated in urban environments because of increased urbanization and automobile use. They move through the environment via stormwater runoff, atmospheric transport, municipal and industrial wastewater, and combustion of organic material (Meador 2008). PAHs are divided into low and high molecular weight compounds based on the number of benzene rings in the molecule. There is also a distinction between parent compounds with a basic ring structure, and alkylated homologs, which can be as toxic or more toxic than the parent compound (Meador 2008). The list of PAH compounds is extensive, but ecotoxicologists generally focus on approximately 40, based on high frequency of occurrence and analytical capabilities. For the purposes of this section, total PAH was based on a sum of 22 compounds, the most complete list that could be compiled based on the range of analytical laboratories used (Appendix 2).

PAHs generally occur in mixtures, and individual compounds can have a wide range of toxic effects. There are only a few PAH sediment toxicity thresholds for *H. azteca* and *C. dilutus*, but there are nine consensus-based sediment quality guideline values that can be applied to the SPoT data set (MacDonald et al. 2000b). Of the 284 sediment samples analyzed for PAH compounds, approximately 15% had at least one exceedance of a consensus-based threshold effect level (TEC) for an individual PAH. Of these samples, approximately half had associated toxicity, but there was no significant relationship between observed toxicity and the number or severity of TEC exceedances or PAH concentrations. There were also no significant trends for individual PAHs or the sum of PAHs between 2008 and 2017 (Figure 10A).

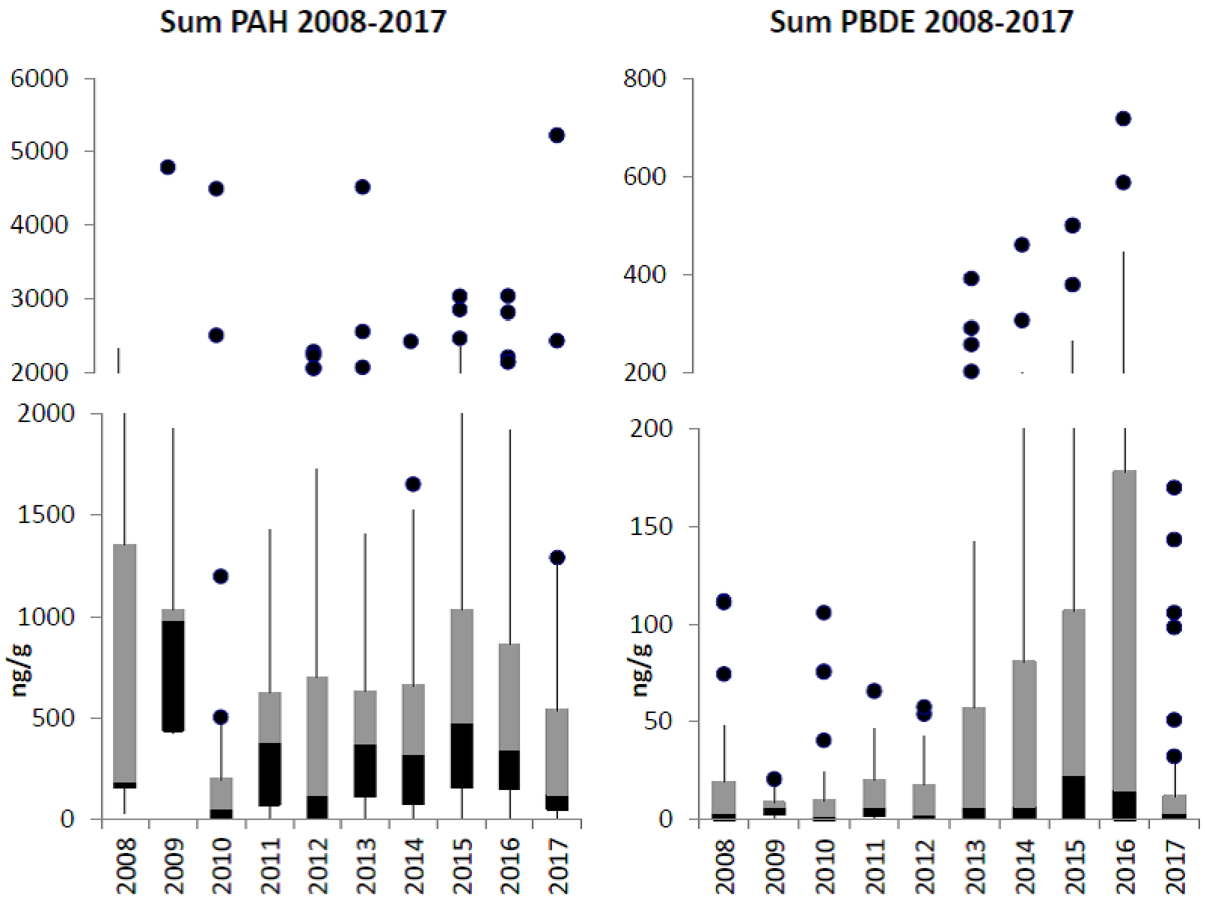


Figure 10. Concentrations of sum PAHs (left), and concentrations of sum PBDEs (right) measured at SPoT Tier II sites.

Polybrominated Diphenyl Ethers

Polybrominated diphenyl ethers (PBDEs) are organobromine compounds that are used as flame retardants in a wide variety of products, including building materials, electronics, furnishings, motor vehicles, airplanes, plastics, polyurethane foams, and textiles. Although PBDEs are not acutely toxic, they can bioaccumulate in higher trophic level organisms. Because of environmental and human health concerns, a number of PBDE formulations have been banned or voluntarily phased out (Sutton et al. 2015).

PBDEs tend to occur in mixtures, but PBDE 209 is the dominant congener in sediments because it is the primary component of the commercial mixture DecaBDE. A close second is PBDE 47. For the purposes of this program, PBDEs were summed based on 13 congeners that were analyzed during most years (Appendix 2), but PBDE 209 was not measured until 2011, and was not measured in 2017 due to a change in analytical laboratory. The sum of PBDEs at SPoT sites were significantly increasing, but this trend was driven by the addition of PBDE 209 measurements (Figure 10B). The trend for sum PBDEs is stable without PBDE 209.

Monitoring data from San Francisco Bay also show a significant downward trend for PBDE 47 in sediments, likely related to a nationwide phase-out, and a state ban of the PentaBDE commercial mixture (Sutton et al. 2015). However, a similar trend was not observed with PBDE 209, likely because the phase-out of this congener did not begin until 2013 (Sutton et al. 2015). Individual trend analysis for PBDE 47 at SPoT sites showed no trend. There were not enough PBDE 209 data to conduct a trend analysis.

Chlorinated Compounds

Legacy Insecticides

Dichlorodiphenyltrichloroethane (DDT) is probably the most well-known of the organochlorine (OC) insecticides due to its environmental legacy. Along with most other OCs (chlordane, dieldrin, endosulfan, hexachlorocyclohexane, etc.), DDT was banned for use in the U.S. in 1972. DDT is considered one of the most insoluble and persistent pesticides ever synthesized (Ware and Whitacre 2004), and it readily bioaccumulates. These chemicals persist in the environment but are not as toxic as many of the current-use pesticides.

Organochlorine pesticides have been tracked at SPoT sites since 2008. Results for total DDT (the sum of six compounds), is presented as representative of the trends of these chemicals in California streams. Statewide, DDT concentrations are not exhibiting any trends, but when broken down by land use, DDT is significantly decreasing in watersheds with open land use at the 5 km radius. It is unlikely DDT, or any of the OC insecticides, are significantly contributing to toxicity.

The published *H. azteca* LC50 for total DDT is 11,000 ng/g ((Nebeker et al. 1989) Appendix 4), and the highest detected concentration in the SPoT data set is 420 ng/g. The highest measured DDT concentrations tend to be detected in Central Coast regional sites that have agricultural influence. There is significant toxicity in some of the samples from these sites, but most of the observed toxicity is related to pyrethroid insecticides. The consensus-based TEC for total DDT (5.28 ng/g) is considerably lower than the *H. azteca* LC50. Although this concentration would be highly protective of the environment, it does not have any relationship to the observed toxicity in SPoT.

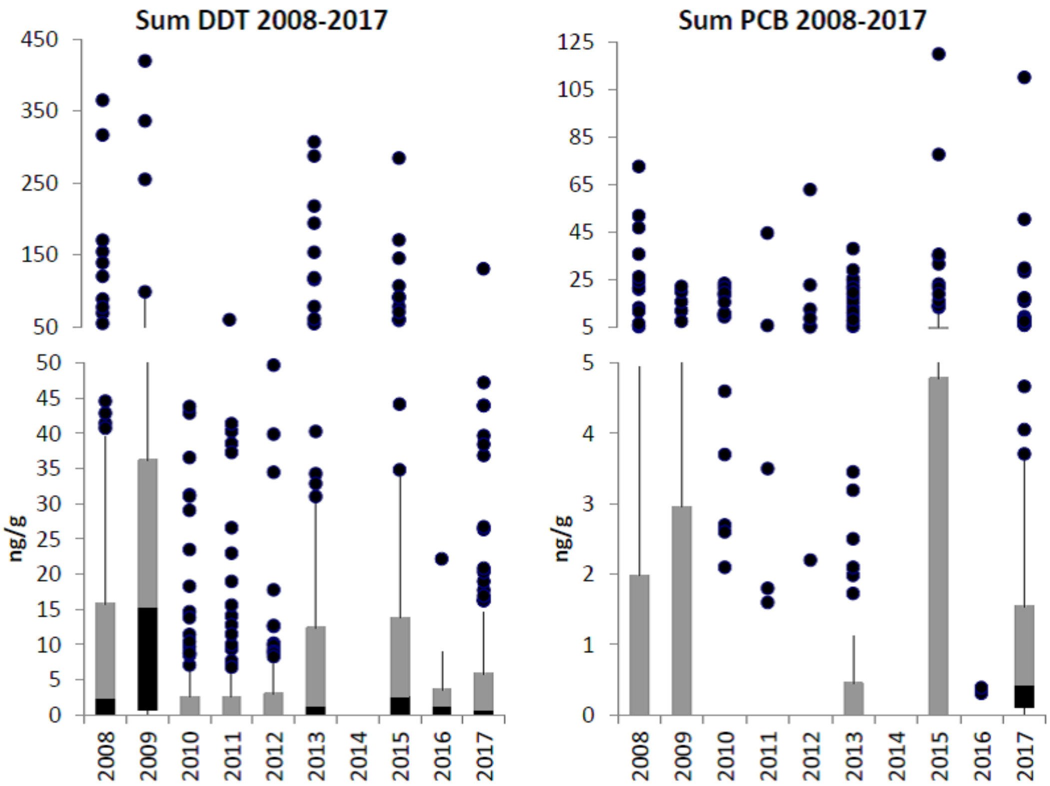


Figure 11. Concentrations of sum DDTs (left), and concentrations of sum PCBs (right).

Polychlorinated Biphenyls

Polychlorinated Biphenyls (PCBs) were used in hundreds of industrial and commercial applications including electrical, heat transfer and hydraulic equipment, plasticizers in paints, plastics and rubber products, and pigments, dyes and carbonless copy paper. They were manufactured domestically until 1979, but because of their stability, they can remain in the environment for long periods, cycling between air, water, and soil. PCBs are generally not acutely toxic, but can bioaccumulate in organisms at the lower end of the food web, and bioconcentrate in higher trophic levels (Beyer and Biziuk 2009). At higher trophic levels, PCBs can cause endocrine and neurological effects (Fonnum and Mariussen 2009).

Much like PBDEs, individual PCB congeners occur in mixtures in the environment, and for the purposes of this program, 25 PCBs were summed to determine trends (Appendix 2). PCBs were measured in watersheds with all land uses, and although concentrations tended to be higher in urban watersheds, there were no significant increases or decreases in PCB concentrations since 2008. There are no reliable PCB toxicity thresholds for the organisms used in SPoT, but there is a consensus-based TEC from MacDonald et al. (2000a). The TEC for total PCB concentrations is

59.8 ng/g, and much like the TEC for total DDT, does not have any relationship to observed toxicity.

Metals

The term "heavy metals" covers a wide range of elements on the periodic table, and there is no widely agreed-upon definition for the term. Most trace metals measured as part of environmental monitoring efforts are naturally occurring, and many are essential as nutrients, but all metals can be toxic at some concentrations. Elevated metals concentrations in sediments can also be indicators of metal contamination released into the environment by human activity. Sources such as wastewater effluent, atmospheric deposition, urban runoff, and copper-based agricultural products all contribute to trace metal concentrations in sediment.

SPoT measures 12 trace metals: aluminum, arsenic, cadmium, chromium, copper, lead, manganese, mercury, nickel, selenium, silver and zinc. There are established toxicity thresholds (*H. azteca* and *C. dilutus* LC50s) for arsenic, cadmium, copper and nickel (Appendix 4), but no individual metal concentration exceeds these metal LC50s. Copper and nickel concentrations at some sites amount to approximately one-half a TU, but there is no significant relationship between any of the individual metals and observed toxicity.

Trend analyses were conducted for copper and zinc as representative metals with clear anthropogenic sources. Copper is not showing any significant trends, either statewide or by land use. Zinc also does not show trends by individual land use and although the trend is subtle, median concentrations of zinc are significantly increasing statewide. Copper concentrations are closely observed within the SPoT program to determine whether or not copper concentrations have been decreasing due to reduced use in automobile brake pads. This trend would likely be most apparent in urban watersheds. Measurable reductions of copper due to brake pad manufacturing content reductions are not expected until the early 2020s (Moran 2016). Zinc is listed as a limiting pollutant in a number of southern California MS4 stormwater management plans. By limiting this pollutant through the design of management practices and controls, other similar pollutants of concern should also be limited. Stormwater permittees can utilize data from southern California SPoT sites to help track significant trends in their watersheds.

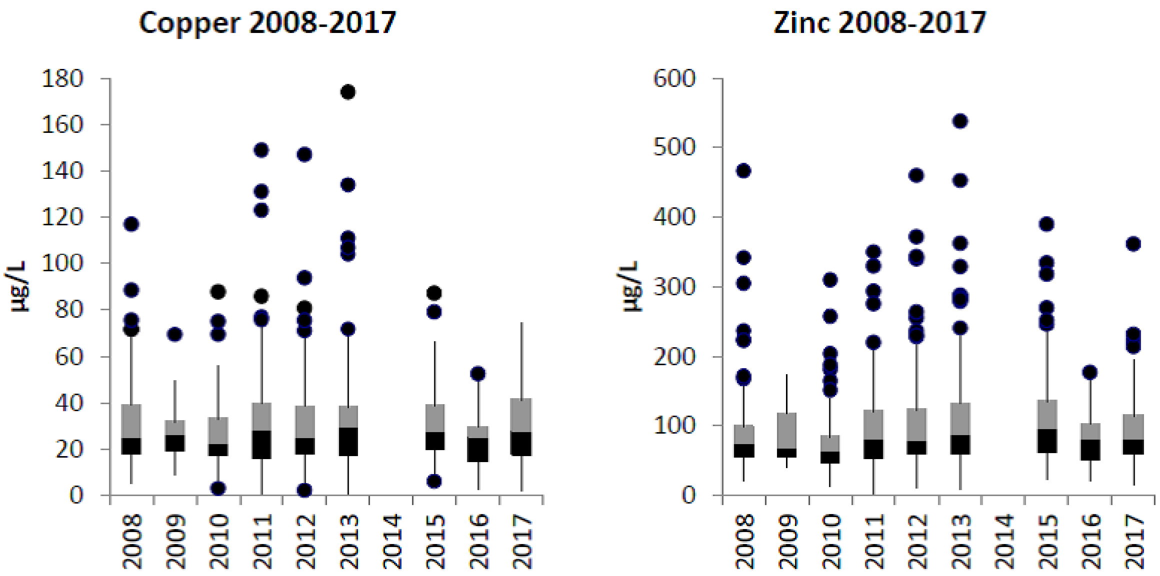


Figure 12. Concentrations of copper (left), and concentrations of zinc (right).

Organophosphate Insecticides

Organophosphate (OP) insecticide use has decreased as pyrethroid and other insecticide use has increased, particularly in urban areas. Most recently, the OP chlorpyrifos is being phased out in California in 2020, following the phase-out of diazinon for residential use in 2001 and chlorpyrifos for residential use in 2005. Many OPs are still used, but detections at SPoT sites have been reduced, and current concentrations are generally well below toxicity thresholds.

A complete suite of OPs were measured in SPoT sediments from 2008 to 2013. During the first years of SPoT monitoring, sediment from some agriculturally influenced sites contained chlorpyrifos at concentrations that could have contributed to toxicity (Phillips et al. 2017), but because of funding limitations, these compounds were not measured in 2014. Organophosphates were measured in a subset of sediments from 2015 and 2016, but further measurements of OPs were suspended beginning in 2017 due to minimal detections and insufficient data to calculate trends.

Section 4 – Interagency Collaborations

Section Highlights

Three collaborative studies are in progress between the State Water Resource Control Board's SPoT Program, and the California Department of Pesticide Regulation and the California Department of Toxic Substance Control, and one intra-agency collaboration is underway between SPoT and Water Board researchers studying constituents of emerging concern.

Past and ongoing collaborations also include monitoring design for the Urban Pesticide Coordinated Monitoring Program, work with bioassessment monitoring programs, and State and Regional Water Board agricultural monitoring, stormwater monitoring and support of 303(d) listings through the Integrated Reporting Process.

Intensive Site Study

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

Four sites were chosen, two existing CDPR urban monitoring stations (Salt Creek and Pleasant Grove Creek), and two existing SPoT stations (Bouquet Canyon Creek and Kirker Creek). All stations previously demonstrated significant toxicity and elevated concentrations of pyrethroids (Ensminger et al. 2013; Phillips et al. 2014; Weston et al. 2005). The four sites were sampled four times per year between 2013 and 2016, and then twice per year in 2017 and 2018. Sediment was analyzed for toxicity to *H. azteca*, as well as pyrethroid pesticides and fipronil, and its degradates. (Fipronil is another common outdoor insecticide that CDPR and registrants are addressing through modified outdoor application instructions.) Trend data were analyzed for both amphipod toxicity endpoints, total pyrethroid and fipronil concentrations, and the sum of pyrethroid and fipronil TUs normalized to organic carbon concentrations.

The four intensive study sites contain a broad range of pyrethroid concentrations from low ng/g to low µg/g (Figure 12), and varying levels of toxicity to amphipod survival and growth (data not shown). Fipronil concentrations were generally well below toxic concentrations for amphipods and chironomids. Pyrethroid and fipronil concentrations at Pleasant Grove Creek were on the low end of the range, and survival toxicity was only observed in one sample. Although pesticide concentrations at this site were low, both significantly increased between 2013 and 2017 (Table 4). The other three sites showed significant decreases in concentrations of one or both pesticides and in all pesticide-related TUs, and two sites demonstrated significant increases in amphipod growth. Kirker Creek had consistently moderate concentrations of pyrethroids, but only demonstrated significant amphipod mortality in one sample and significant reductions in amphipod growth in three samples. Concentrations of pyrethroids were an order of magnitude higher at Salt Creek, where there were many more incidents of toxicity to amphipod survival and growth. Both Kirker and Salt Creek demonstrated significant increases in amphipod growth and significant decreases in pyrethroid organic carbon-normalized TUs (Table 4). Concentrations of pyrethroids at Bouquet Canyon Creek were the highest measured in the SPoT program, and complete mortality continues to be observed in almost every sample collected. Despite this fact, pyrethroid concentrations and the sum of organic carbon- normalized toxic units were significantly decreasing at the site as of 2017.

Data from this collaboration contributed to a recent CDPR publication evaluating temporal and spatial trends of pyrethroid concentrations in California (Budd et al. 2020). In this paper, Budd et al. (2020) determined significant trends in concentrations of several pyrethroids, some of which were reflected in SPoT monitoring. These authors also illuminate the importance of stormwater for pyrethroid transport, as well as the potential long-term sources of pyrethroids in sediments.

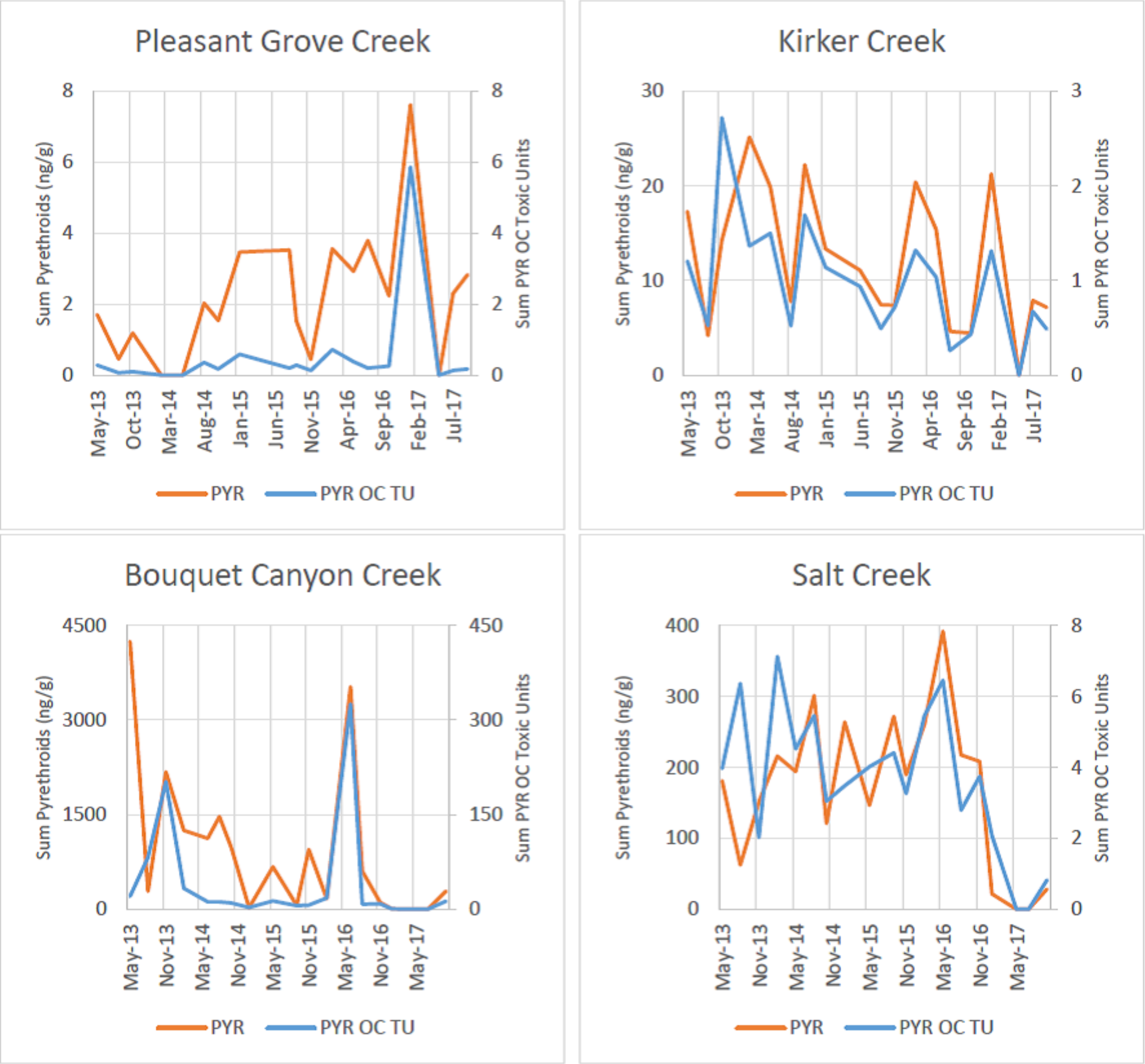


Figure 13. Pyrethroid concentrations (orange) and pyrethroid toxic units (blue) from four sites that were intensively monitored as part of a collaboration between SPoT and Department of Pesticide Regulation.

Table 4. Trends in *Hyalella azteca* survival and growth, as well as concentrations and toxic units of pyrethroids and fipronil from four intensively monitored urban sites from 2013-2017. TU indicates toxic units. Shading indicates significant trends.

Station Name	***H. azteca***		**Pyrethroids**		**Fipronil**	
	Survival	**Growth**	**Sum Conc.**	**Sum OC TU**	**Sum Conc.**	**Sum OC TU**
Pleasant Grove Creek	Stable	Stable	Increase	Stable	Increase	Stable
Kirker Creek	Stable	Increase	Decrease	Decrease	Stable	Decrease
Salt Creek	Stable	Increase	Stable	Decrease	Decrease	Decrease
Bouquet Canyon Creek	Stable	Stable	Decrease	Decrease	Decrease	Decrease

CDPR Surface Water Supplemental Toxicity

In 2014 and 2015, there was an additional collaboration with CDPR integrating Regional SWAMP monitoring for water column toxicity at CDPR's agricultural surface water monitoring sites. The Central Coast and Colorado River Basin Regional Water Quality Boards funded toxicity testing using *H. azteca* and *C. dilutus* at 17 sites. Significant toxicity was observed at sites that were minimally toxic to U.S. EPA's standard three-species tests: *Pimephales promelas, Ceriodaphnia dubia, and Selenastrum* (*Raphidocelis*) *capricornutum* (Anderson et al. 2018). Chemical analysis by CDPR detected a number of current-use pesticides, and toxicity testing results indicated these chemicals have the potential to impact the receiving systems. In addition to monitoring organophosphates and pyrethroids in water, this monitoring was specifically targeting water concentrations of the neonicotinoid insecticide imidacloprid. Neonicotinoids are not expected to partition to sediments due to their high solubility. These data informed a recent SWAMP memo on changing patterns in toxicity and provided recommendations for choosing toxicity test species for pesticide-related projects (https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/workplans/tox_recs_tech_memo.pdf).

This project led to an ongoing collaboration between SPoT and CDPR to conduct toxicity testing on CDPR surface water monitoring samples collected from urban and agricultural watersheds throughout the state. Water column toxicity testing with *H. azteca* (survival) and *C. dilutus* (survival and growth), coupled with CDPR analyses of current-use pesticides in water provided up-to-date information on the risk of emerging contaminants to California watersheds.

Table 5. Amphipod and midge toxicity results from CDPR surface water monitoring sites. Water column toxicity results augment chemical concentrations measured as part of CDPR's Surface Water Monitoring program. PYR indicates sum pyrethroids. IMI indicates imidacloprid. TU indicates toxic units. Shaded cells indicate significant toxicity (T) or TU values greater than 0.5 (>0.5). Chemical concentrations are presented as toxic units for total pyrethroids and imidacloprid.

SPoT Sites	Sample Date	*H. azteca*			*C. dilutus*			
		Survival (% of control)	PYR TU	IMI TU	Survival (% of control)	Growth (mg/ind.)	PYR TU	IMI TU
205GUA020	6/12/2018	98	0	0	95.8	2.51	0	0
205GUA020	8/7/2018	100	0	0	87.5	3.22	0	0
207WAL020	6/12/2018	98	0	0	97.9	2.27	0	0
207WAL020	8/7/2018	96	0	0	91.7	3.96	0	0
309DAV	5/21/2018	98	0	0	91.7	0.895	0	0
309DAV	7/16/2018	100	0	0	87.5	1.49	0	0.01
309DAV	9/17/2018	100	0	0	100	3.79	0	0
309DAV	11/26/2018	74	0	0	89.6	2.5	0	0
723ARGRB1	3/27/2018	58(T)	1.00 (>0.5)	0	87.8	5.69	0.06	0.03
723ARGRB1	10/16/2018	82	0	0	97.9	5.01(T)	0	0.09
723NROTWM	3/27/2018	68(T)	0	0	100	5.39	0	0.05
723NROTWM	10/6/2018	42.5(T)	21.7(>0.5)	0	89.6	5.97	0.01	0.06
Other Sites								
309JON	5/21/2018	80	0.14	0.02	6.25(T)	0.25(T)	0.02	0.42
309JON	9/17/2018	22(T)	0.57(>0.5)	0.01	97.9	2.25	0.06	0.19
309JON	11/26/2018	20(T)	0.49	0	27.1(T)	0.302(T)	0.06	0.03
309TEH	5/21/2018	50(T)	0.52(>0.5)	0.01	81.3	0.567	0.06	0.12
309TEH	9/17/2018	92	0.19	0	100	2.64	0.02	0.01
309TEH	11/26/2018	34(T)	0	0	14.6(T)	0.147(T)	0	0.04
312OFC	11/27/2018	92	0.25	0	77.1	1.71(T)	0.03	0.01
312ORC	5/22/2018	96	0	0.08	0(T)	NA	0	1.85(>0.5)
312ORC	9/18/2018	100	0	0.01	31.3(T)	0.284	0	0.30
312ORC	11/27/2018	86	0	0.01	45.8(T)	0.639(T)	0	0.17
312SMSN74	5/22/2018	86	0	0	75(T)	0.289(T)	0	0.09
312SMSN74	9/18/2018	64(T)	0	0.10	0(T)	NA	0	2.38(>0.5)
312SMSN74	11/27/2018	94.4	0	0	85.4	2.27(T)	0	0.09
519SED008	8/6/2018	96	0	0	75(>0.5)	1.34	0	0.01

Twenty-six water samples from 11 sites were collected and tested throughout 2018. Five of these sites were routine SPoT sites, five were additional toxicity samples collected at CDPR sites within the Central Coast Regional Water Quality Control Board (Region 3), and one was from the Central Valley (Region 5). Significant acute toxicity was observed in 14 samples from seven sites (Table 5). Chronic toxicity to *C. dilutus* was observed in three additional samples from three sites. A full suite of pesticides was analyzed for each sample. Sixteen of 35 insecticides and degradates were detected, 12 of 29 herbicides were detected, and 3 of 23 fungicides and degradates were detected. Chemical contributions to toxicity were determined by comparing measured concentrations with median lethal concentrations (LC50s) and using a TU approach to determine the magnitude of the contribution. Acute amphipod toxicity could be attributed to pyrethroids in half of the toxic samples, which was expected because of the sensitivity of *H. azteca* to this class of chemical. The midge is less sensitive to pyrethroids and more sensitive to imidacloprid, but of the nine samples that were acutely toxic to the midge, only the toxicity of two samples could be attributed to imidacloprid.

SPoT/DTSC Collaboration for Statewide Screening of Chemicals of Emerging Concern

The primary mission of the California Department of Toxic Substance Control (DTSC) is to protect residents and the environment from toxic substances. This is accomplished, in part, through the prioritization of chemicals of emerging concern (CEC) for consideration by DTSC's Safer Consumer Products Program. Because SPoT currently monitors sediment toxicity and contaminants at the base of 90 watersheds statewide, and has identified a number of significant trends, the program was in a good position to provide water sample collection and sediment and water analyses for CECs that DTSC was interested in. Since the beginning of the program, SPoT has adapted to reduce monitoring of some chemical classes and focus on CECs and their potential to contribute to toxicity and environmental impacts. Data from this exercise could inform SPoT's future sampling efforts.

The State Water Resources Control Board proposed a collaboration between SPoT and DTSC to conduct a one-time survey of emerging contaminants at SPoT sites in 2019. Managers and staff from both groups reviewed SPoT sites and potential analytes to formulate a monitoring plan. The final monitoring plan included five CECs to be sampled in sediment (galaxolide, octamethylcyclotetrasiloxane, decamethylcyclopentasiloxane, dodecamethylcyclohexasiloxane, and Quaternary Ammonium Compounds), and one in water (1,3-diphenylguanidine). Data from this project will be submitted to the SWAMP Database and CEDEN, and it will be presented as a stand-alone report from DTSC.

State Water Board Passive Sampling Study

Data from SPoT monitoring have demonstrated significant relationships among land use, pesticide concentration, and toxicity. These results corroborate previous SWAMP toxicity data demonstrating that pesticides are overwhelmingly linked to toxicity. SPoT measures discrete classes of pesticides that are associated with sediments and could actually be underestimating the environmental risk from chronic exposure to emerging water-soluble pesticides and other contaminants. To date, SPoT has not addressed more traditional CECs, which are generally unregulated and include pharmaceuticals, industrial chemicals, consumer product ingredients, plastic additives, surface treatments, flame retardants, food additives, and personal care products. CECs are present in wastewater systems, agricultural and urban runoff, and landfill leachates.

Statewide, CEC monitoring programs have prioritized wastewater treatment plant (WWTP) systems, receiving water downstream of WWTPs, and urban runoff for monitoring (Anderson et.al. 2012). The Statewide Science Panel hypothesized that most CECs occur in trace concentrations in WWTP effluent, however, the larger volume discharged to receiving waters throughout the year results in total mass loadings that are comparable to contaminants such as heavy metals (Phillips et al. 2014). Similarly, the panel hypothesized stormwater runoff is another major source of CECs in receiving water. The total volume of water annually discharged is roughly equivalent to wastewater effluent discharge in southern California Bight (Lyon and Stein 2009). The panel also recognized that discharge from septic systems, concentrated brine disposal, dry weather runoff, agricultural runoff, industrial discharges, groundwater, and atmospheric deposition are additional sources. However, the occurrence data for these sources are limited and have not been evaluated.

Regional CEC monitoring has minimally used passive samplers. Passive samplers are monitoring tools that can measure the concentrations of freely dissolved pollutants more precisely and have generally lower detection limits than grab samples (Charriau et. al. 2016). Research indicates that grab samples are inadequate for capturing episodic discharge events and can lead to a supposition of negative detections by missing pulses of contaminants. In addition to missing the pulses, grab samples generally collect a low volume of water, which is a small fraction of the stream discharge. Passive sampling utilizes solid phase extraction (SPE) media to capture episodic discharge events over longer periods, and can have detection limits orders of magnitude lower than grab sampling. Passive samplers can be used for qualitative detection, or presence/absence, or in some cases can be used for quantitative measurements depending on the device and analyte.

A special study was conducted in 2019 with the goal of determining if passive samplers could provide enhanced information about CECs at SPoT sites, and to compare qualitative concentrations determined with passive samplers to measured concentrations in grab samples and sediment samples.

Sites were chosen for passive sampling based on proximity to, and influence by WWTP outfalls. Sixteen sites were chosen based on these criteria, and six sites were prioritized based on logistics and suitability (Table 6). Passive samplers were deployed during regular SPoT monitoring activities; an initial water sample was collected at the time of deployment. Passive samplers were retrieved approximately three weeks later, and a second water sample was collected. Solid-phase extraction disks (C-18 and HLB) and water samples were all analyzed for the compounds listed in Table 6. A final report from this special project is expected from the State Water Resources Control Board in 2020.

Table 6. SPoT sites measured as part of the passive sampling project, and list of compounds measured from solid-phase extraction media.

Station	Primary Substrate	Days in Field
403STCEST	Sand	20
405SGRA2x	Sand/Mud	20
408CGCS06	Sand	20
412LARWxx	Concrete	20
801CCPT12	Sand/Mud	19
801SARVRx	Sand	19

Compounds	Method
1,4-Dioxane by GCMS	EPA 8270M
OPP low-level	EPA 525.2M
Polyfluoroalkyl Substances (PFAS)	EPA 537M
Neonicotinoids by LC/MS/MS	EPA 538
Semi-volatile Organic Compounds	EPA 625
Tributyltin by GC/MS	Krone, et al, 1989
Polybrominated Diphenyl Ethers (PBDEs) by GC/MS SIM	EPA 1614M
Alkyl Phenols by GCMS	ASTM D7065
PPCP - Hormones by LCMSMS-APCI+	EPA 1694M-APCI
PPCP - Pharmaceuticals by LCMSMS-ESI-	EPA 1694M-ESI-
PPCP - Pharmaceuticals by LCMSMS-ESI+	EPA 1694M-ESI+
Pyrethroid Pesticides by GC/MS/MS	EPA 8270M

Section 5 – Cyanotoxin Special Study

Section Highlight

Microcystin was detected in 58% of samples in 2014, with 14% below the reporting limit (RL), 34% in 2015 (28% <RL), and 62% in 2016 (52% <RL). A significantly higher percentage of samples contained reportable concentrations of microcystins in 2014 as compared to the following two years.

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

In 2013 SPoT began a collaboration with Erin Stanfield and others at California State University Monterey Bay to develop and implement a method to analyze microcystin in sediment extracts. This represents the first statewide survey of microcystins in California stream benthos and provides baseline data for this CEC in California watersheds. Of the 52 sites sampled, 38 sites were categorized as urban, seven were agricultural, and seven were open space. Four urban sites were sampled quarterly to evaluate seasonal variability.

The 2013 results showed detections of microcystins in approximately three-quarters of sediment samples, but there was concern that some of the low detections were due to enzyme-linked immunosorbent assay (ELISA) false positives from matrix interference of humic material and other particles in the sediment extracts. In 2014, the method was revised to include solid-phase extraction as an additional clean up step. Microcystins were detected in eight of the nine Water Quality Control Board Regions, and in watersheds with diverse habitat types and land uses (Siegler et al. in preparation). Microcystin was detected in 58% of samples in 2014 with 14% below the reporting limit (RL), 34% in 2015 (28% <RL), and 62% in 2016 (52% <RL). Although some concentrations were an order of magnitude higher in 2014 than subsequent years, the median of concentrations above the reporting limit were 0.387, 0.481, and 0.783

ng/g for 2014, 2015, and 2016, respectively. This appeared to be a trend of increasing concentrations, but it was not statistically significant. The percentage of samples with detections was similar to those reported by Fetscher et al. (2015) for microcystins in Southern California wadeable streams.

Microcystins in the water column have had a number of effects on fish populations, and occasionally have caused harm to mammals (Backer et al. 2013; Malbrouk and Kestemont 2006; Miller et al. 2010), but the ecological relevance of sediment-bound microcystins is relatively unknown. As part of the microcystin study, the potential for microcystins to bioaccumulate in sediment dwelling invertebrates was assessed. Midge larvae (*C. dilutus*) were exposed to cultures of *Microcystis aeruginosa* (Strain LB 2385, University of Texas, Austin). Following a seven-day exposure, concentrations of 0.017 ug/g (chironomid wet weight) were detected, but microcystins were not detected in the control larvae or in store-purchased larvae. At the beginning of the exposure, measured intercellular microcystins in the culture media were 72 +/- 6 µg/L and the extracellular concentration was 41 +/- 4 µg/L. By the end, extracellular microcystins were 1.5 +/- 0.8 µg/L. Toporowska et al. (2014) reported a 61% decrease in survival of riverine *C. dilutus* larvae after a 96-hour exposure to a concentration of 3,320 µg/L microcystin-LR, and Ali (1990) reported 52 to 84 percent of food in the guts of *C. crassicaudaus* to be cyanobacteria, indicating their importance as a food source. *Chironomus dilutus*, as a food source for fish and other animals, can act as a potential mechanism for trophic transfer of microcystins into the ecosystem.

Monitoring microcystins bound to stream sediments may be an indicator of harmful algal blooms upstream or in-stream toxin production. Results for 2017 and 2018 were produced using ELISA kits with higher reporting limits (MDL = 0.42 ng/g, RL= 0.90 ng/g), as compared to the older version of the kit (MDL = 0.15 ng/g, RL = 0.30 ng/g), making direct comparisons to previous data sets impossible, but still allowing for the reporting of extreme concentrations. 2018 will likely be the final year of the microcystin study, as more information is needed on the ecological relevance of sediment bound microcystins.

Additional information on the monitoring of HABs in California can be found at: https://www.waterboards.ca.gov/water_issues/programs/swamp/freshwater_cyanobacteria.html

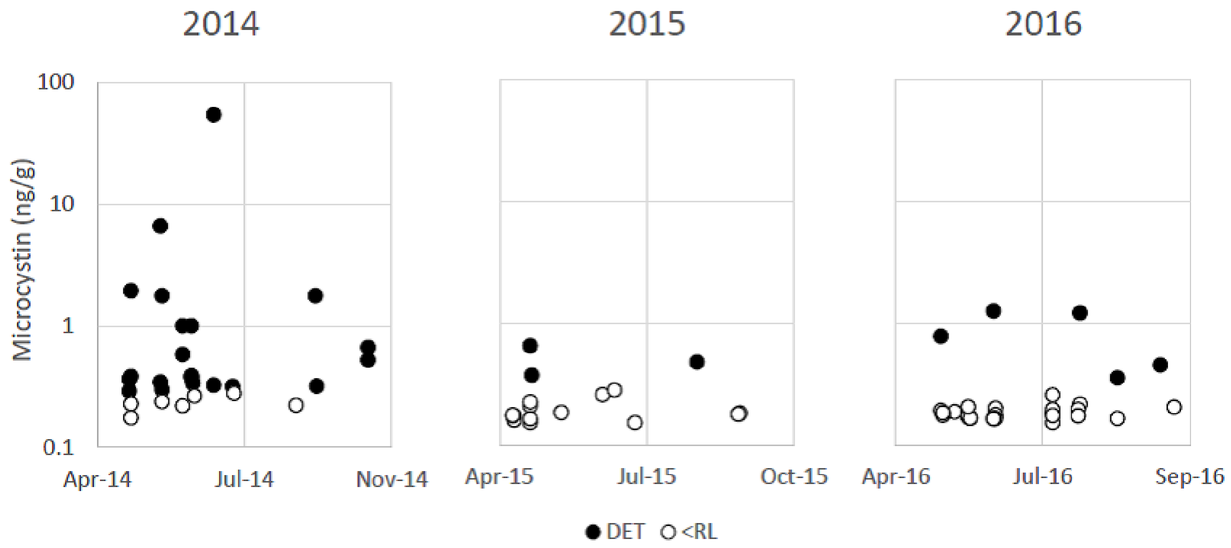


Figure 14. Detected and detected but not quantified (<RL = 0.3 ng/g) concentrations of microcystin equivalents at a subset of 50 SPoT sites.

Section 6 – Trends at Individual Sites and Regional Summaries

All of the tables in this section are similarly configured. Toxicity is presented as the mean percent control from the first year of sampling to 2018.

Toxicity results from multiple years were summarized using the following criteria: sites with no toxic samples were coded green and marked “NT” for non-toxic; sites with at least one toxic sample were coded yellow and marked “ST” for some toxicity; sites with at least one sample exceeding the high toxicity threshold were coded orange and marked “MT” for moderate toxicity, and sites with an average survival less than the high toxicity threshold were coded red and marked “HT” for high toxicity.

Statistically significant trends are based on Mann Kendall analysis of median toxicity response (to 2018) or median contaminant concentrations (to 2017) and are noted with arrows. NA indicates not analyzed.

Region 1 – North Coast

The lower watersheds of most sites in Region 1 are dominated by open land use at the 5 km scale. Smith River (103SM1009) has sufficient cover of developed open space to place it in the urban land use category, and Laguna de Santa Rosa (114LAGWOH) was classified as agricultural based on the 2016 National Land Cover Database. Most sites have had a single incidence of moderate toxicity, and the Navarro River (113NA3269) has been moderately toxic in four of seven years. Two sites were tested with *C. dilutus* in 2018 and did not show any toxicity to midge survival or growth. 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, but overall, this region has the lowest pesticide concentrations in the state. Two sites in Region 1 were removed from the SPoT list in 2019, Smith River (103SM1009) and Eel River – South Fork at Myers Flat (111SF0933).

Region 2 – San Francisco Bay

Eight of the eleven watersheds sampled in Region 2 are classified as urban at the 5 km scale. Only Sonoma Creek (206SON010) was influenced by agriculture based on the NLCD, and only on the 1 km and 5 km scales. Although most of the sites in the region have urban influences, there continues to be a trend of decreasing toxicity to amphipods. Five sites had significant trends of increasing amphipod survival in toxicity tests, and two of these sites had significantly increasing amphipod growth. Three sites also had significant increases in midge survival. There were two sites that were highly toxic to amphipods (Kirker Creek 207KIR020, and Walker Creek 201WLK160), but there have been four sites that were highly toxic to midge survival or growth (San Leandro Creek 204SLE030, Coyote Creek 205COY060, Kirker Creek 207KIR020 and Laurel Creek 207LAU020). Despite a statewide increase in pyrethroid pesticides in urban watersheds, two sites had significant decreases of pyrethroids, and fipronil decreased at one site. A significant decrease in PAHs was observed in Guadalupe Creek (205GAU020) and a decrease in PBDEs was observed in Walnut Creek (207WAL020). Lagunitas Creek was removed from the SPoT site list and last sampled in 2017 (201LAG125).

Region 3 – Central Coast

At the 5 km scale, six of the Region 3 watersheds are classified as urban. Of the remaining sites tested, five are classified as open and two are classified as agricultural. Tembladero Slough (309TDW) and the Santa Maria River (312SMA) sites have been consistently toxic during the first five years of SPoT, but the Tembladero Slough has continued to show significantly decreasing amphipod survival, whereas the Santa Maria River has shown a significant increase in survival in recent years. Although the Santa Maria River is not classified as agricultural at the 5 km scale, this site has a significant agricultural input from Orcutt Creek. Tembladero Slough is classified as agricultural but has shown significantly decreasing pyrethroid concentrations. The Pajaro River is also showing a significant increase in amphipod survival. Most Region 3 sites were tested with *C. dilutus*, and Mission Creek (315MIS) has been consistently highly toxic. Pyrethroid toxic units for the midge have been greater than one, but fipronil concentrations are low. Mission Creek also has significantly increasing pyrethroid concentrations, but little toxicity to amphipods. There were few other significant trends measured in Region 3, including significantly increasing fipronil concentrations in Arroyo Grande Creek (310ARG).

Region 4 – Los Angeles

Seven of the eight sites in Region 4 are classified as urban at the 5 km scale. No sites are solely agriculture at the 5 km scale, but two sites have agriculture mixed with urban or open land use (Sespe Creek 403STSSSP and Calleguas Creek 408CGCS06). Region 4 continues to have the greatest number of toxic sites in the state. Three sites have average amphipod survival that categorize them as moderately toxic (having had at least one highly toxic sample), and two sites have averages that classify them as highly toxic (average less than 38.6% high toxicity threshold). Three sites had significantly increasing pyrethroid concentrations, and Bouquet

Canyon Creek continues to have the highest measured concentrations of pyrethroids (403STCBQT). Considering the large urban landscape, concentrations of fipronils did not have an increasing trend, and although Bouquet Canyon Creek is responsible for the highest concentrations of fipronils in the state, these chemicals were significantly decreasing at this site. Four sites also had at least one sample that was highly toxic to midge survival. Ballona Creek (404BLNAxx) and San Gabriel River (408CGCS06) had significant increases in concentrations of urban and chlorinated chemicals.

Region 5 – Central Valley

Approximately one-third of SPoT sites are in Region 5, and at the 5 km scale, most of these watersheds are characterized as agricultural or open, but five watersheds are characterized as urban. The majority of the sites in Region 5 have never been toxic and generally have low concentrations of measured chemicals, including pesticides. Eight sites in the region were toxic to amphipod survival or growth, and four other sites were toxic to midge survival or growth. Marsh Creek (541MERECY) and Del Puerto Creek (541STC516) continue to be the most toxic sites. Marsh Creek is influenced by urban land use and continues to have the highest concentrations of pyrethroids in the region, but fipronil concentrations remain low in the region. There were a number of significant contaminant trends, most notably five sites with increasing pyrethroid concentrations. Four sites were removed from the SPoT list: Pit River (526PRFALR) was last sampled in 2017, Tuolumne River (535STC210) (2016), TID Harding Drain (535STC501) (2016), and the South Fork Kern River (554SKR010) (2016).

Region 6 – Lahontan

Only two of the ten Region 6 sites are characterized as urban at the 5 km scale, and the remainder are characterized as open. To date, there have been no samples toxic to amphipod survival, but one sample was toxic to amphipod growth. Three sites were tested with the midge beginning in 2015, and all three have had at least one sample that was toxic to one of the two midge endpoints. There have only been a few significant upward or downward trends in chemical concentrations. Even though most of these sites are classified as being in watersheds dominated by open land uses, pyrethroids were detected at nine of ten sites, and fipronils were detected at two of the three urban sites. Two sites were removed from the SPoT list and last sampled in 2016: Lower Owens River (603LOWSED) and Deep Creek (628DEPSED).

Region 7 – Colorado River Basin

The three Region 7 sites that are evaluated for SPoT are also routinely monitored as part of other Regional Water Board programs. The Coachella Valley Stormwater Channel Outlet (719CVSCOT) is characterized as open at the 5 km scale, whereas the Alamo River Outlet (723ARGRB1) and New River Outlet (723NROTWM) are characterized as agricultural watersheds. Coachella Valley has never been toxic, but the southern river outlets have been moderately toxic intermittently. Both sites were highly toxic in 2013, and Alamo River was highly toxic a second time in 2016. 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 (Phillips et al. 2007). Despite this finding, concentrations of pyrethroids are significantly decreasing at the New River site. Region 7 samples were tested with the midge in 2018, but none of the samples were significantly toxic.

Region 8 – Santa Ana

Three of the four sites in the Santa Ana Region are classified as urban at the 5 km scale. The fourth site, San Jacinto Creek (802SJCREF), was one of the five SPoT reference sites, and was classified as open, but has been removed from the SPoT list for 2018. 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 historically been significantly toxic. In the last few years, San Diego Creek has demonstrated an increasing trend in amphipod survival, but still exhibits some toxicity to the midge growth endpoint. Chino Creek amphipod toxicity is stable, and there has been at least one sample that was highly toxic to midge survival from this site. Significant increases were observed for PAHs, PBDEs, and zinc at Chino Creek. Fipronil was measured at two sites, but concentrations were stable.

Region 9 – San Diego

All but one of the Region 9 sites are characterized as urban at the 5 km scale. When considering both tests organisms and all toxicity endpoints, no sites in the region have remained non-toxic. Mostly moderate toxicity has been observed at San Juan Creek (901SJSJC9), Escondido Creek (904ESCOxx), San Dieguito River (905SDSDQ9), and Sweetwater River (909SWRWSx). The Tijuana River (911TJHRxx) is the second most toxic site in the state.

This site also has the highest average concentration of total pyrethroids in the region and has consistently been one of the most pyrethroid-contaminated sites based on SPoT monitoring. There were a number of increasing and decreasing trends in the region, most notable were the significant increases in PBDEs in San Diego River (907SDRWAR), Sweetwater River, and Tijuana River. Fipronil concentrations significantly increased in San Dieguito River but were lower than concentrations at other Region 9 sites.

Table 7. Summary toxicity and chemistry data for sites sampled in Region 1. (Note: Tables 7-15: Statistically significant trends are noted with arrows. Toxicity color scheme is section introduction. PYR indicates pyrethroids. FIP indicates fipronils. Cu indicates copper. Zn indicates zinc. NA indicates not analyzed.)

Station Code	**Land Use**	**First Year**	***H. azteca***		***C. dilutus***		**Sum PYR**	**Sum FIP**	**Sum PAH**	**Sum PBDE**	**Sum DDT**	**Sum PCB**	**Cu**	**Zn**
			Mean Surv.	**Mean Growth**	**Mean Surv.**	**Mean Growth**								
			% of Control		**% of Control**		**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**µg/g**	**µg/g**
Smith River 103SM1009	Urban	2008	90.1 (ST)↓	125 (NT)	NA	NA	0.018	NA	NA	NA	0	0.026	36.5	76.0
Klamath River 105KLAMKK	Open	2008	97.9 (NT)	131 (NT)	NA	NA	0	NA	NA	NA	0	0.005	39.1	77.3
Mad River 109MAD101	Open	2008	91.6 (ST)	162 (NT)	NA	NA	0.020	NA	NA	NA	0	0.016	28.3	59.2
Eel River (Fernbridge) 111EELFRN	Open	2008	93.1 (ST)	187 (NT)	NA	NA	0.061	NA	NA	NA	0	0.020	23.0	56.6
Eel River (Myers Flat) 111SF0933	Open	2008	91.9 (ST)	170 (NT)	NA	NA	0.154	NA	NA	NA	0	0.122	21.7	52.2
Navarro River 113NA3269	Open	2010	76.2 (ST)	156 (NT)	NA	NA	0	NA	NA	NA	0	0	19.9	43.6
Laguna de Santa Rosa 114LAGWOH	Agric.	2008	93.4 (ST)↓	124 (ST)	92.5 (NT)	113.7 (NT)	0.632	NA	NA	NA	3.11	0	18.9	69.4
Russian River 114RRDSDM	Open	2008	102 (NT)	140 (NT)	90.0 (NT)	109.2 (NT)	2.32	NA	NA	NA	0.842	0.200	31.6	71.9

Table 8. Summary toxicity and chemistry data for sites sampled in Region 2.

Station Code	Land Use	First Year	*H. azteca*		*C. dilutus*		Sum PYR	Sum FIP	Sum PAH	Sum PBDE	Sum DDT	Sum PCB	Cu	Zn
			Mean Surv.	Mean Growth	Mean Surv.	Mean Growth								
			% of Control		% of Control		ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	µg/g	µg/g
Lagunitas Creek 201LAG125	Open	2008	98.9 (NT)	120 (NT)	NA	NA	1.53	NA	NA	NA	0.031	0.058	22.7 ↑	55.3 ↑
Walker Creek 201WLK160	Open	2008	80.1 (MT)	138 (NT)	NA	NA	0.985	NA	NA	NA	0	0.041	16.5	45.0
Alameda Creek 204ALA020	Urban	2008	99.4 (NT)↑	122 (ST)	92.0 (ST)	77.6 (ST)	5.28 ↓	0.450	150	2.08	3.70	1.18	28.6	83.6
San Leandro Creek 204SLE030	Urban	2008	89.6 (ST)	174 (NT)	34.3 (HT)	106 (NT)	34.8	1.25	1884	41.4	49.9	24.0	51.0	308
San Mateo Creek 204SMA020	Urban	2008	90.8 (ST)↑	99.3 (ST)	98.9 (NT)	109 (NT)	30.7	1.85 ↓	1590	10.6	62.1	11.1	52.0	152
Coyote Creek 205COY060	Urban	2008	94.2 (ST)↑	108 (ST)↑	103 (NT)↑	67.2 (MT)	93.1	1.88	1170	34.2	19.6	15.7	45.2 ↑	183 ↑
Guadalupe Creek 205GUA020	Urban	2008	94.2 (ST)	140 (NT)	104 (NT)↑	113 (NT)	42.7	0.955	1838 ↓	35.3	32.0	55.8	62.3	244
Sonoma Creek 206SON010	Open	2008	97.8 (NT)	114 (NT)	110 (NT)	105 (NT)	12.8	NA	NA	NA	0.399	0.346	28.4	77.5
Kirker Creek 207KIR020	Urban	2008	85.3 (MT)	102 (ST)	95.9 (NT)	167 (MT)	23.5	2.90	169	3.85	0.638	1.95	33.9	163
Laurel Creek 207LAU020	Urban	2008	95.6 (ST)↑	127 (ST)↑	78.2 (ST)	78.3 (MT)	9.56 ↓	0.247	76.0	2.78	0.257	0.298	25.9 ↓	79.7 ↓
Walnut Creek 207WAL020	Urban	2008	86.7 (ST)↑	136 (ST)	101 (NT)↑	157 (ST)	26.2	0.477	960	8.35 ↓	4.43	4.60	34.6	129

Table 9. Summary toxicity and chemistry data for sites sampled in Region 3.

Station Code	**Land Use**	**First Year**	***H. azteca***		***C. dilutus***		**Sum PYR**	**Sum FIP**	**Sum PAH**	**Sum PBDE**	**Sum DDT**	**Sum PCB**	**Cu**	**Zn**
			Mean Surv.	**Mean Growth**	**Mean Surv.**	**Mean Growth**								
			% of Control		**% of Control**		**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**µg/g**	**µg/g**
San Lorenzo River 304SLRWAT	Urban	2011	100 (NT)	172 (NT)	97.8 (NT)	145 (NT)	0.218	0.035	85.0	0.839	0.571	0.155	5.90	38.0
Soquel Creek 304SOK	Urban	2008	99 (NT)	168 (NT)	96.9 (NT)	144 (NT)	1.13	0.080	301	1.04	0.791	0.019	12.4	52.7
Pajaro River 305THU	Agric.	2008	101 (NT)↑	162 (NT)	98.7 (NT)	160 (NT)	8.95	0	152	1.57	123	0.093	23.1	77.5
Carmel River 307CML	Urban	2008	95.0 (NT)	157 (ST)	NA	NA	23.1	NA	NA	NA	0.558	0.180	19.1 ↑	110 ↑
Salinas River 309DAV	Open	2008	91.0 (ST)	136 (MT)	91.1 (NT)	111 (NT)	41.8	NA	NA	NA	75.8	5.34	34.1	111
Tembladero Slough 309TDW	Agric.	2008	18.5 (HT)↓	98.8 (ST)	94.9 (NT)	105 (NT)	65.2 ↓	NA	NA	NA	119	7.94	32.0	123
Arroyo Grande Creek 310ARG	Urban	2008	89.9 (ST)	127 (NT)	82.0 (ST)	144 (NT)	25.3	0.289 ↑	175	3.70	73.7	0.172	21.0	107 ↑
San Luis Obispo Creek 310SLB	Open	2008	98.5 (NT)	143 (NT)	89.9 (NT)	124 (NT)	3.05	NA	NA	NA	0.770	2.76	29.9 ↑	79.5 ↑
Santa Maria River 312SMA	Open	2008	54.2 (MT)↑	97.5 (ST)↑	100 (NT)	186 (NT)	26.2	NA	NA	NA	172	0.169	24.9	83.3
San Antonio Creek 313SAI	Open	2008	94.5 (ST)	143 (NT)	94.9 (NT)	108 (NT)	4.24	NA	NA	NA	5.64	0.000	10.3	42.4
Santa Ynez River 314SYN	Open	2011	99.3 (NT)	154 (NT)	96.3 (NT)	166 (NT)	5.25	NA	NA	NA	1.79	0.009	19.6	65.4
Atascadero Creek 315ATA	Urban	2008	96.4 (ST)	159 (NT)	95.0 (ST)	144 (NT)	11.5	0.384	247	1.58	6.15	3.71	18.6	50.7
Mission Creek 315MIS	Urban	2008	96.8 (NT)	187 (NT) ↑	24.4 (HT)	182 (NT)	15.8 ↑	2.63	1001	9.92	4.20	0.766	22.0	104

Table 10. Summary toxicity and chemistry data for sites sampled in Region 4.

Station Code	Land Use	First Year	*H. azteca*		*C. dilutus*		Sum PYR	Sum FIP	Sum PAH	Sum PBDE	Sum DDT	Sum PCB	Cu	Zn
			Mean Surv.	Mean Growth	Mean Surv.	Mean Growth								
			% of Control		% of Control		ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	µg/g	µg/g
Ventura River 402VRB0xx	Urban	2008	97.5 (NT)	166 (NT)	99.4 (NT)	204 (NT)	8.98	5.20	272	49.9	1.31	7.94	21.5 ↑	84.2 ↑
Bouquet Canyon Ck. 403STCBQT	Urban	2010	1.5 (HT)	NA	55.1 (MT)	166 (NT)	1663	69.3 ↓	608	25.2	1.79	3.91	92.7	192
Santa Clara River 403STCEST	Urban	2008	97.2 (NT)	169 (NT)	NA	NA	11.0 ↑	NA	NA	NA	11.8	0.209	16.0	52.8
Sespe Creek 403STCSSP	Open	2008	99.9 (NT)	192 (ST)	96.2 (NT)	103 (NT)	8.36	NA	NA	NA	1.50	0.330	25.6	88.5
Ballona Creek 404BLNAxx	Urban	2008	28.8 (HT)↓	87.9 (ST)	53.7 (MT)	174 (NT)	396 ↑	25.3	1988 ↑	58.5	28.5	38.1 ↑	75.3	328
San Gabriel River 405SGRA2x	Urban	2008	42.9 (MT)↓	99.1 (ST)	68.3 (MT)	103 (NT)	142	5.63	1416 ↑	31.5 ↑	10.5 ↑	14.2 ↑	40.9	175
Calleguas Creek 408CGCS06	Urban	2008	79.5 (MT)	148 (ST)	98.8 (NT) ↓	121 (ST)	13.5 ↑	2.06	89.2	3.13	58.1	2.89	17.4	67.3 ↑
Los Angeles River 412LARWxx	Urban	2010	81.4 (MT)	138 (ST)	68.5 (MT)	242 (NT)	101	7.03	724 ↑	26.9	4.83	7.02	31.3	195

Table 11. Summary toxicity and chemistry data for sites sampled in Region 5.

Station Code	Land Use	First Year	*H. azteca*		*C. dilutus*		Sum PYR	Sum FIP	Sum PAH	Sum PBDE	Sum DDT	Sum PCB	Cu	Zn
			Mean Surv.	Mean Growth	Mean Surv.	Mean Growth								
			% of Control		% of Control		ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	µg/g	µg/g
Big Chico Creek 504BCHROS	Urban	2008	103 (NT)↓	150 (NT)	93.7 (NT)	222 (NT)	5.75	0.607	794	9.48	28.1	1.25	36.5	76.4
Sacramento Riv. (H.C.) 504SACHMN	Agric.	2008	103 (NT)↓	158 (NT)	61.8 (ST)	94.4 (NT)	0.878 ↑	NA	NA	NA	0	0.002	40.4	111
Sacramento Riv. (B.F.) 508SACBLF	Open	2008	97.6 (NT)	165 (NT)	NA	NA	1.66	NA	NA	NA	0	0.006	65.4	179
Clarksburg Marina 510LSAC08	Urban	2008	101 (NT)	130 (NT)	NA	NA	0.623	NA	NA	NA	1.29	0.005	36.0	103
Cache Creek 511CAC113	Agric.	2008	101 (NT)	157 (NT)	NA	NA	0.742 ↓	NA	NA	NA	0.652	0.012	31.3	68.8
Sacramento Slough 515SACKNK	Agric.	2008	100 (NT)	118 (NT)	NA	NA	2.65	NA	NA	NA	10.8	0.032	58.2 ↑	103
Yuba River 515YBAMVL	Agric.	2008	100 (NT)↑	147 (NT)	97.3 (NT)	110 (ST)	1.38	0	141	3.68 ↓	3.03 ↑	0.125	32.8	64.9
American River 519AMNDVY	Urban	2008	100 (NT)↑	147 (NT)	101 (NT)	142 (ST)	1.13	0	52.5	0.489 ↓	0.289	0.176	28.3 ↓	64.8 ↓
Bear River 519BERBRY	Agric.	2008	102 (NT)↑	128 (NT)	NA	NA	0.622	NA	NA	NA	0	0.010	43.8 ↑	77.6
Feather River 519FTRNCS	Agric.	2008	102 (NT)	146 (NT)	NA	NA	0.508	NA	NA	NA	0.341	0.025	36.1	69.7
Butte Slough 520BUTPAS	Agric.	2008	101 (NT)↑	127 (NT)	NA	NA	1.42	NA	NA	NA	2.43	0.017	49.6	99.8 ↑
Colusa Basin 520CBDKLU	Agric.	2008	100 (NT)	108 (NT)	NA	NA	4.60	NA	NA	NA	8.04	0.013	59.1	106
Sacramento Riv. (Col.) 520SACLSA	Open	2008	104 (NT)↑	146 (NT)	101 (NT)	141 (ST)	0.394 ↑	0	26.7	0.080	0.526	0.122	40.8	111
Pit River 526PRFALR	Open	2008	105 (NT)	153 (NT)↑	NA	NA	0.074	NA	NA	NA	0.197	0.002	21.1	53.0
Cosumnes River 531SAC001	Open	2008	101 (NT)	157 (NT)	NA	NA	0.597	NA	NA	NA	0.257	0.024	35.3	104

Station Code	Land Use	First Year	*H. azteca*		*C. dilutus*		Sum PYR	Sum FIP	Sum PAH	Sum PBDE	Sum DDT	Sum PCB	Cu	Zn
			Mean Surv.	Mean Growth	Mean Surv.	Mean Growth								
			% of Control		% of Control		ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	µg/g	µg/g
Sutter Creek 532AMA002	Open	2010	100 (NT)	163 (NT)	NA	NA	4.29	NA	NA	NA	0	0	31.4	81.7
Bear Creek 535MER007	Agric.	2008	69.7 (MT)↓	155 (ST)↓	94.9 (NT)	278 (NT)	6.44 ↑	NA	NA	NA	0.857	0	25.9	63.3
Merced River 535MER546	Agric.	2008	103 (NT)	224 (NT)	101 (NT)	253 (NT)	0.673	NA	NA	NA	0.460	0	18.9	59.1 ↑
Dry Creek 535STC206	Urban	2008	90.0 (ST)	153 (ST)	98.1 (NT)	169 (NT)	44.1	1.45	651	10.5	3.02 ↑	4.08 ↑	23.5	94.5
Tuolumne River 535STC210	Open	2008	94.3 (NT)	182 (NT)	NA	NA	0.227 ↑	NA	NA	NA	2.53	0	22.1	76.6
TID 5 Harding Drain 535STC501	Agric.	2008	100 (NT)↑	196 (NT)↑	NA	NA	3.24	NA	NA	NA	0.968	0	12.3	57.8
San Joaquin R. (Crows) 535STC504	Agric.	2008	104 (NT)	165 (NT)	100 (NT)	208 (NT)	2.34	NA	NA	NA	3.93	0	43.0	112
San Joaquin R. (Land.) 541MER522	Agric.	2008	106 (NT)	196 (NT)	NA	NA	0.362	NA	NA	NA	0.667	0	32.9 ↓	91.5
Mud Slough 541MER542	Open	2008	101 (NT)	193 (NT)	NA	NA	0.141	NA	NA	NA	0.108	0	10.9	36.2
Marsh Creek 541MERECY	Urban	2010	28.1 (HT)	87.7 (ST)	103 (NT)↑	142 (NT)	77.9 ↓	1.10	262	7.42	24.4	0.860	29.3	165
San Joaquin R. (A.W.) 541SJC501	Agric.	2008	103 (NT)↓	206 (NT)	NA	NA	1.49	NA	NA	NA	2.97	0	29.7	100
Orestimba Creek 541STC019	Agric.	2008	81.5 (MT)	89.8 (ST)	100 (NT)	251 (NT)	10.9	NA	NA	NA	68.7	0.032	31.4	71.9
Del Puerto Creek 541STC516	Agric.	2010	39.6 (MT)	93.7 (ST)↓	82.3 (NT)	115 (NT)	28.3	NA	NA	NA	31.6	0.075	40.5	91.3
Mokelumne River 544SAC002	Agric.	2010	100 (NT)	190 (NT)	NA	NA	0.884	NA	NA	NA	0.833	0	28.2	120
Kings River 551LKI040	Agric.	2008	93.4 (NT)	121 (NT)	NA	NA	1.27	NA	NA	NA	2.37	0.228	19.9	63.9
S.F. Kern River 554SKR010	Open	2008	102 (NT)	167 (NT)	NA	NA	0.031	NA	NA	NA	0	0	25.9	66.6

Station Code	**Land Use**	**First Year**	***H. azteca***		***C. dilutus***		**Sum PYR ng/g**	**Sum FIP ng/g**	**Sum PAH ng/g**	**Sum PBDE ng/g**	**Sum DDT ng/g**	**Sum PCB ng/g**	**Cu µg/g**	**Zn µg/g**
			Mean Surv.	**Mean Growth**	**Mean Surv.**	**Mean Growth**								
			% of Control		**% of Control**									
Cross Creek 558CCR010	Agric.	2008	98.8 (NT)	133 (ST)	NA	NA	0.848	NA	NA	NA	1.04	0.597	37.0	59.8
Packwood Creek 558PKC005	Agric. /Urban	2008	87.8 (MT)↑	134 (ST)↑	92.4 (NT)	190 (NT)	14.5	NA	NA	NA	12.9	0.692	21.8	94.0
Tule River 558TUR090	Agric.	2008	87.2 (MT)↓	145 (NT)	NA	NA	1.54 ↑	NA	NA	NA	1.53	0.021	18.5	68.6 ↑

Table 12. Summary toxicity and chemistry data for sites sampled in Region 6.

Station Code	**Land Use**	**First Year**	***H. azteca***		***C. dilutus***		**Sum PYR ng/g**	**Sum FIP ng/g**	**Sum PAH ng/g**	**Sum PBDE ng/g**	**Sum DDT ng/g**	**Sum PCB ng/g**	**Cu µg/g**	**Zn µg/g**
			Mean Surv.	**Mean Growth**	**Mean Surv.**	**Mean Growth**								
			% of Control		**% of Control**									
Bishop Creek 603BSP002	Open	2008	99.5 (NT)	138 (NT)	95.2 (ST)	206 (NT)	2.72	0	267	1.50	0.823	0.086	19.3 ↑	77.3
Lower Owens River 603LOWSED	Open	2008	98.1 (NT)	190 (NT)	NA	NA	0.425	NA	NA	NA	0	0	10.6 ↓	38.6 ↓
Deep Creek 628DEPSED	Open	2010	101 (NT)	201 (NT)	NA	NA	0.503 ↓	NA	NA	NA	0	0	10.5	63.2
West Walker River 631WWKLAR	Open	2008	98.2 (NT)	201 (NT)	NA	NA	0	NA	NA	NA	0	0.067	38.0	81.8
W.F. Carson Creek 633WCRSED	Open	2008	97.1 (NT)	149 (ST)	NA	NA	3.37	NA	NA	NA	0	0.104	25.3	77.8
Upper Truckee River 634UTRSED	Urban	2008	97.8 (NT)↑	181 (NT)	89.9 (ST)	140 (NT)	0.043	0.152	88.4	0.307	0	0.081	22.3	89.5
Martis Creek 635MARSED	Open	2008	97.9 (NT)	140 (NT)	NA	NA	0.913	NA	NA	NA	0	0.170	22.9	93.8
Lower Truckee River 635TRKSED	Open	2008	100 (NT)	153 (NT)	NA	NA	2.61	NA	NA	NA	0	5.25 ↑	23.0	73.5
Trout Creek 635TROSED	Urban	2008	101 (NT)	147 (NT)↓	94.3 (NT)	112 (ST)	1.54	0.007	1480	7.02	0.160 ↑	7.56	20.1	87.6
Susan River 637SUS001	Open	2008	101 (NT)	177 (NT)	NA	NA	0.259	NA	NA	NA	0	0.047	35.9	68.1

Table 13. Summary toxicity and chemistry data for sites sampled in Region 7.

Station Code	**Land Use**	**First Year**	***H. azteca***		***C. dilutus***		**Sum PYR**	**Sum FIP**	**Sum PAH**	**Sum PBDE**	**Sum DDT**	**Sum PCB**	**Cu**	**Zn**
			Mean Surv.	**Mean Growth**	**Mean Surv.**	**Mean Growth**								
			% of Control		**% of Control**		**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**µg/g**	**µg/g**
Coachella Valley S.W. 719CVSCOT	Open	2008	99.9 (NT)	134 (NT)	103 (NT)	152 (NT)	4.27	NA	NA	NA	13.9	0.000	34.2	119
Alamo River 723ARGRB1	Agric.	2008	77.8 (MT)	118 (ST)	101 (NT)	107 (NT)	7.71	NA	NA	NA	22.2	0.002	17.4 ↑	59.7 ↓
New River 723NROTWM	Agric.	2008	76.2 (MT)↑	100 (ST)	103 (NT)	132 (NT)	13.6 ↓	NA	NA	NA	21.8 ↓	0.022	18.2	57.4

Table 14. Summary toxicity and chemistry data for sites sampled in Region 8.

Station Code	**Land Use**	**First Year**	***H. azteca***		***C. dilutus***		**Sum PYR**	**Sum FIP**	**Sum PAH**	**Sum PBDE**	**Sum DDT**	**Sum PCB**	**Cu**	**Zn**
			Mean Surv.	**Mean Growth**	**Mean Surv.**	**Mean Growth**								
			% of Control		**% of Control**		**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**ng/g**	**µg/g**	**µg/g**
Chino Creek 801CCPT12	Urban	2010	64.1 (MT)	136 (ST)	79.5 (MT)	104 (ST)	92.1	3.53	677 ↑	34.3 ↑	2.96	2.56	39.3	201 ↑
Santa Ana River 801SARVRx	Urban	2008	92.9 (NT)	165 (NT)	NA	NA	13.8	NA	NA	NA	5.49	1.03	24.2	97.7
San Diego Creek 801SDCxxx	Urban	2008	48.1 (MT)↑	109 (ST)	98.6 (NT)	104 (ST)	96.5	5.46	341	4.75	18.3	1.14	22.8	101
San Jacinto River 802SJCREF	Open	2008	101 (NT)	264 (NT)	NA	NA	0.422	NA	NA	NA	0.295	1.71	7.36	93.8

Table 15. Summary toxicity and chemistry data for sites sampled in Region 9.

Station Code	Land Use	First Year	*H. azteca*		*C. dilutus*		Sum PYR	Sum FIP	Sum PAH	Sum PBDE	Sum DDT	Sum PCB	CU	ZN
			Mean Surv.	Mean Growth	Mean Surv.	Mean Growth								
			% of Control		% of Control		ng/g	ng/g	ng/g	ng/g	ng/g	ng/g	µg/g	µg/g
San Juan Creek 901SJSJC9	Urban	2008	78.4 (ST)	124 (ST)	76.9 (MT)	101 (ST)	59.2 ↑	5.69	399	10.8	5.89	0.574	22.2 ↑	94.0
Santa Margarita R. 902SSMR07	Open	2008	101 (NT)	227 (NT)	94.1 (ST)	100 (NT)	2.97 ↓	0	14.3	0.236 ↓	6.70 ↓	0.339	14.2 ↓	52.8 ↓
San Luis Rey River 903SLRRBB	Urban	2011	94.2 (ST)	155 (NT)	105 (NT)	142 (MT)	1.06	0.267	115	0.760	9.72	0.698	19.8 ↑	84.8
Escondido Creek 904ESCOxx	Urban	2008	84.7 (ST)↓	111 (ST)	109 (NT)↑	105 (MT)	20.0	3.48	338	3.33	1.29	0.761	31.2 ↓	117 ↓
San Dieguito River 905SDSDQ9	Urban	2010	87.0 (MT)↑	158 (NT)	103 (NT)	175 (ST)	0.379	0.172 ↑	119 ↑	0.263 ↓	0.185	0.006	18.9	89.2
Peñasquitos Creek 906LPLPC6	Urban	2008	89.8 (NT)	109 (ST)↓	93.8 (ST)	72.3 (MT)	141	9.06	615 ↑	13.1	0.228 ↑	0.724	42.0	202
San Diego River 907SDRWAR	Urban	2009	91.7 (NT)	110 (ST)	89.2 (ST)	123 (NT)	75.1	11.2	1585	23.4 ↑	11.5	11.2	48.2	261
Sweetwater River 909SWRWSx	Urban	2011	81.6 (ST)	95.9 (ST)	98.3 (NT)↑	143 (ST)	44.8 ↑	5.05	543	4.25 ↑	8.47 ↑	0.742	26.9	135
Tijuana River 911TJHRxx	Urban	2008	27.9 (ST)	126 (ST)↓	40.5 (MT)	56.7 (MT)↑	331	1.95	417	149 ↑	4.04	10.9	67.0	237

Section 7 – Recommendations for Future SPoT Monitoring

SPoT is detecting trends in toxicity and current-use chemicals, particularly pesticides, thus meeting the primary goals of the project. As the project has matured, it has broadened its collaborations with other agencies and programs and increased its focus on CECs, such as fipronil and microcystin. Although toxicity testing results demonstrate the presence of bioavailable contaminant mixtures in toxic concentrations, the analysis of these chemicals is limited by a static analyte list. Traditional environmental monitoring programs have focused on the targeted analysis of hydrophobic contaminants, but recent advances in chemical analysis have demonstrated the presence of a wide range of polar chemicals in sediments (Massei et al. 2018). Many of these chemicals could be contributing to the type of whole organism toxicity that is monitored by SPoT but could also be contributing to a number of sub-lethal impacts on biota.

Continued frequent monitoring of legacy contaminants, such as the organochlorine pesticides and PCBs should be minimized to allow for increased measurements of newer contaminants that could be contributing to the observed toxicity. SPoT has begun to monitor legacy contaminants once every five years to maintain tracking of long-term trends. The hydrocarbons (PAHs) and PBDEs monitored in urban watersheds could also be tracked less frequently while still maintaining trend monitoring. SPoT Science Leads, the SPoT Scientific Review Committee, and the State Water Board will be deciding analysis frequency for the 2021 sampling season.

A pilot project using non-targeted analysis will begin during the 2020 sampling season. Use of non-targeted analysis will allow for the identification of new CECs (Ferguson et al. 2019), and allow for regulators and the SPoT program to focus resources on emerging compounds. Follow-up targeted analysis would quantify concentrations and establish baseline information for trend analysis. Potential risk to biota could be determined with coupled effects-based tools (in addition to the toxicity testing already conducted), such as behavioral endpoints, and eventually bioanalytical monitoring or analysis of adverse outcomes pathways (Connon et al. 2019).

Suggestions for new targeted analysis include perfluoroalkyl and polyfluoroalkyl substances (PFAS), as well as contaminants of emerging concern identified by CDPR or the State Water Board in partnership with the San Francisco Estuary Institute’s Emerging Contaminants Workgroup and DTSC. Consideration should also be given to quaternary ammonium compounds (QACs), due to their extraordinarily heavy use in response to COVID-19 pandemic. SPoT would also like to add a representative of DTSC’s Safer Consumer Product Program to the Scientific Review Committee so that DTSC annual monitoring priorities can be clearly communicated. Suggestions for other analyte groups will come from planned State Water

Board workshops that will identify various program data needs, and will be working with SPoT on areas to focus monitoring efforts. These workshops are part of Water Board driven monitoring and efforts to expand the use of SPoT data. Embracing new tools for environmental monitoring, including non-target analysis and effects-based biological measurements will allow SPoT to be at the forefront of emerging chemical trends and their effects on resident biota.

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) (https://www.waterboards.ca.gov/water_issues/programs/swamp/mission.html), 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 uses that are assessed pertain to 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, or can provide, 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. Supporting uses of SPoT data are listed under each Level 2 question.

Level 1 Assessment Questions:

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

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

1) Are beneficial uses impacted?

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

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

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

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

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

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

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

2) Are conditions getting better or worse?

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

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

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

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

Reference conditions: As described above.

Spatial and Temporal Scale: As described above.

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

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

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

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

Certainty / precision: As described above.

Reference conditions: As described above.

Spatial and Temporal Scale: As described above.

4) What's causing the problem?

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

Supports: 305(b), TMDL, basin planning, county land use planning, pesticide surface water regulations and CDPR pesticide registration (especially for pyrethroids).

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

Certainty/precision: High.

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

Spatial and Temporal Scale: As described above.

5) Are solutions working?

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

Supports: TMDL, management practice implementation programs (e.g. CDPR pyrethroid label changes, or reduction of copper in brake pad production), 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. Some effort has been made to standardize reporting of practices implemented, land area affected, volume of water treated, and effectiveness of treatment (e.g., International Stormwater Best Management Practice Database – http://www.bmpdatabase.org/). It is anticipated that improvements in this area will improve precision of analyses to determine whether implemented solutions are effective.

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

Spatial and Temporal Scale: As described above.

Appendix 2: Methods

Site Selection and Survey Timing

A number of factors were considered when selecting SPoT sites (Hunt et al. 2012). The most important factors included location in a large watershed with heterogeneous land cover; location at or near the base of a watershed, defined as the confluence with either an ocean, lake, or another stream of equal or greater stream order; and location where site-specific conditions are appropriate for the indicators selected (e.g., depositional areas, sufficient flow, appropriate channel morphology, substrate). 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.

SPoT surveys are timed so that sediment is collected from recent stream bed deposits during base flow periods after the high flow season, when most sediment and pollutant transport and loading take place. Fine grained sediments are targeted for sample collection. Fine sediment particles can be found in thin layers throughout the channel, or in specific areas dominated by deep deposits of fine sediment. SPoT emphasizes collecting fine-grained depositional sediments because contaminants associate with smaller size fractions. Fine sediment particles accumulate in low energy depositional areas and can be found throughout the channel at many sites in thin layers covering other dominant substrate. SPoT results should not be construed as a characterization of the entire stream in which study sites were located. Rather, they are intended as relative indicators of the annual pollutant mobilization and transport within target watersheds, which is a useful measurement for evaluating annual trends.

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

Indicators and Parameters Measured

SPoT indicators were selected to measure contaminants previously demonstrated to be of concern in California streams, as well as to 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), resulting in the following selections:

1. Toxicity – 10-day growth and survival test with the representative freshwater amphipod *Hyalella azteca*, to estimate biological effects of contaminants. A 10-day growth and survival test with *Chironomus dilutus* was added to the Tier II list for the 2015 season and expanded to other sites in 2018.

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

3. Tier II Contaminants – A subset of sediments from the most urban watersheds was also measured for PAHs and PBDEs. Fipronil was added to the Tier II list in 2013.

4. TOC and sediment grain size.

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

Participating Laboratories and Data Storage and Management

The California Department of Fish and Wildlife Water Pollution Control Laboratory and Southern California Coastal Research Project (trace organics), the Marine Pollution Studies Laboratory at Moss Landing (trace metals), and the UC Davis Marine Pollution Studies Laboratory at Granite Canyon (toxicity). Microcystin-LR was analyzed by Cal State University Monterey Bay (starting in 2013). All methods and quality assurance/quality control requirements are listed in the SPoT Quality Assurance Project Plan (SPoT 2019).

All data collected for this study are maintained in the SWAMP Database, which is managed by the SWAMP Information Management and Quality Assurance Center (https://www.waterboards.ca.gov/water_issues/programs/swamp/swamp_iq/). The complete dataset includes quality assurance data (quality control samples and blind duplicates), and ancillary information (specific location information and collection descriptions). Data for the SPoT program can be accessed from the CEDEN Database query system (http://www.ceden.org/).

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 activities 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 at California State University, Chico (http://www.gic.csuchico.edu/index.html). The entire drainage area specific to each SPoT site was delineated using automated scripts based on digital elevation models. Each delineation file was reviewed by Geographic Information Center 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.

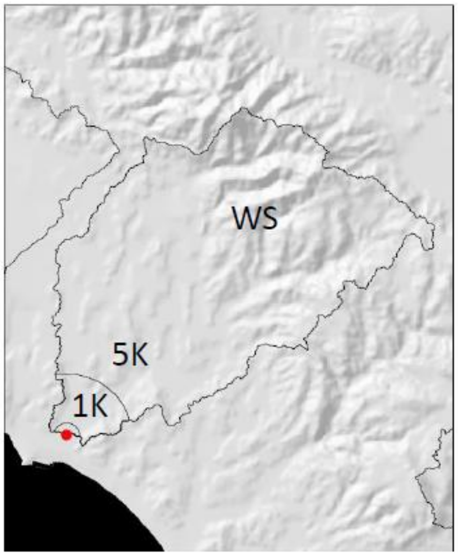


Figure A1. A depiction of watershed delineation. The red dot designates the site at the bottom of the watershed (WS, larger polygon). The semi-circular smaller areas are watershed areas 1 km (1K) and 5 km (5K) from the site.

Drainage area shape files were used to extract land cover grids from the NLCD (Homer et al. 2020). Land use categorization followed the same criteria as the Perennial Streams Assessment (Ode et al. 2011). The following NLCD categories were used in the analyses relating land cover to water quality. *Urban* included developed open space and low, medium, and high intensity developed areas (NLCD 21, 22, 23, 24). *Agricultural* land cover was represented by pasture/hay and cultivated crops (NLCD 81 and 82). For the purposes of trend analyses by land use, pollutant concentrations were compared to continuous percent land cover data as percent urban, percent agricultural, and percent open. For analyses based on comparisons among watershed types, watershed areas were characterized as urban if they had greater than 25% urban cover at the 5 km scale. This characterization is in line with studies indicating stream degradation where impervious surface cover exceeds 10% (Schueler 1994). Watershed areas were characterized as agricultural if they had greater than 50% cultivated crop cover. The remaining watershed areas were characterized as *open*. Based on NLCD 2016, one site was categorized as both urban and agricultural (558PKC005).

Toxicity Testing and Statistical Analyses

Toxicity tests with *Hyalella azteca* and *Chironomus dilutus* were conducted following U.S. EPA standard methods (U.S. EPA 2000), and the acute toxicity of sediment samples was determined using the U.S. EPA's test of significant toxicity (Denton et al. 2011; Diamond et al. 2011; U.S. EPA 2010). Significant chronic toxicity was determined with a separate-variance t-test and comparison to an 80% threshold.

For any given year, sites that were not toxic were coded green, sites that were significantly toxic were coded yellow, and sites that were highly toxic (had percent survival lower than the high toxicity threshold for *Hyalella azteca,* 38.6%) were coded red (Anderson et al. 2011). Toxicity results from multiple years were summarized using the following criteria: sites with no toxic samples were coded green for non-toxic, sites with at least one toxic samples were coded yellow for some toxicity, sites with at least one sample below the high toxicity threshold were coded orange for moderate toxicity, and sites with an average survival less than the high toxicity threshold were coded red for high toxicity.

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 (see table below). All detected pyrethroids were summed where indicated, and pyrethroids were also summed as carbon normalized toxic units (Amweg et al. 2005). Significant trends were determined using Mann Kendall tests, and all statistical analyses were conducted using Q1 Macros for Excel (KnowWare International, Inc.).

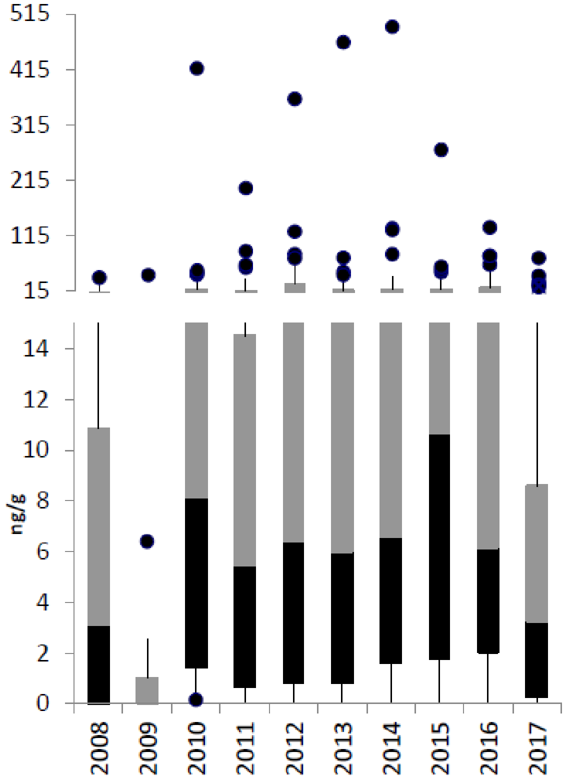
Table A1. List of individual compounds that make up various chemical sums.

Sum DDTs	DDD(o,p'), DDD(p,p'), DDE(o,p'), DDE(p,p'), DDT(o,p'), DDT(p,p')
Sum PCBs	Congeners: 8, 18, 44, 49, 52, 66, 70, 99, 101, 105, 110, 118, 128, 149, 151, 153, 156, 170, 177, 180, 187, 194, 201, 206, 209
Sum PBDEs	Congeners: 17, 25, 28, 33, 47, 66, 85, 99, 100, 138, 153, 154, 183, 190, 209
Sum PAHs	Acenaphthene, Acenaphthylene, Anthracene, Benz(a)anthracene, Benzo(a)pyrene, Benzo(b)fluoranthene, Benzo(e)pyrene, Benzo(g,h,i)perylene, Benzo(k)fluoranthene, Biphenyl, Chrysene, Dimethylnaphthalene, 2,6-, Fluoranthene, Fluorene, Methylnaphthalene, 1-, Methylnaphthalene, 2-, Methylphenanthrene, 1-, Naphthalene, Perylene, Phenanthrene, Pyrene, Trimethylnaphthalene, 2,3,5-
Sum Pyrethroids	Bifenthrin, Cyfluthrin, Cypermethrin, Deltamethrin, Esfenvalerate, Fenpropathrin, lambda-Cyhalothrin, Permethrin
Sum Fipronils	Fipronil, Fipronil Amide, Fipronil Desulfinyl, Fipronil Desulfinyl Amide, Fipronil Sulfide, Fipronil Sulfone

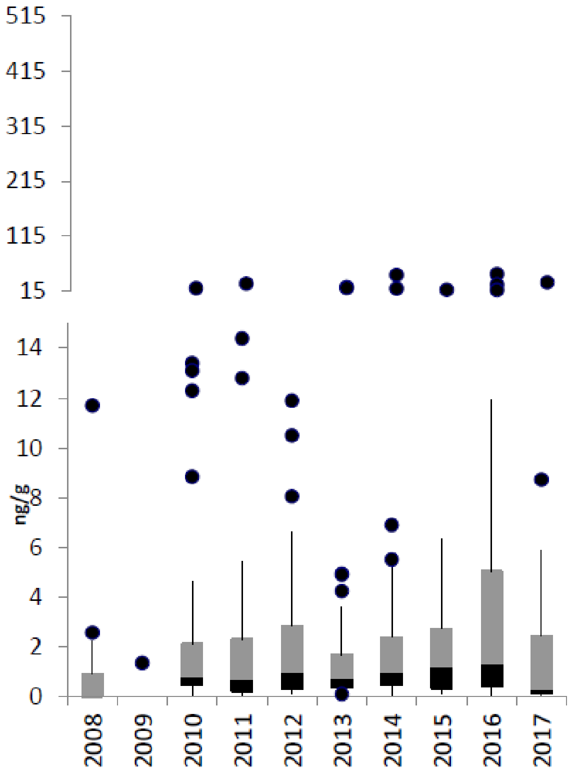
Analysis of Microcystin

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

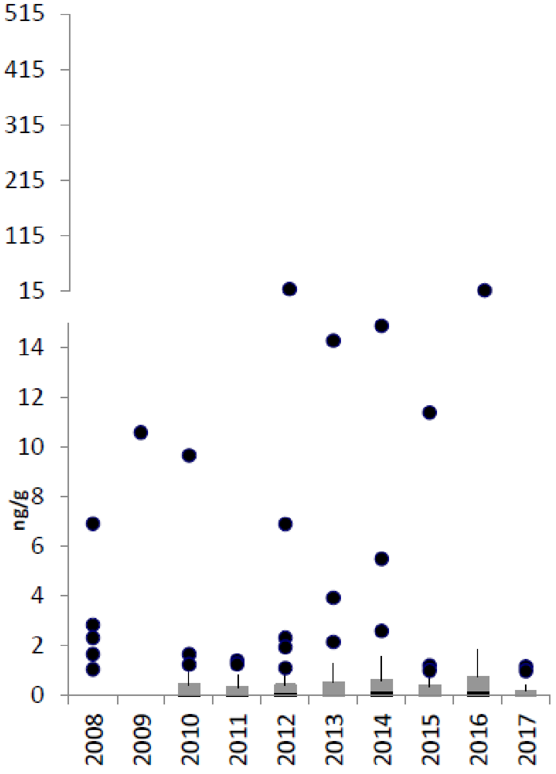
Appendix 3: Plots of Individual Pyrethroids by Land Use



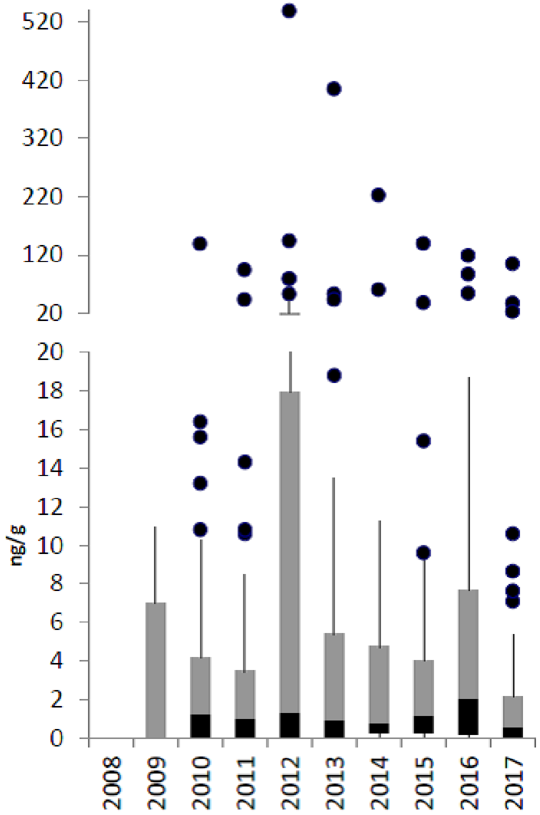
Bifenthrin (Urban)

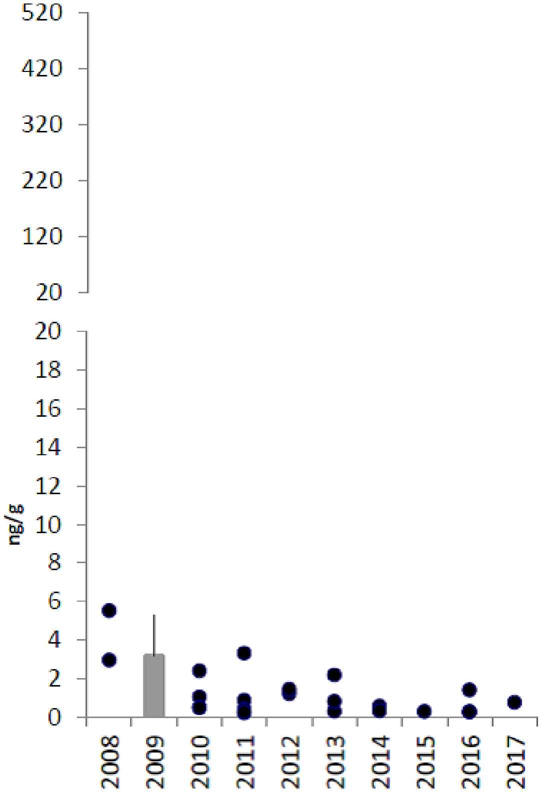


Bifenthrin (Agriculture)



Bifenthrin (Open)


Cyfluthrin (Urban)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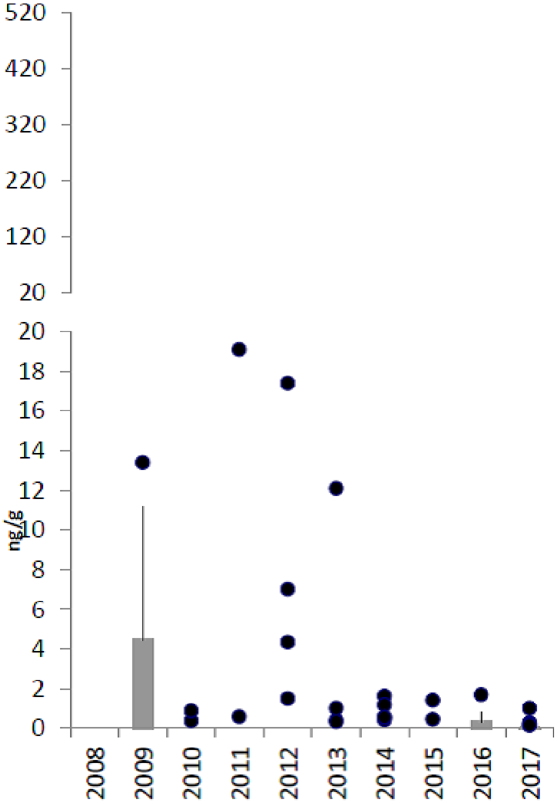
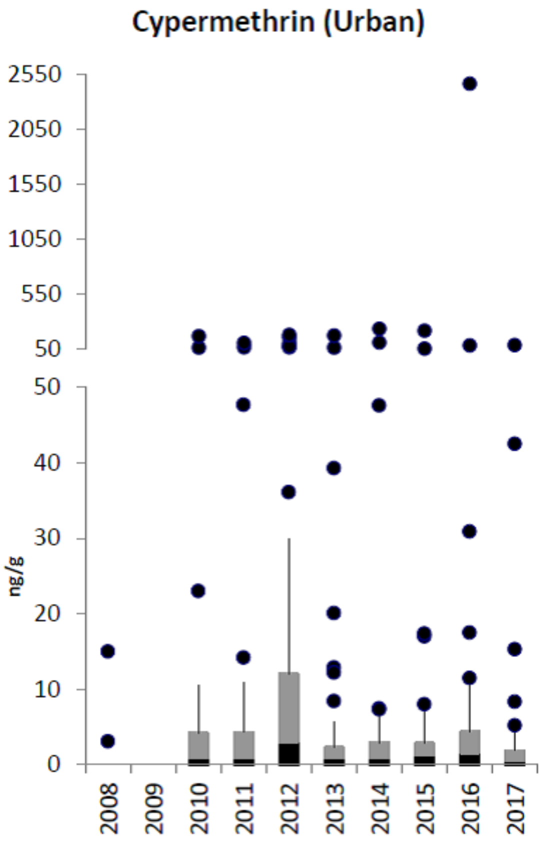

Cyfluthrin (Open)


Cypermethrin (Urban)
2550
2050
1550
1050
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30
20
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ng/g
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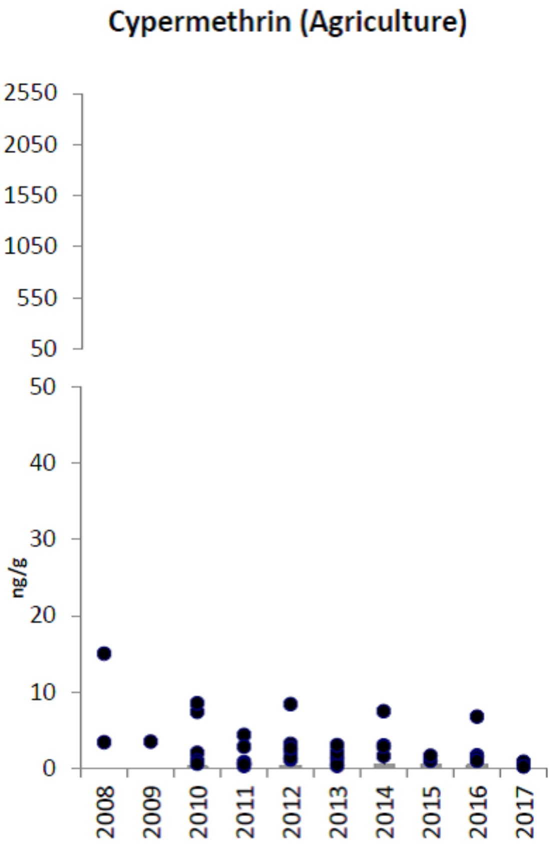
Cypermethrin (Agriculture)
2550
2050
1550
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ng/g
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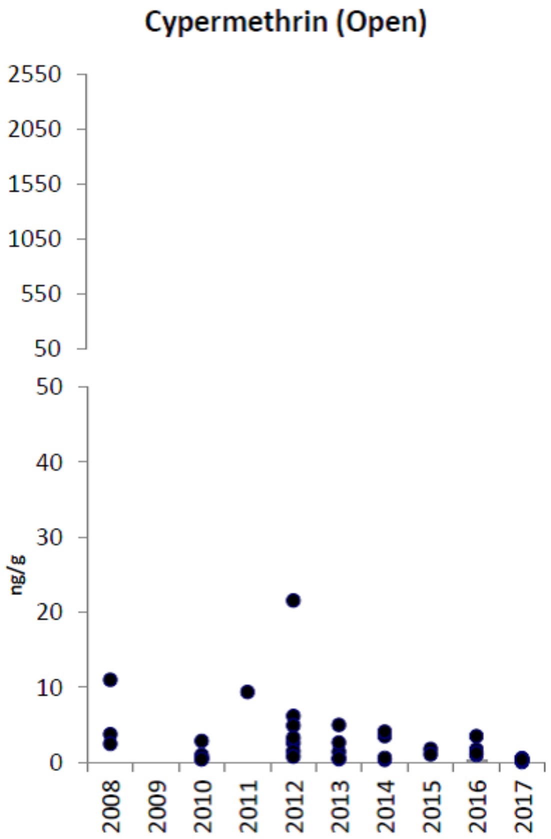
Cypermethrin (Open)
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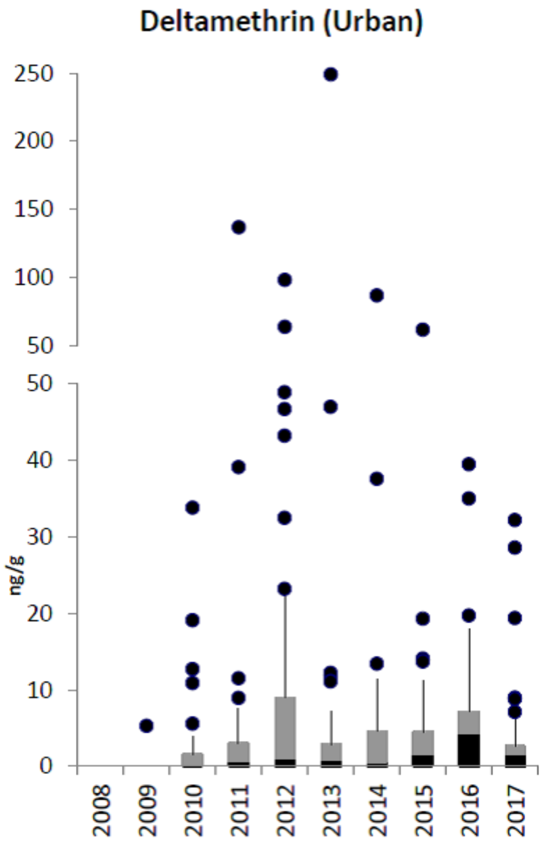
Deltamethrin (Urban)
250
200
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100
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ng/g
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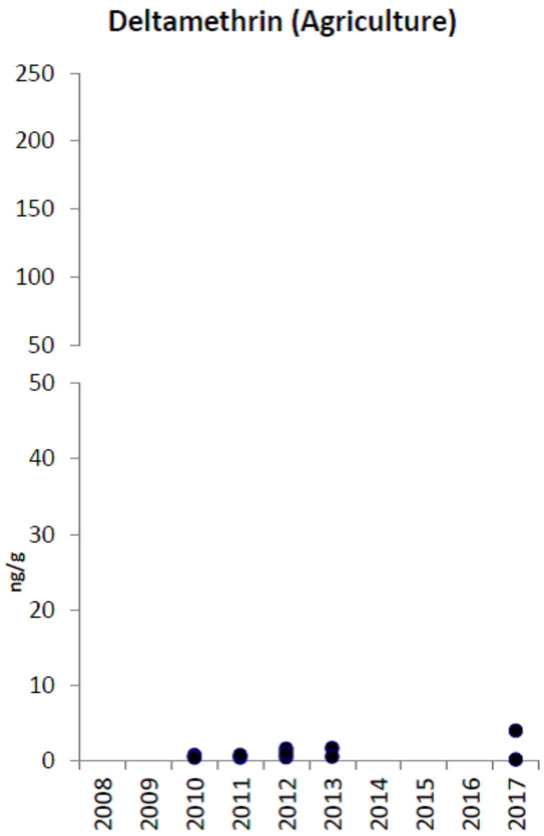
Deltamethrin (Agriculture)
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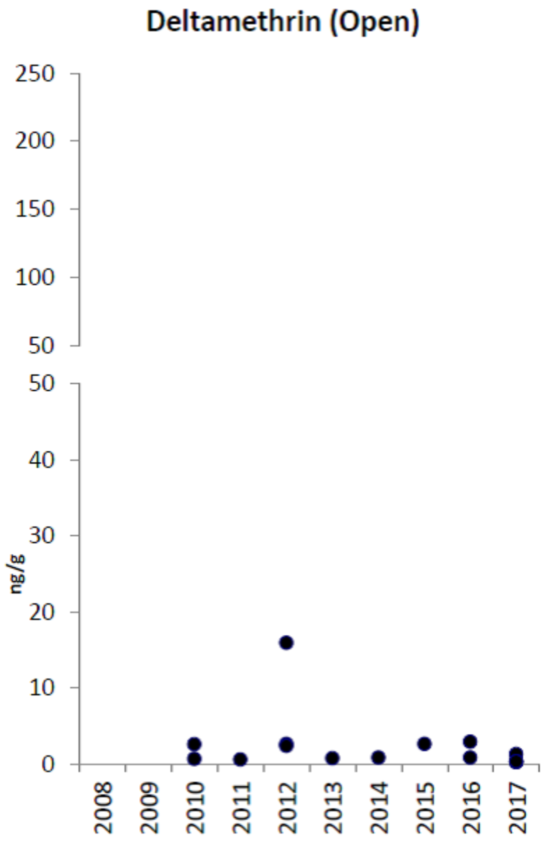
Deltamethrin (Open)
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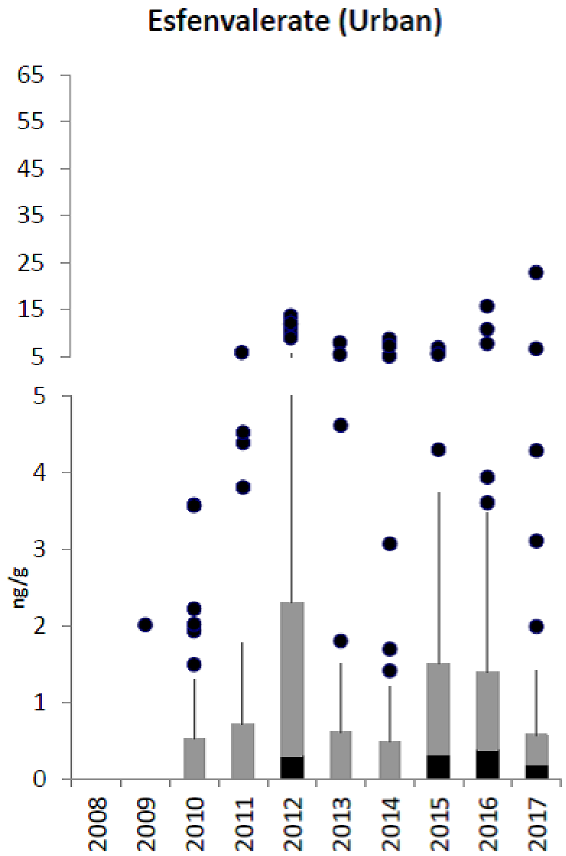
Esfenvalerate (Urban)
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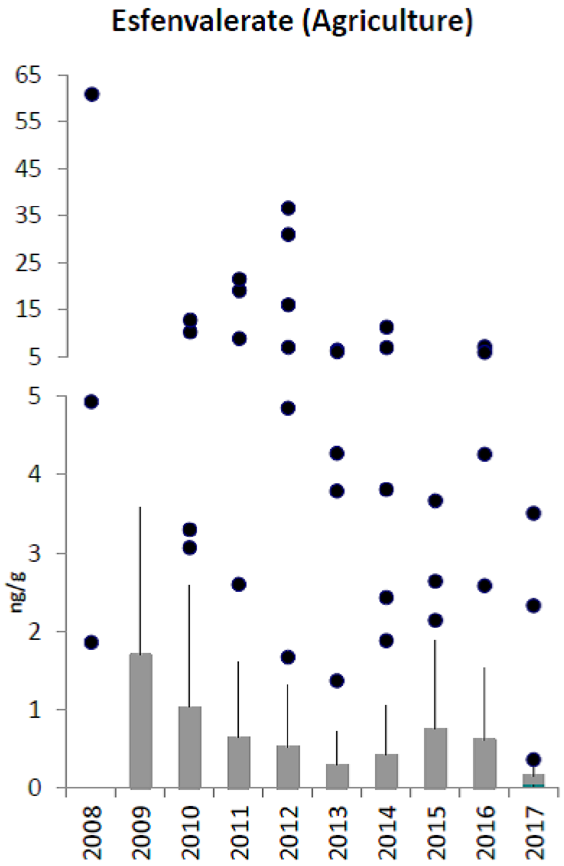
Esfenvalerate (Agriculture)
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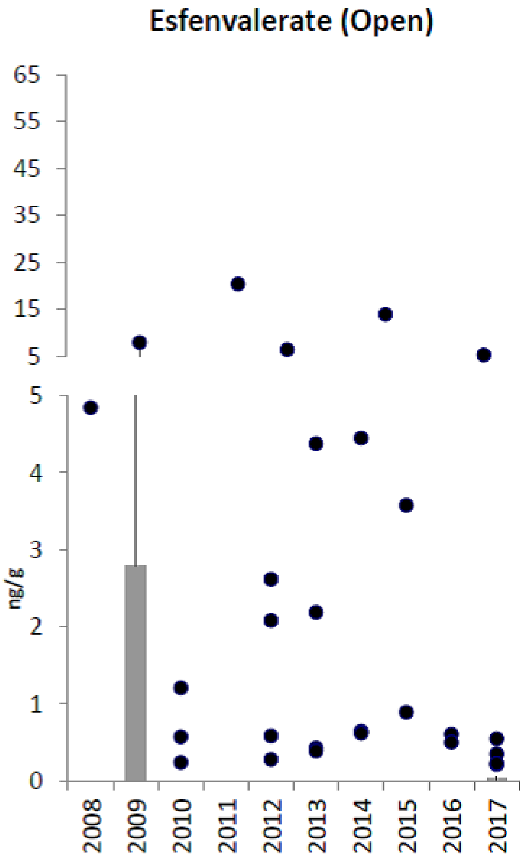
Esfenvalerate (Open)
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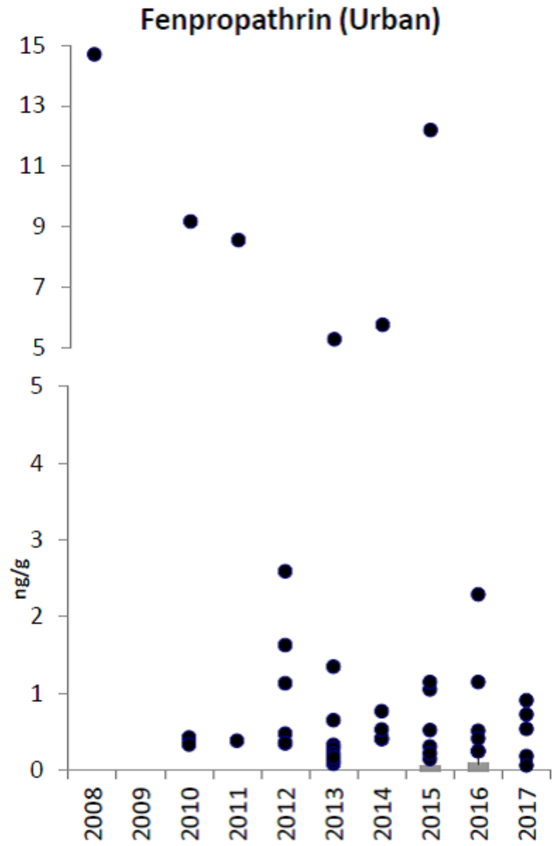
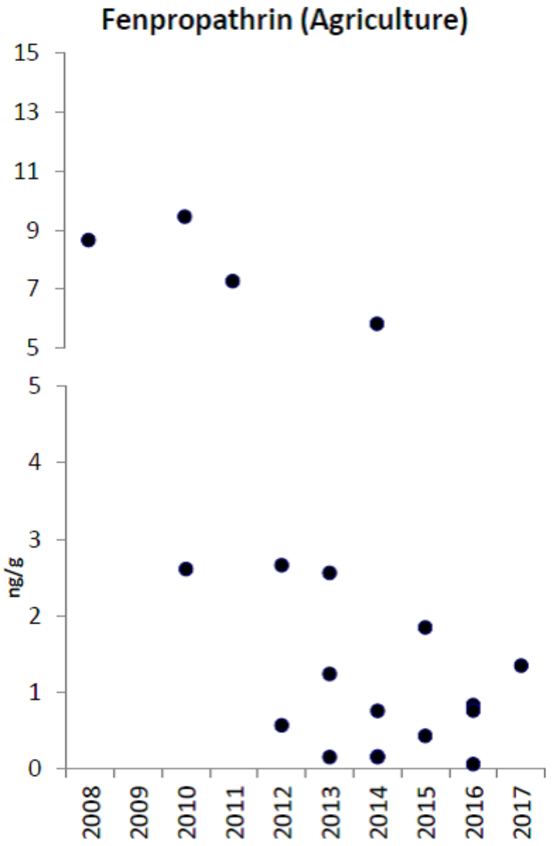
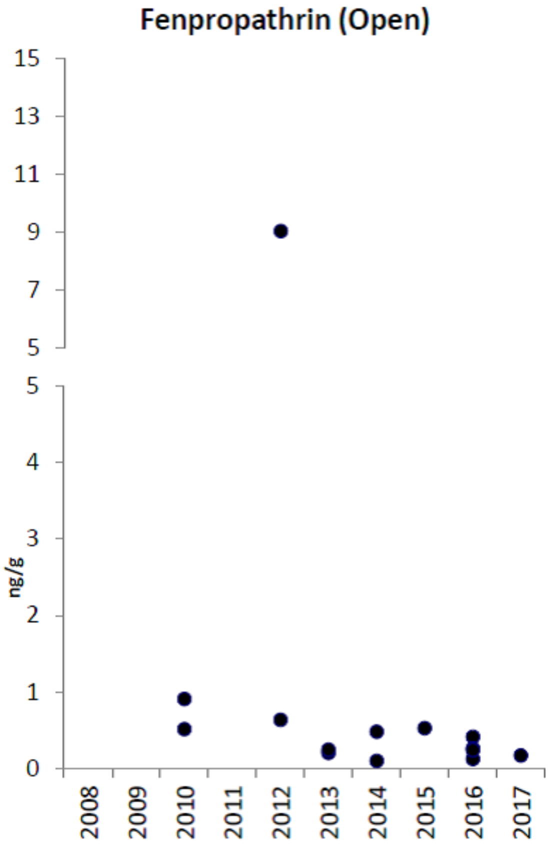


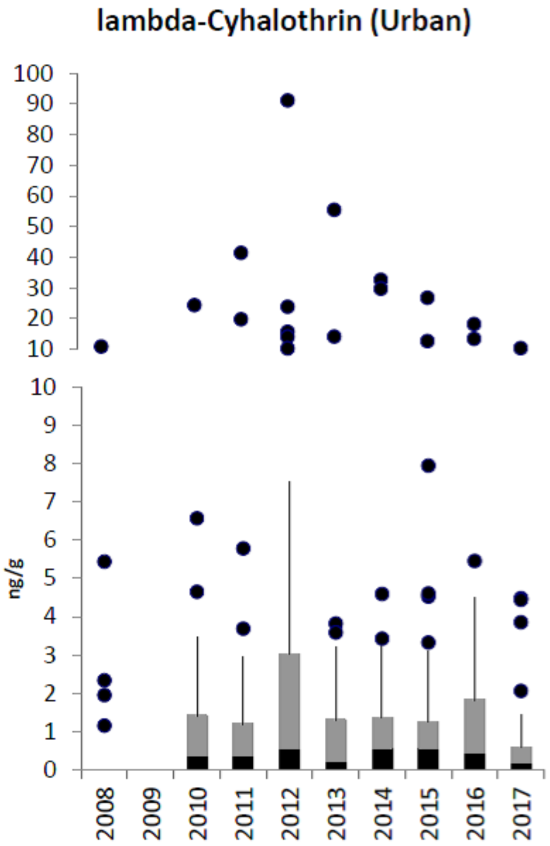
Fenpropathrin (Urban)

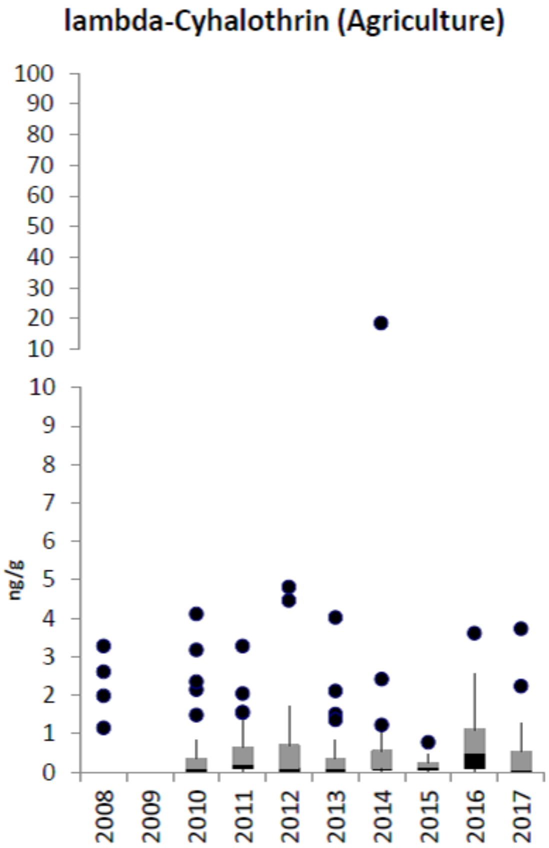


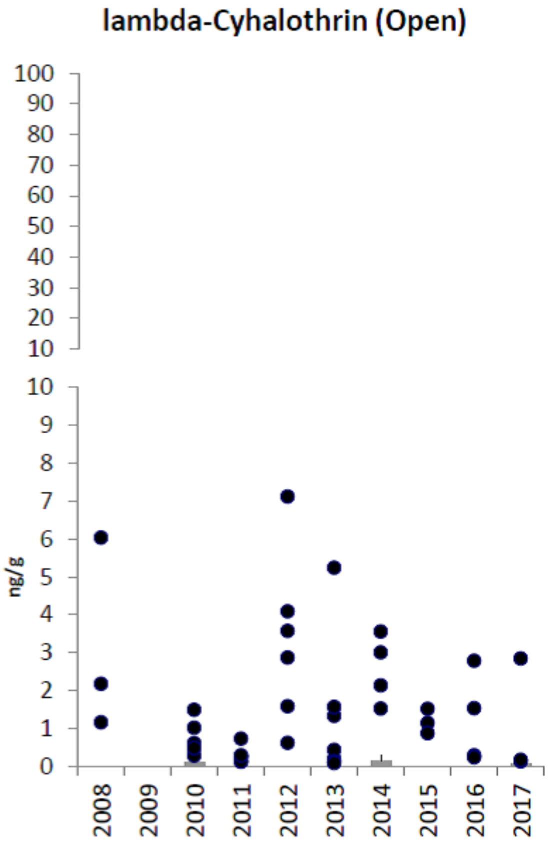
Fenpropathrin (Agriculture)

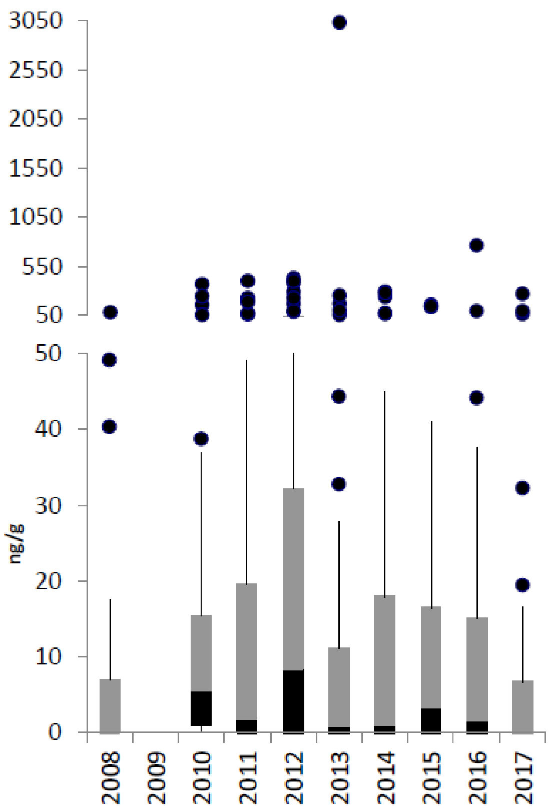


Fenpropathrin (Open)

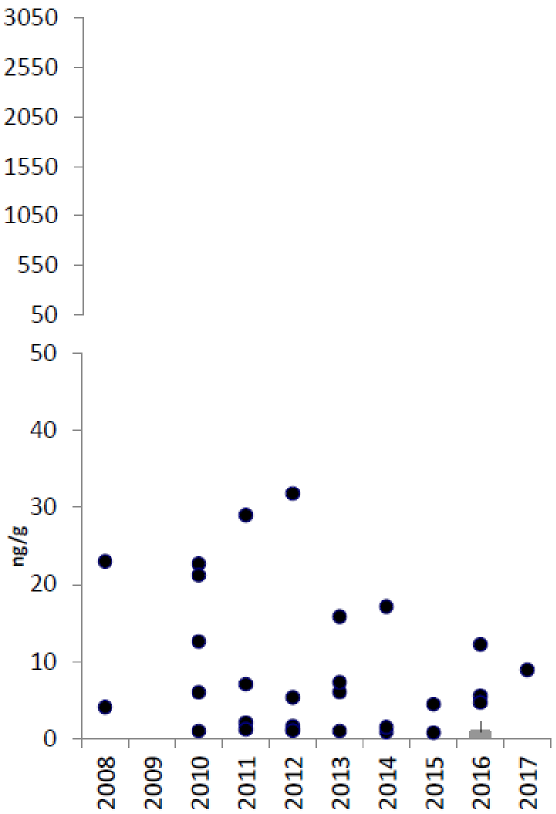

lambda-Cyhalothrin (Urban)


lambda-Cyhalothrin (Agriculture)

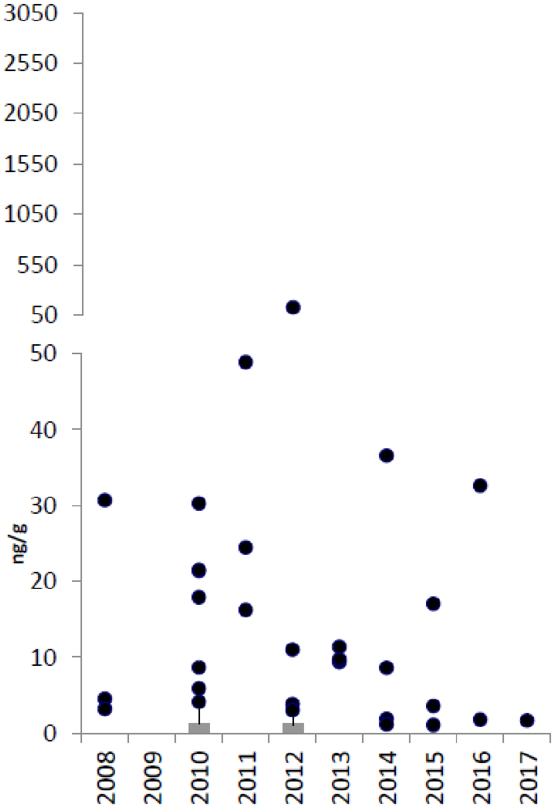

lambda-Cyhalothrin (Open)



Permethrin (Urban)



Permethrin (Agriculture)



Permethrin (Open)

Appendix 4: Toxicity Threshold Evaluation Concentrations

The relationships between organism mortality and sediment chemical concentrations are investigated by comparing survival to individual chemical threshold values. Where possible, 10-day median LC50s derived from spiked sediment toxicity studies were used to evaluate chemistry data. Median lethal concentrations are preferable because they are derived from exposure experiments with single chemicals. Consensus-based TECs were used when spiked-sediment LC50s were not available (MacDonald et al. 2000b). The TEC provides some predictive ability but is not derived from direct dose-response experiments. More LC50 values are available for the amphipod than the midge, but 27 chemicals were represented by one or both organisms. In addition to the LC50s, 29 consensus-based TECs are listed.

Table A2. Ten-day median effect concentrations for *H. azteca* and *C. dilutus*.

Contaminant	**Endpoint**	***Hyalella azteca***		***Chironomus dilutus***	
Pyrethroids		**ng/g**	**ug/g OC**	**ng/g**	**ug/g OC**
Bifenthrin	Survival	12.9	0.52	634	6.2, 25.7
		(Amweg et al. 2005)		(Maul et al. 2008) (Xu et al. 2007)	
Cyfluthrin	Survival	13.7	1.08	65.9	2.34
		(Amweg et al. 2005)		(Xu et al. 2007)	
Cyhalothrin	Survival	5.6	0.45	27.2	2.8
		(Amweg et al. 2005)		(Maul et al. 2008)	
Cypermethrin	Survival	14.9	0.38		
		(Maund et al. 2002)			
Deltamethrin	Survival	9.9	0.79		
		(Amweg et al. 2005)			
Esfenvalerate	Survival	41.8	1.54		
		(Amweg et al. 2005)			
Fenpropathrin	Survival	177	8.90	65.4	2.36
		(Ding et al. 2011)		(Xu et al. 2007)	
Permethrin	Survival	201	10.9	169	24.5
		(Amweg et al. 2005)		(Maul et al. 2008)	
Fipronils		**ng/g**	**ug/g OC**	**ng/g**	**ug/g OC**
Fipronil	Survival		13.3	0.90	0.13
		(Bower and Tjeerdema 2017; Picard 2015d)		(Maul et al. 2008)	
Fipronil Sulfide	Survival		56	1.105	0.16
	Growth		19		
		(Bower and Tjeerdema 2017; Picard 2015a)		(Maul et al. 2008)	
Fipronil Sulfone	Survival		10	0.83	0.12
	Growth				>0.20
		(Bower and Tjeerdema 2017; Picard 2015b)		(Maul et al. 2008)	
Fipronil Desulfinyl	Survival		181		57

Contaminant	**Endpoint**	***Hyalella azteca***		***Chironomus dilutus***	
	Growth		69		7.78
		(Bower and Tjeerdema 2017; Picard 2015c)		(Bower and Tjeerdema 2017; Putt 2001)	
Organophosphates		**ng/g**	**ug/g OC**		
Chlorpyrifos	Survival	399	1.77		
		(Amweg and Weston 2007; Brown et al. 1997)			
Diazinon	Survival	1085	54.6		
Methyl Parathion	Survival	6362	318		
		(Ding et al. 2011)			
Organochlorines		**ng/g**	**ug/g OC**		
Total DDT	Survival	11,000 (3% TOC)	367 (3% TOC)		
		(Nebeker et al. 1989)			
DDD	Survival		1300		
DDE	Survival		8300		
		(Weston et al. 2004)			
Dieldrin	Survival		2000 (Mean)		
		(U.S. EPA 2003)			
Endrin	Survival	4,400 (3% TOC)	147 (3% TOC)		
		(Nebeker et al. 1989)			
Methoxychlor	Survival		85.8		
alpha Endosulfan	Survival		51.7		
Endosulfan sulfate	Survival		873		
		(Weston et al. 2004)			
PAHs		**ng/g**	**ug/g OC**	**ng/g**	**ug/g OC**
Fluoranthene	Survival		1,077		1,336
		(Suedel et al. 1993)		(Suedel et al. 1993)	
Metals		**µg/g**		**µg/g**	
Arsenic	Survival	532		642	
		(Liber et al. 2011)		(Liber et al. 2011)	
Cadmium	Survival	170			
		Chen et al. unpublished (review)			
Copper	Survival	260			
		MPSL Unpublished Data			
Nickel	Survival	521		>3,286	
		(Liber et al. 2011)		(Liber et al. 2011)	

Table A3. Consensus-based threshold effect concentrations (MacDonald et al. 2000b).

Metals	**ug/g**	**PAHs**	**ng/g**
Arsenic	9.79	Anthracene	57.2
Cadmium	0.99	Fluorene	77.4
Chromium	43.4	Naphthalene	176
Copper	31.6	Phenanthrene	204
Lead	35.8	Benz[a]anthracene	108
Mercury	0.18	Benzo(a)pyrene	150
Nickel	22.7	Chrysene	166
Zinc	121	Dibenz[a,h]anthracene	33
		Fluoranthene	423
Organochlorines	**ng/g**	Pyrene	195
Chlordane	3.24	Total PAHs	1610
Dieldrin	1.9		
Sum DDD	4.88	**PCBs**	**ng/g**
Sum DDE	3.16	Total PCBs	59.8
Sum DDT	4.16		
Total DDTs	5.28		
Endrin	2.22		
Heptachlor epoxide	2.47		
gamma-BHC	2.37		

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