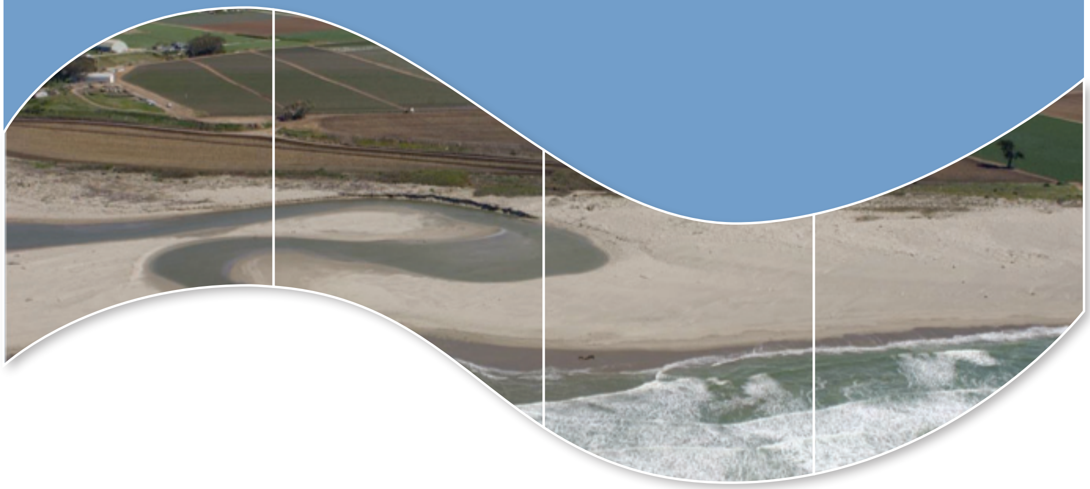

Surface Water Ambient Monitoring Program

STATEWIDE PERSPECTIVE ON CHEMICALS OF CONCERN AND CONNECTIONS BETWEEN STREAM WATER QUALITY AND LAND USE

STREAM POLLUTION TRENDS PROGRAM (SPoT)

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SPoT Report: Field Year 2008
First Report

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List of Acronyms

BOG	Bioassessment Oversight Group that directs the SWAMP bioaccumulation monitoring program.
DDT	Dichlorodiphenyltrichloroethane, synthetic organochlorine pesticide known for its persistent toxicity and banned in the United States in 1972
DFG	California Department of Fish and Game
GIC	The Geographic Information Center at California State University, Chico.
MPSL	Marine Pollution Studies Laboratory, consisting of the toxicology laboratory at Granite Canyon, and the logistics, data management, and trace metal analytical laboratory at Moss Landing.
NAWQA	National Water Quality Assessment, a program of the US Geological Survey.
NLCD	National Land Cover Dataset
PAH	Polycyclic aromatic hydrocarbons, a suite of organic pollutants produced through combustion of fossil fuels
PBDE	Polybrominated diphenyl ethers, which are widely employed as flame-retardants. In 2006 the State of California began prohibiting the manufacture, distribution, and processing of pentaBDE and octaBDE products.
PCB	Polychlorinated biphenyls, a group of industrial compounds widely used for their insulating properties. PCB production was banned in the United States in 1979.
PEC	Probable effect concentration, an empirically derived sediment quality objective that sets a concentration above which toxicity is expected to occur (MacDonald et al., 2000). PEC values are shown in Appendix 3, Table 14.
PSA	Perennial Streams Assessment, the SWAMP statewide program measuring ecological indicators at probabilistically selected sites in California streams.
SPoT	Stream Pollution Trends monitoring program.
SWAMP	Surface Water Ambient Monitoring Program
TEC	Threshold effect concentrations, an empirically derived sediment quality objective that sets a concentration below which toxicity is not expected to occur (MacDonald et al., 2000). TEC values are shown in Appendix 3, Table 14.
TMDL	Total Maximum Daily Load
TOC	Total organic carbon
USGS	United States Geological Survey

EXECUTIVE SUMMARY E

The California Surface Waters Ambient Monitoring Program (SWAMP) is tasked with assessing water quality in all of California's surface waters. The program conducts monitoring directly and through collaborative partnerships, and provides numerous information products designed to support water resource management in California. The Stream Pollution Trends (SPoT) program is a statewide monitoring effort focused on the SWAMP priority of assessing the levels to which aquatic life beneficial uses are supported in California streams (SWAMP 2010). The program has three primary goals:

1. Determine long-term trends in stream contaminant concentrations and effects statewide.
2. Relate water quality indicators to land-use characteristics and management effort.
3. Establish a network of sites throughout the state to serve as a backbone for collaboration with local, regional, and federal monitoring.

The SPoT program is specifically designed to fill critical information needs for state, regional and local resource management programs, including Clean Water Act (CWA) §303d impaired waters listing, CWA §305b condition assessment, total maximum daily load (TMDL) assessment and allocation, non-point source program water quality assessment, stormwater and agricultural runoff management, pesticide registration and labeling, and local land use planning.

SPoT is a long-term trends monitoring program that will help managers understand how water quality conditions are changing over time in relation to land use change and resource management practice implementation. This report covers the first annual survey, so trends assessment will not begin until the second and third year surveys are included in the next SPoT report (due in 2012). The focus of this report is on identifying chemicals of concern and the watershed land uses associated with their presence in California streams. The data collected can be used in a space-for-time-swap approach to estimate the effect that further land use change (such as increasing urbanization) would have on stream water quality in California.

The results indicate that, on a statewide basis, levels of most measured pollutants in stream sediment increased as urban land cover in their watersheds increased. Industrial compounds, some metals, and many pesticides were found at higher concentrations in urban watersheds than in agricultural or other watersheds statewide.

Pyrethroid pesticides were detected in stream sediments from more than half of the SPoT watersheds, and were measured at concentrations associated with toxicity in more than a quarter of the total samples. DDTs and PCBs, both banned for more than three decades, are still commonly detected in California streams, with DDTs frequently exceeding sediment quality guidelines. PBDEs and PAHs were common in urban areas, and mercury was above guideline values in a small number of samples from urban watersheds and watersheds where it is geologically abundant.

The data presented here describe the baseline condition for the SPoT long-term trends assessment. They also demonstrate a significant relationship between land use and stream pollution, and provide data directly relevant to a number of agency water quality protection programs.

SECTION 1
INTRODUCTION

Clean freshwater is California's most precious natural resource. It flows through streams that drain watersheds subject to constantly changing levels of human activity. Understanding the connections between these human activities, the changing landscape, and the quality of our waters is essential for the preservation of aquatic life, human health, and the prosperity of California's economy. As the population grows, foothills are converted to residential and agricultural use, agricultural lands are converted through urban and suburban development, and regulatory programs and conservation practices are implemented to maintain and restore stream condition in this ever changing environment.

The Stream Pollution Trends (SPoT) program is designed to improve our understanding of watersheds and water quality by monitoring changes in both over time, evaluating impacts of development, and assessing the effectiveness of regulatory programs and conservation efforts at a watershed scale. The overall goal of this long-term trends assessment program is to detect meaningful change in the concentrations of stream-borne contaminants and their biological effects in large watersheds at time scales appropriate to management decision making.

The three specific program goals are to:

1. Determine long-term trends in stream contaminant concentrations and effects statewide.
2. Relate water quality indicators to land-use characteristics and management effort.
3. Establish a network of sites throughout the state to serve as a backbone for collaboration with local, regional, and federal monitoring.

SPoT sampling locations were selected to provide a statewide network of sites at the drainage points of large watersheds to support collaboration with watershed-based monitoring programs throughout the state. To establish this network, SPoT staff met with Regional Board monitoring coordinators and stormwater agencies to develop a coordinated monitoring design. 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 monitoring sites for the Municipal Regional Stormwater NPDES Permit (CRWQCB-SFR, 2011). SPoT sites in the Central Coast and Central Valley Regions are shared by the Cooperative Monitoring Program for Agriculture and Irrigated Lands Program, respectively (Appendix 1). In most cases, the SPoT assessments of sediment toxicity and chemistry complement water column measurements made by cooperating programs.

The SPoT program indicators are measured in stream sediment because this matrix best accommodates program goals. Most trace metal and organic pollutants that enter streams adhere to suspended sediment particles and organic matter, and this sediment-associated phase is the major pathway for contaminant loading in streams and downstream waterways (Karickhoff 1984, DiToro et al. 1991, Foster and Charlesworth 1996). In addition, 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 from recent stream bed deposits during base flow periods after the high water season when most sediment and pollutant transport takes place.

The SPoT program complements the other three SWAMP statewide monitoring programs: the Perennial Streams Assessment (PSA), the Reference Condition Management Program (RCMP), and the bioaccumulation monitoring program of the Bioaccumulation Oversight Group (BOG). The PSA measures ecological endpoints related to macroinvertebrate and algal communities, and uses a probabilistic design to assess aquatic health in perennial, wadeable streams statewide. PSA and RCMP provide a baseline assessment of high quality streams, and provides direct evidence of aquatic life condition statewide. The BOG program measures contaminant concentration in sport fish collected on a rotating basis from streams, lakes and coastal waters.

SPoT complements the PSA by focusing on the magnitude of pollution in streams, using toxicological endpoints to establish causal connections between these chemicals and biological impacts, and by analyzing land cover as part of a watershed-scale evaluation of the sources of pollutants affecting aquatic life. The PSA contributes to the attainment of SPoT goals by assessing the overall health of wadeable perennial streams, and by testing assumptions about the status of reaches upstream of the intensive land uses that might be found associated with pollutants measured by SPoT. SPoT complements the BOG by identifying watershed sources for contaminants measured in fish from downstream water ways. The BOG complements SPoT by providing perspectives on the fate and human health aspects of pollutants in streams, particularly as related to their uptake in fish tissue and risk associated with human consumption. PSA, RCMP, BOG, and SPoT together provide freshwater data similar to those used in other programs to develop sediment quality objectives (SQOs) in marine and estuarine habitats. Co-location of sites or addition of specific indicators across the PSA, BOG, and SPoT programs could allow for development of freshwater SQOs for California in the near future (SWAMP 2010).

SPoT was specifically designed to provide data directly useful for regulatory programs and conservation initiatives. SPoT data can be incorporated directly into Clean Water Act § 303[d] listing of impaired waters, as well as into the statewide status assessments required by § 305[b]. Eight SPoT sites are located in priority watersheds for the US EPA Measure W program (also known as the Watershed Improvement Measure (WIM) or SP-12). The focus on causes and sources of pollutants in watersheds feeds directly into Total Maximum Daily Load program efforts to quantify pollutant loadings and understand sources and activities that contribute to those loadings. By coordinating with local and regional programs, SPoT provides statewide context for local results, and provides information useful for local management and land use planning activities. SPoT is also specifically designed to assist with the watershed-scale effectiveness evaluation of management actions implemented to improve water quality, such as pesticide reduction or irrigation management on farms, and installation of stormwater treatment devices or low impact development in urban areas. Use of SPoT data for watershed scale evaluations of management practice effectiveness is currently limited by the lack of a comprehensive and standardized reporting system for practice implementation, as will be discussed further in this report.

SECTION 2
ASSESSMENT QUESTIONS AND LINKS TO WATER QUALITY PROGRAMS

SPOT IN THE SWAMP ASSESSMENT FRAMEWORK

The following is a summary of SPoT program elements in the context of the SWAMP Assessment Framework (Bernstein, 2010), with linkages to regulatory and resource management programs that can incorporate SPoT data. The SWAMP Assessment Framework provides guidance and context for developing question-driven monitoring to provide water quality information directly useful for resource management. This summary specifies the beneficial uses and water body types targeted by SPoT, states the assessment questions SPoT addresses, and lists the resource management programs to which SPoT provides essential information. Level 1 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.

Beneficial use assessed:	Aquatic life protection
Water body type assessed:	Streams, ranging from ephemeral creeks to large rivers

Level 1 Assessment Questions:

I. Are our aquatic ecosystems healthy?

II. What stressors and processes affect our water quality?

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

Are beneficial uses impaired?

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

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

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

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

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

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

Temporal scale: Surveys on an annual basis over an extended period (> 10 years).

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 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 scale: State of California, as described above.

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

What is the magnitude and extent of any problems?

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

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

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

Certainty / precision: as described above.

Reference conditions: as described above.

Spatial scale: as described above.

Temporal scale: as described above.

What's causing the problem?

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

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

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

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

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

Spatial scale: as described above.

Temporal scale: as described above.

Are solutions working?

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

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

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

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

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

Spatial scale: as described above.

Temporal scale: as described above.

SECTION 3 METHODS

MONITORING OBJECTIVES

Program methods were selected to meet six monitoring objectives:

1. Determine concentrations of a suitable suite of contaminants in depositional sediment collected near the base of large California watersheds;
2. Determine whether these depositional sediments are toxic to representative organisms;
3. Quantify ancillary parameters such as land cover and impervious surface area, available from the National Land Cover Dataset and other public sources;
4. Conduct surveys once per year on a continuing basis;
5. Analyze data to evaluate relationships between contaminant concentrations, toxicity, and land cover metrics;
6. In future years (when data from multiple annual surveys are available) conduct trends analyses to detect the direction, magnitude, and significance of change in the above parameters over time.

MONITORING DESIGN

The monitoring design benefitted from experience and information available from 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.

SPoT employs a targeted monitoring design to enable trend detection on a site-specific basis. To serve their purpose as integrator sites, SPoT sites were located at the base of large watersheds containing a variety of land uses. Because depositional sediment is needed for sample collection, sites were targeted in locations with slow water flow and appropriate micro-morphology, to allow deposition and accumulation. The SPoT program considered creating a sample frame that included all possible sites that fit this description, but the necessary information to generate such a frame did not exist.

SPoT and NAWQA use integrator sites because both programs focus on understanding causes of water quality impairment. The connection with land use is a major part of the assessment, and targeted sites allow greater discretion to adjust to significant land cover variation in low watershed areas. One of the three main goals of SPoT was to form a statewide network of sites that provides statewide context for the findings of local and regional programs. A targeted approach allowed the SPoT program flexibility to link to established sites from other programs.

SITE SELECTION

In 2008, 92 sites were surveyed to census about half of the nearly 200 major hydrologic units (8-digit HUCs) in California. Site selection criteria included:

1. Availability of fine-grained depositional sediment (see note below);
2. Location in a large watershed with heterogeneous land cover, in most cases on the order of an 8-digit hydrologic unit code (8-digit HUC = USGS Cataloging Unit);
3. One site per large watershed (except in some very large watersheds, such as the Sacramento, in which sites were selected in large sub-watersheds);
4. 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;
5. Availability of previous data on sediment contaminant concentrations, biological impacts, or other relevant water quality data;
6. Location where site-specific conditions are appropriate for the indicators selected (e.g., depositional areas, sufficient flow, appropriate channel morphology, substrate);
7. Availability of safe access, either by boat or wading;
8. Location near stream gauges where possible;
9. Co-location, where possible and appropriate, with key sites from cooperative programs;
10. Priority ranking assigned by SWAMP Regional Monitoring Coordinator for cooperation with Regional SWAMP monitoring programs;
11. Preference given to large tributaries rather than multiple main stem sites on multi-HUC rivers.

Note on targeting of fine sediments

During field surveys at most SPoT sites, fine sediment particles were found in thin layers throughout the channel. Some sites were dominated by deep deposits of fine sediment. At many sites, however, there were fewer locations where fine sediment accumulated in layers thick enough to allow efficient sample collection (> 2 cm). Hall et al. mapped fine sediment distributions at 99 transects in three California streams, each designated as either agricultural, urban or residential. They estimated that an average of 17% of the stream bed was characterized as “depositional” (Hall et al. 2010; Hall et al. in press). 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 matrix for evaluating annual trends.

REFERENCE SITES

Reference sites were included in the monitoring design for quality assurance purposes, and to provide information on temporal trends in the absence of significant contaminant-related land use change. Reference site data were also expected to anchor the low end of contaminant gradients for correlation analyses. Five large watersheds with relatively low levels of human activity were selected across the state, representing the north coast, Bay Area, Sierra foothills, Coast Range, and southern inland areas. Sites in these watersheds were selected based on the same criteria as above for other SPoT sites. The SPoT Scientific Review Committee recommended using the USGS NAWQA reference sites for the Santa Ana, San Joaquin, and Sacramento study units. Of these NAWQA sites, two were used for SPoT: Tuolumne River at Old La Grange bridge 535STC210 (San Joaquin) and San Jacinto River Reference Site 802SJCREF (Santa Ana). The Sacramento study unit site was abandoned for lack of access to locations with sufficiently fine-grained sediment.

SURVEY TIMING

SPoT surveys were timed so that sediment was collected from recent stream bed deposits during base flow periods after the high water season when most sediment and pollutant transport takes place. In general, surveys preceded from coastal southern California in late spring, to coastal central California in early summer, the Central Valley in mid-summer, the eastern Sierra in late summer, and the North Coast and Colorado River Basins in the fall. Surveys began April 28 and ended October 29, 2008 (Appendix 1).

INDICATORS AND MEASUREMENT PARAMETERS

SPoT indicators were selected to measure contaminants previously demonstrated to be of concern in California streams, as well as assess toxicity to a representative benthic crustacean of a resident genus. The criteria for indicator selection included

1. Stability over intermediate time scales (weeks to months) to minimize the effects of intra-annual variability on the evaluation of long-term trends;
2. Biological indicators sensitive to contaminants;
3. Feasibility;
4. Reasonable cost;
5. Use of established methods comparable to SWAMP indicators and widely accepted in the scientific and regulatory communities;
6. Usefulness for investigating relationships between contaminants and effects;

7. Coverage of analyte lists that are sufficient for statewide application in order to detect relevant trends in different regions; and
8. Usefulness for investigating sources and causes of impairment.

Based on these criteria, the following indicators were selected:

1. Sediment trace metals: Ag, Al, As, Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn;
2. Sediment trace organics: organophosphate, organochlorine, and pyrethroid pesticides, and PCBs;
3. Total phosphorus, total organic carbon, and sediment grain size;
4. Sediment toxicity, using the 10-d growth and survival test with the representative freshwater amphipod Hyalella azteca, to estimate biological effects of contaminants;
5. At a subset of 32 primarily urban sites (labeled Tier 2 sites), sediments were also measured for polycyclic aromatic hydrocarbons (PAHs) and polybrominated diphenyl ethers (PBDEs).

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, in accordance with previous studies evaluating sediment quality guidelines, where appropriate (MacDonald et al., 2000). All detected pyrethroids were summed together where indicated, and pyrethroids were also summed as carbon normalized toxic units (Amweg et al. 2005). For many analyses, 8 relatively toxic trace metals (As, Cd, Cr, Cu, Pb, Hg, Ag, Zn; Mahler et al., 2006) were summed to provide an overall characterization of measured levels in sediment. Trace metals were also interpreted as the sum of four metals commonly released into the environment by human activity, and less affected by geologic abundance in California (Cd, Cu, Pb, Zn; Mahler et al., 2006; Bonifacio et al., 2010; Topping and Kuwabara, 2003).

A subset of the sediment sample was sieved to 63 um so that trace metal concentrations could be measured in both sieved (fine grained) and unsieved (whole) sediment. Sediments were dry sieved on Nytex screens, with separate sieves used for each sample.

ANALYTICAL CHEMISTRY AND TOXICITY TEST METHODS

All chemical analyses and toxicity tests were performed by SWAMP laboratories: the DFG Water Pollution Control Laboratory (trace organics), the Marine Pollution Studies Laboratory at Moss Landing (MPSL, trace metals), and the UC Davis MPSL at Granite Canyon (toxicity). Analytical methods are listed in Table 4 of the SPoT Quality Assurance Project Plan (QAPP): http://www.waterboards.ca.gov/water_issues/programs/swamp/qapp/qapp_spot_strms_pollute_final.pdf

FIELD METHODS

Detailed field methods are described in the SPoT Quality Assurance Project Plan: http://www.waterboards.ca.gov/water_issues/programs/swamp/qapp/qapp_spot_strms_pollute_final.pdf

QUALITY ASSURANCE AND QUALITY CONTROL (QA/QC)

The QA/QC requirements for the SPoT program are described in detail in the appendix to the SPoT Quality Assurance Project Plan: http://www.waterboards.ca.gov/water_issues/programs/swamp/qapp/qapp_spot_strms_pollute_final.pdf. The results of QA measurements for the 2008 surveys are provided in Appendix 3 of this report.

DATA MANAGEMENT

All data collected for this study are maintained in the SWAMP database, which is managed by the data management team at Moss Landing Marine Laboratories (http://swamp.mpsl.mlml.calstate.edu/). The complete dataset includes QA data (quality control samples and blind duplicates) and additional ancillary information (specific location information, and site and collection descriptions). The complete dataset from this study is also available on the web at http://www.ceden.org/. Data for the SPoT program can be accessed from the CEDEN query system, http://www.ceden.us/AdvancedQueryTool . The procedure for obtaining only SPoT data is as follows: 1. Press the “Select” button next to the Project link. 2. Highlight the “SWAMP Stream Pollution Trends” and click on “Done”. 3. At the bottom of the screen determine whether to include QA data or not as well as whether to download the data as an Excel or text file. By selecting “Toxicity” in the Result Category, one can go through the same steps to download SPoT Toxicity data as well.

GEOGRAPHIC INFORMATION SYSTEM ANALYSES

Anthropogenic contaminant concentrations in streams are influenced by the mobilization of pollutants in their watersheds. The analyses described here evaluate the strength of relationships between human activity in watersheds, as indicated by land cover, and pollutant concentrations in recently deposited stream sediment. Watershed delineations and land cover data extractions were conducted by the Geographic Information Center at CSU, 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 (DEMs). Each delineation file was reviewed by GIC and SPoT program staff for accuracy. Reviews included comparisons to National Hydrologic Dataset catchments, and Google Earth® images of drainage areas as kml files. Drainage areas near the site were delineated with 1 km and 5 km radius buffers to create the 1K and 5K drainage areas for analysis (along with analyses of the entire drainage area and whole watershed; Figures 1 and 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.

Drainage area shapefiles were used to extract land cover grids from the National Land Cover Dataset (NLCD, Figure 3). The following NLCD categories were used in the analyses relating land cover to water quality:

NLCD 21: Developed, open space, including areas with a mixture of some constructed materials, but mostly vegetation in the form of lawn grasses, such as large-lot single-family housing units, parks, and golf courses.

NLCD 22, 23, 24: Low, Medium, and High Intensity Developed. These were combined to represent "urban" land cover for the report analyses.

NLCD: 82: Cultivated crops. This was the category used to represent "agricultural" land cover for the report analyses.

All other NLCD categories were combined into the "other" category for the report analyses.

Impervious surface area data were obtained from the National Land Cover Dataset (Imperv_nlc; NLCD2006 Percent Developed Imperviousness).

In correlation analyses, pollutant concentrations were compared to continuous percent land cover data (as % urban, % agricultural, and % other land cover types). For analyses based on comparisons among watersheds types, watershed areas were characterized as "urban" if they had greater than 10% urban cover (NLCD categories 22 + 23 + 24). This characterization is in line with studies indicating stream degradation where impervious surface cover exceeds 10% (e.g., Schueler 1994). Watershed areas were characterized as "agricultural" if they had greater than 25% crop cover (82). Watershed areas were characterized as "urban-ag" if they had greater than both 10% urban and 25% agricultural land cover. At the whole watershed scale, the Tembladero Slough site was the only site meeting the urban-ag criteria.

STATISTICAL ANALYSES

Multivariate Spearman rank correlations were used for all statistical evaluations of relationships between pollutants, toxicity, land cover, TOC, and/or grain size. The Wilcoxon test was used to determine the statistical significance of differences in results binned by land use category. All analyses were done using JMP ® 9.0.0 software (SAS Institute, Inc., 2010). The statistical significance of observed toxicity was determined according to the methods described in Anderson et al. (2011).

Tables in the Results section provide probability (p) values indicating the strength of relationship among variables in the multiple correlations. These p values have not been adjusted to account for the number of simultaneous comparisons made (e.g., Bonferroni adjustment). There is debate in the statistical literature about the value of adjusting alpha values to account for inference based on many simultaneous tests (Perneger 1998). Alpha adjustments were not made here because we are not interested in whether all null hypotheses are true simultaneously, but rather which relationship are of greatest interest in exploring connections between land use and stream pollution.

Figure 1. SPoT sites and watersheds. Additional site information is found in Appendices 1 and 2.

Figure 2. Drainage area delineation for watershed areas draining to SPoT sites. The largest polygon is the site's whole watershed (WS). The semi-circular smaller areas are watershed areas 1 km (1K) and 5 km (5K) upstream.

Figure 3. **National Land Cover Dataset grids overlaying SPoT watersheds.** Each color represent one of the 36 NLCD categories.

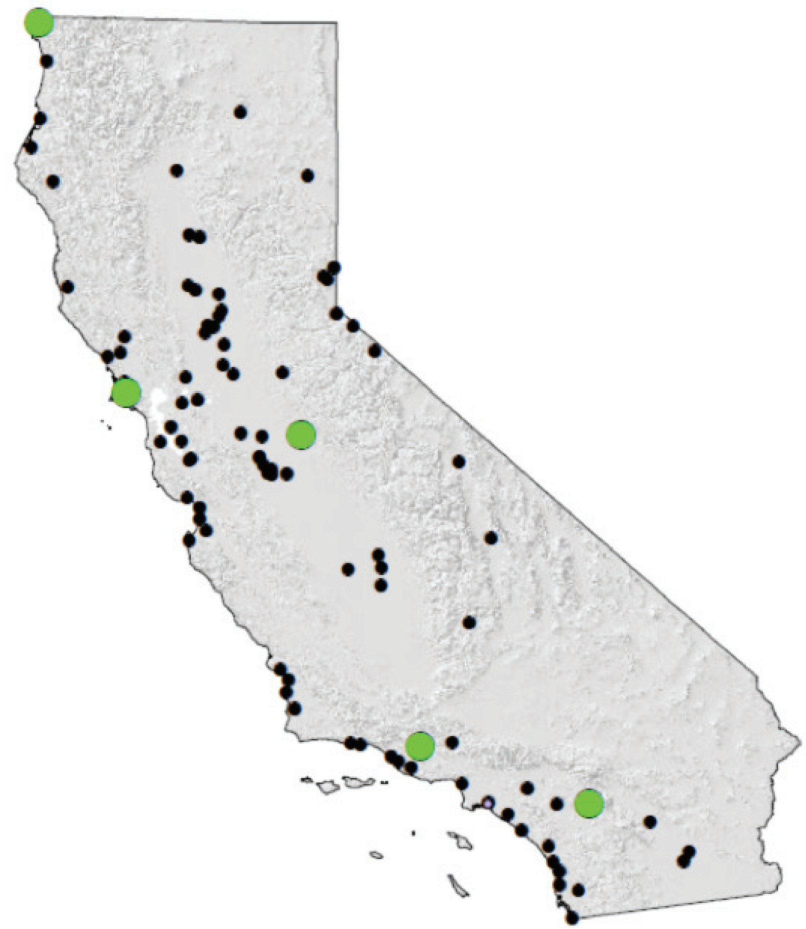

Figure 4. Location of SPoT reference sites (green circles), and additional SPoT sites (black circles). Additional site information is found in Appendices 1 and 2.

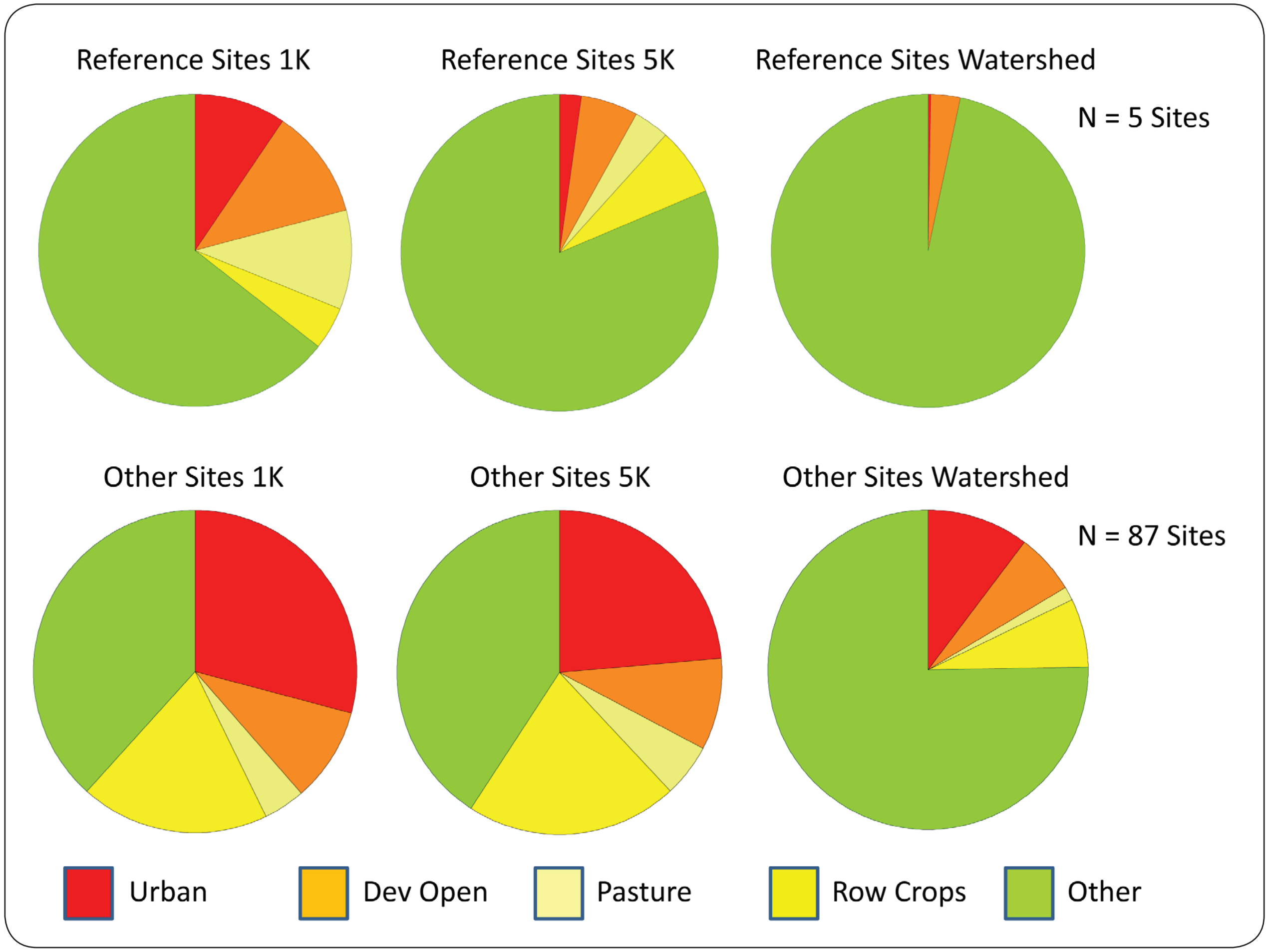

Figure 5. Land cover distributions in reference sites compared to other SPoT sites at the three watershed scales of analysis. Legend colors from left to right are shown clockwise from noon.

SECTION 4 RESULTS

COMPARISON OF REFERENCE SITES TO OTHER SPOT SITES

All classes of chemicals had lower concentrations in sediments collected from designated reference sites than in sediments from other SPoT sites (Figures 6 - 12).

Trace metals

The sum concentration of cadmium, copper, lead and zinc, the four primarily anthropogenic metals of concern, was lower in reference site sediments than elsewhere (Fig. 7). The mean concentration for the sum of eight metals is slightly higher at reference sites than at other sites. These eight metals include the four above plus arsenic, chromium, mercury, and silver, and their distributions are often determined by geological abundance. All reference sites were located relatively short distances downstream of mountainous areas within their watersheds. The Lagunitas Creek reference site watershed contains serpentine outcroppings of the Franciscan formation, and the other reference site watersheds had moderate to high levels of historic mining activity.

Total phosphorus concentrations were lower in reference site sediments. Phosphorus can be geologically abundant in certain areas, and can also be elevated by urban and agricultural fertilizer applications or soil disturbance associated with land development.

Trace organics

Concentrations of organic pollutants were generally low in reference site sediments, with means lower than the means for other SPoT sites (Figs. 8 - 10). PCBs and DDTs were low for all reference sites. Total pyrethroid pesticide concentrations were elevated in sediment from the Lagunitas Creek reference site (201LAG125), with just over 1 toxic unit measured there (Figs. 10 and 19). This watershed has low urban and agricultural land coverage (< 1%) and approximately 5% urban open space. There are clusters of residential areas upstream.
(A sample with one toxic unit has a concentration equal to the LC50 for the measured chemical, and thus should cause mortality in half the test organisms exposed to it.)

Tier 2 analyte classes (PBDEs and PAHs) were detected in sediment from only one reference site (San Jacinto Creek, 802SJCREF). The San Jacinto Creek PBDE concentration was 0.586 ng/g dw, compared to the overall mean of 16.4 ng/g dw. The San Jacinto Creek PAH concentration was 144.63 ng/g dw, compared to the overall mean of 757.27 ng/g dw.

Toxicity

No significant toxicity was observed in sediments collected from reference sites, compared to a range of toxicity levels observed in sediments from other SPoT sites (Fig. 11).

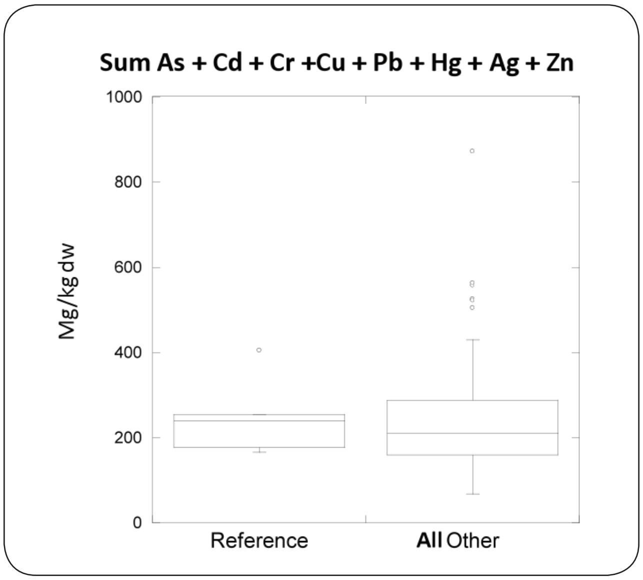

Figure 6. Sediment concentrations of 8 trace metals in reference and other SPoT sites.

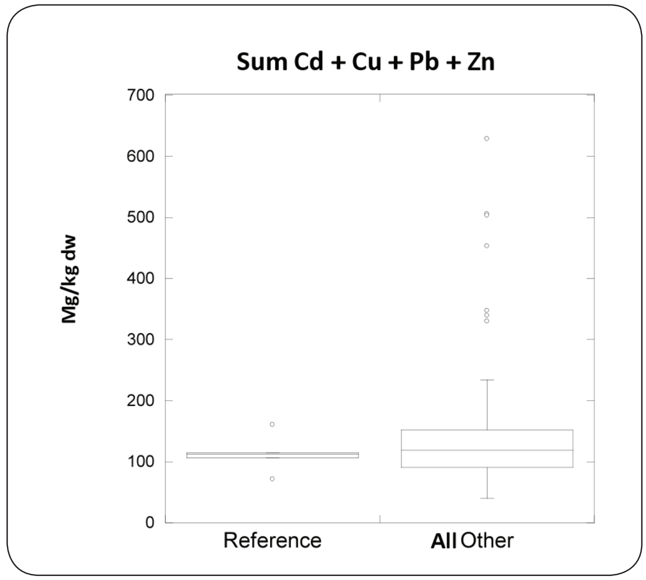

Figure 7. Sediment concentrations of 4 trace metals in reference and other SPoT sites.

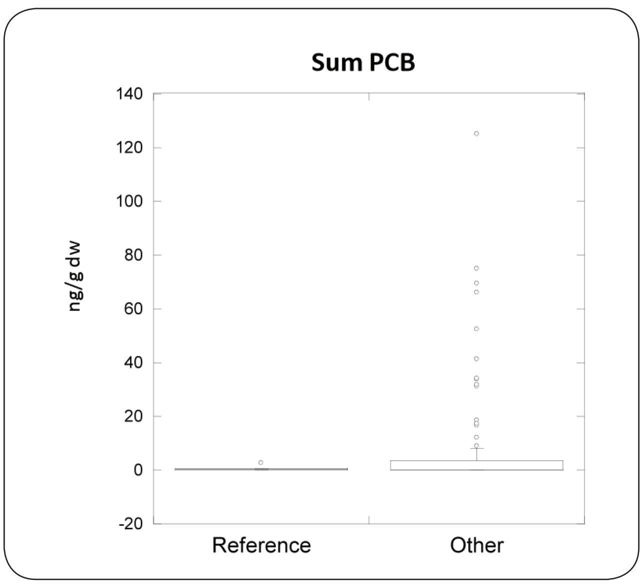

Figure 8. Sediment concentrations of PCBs in reference and other SPoT sites.

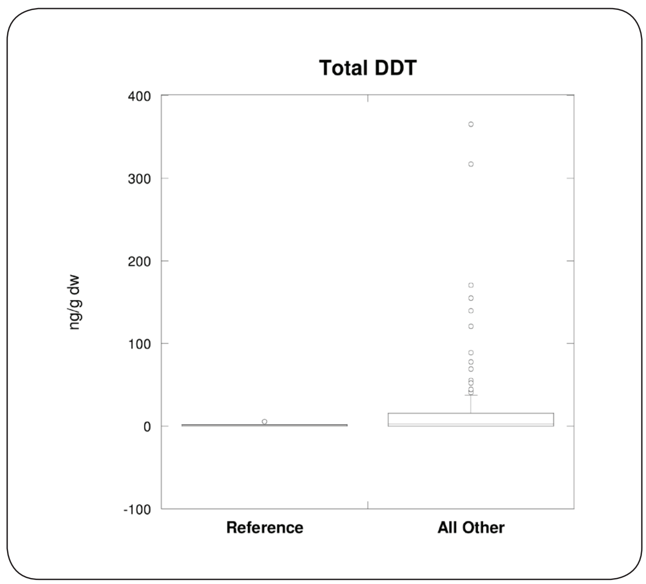

Figure 9. Sediment concentrations of DDTs in reference and other SPoT sites.

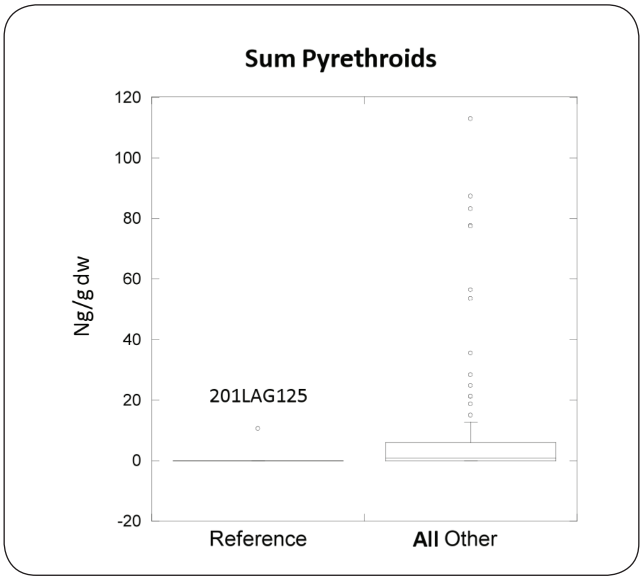

Figure 10. Sediment concentrations of pyrethroids in reference and other SPoT sites.

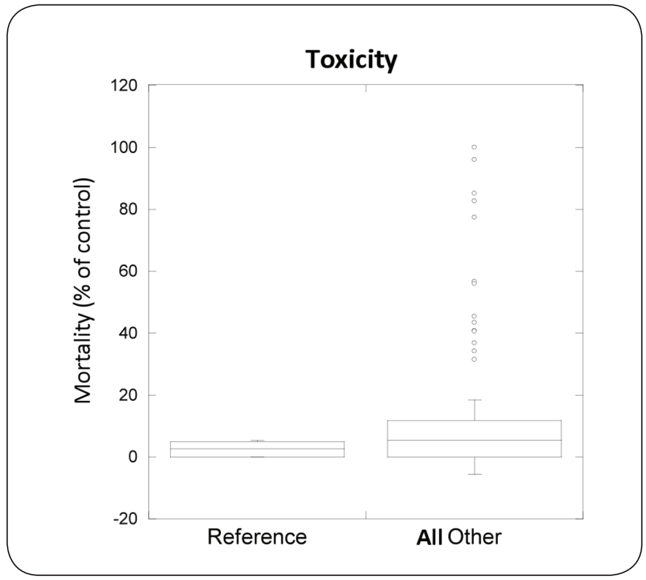

Figure 11. Sediment toxicity in reference and other SPoT sites.

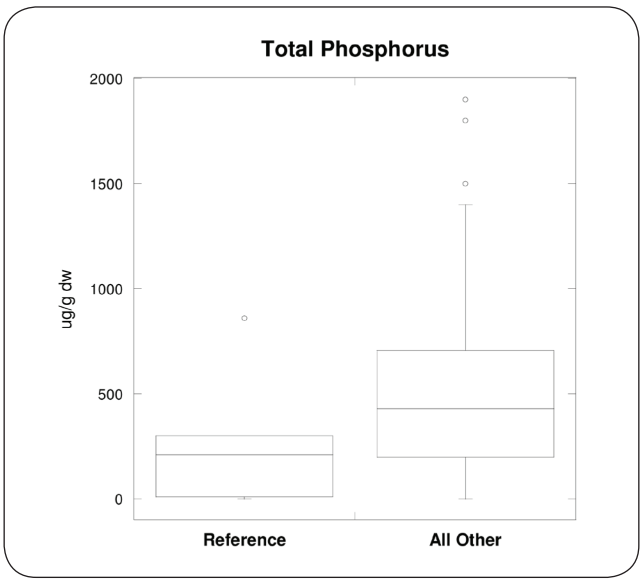

Figure 12. Sediment concentrations of total phosphorus in reference and other SPoT sites.

SEDIMENT CHARACTERISTICS: GRAIN SIZE AND TOC

At the majority of SPoT sites, fine sediment particles were found throughout the channel in thin layers covering other dominant substrate, including sand, cobble, boulders, concrete, and woody debris. This fine sediment formed deeper layers in pockets and larger depressions where micro-hydrological and geomorphic conditions favored deposition. These deeper depositional areas were targeted for sample collection because they allowed the most effective collection of fine material. In some sampling areas, fine sediments formed large and deep deposits across the channel.

While field teams were trained to collect the finest material available, a number of samples were composed primarily of grains larger than 63 um (Figure 13a). None of these samples contained substantial amounts of coarse sand or larger particles, but grains larger than 63 um made up the larger fraction in 37% of the samples.

Field teams were also trained to avoid or remove conspicuous debris, including leaves and other large organic material. TOC content cannot be readily determined in the field, and the sampling protocol has no set criterion for TOC concentration. Measured TOC values ranged from 0.23% to 16.29%, with a mode between 1 and 1.5% (Fig. 13b). There were three samples with TOC greater than 7.6%: San Leandro Creek (11.6%), Ballona Creek (12.5%), and Lower Owens River (16.3%).

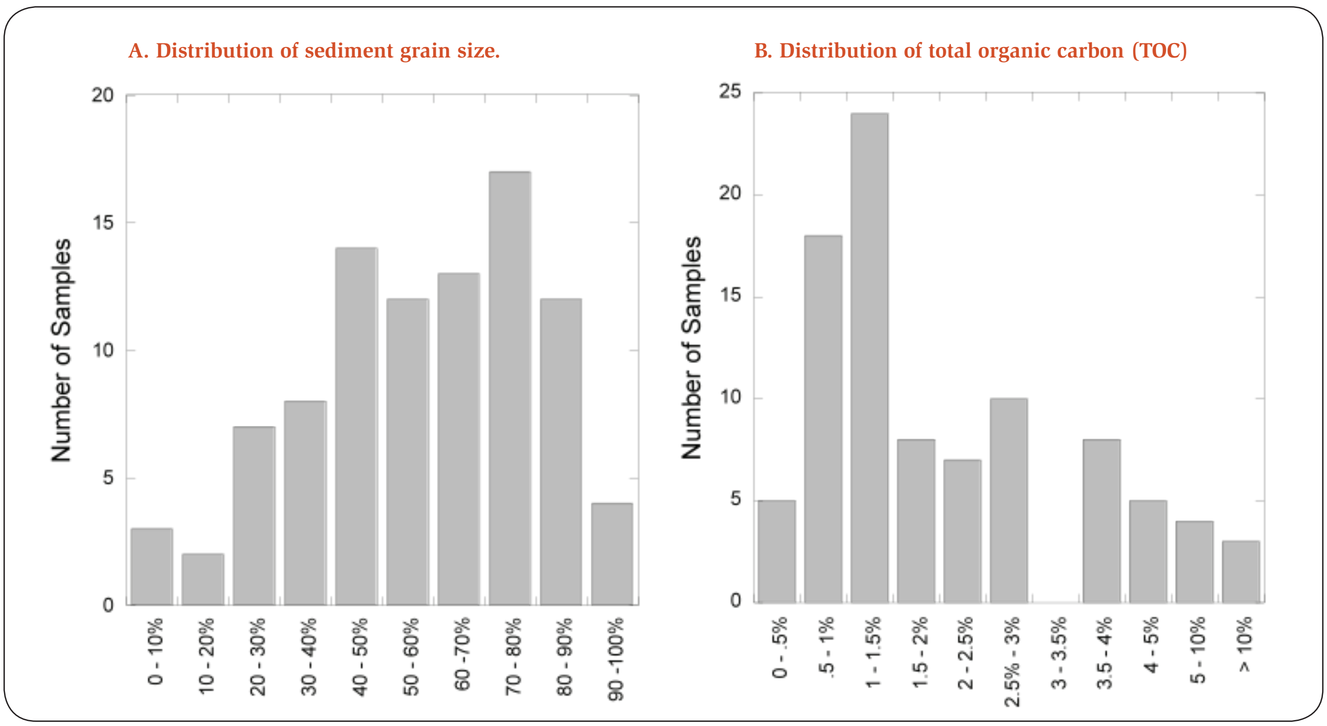

Figure 13. Sediment characteristics. (A) Percent fines: numbers of samples with given percentages of sediment < 63 um. (B) Percent TOC: numbers of samples with given percentages of TOC content.

STATEWIDE SPATIAL DISTRIBUTION OF POLLUTANTS

Trace metals

Stream sediment concentrations of cadmium, copper, lead and zinc tended to be highest in the San Francisco Bay and Los Angeles area watersheds (Fig. 14). Sediments from San Leandro Creek (SF Bay area), and Ballona Creek and San Gabriel River (Los Angeles area) were in the highest quartile for the range of concentrations. The distribution of second and third quartile metals concentrations was not as strongly related to urban land cover.

Mercury concentrations exceeding probable effects concentrations (PECs) were found in sediments from watersheds with geologic abundance and historic mining activity (Fig. 15). This was also the case for samples exceeding the lower TECs (threshold effects concentrations), though the Ballona Creek sample also exceeded TECs, even though it came from an urban area isolated from geologic sources.

Trace organics

Total PCBs exceeded TECs in urban watersheds near San Francisco and Los Angeles (Fig. 16). Most PCB detections were in sediments from coastal and urban watersheds, though they were also detected in a few more remote locations, such as in the Kern and San Jacinto Rivers. PCBs were seldom detected in sediments from agricultural and rural areas.

Despite being banned in California for nearly 40 years, persistent DDTs were found in sediments from most urban and agricultural watersheds, including many samples that exceeded TECs (Fig. 17). None of the DDT concentrations exceeded the LC50 for *Hyalella azteca*. Samples in which DDTs were not detected were predominantly located within rural and mountainous watersheds.

Organophosphate pesticides were detected in relatively few samples. Chlorpyrifos was detected in 11 samples, with only three of these above reporting limits. The highest chlorpyrifos concentration was in the Santa Maria River sample (71 ng/g), though this was below known toxic concentrations for Hyalella (LC50 = 399 ng/g; Brown et al. 1997). Diazinon and malathion were detected in only one sample each (Santa Maria River and Tule River, respectively), neither of which exceeded known toxic concentrations.

Pyrethroid pesticides were detected in 55% of the samples statewide (51 of 92). The highest concentrations were measured in sediments collected from urban watersheds, plus two agricultural watersheds along the central coast (Santa Maria River and Tembladero Slough; Fig. 18).

Sediment total pyrethroid concentrations were also viewed in terms of organic carbon normalized toxic units (TUs; Fig. 19). A sample with one toxic unit has a concentration equal to the LC50 for the measured chemical, and thus should cause mortality in half the test organisms exposed to it. The pyrethroid toxic unit data show a different spatial pattern than the dry weight data because of variation in sample total organic carbon content (TOC) and differences in the contributions of individual pyrethroids to each sample's total.

For example, the Tijuana River sample (southernmost site on the maps) had a relatively high total pyrethroid dry weight concentration, but a relatively low toxic unit value because of the high TOC content (7.6%) and the high proportion of permethrin relative to the other pyrethroids. (Permethrin is less toxic than the other pyrethroids measured.) On the other hand, the highest pyrethroid toxic unit value (10.96 TU) was measured in a sample from Packwood Creek (Tulare basin). This sample had low TOC and was comprised entirely of cypermethrin, which is more toxic. Viewing the pyrethroid data as toxic units also shows high levels in urban and many agricultural areas, and lower TUs in rural or mountainous watersheds.

PBDEs and PAHs were measured only at Tier II SPoT sites located mostly in urban areas. As with the four trace metals, the highest PBDE concentrations were measured in sediments from San Leandro Creek (SF Bay area) and Ballona Creek (Los Angeles area; Fig. 20). Most other sites were in the lower two quartiles of the concentration range, having less than half the highest concentration measured (121 ng/g at Ballona Creek).

Sediment PAH concentrations were generally highest in the San Francisco Bay area, with one surprising exception: the highest total PAH value was measured in sediment from the Mokelumne River site in the Sierra foothills (Fig. 21). The total PAH concentration was 3567 ng/g dw, and the sum for 13 PAHs (Swartz 1999) was 2836 ng/g, which exceeds the TEC value of 1610 ng/g. Two other sites (marked by the other two cross symbols on Fig. 21) exceeded the TEC: Walnut Creek at Concord Ave (2536 ng/g total) and Guadalupe Creek at the USGS gauging station (2624 ng/g total). Samples from these three sites also exceeded TEC levels for a number of individual PAH compounds, including benz[a]anthracene, benzo[a]pyrene, fluoranthene (except Walnut Creek), and pyrene (except Guadalupe). For confirmation, the Mokelumne River sample was re-extracted and re-measured, with similar results. This site is on a relatively high gradient reach with a natural streambed and ample riparian vegetation. Sparse development upstream includes a hydroelectric power house (5 km upstream) and widely separated rural communities much further up in the foothills. The two-lane Highway 49 crosses the Mokelumne just upstream of the site, and the high PAH result may have been due to a spill or dumping incident. Further investigation is planned.

Toxicity

Significant toxicity was observed in 24% of the sediment samples collected, with 6.5% (6 of 92) identified as highly toxic (Fig. 22). Highly toxic samples were collected from agricultural watersheds in the Tulare basin and central coast, in urban areas of southern California, and in the Tijuana River. Other toxic samples were collected from a wide range of watershed types, including those along the north coast, the Sierra Nevada and urban and agricultural areas across the state.

CHEMICAL CONCENTRATIONS RELATIVE TO THRESHOLDS

Pyrethroid pesticides show cause for concern in terms of potential for acute biological effects. At least one pyrethroid pesticide was detected in 55% of the sediment samples collected statewide, and 26 of 92 samples

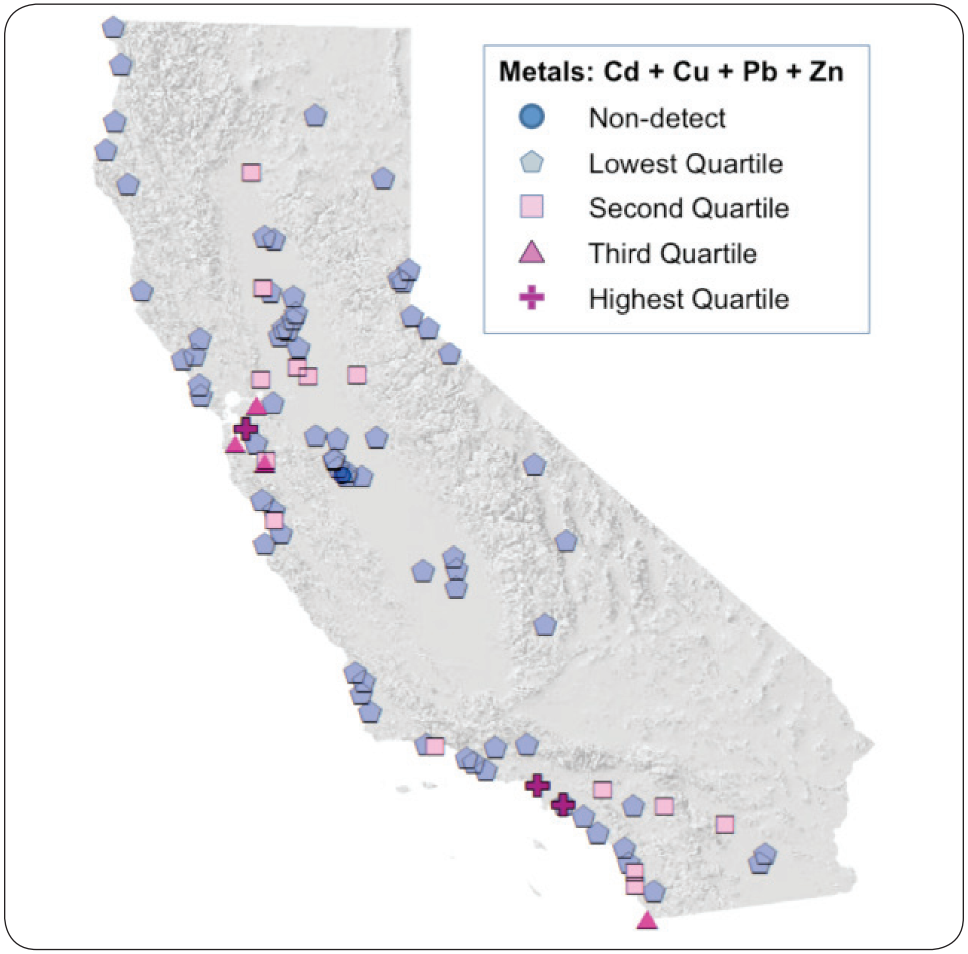

Figure 14. Distribution of sum of Cd, Cu, Pb, and Zn in unsieved stream sediment. "Quartile" cutoffs are at 25%, 50% and 75% of the maximum concentration.

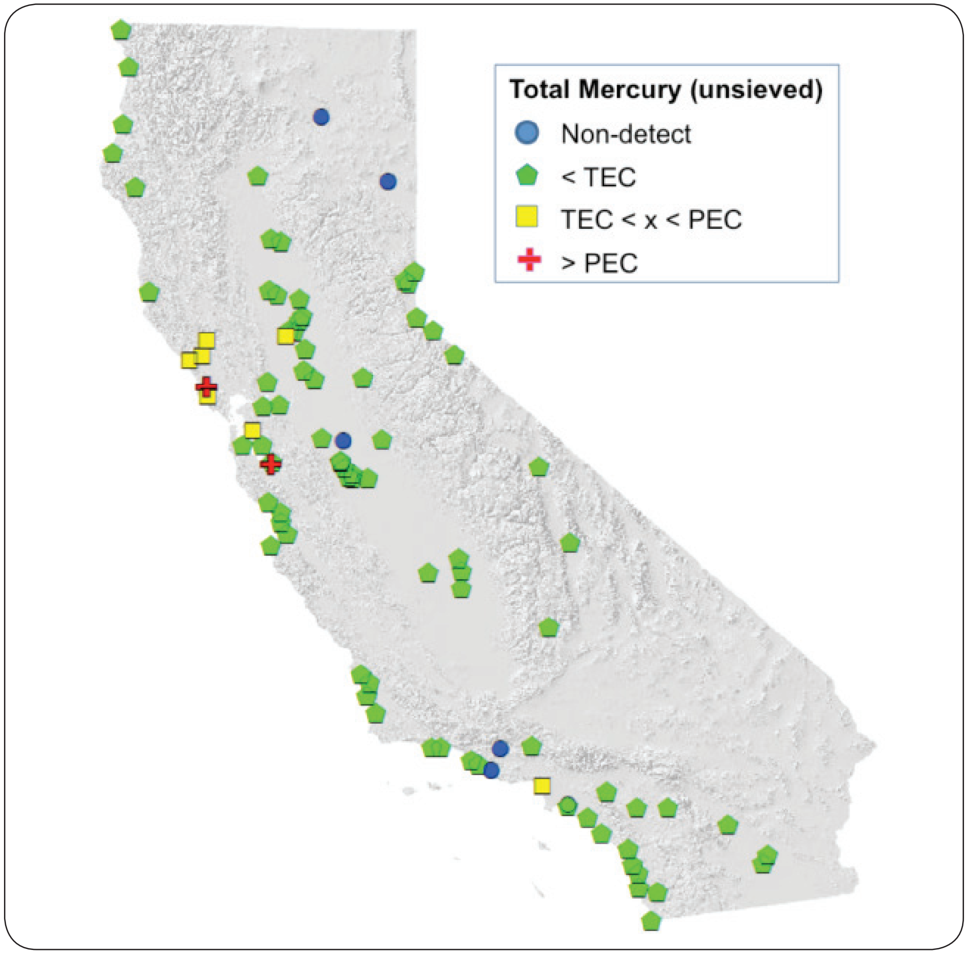

Figure 15. Distribution of mercury in unsieved stream sediment.

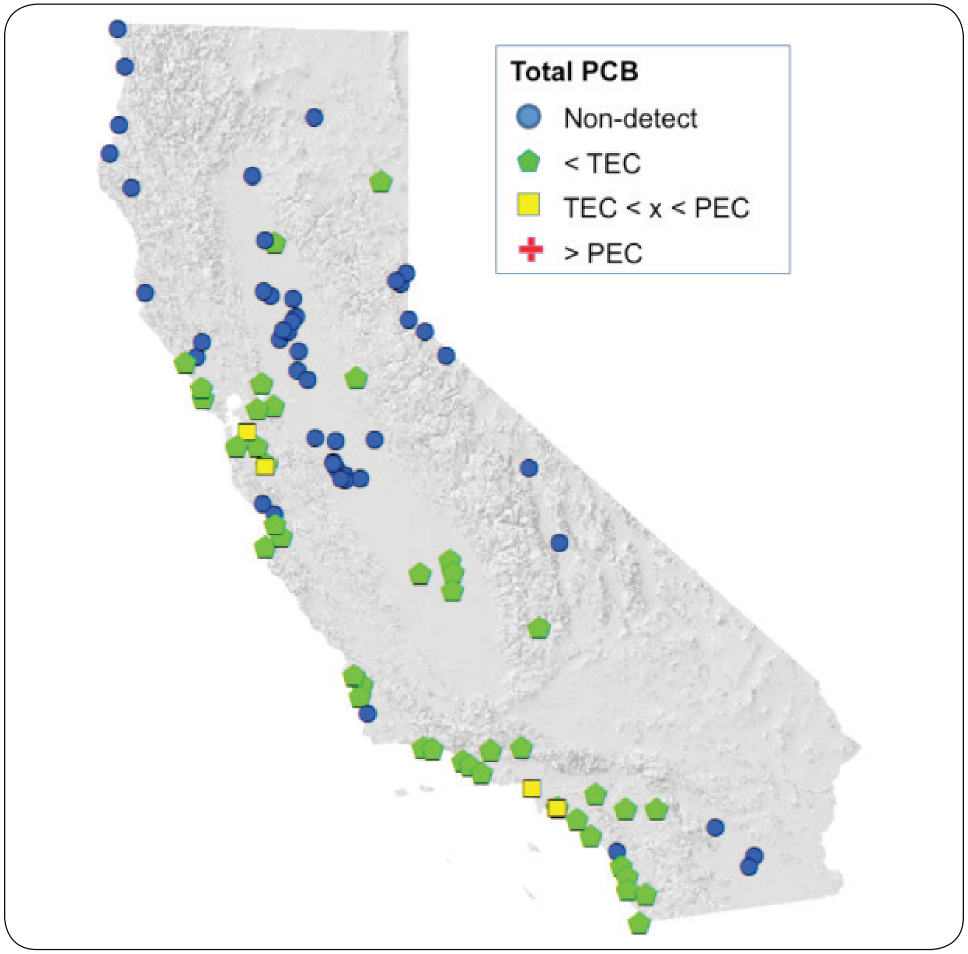

Figure 16. Distribution of PCBs in stream sediment.

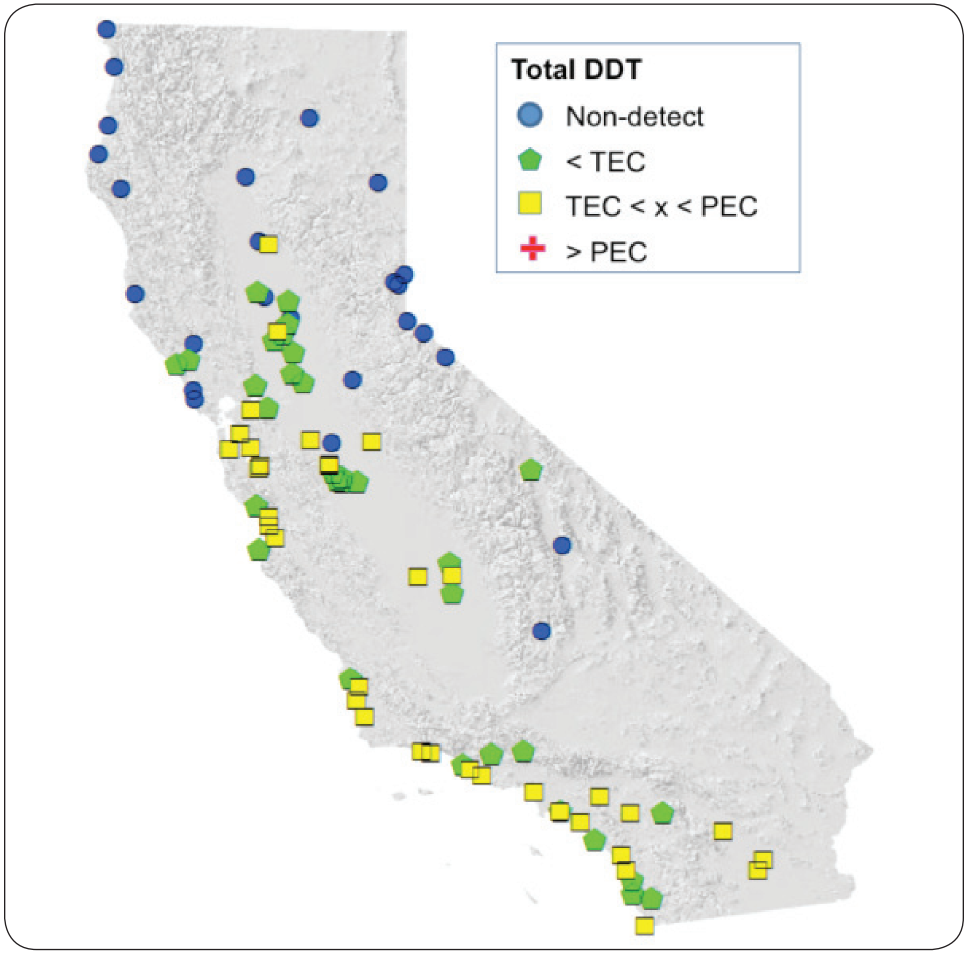

Figure 17. Distribution of DDTs in stream sediment.

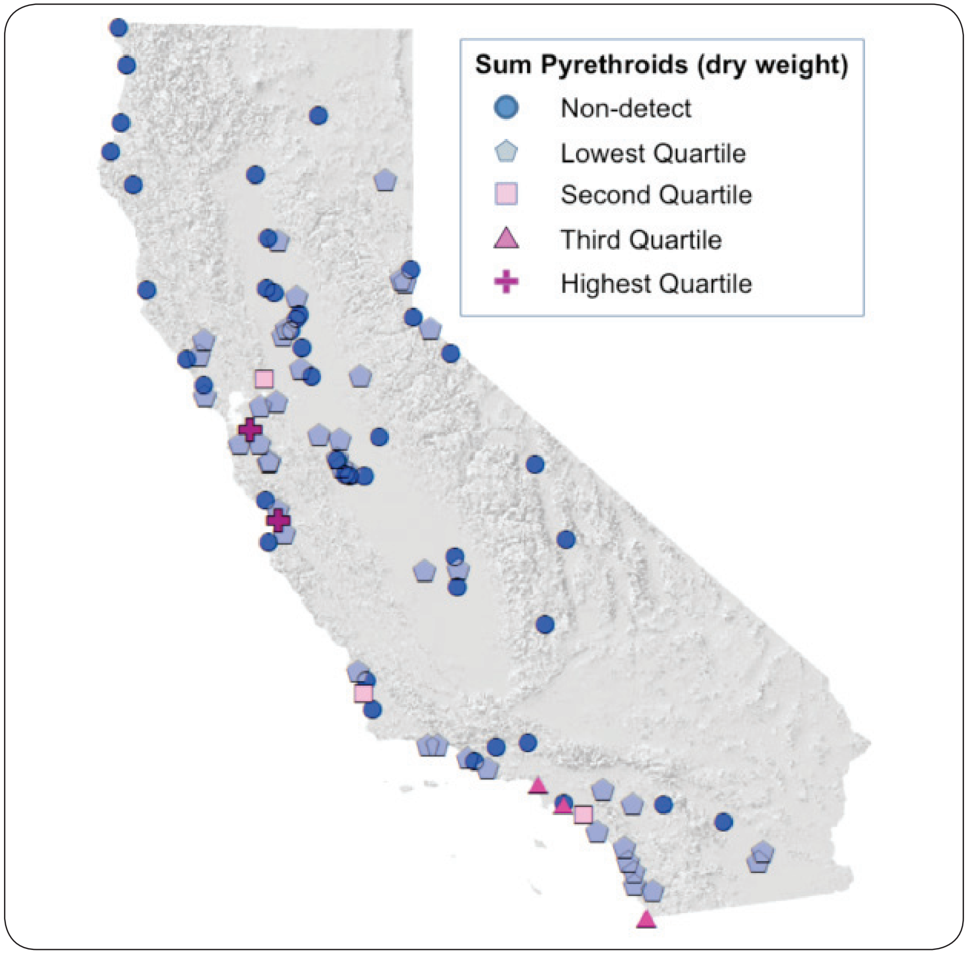

Figure 18. Distribution of pyrethroids in stream sediment. "Quartile" cutoffs are at 25%, 50% and 75% of the maximum concentration.

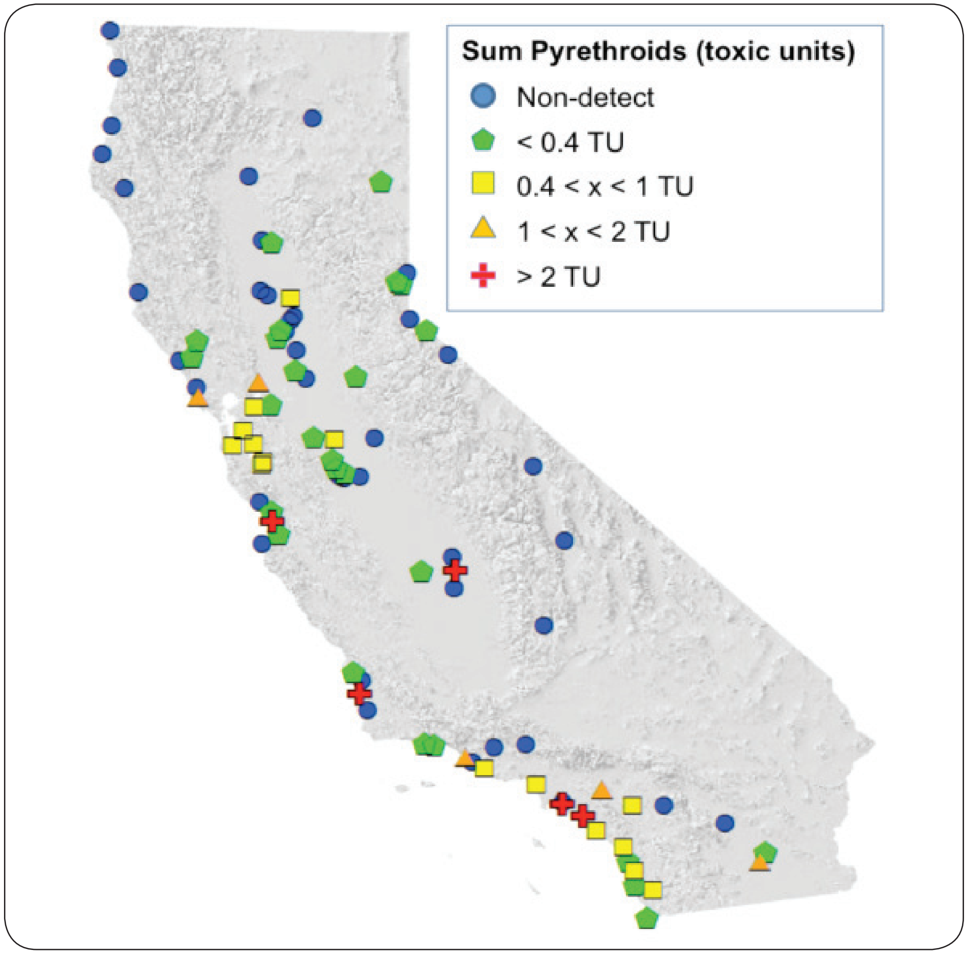

Figure 19. Distribution of pyrethroids as toxic units in stream sediment.

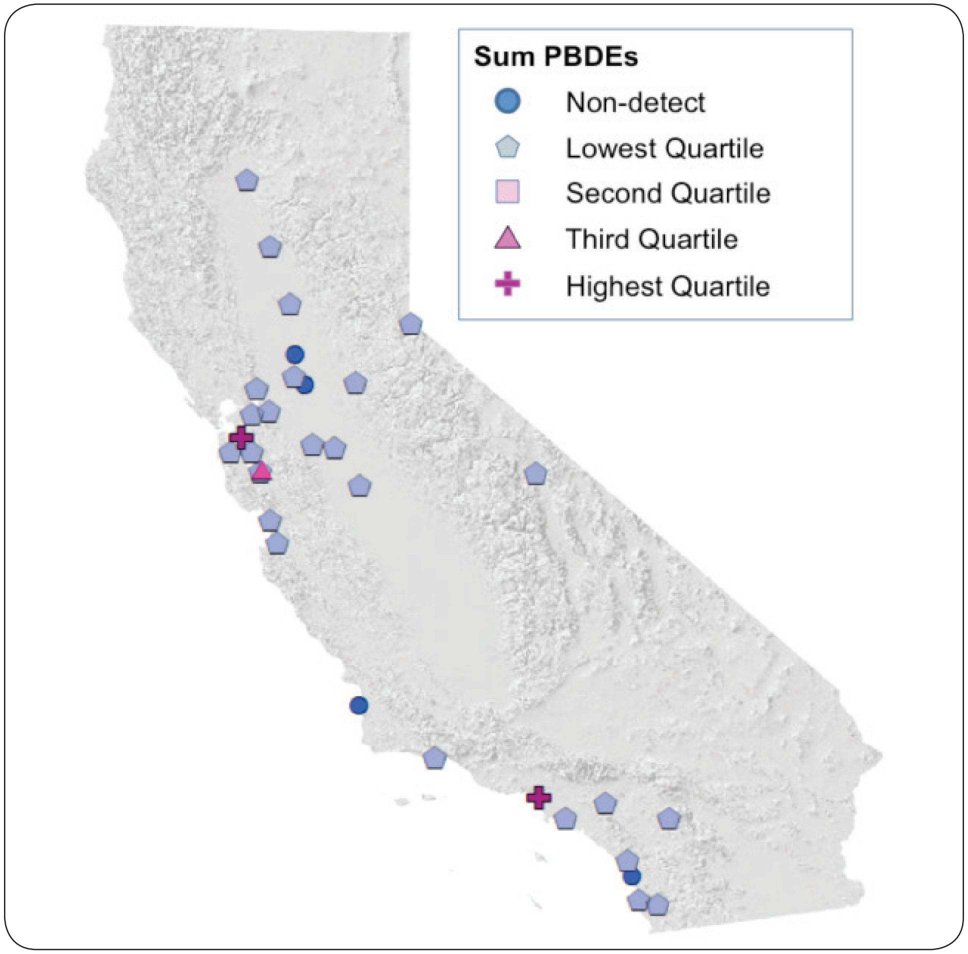

Figure 20. Distribution of PBDEs in stream sediment. "Quartile" cutoffs are at 25%, 50% and 75% of the maximum concentration.

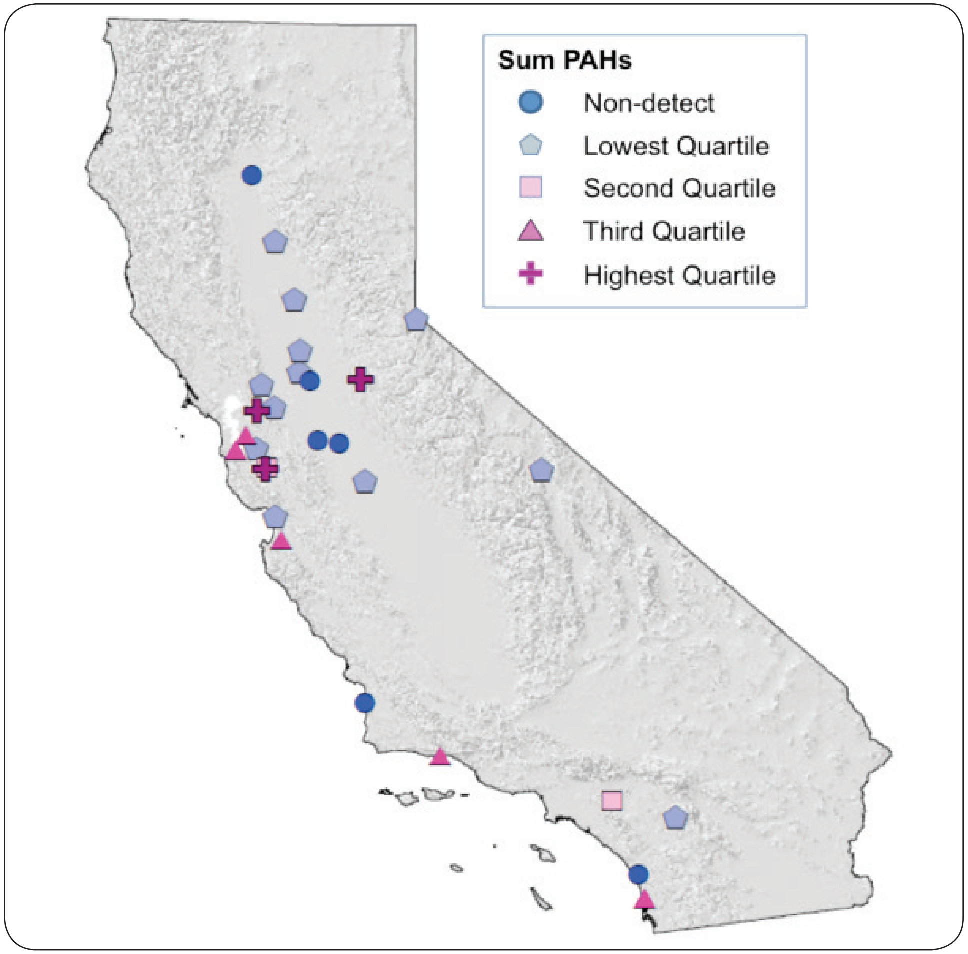

Figure 21. Distribution of PAHs in stream sediment. "Quartile" cutoffs are at 25%, 50% and 75% of the maximum concentration.

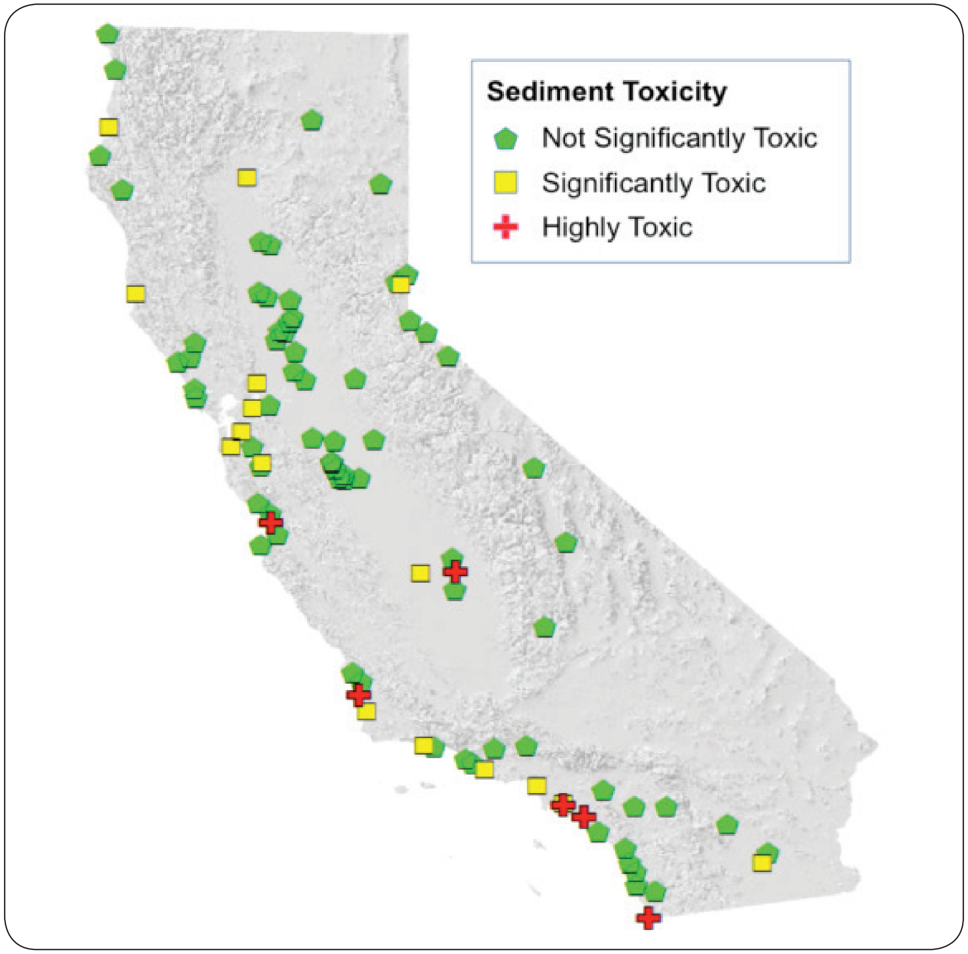

Figure 22. Distribution of observed toxicity in stream sediment.

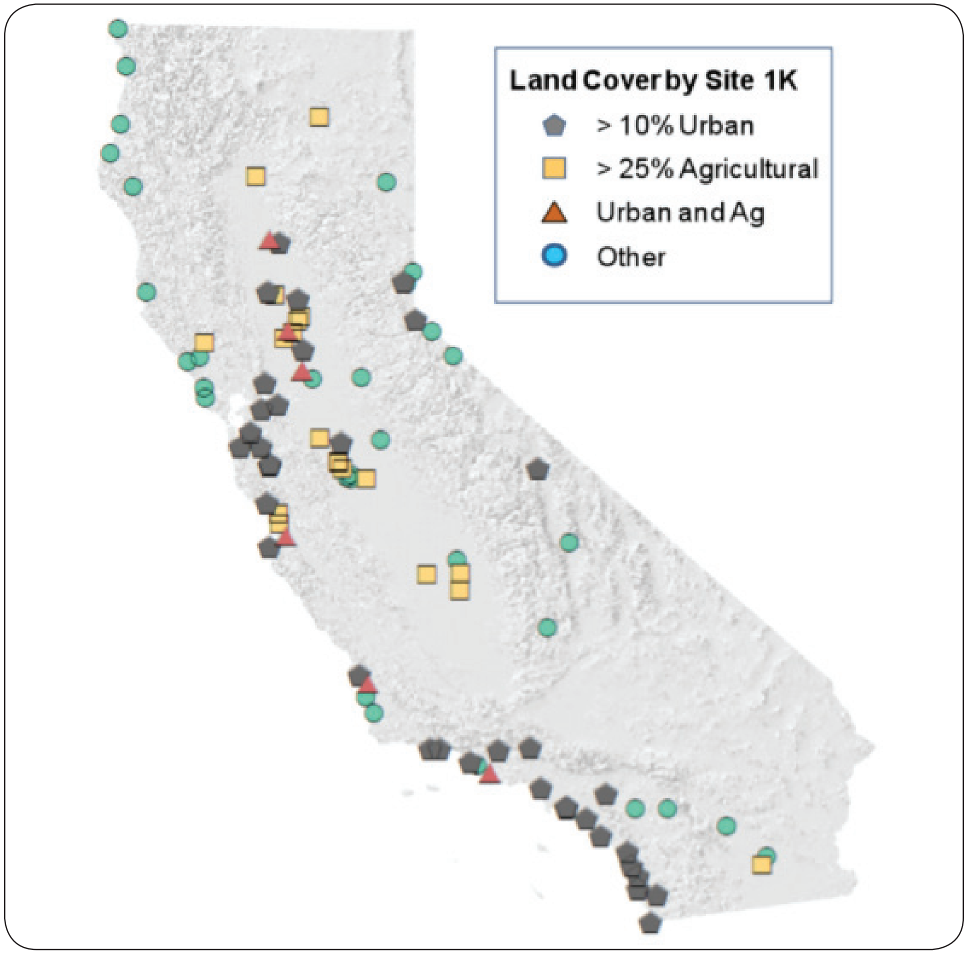

Figure 23. Characterization of land cover in the 1 km drainage area to each site.

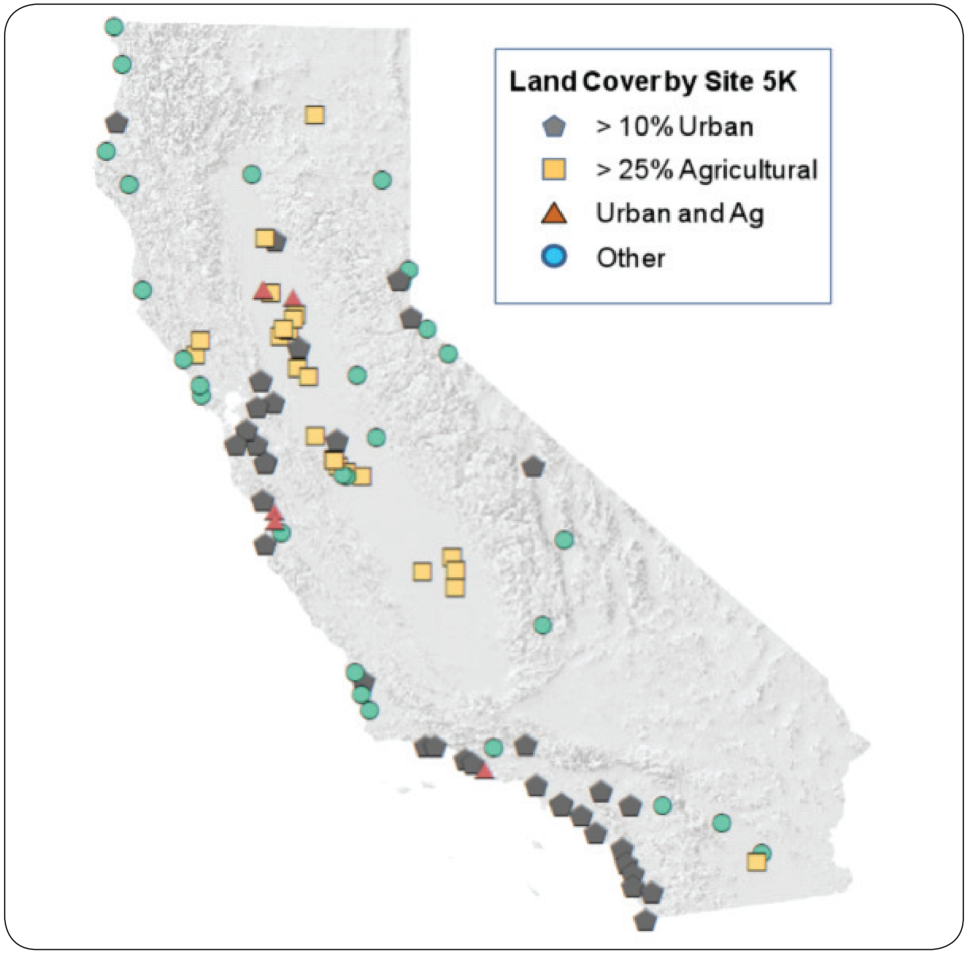

Figure 24. Characterization of land cover in the 5 km drainage area to each site.

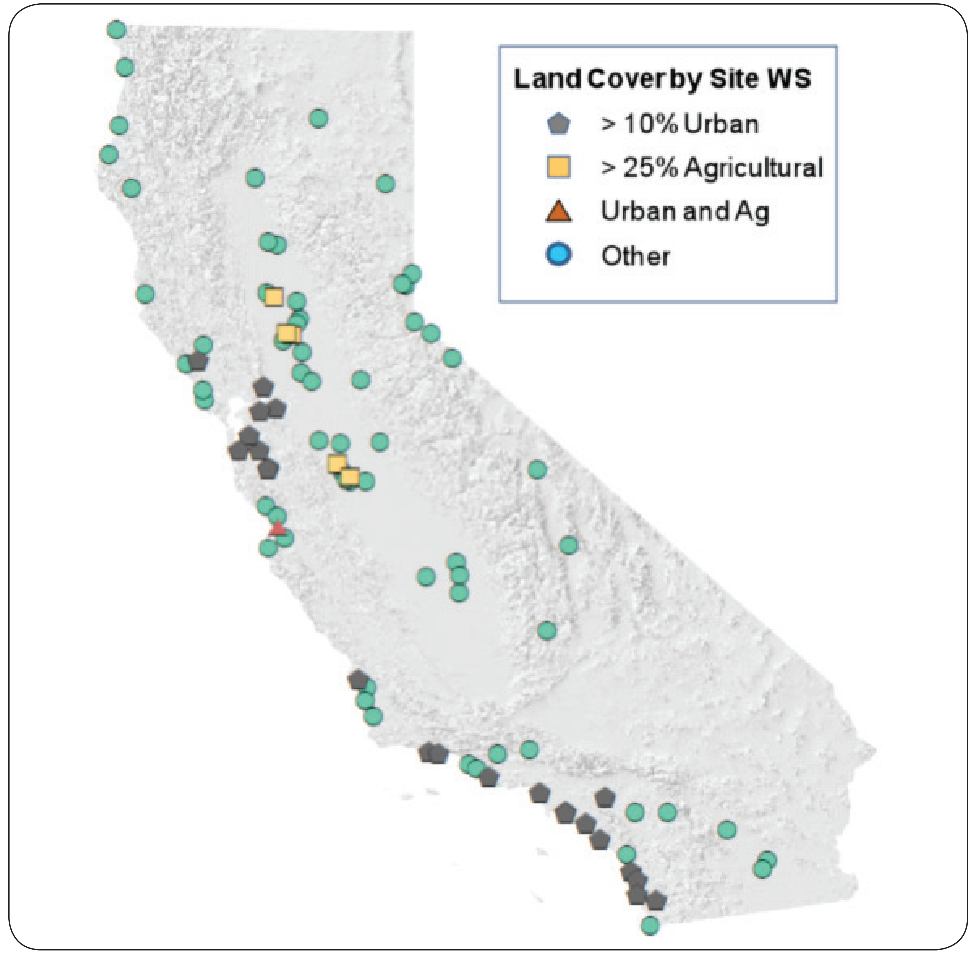

Figure 25. Characterization of land cover in the entire watershed drainage area to each site.

(28%) exceeded 0.4 toxic units, a value associated with acute toxicity in previous studies (Holmes et al. 2008). Bifenthrin, one of the more toxic pyrethroids, was detected in 44 of 92 samples (48%).

Organophosphate pesticides were detected in 12 of 92 sediment samples, and were not measured at concentrations associated with toxicity in any samples from this survey. Organophosphates are generally more water soluble and less persistent than pyrethroids, and thus less likely to accumulate in sediments deposited far downstream of application areas.

Legacy DDTs continue to be found at concentrations above TEC values in a large number of watersheds across the state. From a statewide perspective, these appear to remain a concern for biological effects associated with bioaccumulation (Davis et al. 2010). While mercury, PCBs, and other compounds have been shown to be of concern in local or regional studies, they were not measured at sediment concentrations above TECs in many of the low watershed sites in this study.

The herbicide oxadiazon was detected in 35 samples with a high concentration of 140 ng/g, though all but two samples had concentrations less than 20 ng/g. These concentrations are below known toxicity levels for aquatic organisms. This oxadiazole herbicide is registered for commercial use on golf courses (~77% of total use) and in apartment/condominium complexes, parks, athletic fields, playgrounds, and cemeteries. It is not registered for use on food crops (USEPA, 2011). As shown below, increased sediment oxadiazon concentrations correlated with increased developed open space land cover.

Trace metal concentrations exceeded sediment quality guidelines at many sites (Table 1). Nickel and chromium had the highest numbers of exceedences for both TECs and PECs. Both metals are geologically abundant, particularly in areas of serpentine soils, such as those common in the Franciscan formation of the central and northern coast ranges (Bonifacio et al., 2010; Topping and Kuwabara, 2003). Both are also used in various industrial applications, so natural sources cannot be assumed for all elevated samples. Arsenic exceeded the PEC in the Lower Owens River sample. Lead exceeded the PEC in the San Gabriel River sample. The mercury PEC was exceeded in samples from two Bay area watersheds, and the San Leandro Creek sample exceeded the PEC for zinc.

STREAM POLLUTION AND WATERSHED LAND COVER

Many pollutants tend to covary with each other and with sediment grain size and TOC content (Karickhoff 1984, DiToro et al. 1991, Foster and Charlesworth 1996). This can be explained generally by the affinity of organic chemicals for TOC, by the tendency of organic matter and fine sediment to deposit in similar areas of slower moving water, and by the economic forces that aggregate pollutant-generating activities in certain watershed locations, such as in urban or agricultural areas. Trace metals generally associate with fine sediment, and fine sediment (% fines, < 63 um) was significantly correlated with sediment TOC content in this data set ($p = 0.0001$).

Table 1
Number of sites with measured sediment concentrations of trace metals above sediment quality guidelines. TEC = threshold effect concentration. PEC = probable effects concentration (MacDonald et al., 2000). Site names given in Appendix 1.
Note: TEC and PEC values are shown in Appendix 3, Table 14.

Chemical	Number of Sites Exceeding		
	TEC	PEC	Sites > PEC
Arsenic	17	1	603LOWSED
Cadmium	11	0	NONE
Chromium	68	30	MANY
Copper	34	0	NONE
Lead	7	1	845SGRDRE
Mercury	9	2	205GUA020
			201WLK160
Nickel	65	34	MANY
Zinc	19	1	204SLE030

Table 2
Probability values for multivariate Spearman rank correlations comparing impervious surface cover with pollution indicators at the three watershed scales. Correlation coefficients were positive for all pollutants, and negative for amphipod survival, indicating increased impact with increased impervious surface cover for all comparisons. Asterisks indicate statistical significance (α = 0.05).
NOTE: Alpha values are not adjusted for multiple comparisons (see Methods).

Chemical	Watershed Scale		
	1	5	W
Sum 8	0.0160	0.066	0.125
Sum 8 Metals	0.0015	0.0317	0.114
Cd+Cu++Pb+Z	0.0002	0.0010	<0.0001
Cd+Cu+Pb+Zn	<0.0001	<0.0001	<0.0001
Total	0.0011	<0.0001	<0.0001
Total	<0.0001	<0.0001	<0.0001
Sum	<0.0001	<0.0001	<0.0001
Sum	0.0018	0.0145	0.056
PBDE	<0.0001	<0.0001	0.0008
Total	0.515	0.312	0.273
Amphipod	0.0051	0.0001	0.0290

Impervious surfaces

Percentage of watershed area covered by impervious surfaces at all three scales were positively correlated with increases in sediment toxicity and sediment concentrations of all pollutant classes. These correlations were statistically significant for all indicators except total phosphorus and the sum of eight metals at the larger watershed scales (Table 2, Figures 26 – 27).

Land Cover Categories

Characterizations of overall land cover in the watershed areas draining to each site are shown in Figures 23 - 25. At all watershed scales, there were significant positive correlations between increased urban land cover and increased stream sediment toxicity and concentrations of total DDTs, total PCBs, total PAHs, PBDEs, bifenthrin, total pyrethroids, and trace metals (as sum Cd, Cu, Pb, Zn; sieved and unsieved; Table 3).

Some pollution indicators correlated significantly with increasing crop cover at some watershed scales: DDT and toxicity at the whole watershed scale, and oxadiazon at the 1K and 5K scales. The herbicide oxadiazon correlated significantly with developed open space at all watershed scales, reflecting its use for golf courses, parks, and similar open space.

It is important to note that these correlations are observed at the statewide level over a population of integrator sites located at the base of large watersheds with heterogeneous land use. Other types of relationships might emerge from data collected within a single region or watershed.

Relationships between pollutant indicators and urban land use were similar among the chemical classes, and were similar to pollutant relationships with impervious surface cover (e.g., Figs. 26-29). For each of these relationships, the larger the drainage area analyzed, the stronger the correlation between pollutant and land cover variables. The trend line slopes increase from 1K to 5K to whole watershed comparisons. This is consistent with the reasoning that if a watershed area 1 km upstream of a site was characterized by a high proportion of urban land cover, it is still possible that much of the rest of the watershed could be in open space or other land cover. The 5 km-scale land cover characterizations are intermediate. At the whole watershed scale of land cover characterization (WS), a high proportion of urban cover indicates substantially greater urban influence throughout the entire area draining to the stream site, and this is reflected in stronger relationships with pollutant concentrations and toxicity.

Space for time analysis

The SPoT program is designed to measure long-term trends in stream pollution. However, this report covers the first annual survey, so temporal trends cannot be evaluated. In the absence of time series data, the relationships between pollution levels and land use can be used to estimate how stream pollution levels might change over time with change in land use (NRC 2002). On the statewide level, the strongest relationships observed for nearly all pollution indicators were with urban land cover. It is reasonable to assume, all else remaining equal, that increasing urbanization will be associated with increasing pollutant levels in streams draining these watersheds.

For example, as a rough approximation, and assuming continued levels of pyrethroid use as a function of urban area, a watershed that develops from 20% to 40% urban land cover might expect to see stream sediment pyrethroid concentrations rise from about 15 ng/g to about 25 ng/g over that period (see Fig. 28). Given that samples from sites in many watersheds had pyrethroid concentrations near threshold levels for toxicity, such a change would result in increased potential for acute adverse effects to aquatic life in these streams. There are many factors that may change over time, and this is not meant as a quantitative prediction, but the space for time analysis approach can be used to identify processes of concern for resource management and land use planning.

Table 3
Correlations between water quality parameters and land cover categories generated using nonparametric multivariate Spearman's ρ test. Statistically significant relationships ($\alpha < 0.05$) are marked with asterisks. Positive coefficients indicate that the measured chemical concentration increased as the specified land cover type increased (bold when significant). Negative coefficients for survival in toxicity tests indicate test organism survival decreased as the specified land cover type increased (bold when significant). Dev_Open = developed open space, such as urban parks; Past = pasture/hay. The "Plot" is a visualization of the direction and strength of each relationship.
NOTE: Alpha values are not adjusted for multiple comparisons (see Methods).

Variable	by Variable	Spearman	Prob	Plot
Sum 8 Metals	Urban_1K	0.2327	**0.0256***	
	Dev_Open	-0.0031	0.9764	
	Past_1k	-0.2116	0.0429*	
	Crop_1K	0.0454	0.6673	
	Urban_5K	0.1912	0.0679	
	21_5K	0.0244	0.8178	
	Past_5K	-0.1621	0.1226	
	Crops_5K	0.0486	0.6457	
	Urban_WS	0.1327	0.2072	
	21_WS	0.1339	0.2033	
	Past_WS	-0.1137	0.2803	
	Crops_WS	-0.0618	0.5583	

Variable	by Variable	Spearman	Prob	Plot
Sum 8 Metals Sieved	Urban_1K	0.3035	**0.0033***	
	Dev_Open	0.0929	0.3785	
	Past_1k	-0.2230	0.0326*	
	Crop_1K	0.0591	0.5758	
	Urban_5K	0.2272	**0.0294***	
	21_5K	0.1519	0.1484	
	Past_5K	-0.1552	0.1395	
	Crops_5K	-0.0028	0.9788	
	Urban_WS	0.1367	0.1937	
	21_WS	0.2028	0.0525	
	Crops_WS	-0.0650	0.5380	
	Past_WS	-0.1367	0.1938	
Cd+Cu+Pb+Zn	Urban_1K	0.3401	**0.0009***	
	Dev_Open	0.0145	0.8907	
	Past_1k	-0.2767	0.0076*	
	Crop_1K	-0.0997	0.3446	
	Urban_5K	0.3259	**0.0015***	
	21_5K	0.0514	0.6263	
	Past_5K	-0.1740	0.0971	
	Crops_5K	-0.0536	0.6120	
	Urban_WS	0.3764	**0.0002***	
	21_WS	0.2099	0.0446*	
	Past_WS	-0.1242	0.2382	
	Crops_WS	-0.1275	0.2258	
Cd+Cu+Pb+Zn Sieved	Urban_1K	0.4746	**<0.0001***	
	Dev_Open	0.1486	0.1574	
	Past_1k	-0.3189	0.0019*	
	Crop_1K	-0.0802	0.4475	
	Urban_5K	0.4063	**<.00001***	
	21_5K	0.2126	**0.0418***	
	Past_5K	-0.1955	0.0618	
	Crops_5K	-0.1035	0.3260	

Variable	by Variable	Spearman	Prob	Plot
Cd+Cu+Pb+Zn Sieved	Urban_WS	0.3823	**0.0002***	
	21_WS	0.3045	**0.0032***	
	Past_WS	-0.2140	0.0405*	
	Crops_WS	-0.1759	0.0934	
Sum DDT	Urban_1K	0.3329	**0.0012***	
	Dev_Open	-0.0340	0.7479	
	Past_1k	-0.0016	0.9879	
	Crop_1K	0.1749	0.0954	
	Urban_5K	0.4528	**<0.0001***	
	21_5K	0.2780	**0.0073***	
	Past_5K	0.0729	0.4899	
	Crops_5K	0.1971	0.0596	
	Urban_WS	0.4828	**<0.0001***	
	21_WS	0.3716	**0.0003***	
	Past_WS	0.0972	0.3565	
	Crops_WS	0.2897	**0.0051***	
Sum PCB	Urban_1K	0.4993	**<0.0001***	
	Dev_Open	0.1671	0.1113	
	Past_1k	-0.1207	0.2516	
	Crop_1K	-0.2097	0.0448*	
	Urban_5K	0.5723	**<.0001***	
	21_5K	0.4392	**<.0001***	
	Past_5K	-0.2065	0.0483*	
	Crops_5K	-0.2961	0.0042*	
	Urban_WS	0.5113	**<0.0001***	
	21_WS	0.5387	**<0.0001***	
	Past_WS	-0.3483	0.0007*	
	Crops_WS	-0.2571	0.0134*	
Pyrethroids	Urban_1K	0.4812	**<0.0001***	
	Dev_Open	0.0686	0.5156	
	Past_1k	-0.0777	0.4617	
	Crop_1K	-0.0968	0.3588	

Variable	by Variable	Spearman	Prob	Plot
Pyrethroids	Urban_5K	0.5579	**<0.0001***	
	21_5K	0.2915	0.0048*	
	Past_5K	-0.1355	0.1977	
	Crops_5K	-0.1375	0.1914	
	Urban_WS	0.5399	**<0.0001***	
	21_WS	0.4342	**<0.0001***	
	Past_WS	-0.1771	0.0913	
	Crops_WS	-0.1080	0.3055	
Bifenthrin	Urban_1K	0.5765	**<0.0001***	
	Dev_Open	0.1449	0.1681	
	Past_1k	-0.0794	0.4517	
	Crop_1K	-0.1460	0.1651	
	Urban_5K	0.6270	**<0.0001***	
	21_5K	0.4414	**<0.0001***	
	Past_5K	-0.0992	0.3470	
	Crops_5K	-0.1892	0.0708	
	Urban_WS	0.6536	**<0.0001***	
	21_WS	0.5760	**<0.0001***	
	Past_WS	-0.0772	0.4645	
	Crops_WS	-0.0370	0.7264	
Oxadiazon	Urban_1K	0.5206	**<0.0001***	
	Dev_Open	0.1518	0.1487	
	Past_1k	-0.1055	0.3170	
	Crop_1K	-0.2397	0.0214*	
	Urban_5K	0.6010	**<0.0001***	
	21_5K	0.4781	**<0.0001***	
	Past_5K	-0.1890	0.0712	
	Crops_5K	-0.2831	0.0062*	
	Urban_WS	0.6154	**<0.0001***	
	21_WS	0.6326	**<0.0001***	
	Past_WS	-0.2067	0.0481*	
	Crops_WS	-0.1845	0.0784	

Variable	by Variable	Spearman	Prob	Plot
Sum PAH	Urban_1K	0.4702	**0.0116***	
	Dev_Open	0.1056	0.5927	
	Past_1k	-0.4512	0.0160*	
	Crop_1K	-0.3871	0.0418*	
	Urban_5K	0.4598	**0.0138***	
	21_5K	0.2956	0.1268	
	Past_5K	-0.5663	0.0017*	
	Crops_5K	-0.4906	0.0080*	
	Urban_WS	0.3799	**0.0462***	
	21_WS	0.3859	**0.0425***	
	Past_WS	-0.6590	0.0001*	
	Crops_WS	-0.5961	0.0008*	
Sum PBDE	Urban_1K	0.6784	**<0.0001***	
	Dev_Open	-0.0460	0.8024	
	Past_1k	-0.2914	0.1057	
	Crop_1K	-0.3652	0.0399*	
	Urban_5K	0.6751	**<0.0001***	
	21_5K	0.2510	0.1659	
	Past_5K	-0.4287	0.0144*	
	Crops_5K	-0.3716	0.0362*	
	Urban_WS	0.5672	**0.0007***	
	21_WS	0.4546	**0.0090***	
	Past_WS	-0.3838	0.0301*	
	Crops_WS	-0.3743	0.0348*	
Total Phosphorus	Urban_1K	0.0458	0.6646	
	Dev_Open	-0.0171	0.8713	
	Past_1k	0.0267	0.8004	
	Crop_1K	-0.1476	0.1603	
	Urban_5K	0.1166	0.2685	
	21_5K	0.0760	0.4718	
	Past_5K	-0.0135	0.8983	
	Crops_5K	-0.0913	0.3866	

Variable	by Variable	Spearman	Prob	Plot
Total Phosphorus	Urban_WS	0.1314	0.2117	
	21_WS	0.0528	0.6172	
	Past_WS	-0.0776	0.4624	
	Crops_WS	-0.1459	0.1654	
Amphipod Survival	Urban_1K	-0.2739	**0.0083***	
	Dev_Open	-0.0051	0.9617	
	Past_1k	0.1372	0.1923	
	Crop_1K	0.1015	0.3357	
	Urban_5K	-0.3784	**0.0002***	
	21_5K	-0.2059	**0.0489***	
	Past_5K	0.0753	0.4754	
	Crops_5K	0.1763	0.0928	
	Urban_WS	-0.2215	**0.0339***	
	21_WS	-0.2381	**0.0223***	
	Past_WS	0.1997	0.0563	
	Crops_WS	0.2350	0.0241*	

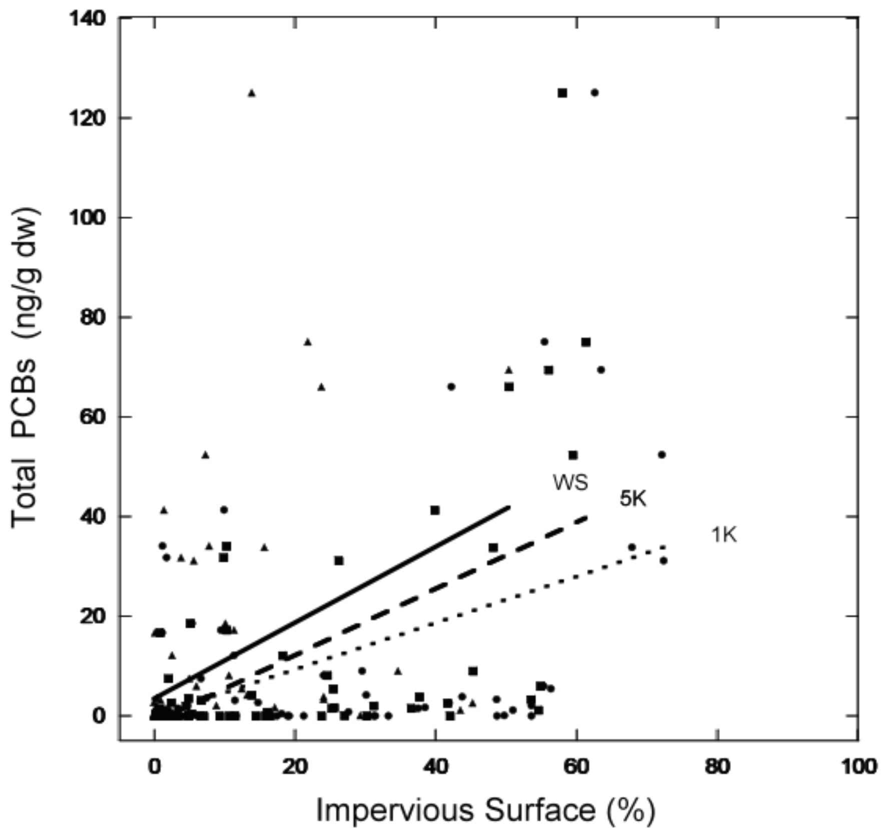

Figure 26. Sediment total PCB concentration plotted against impervious surface cover. Correlation coefficients given in Table 3. ▲ = whole watershed, ■ = 5K, ● = 1K.

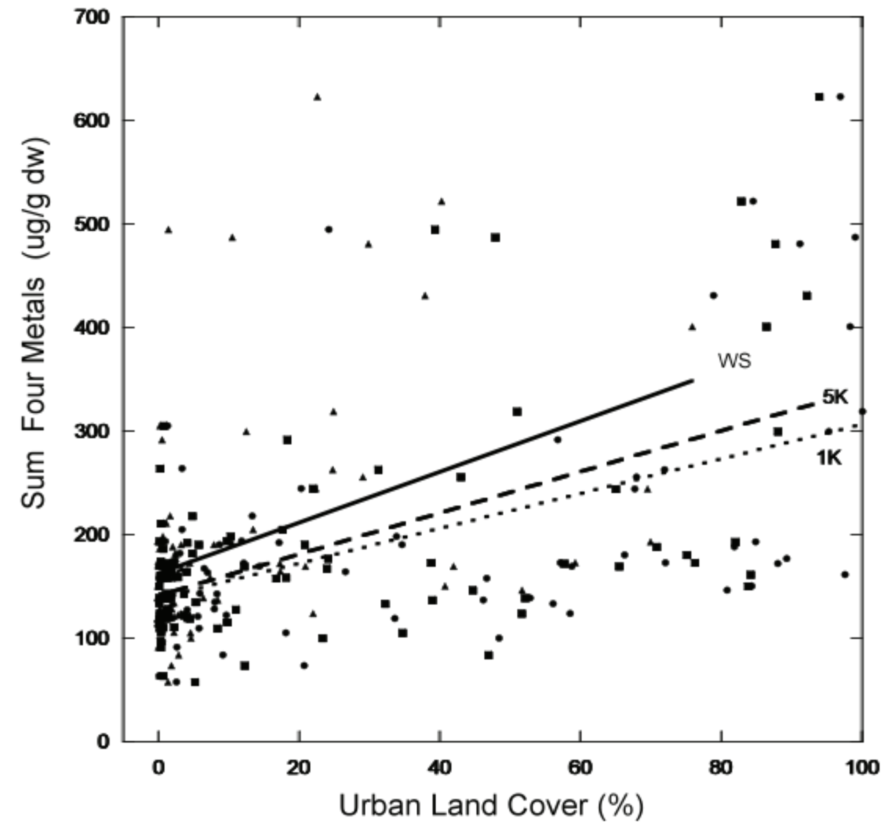

Figure 27. Four metals in sieved sediment plotted against urban land cover. Coefficients given in Table 3. ▲ = whole watershed, ■ = 5K, ● = 1K.

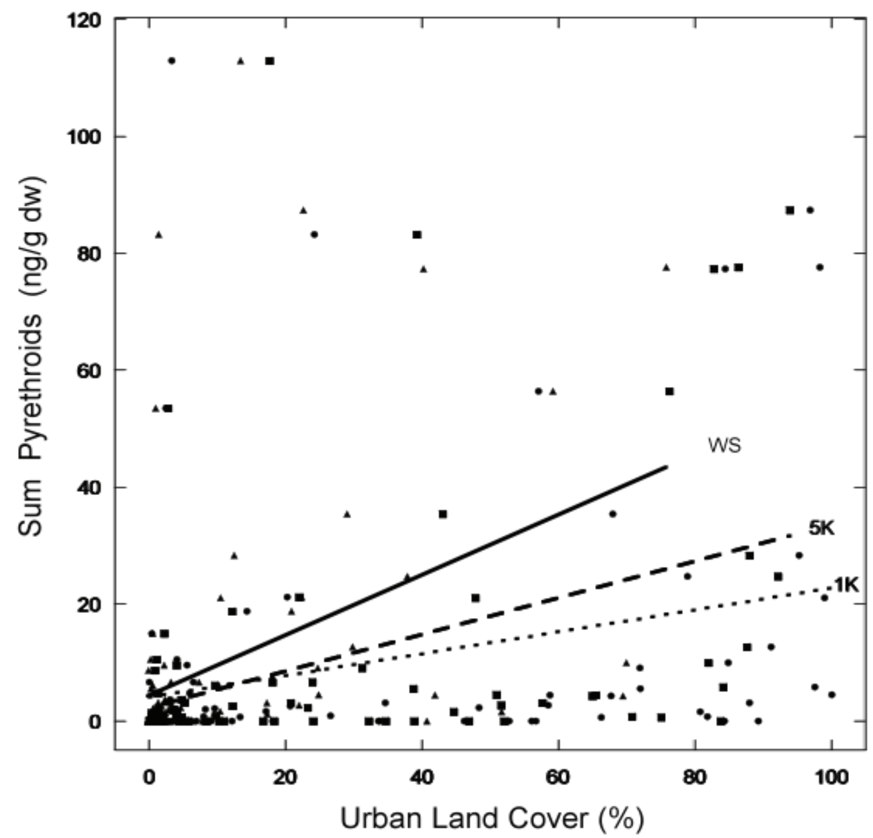

Figure 28. Sediment pyrethroid concentration plotted against urban cover. Correlation coefficients given in Table 3. ▲ = whole watershed, ■ = 5K, ● = 1K.

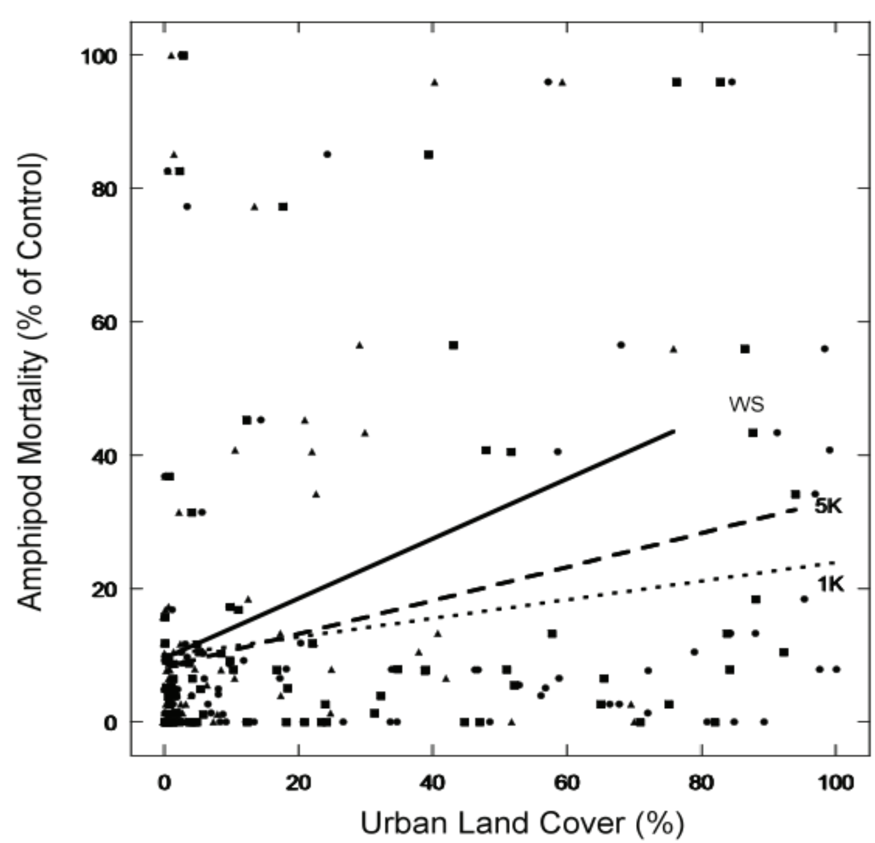

Figure 29. Sediment toxicity plotted against urban cover. Correlation coefficients given in Table 3. ▲ = whole watershed, ■ = 5K, ● = 1K.

STREAM POLLUTION INDICATORS BY LAND COVER CATEGORY

On a statewide basis, watershed areas with greater than 10% urban land cover had consistently higher sediment toxicity and pollutant concentrations than did watersheds characterized by agricultural or other land cover types (Figures 30 – 38). Differences among land cover categories were statistically significant for PCBs, metals, pyrethroids, DDTs, and PBDEs (Wilcoxon test, $\alpha < 0.05$; Table 4).

Table 4

Probability values for non-parametric Wilcoxon test comparisons among land cover categories at the 1 km scale. Data are the same as displayed in the 1K graphs in Figures 30 – 38. Asterisks indicate significant differences among land cover categories.

Total PCBs	< 0.0001*
Cd+Cu+Pb+Zn sieved	0.0003*
Sum Pyrethroids	0.0016*
Total DDTs	0.0057*
Total PBDEs	0.0273*
Sum PAH	0.1673
Toxicity	0.1720
Mercury sieved	0.8577

Trace metals as a sum of four elements commonly used in commercial, industrial, and transportation applications (cadmium, copper, lead, and zinc) were markedly higher in urban watersheds than in those with greater than 25% agricultural land cover or those with less urban or agricultural cover (Fig. 31). These metals tend to be more acutely toxic to many aquatic organisms. Sediment concentrations of mercury tended to reflect local watershed conditions rather than evidence strong statewide trends (Fig. 32). Differences among watersheds were not as pronounced for the sum of eight trace metals (Fig. 30). Some of these eight metals are locally abundant geologically (e.g., chromium, nickel, and mercury) or associated with historic mining activity (e.g., mercury and silver).

The legacy pesticide DDT (as total DDT) was found at higher sediment concentrations in urban watersheds than in agricultural or other watersheds (Fig. 33). This may reflect past urban use relative to agricultural applications, but perhaps is more reflective of urban development over previously agricultural lands during the years since DDTs were banned in the early 1970s. Early mosquito abatement programs may also have contributed substantial DDT to urban environments. Like other relatively insoluble organic compounds, DDTs adhere to soil particles, and DDTs persist for many decades, perhaps later mobilized by soil disturbance associated with urban and residential development.

It is not surprising that PCBs, PAHs and PBDEs were measured at higher sediment concentrations in urban watersheds (Figs. 34 – 36). PCBs were used primarily in industrial applications, petrogenic PAHs are by-products of fossil fuel combustion, and PBDEs are industrially manufactured and commercially used flame retardants. PCB use has been banned for decades and PBDEs are subject to strict recent regulation, so the trend analysis of these classes of chemicals should provide interesting markers of pollutant fate and transport.

Pyrethroids are current use insecticides for agricultural, residential, commercial and industrial applications. Given this variety of usage, the higher sediment concentrations in urban watersheds are striking (Fig. 37). This is a statewide analysis of the sum of all pyrethroids measured, and different pyrethroid pesticides are used in different applications (e.g. commercial vs. agricultural (Spurlock and Lee 2008). However, when summed on a toxic unit basis (indicating potential for acute adverse biological effects), sediment pyrethroids appear to be of greater concern in urban watersheds (Fig. 19). Given the higher sediment pollutant concentrations, it's not surprising that stream sediment toxicity was also highest in urban watersheds (Fig. 38). These results can be compared to the statewide evaluation of toxicity results from nine years of SWAMP studies which demonstrates more comparable levels of toxicity between urban and agricultural areas (Anderson et al. 2011).

Initial results from subsequent SPoT surveys indicate that the level of sediment toxicity presented here may be an underestimate. The test temperature for the present study was 23°C, the standard temperature for the Hyalella test protocol. Many California streams are much cooler, particularly during and after winter runoff events. Tests conducted at 15°C in subsequent SPoT surveys indicated substantially higher observed amphipod mortality, a result consistent with toxicity due to pyrethroid pesticides (data forthcoming). In addition, toxicity was measured using 10-day tests, while the amphipod life-cycle is on the order of two months. Longer exposures typically result in greater observed toxicity.

EFFECTS OF SIEVING

Trace metals were measured on both whole sediments and sediments sieved to less than 63 um. Because trace metals bind preferentially to smaller sediment size fractions, particularly clays, concentrations measured on sieved sediment can be compared across watersheds with less variability related to differences in grains sizes among samples. Concentrations in unsieved sediments are the total metal concentrations and can be compared to thresholds for biological effects.

In a comparison of concentrations of the 11 trace metals measured in 92 field samples plus duplicates (n = 1128), the sieved sediment had higher metal concentrations in 83% of the sample/element combinations. The average relative percent difference (RPD) between sieved and unsieved measurements from the same

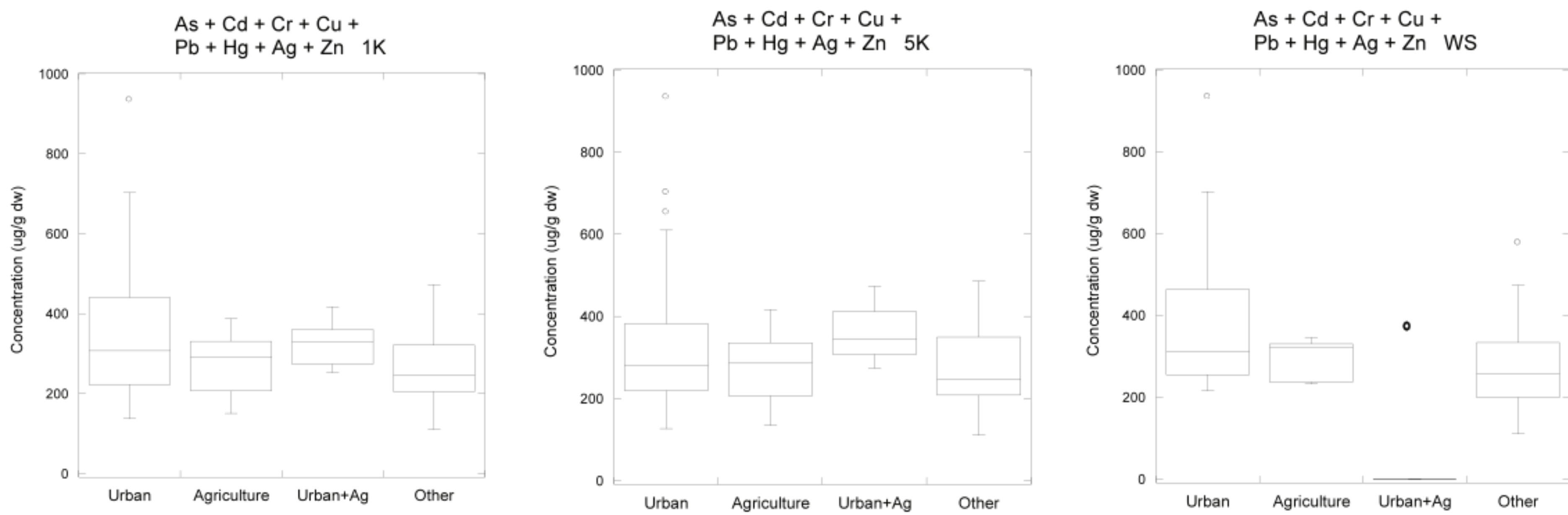

Figure 30. Concentrations of eight metals in sieved sediment by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

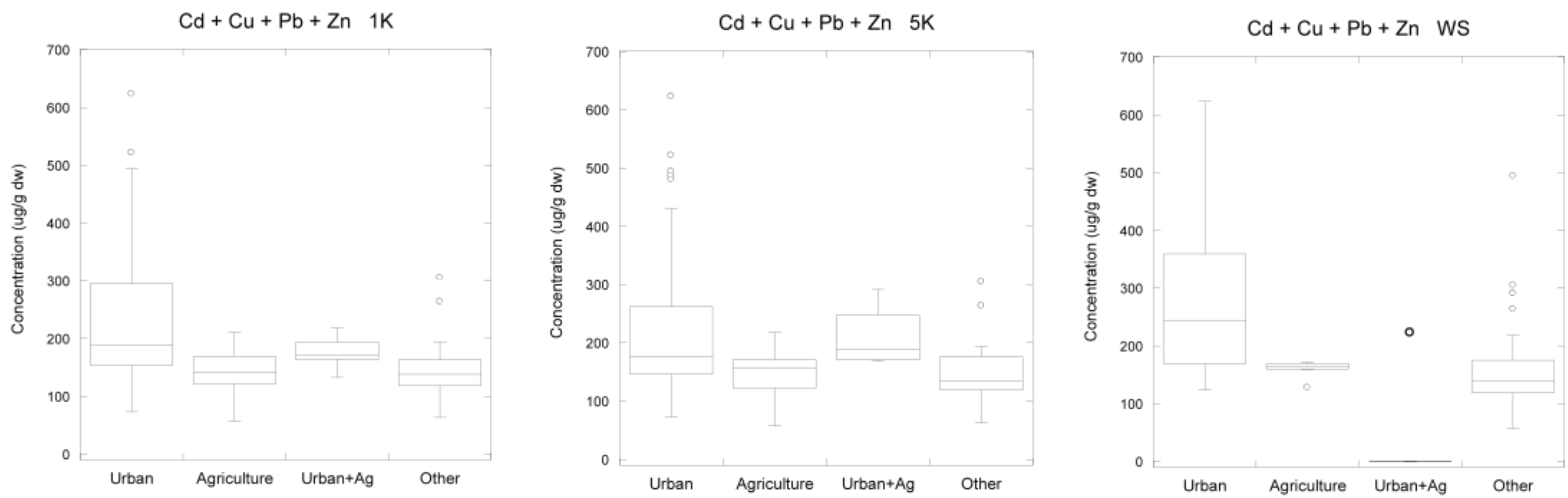

Figure 31. Concentrations of four metals in sieved sediment by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

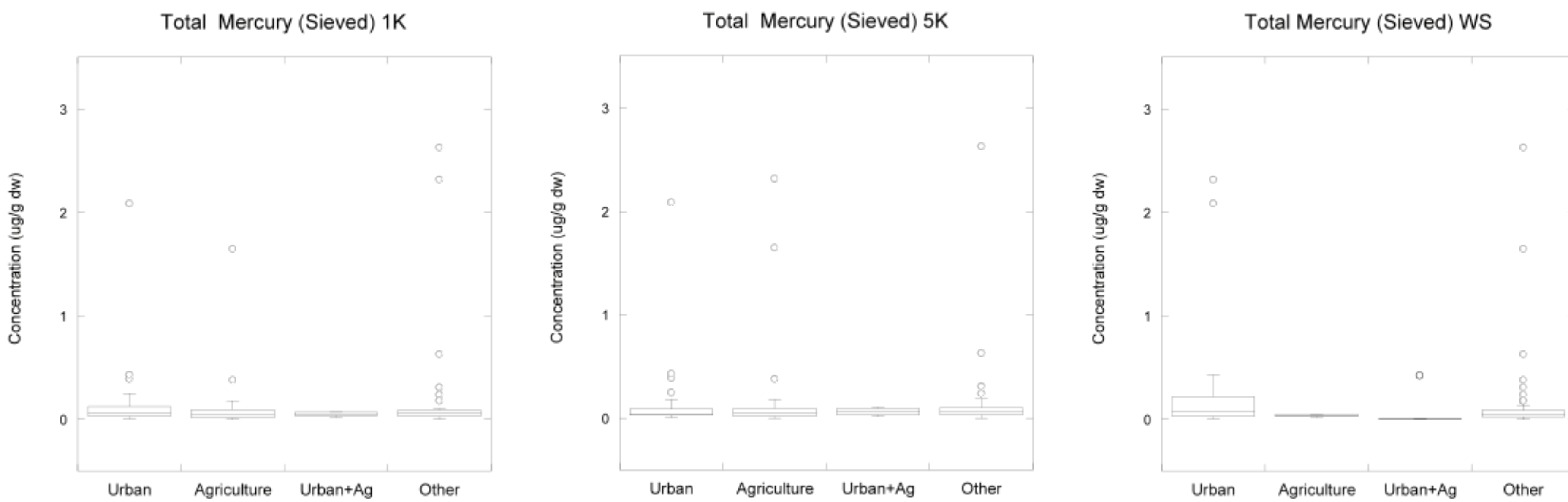

Figure 32. Concentrations of mercury in sieved sediment by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

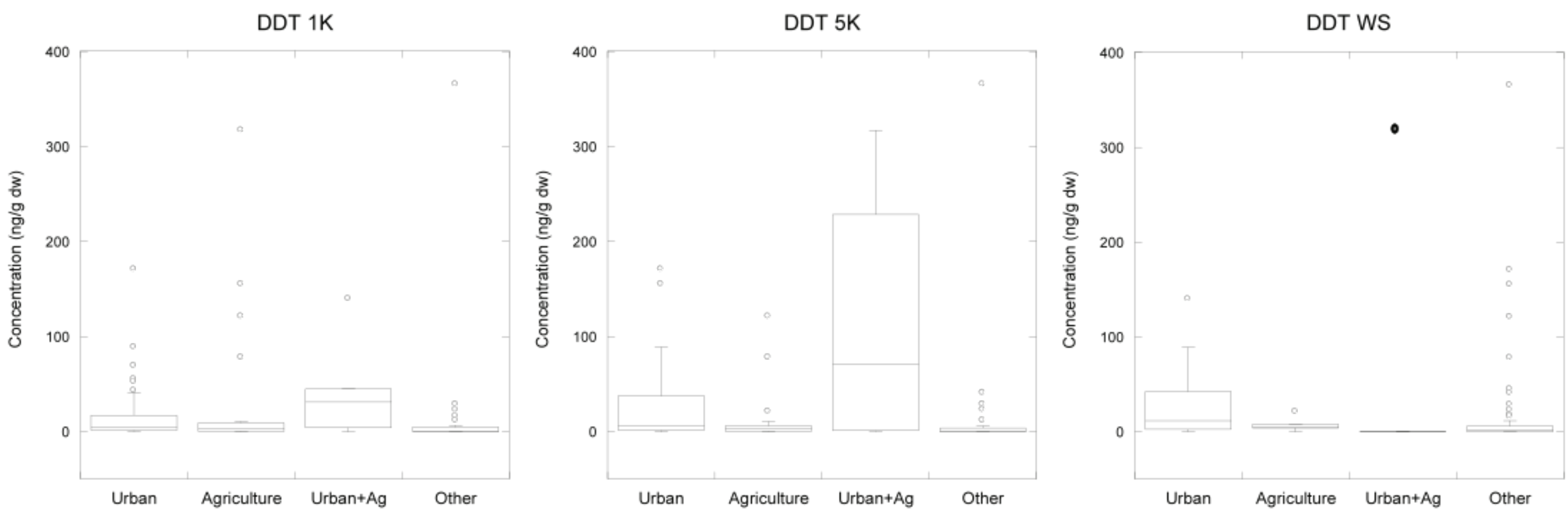

Figure 33. Sediment concentrations of DDTs by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

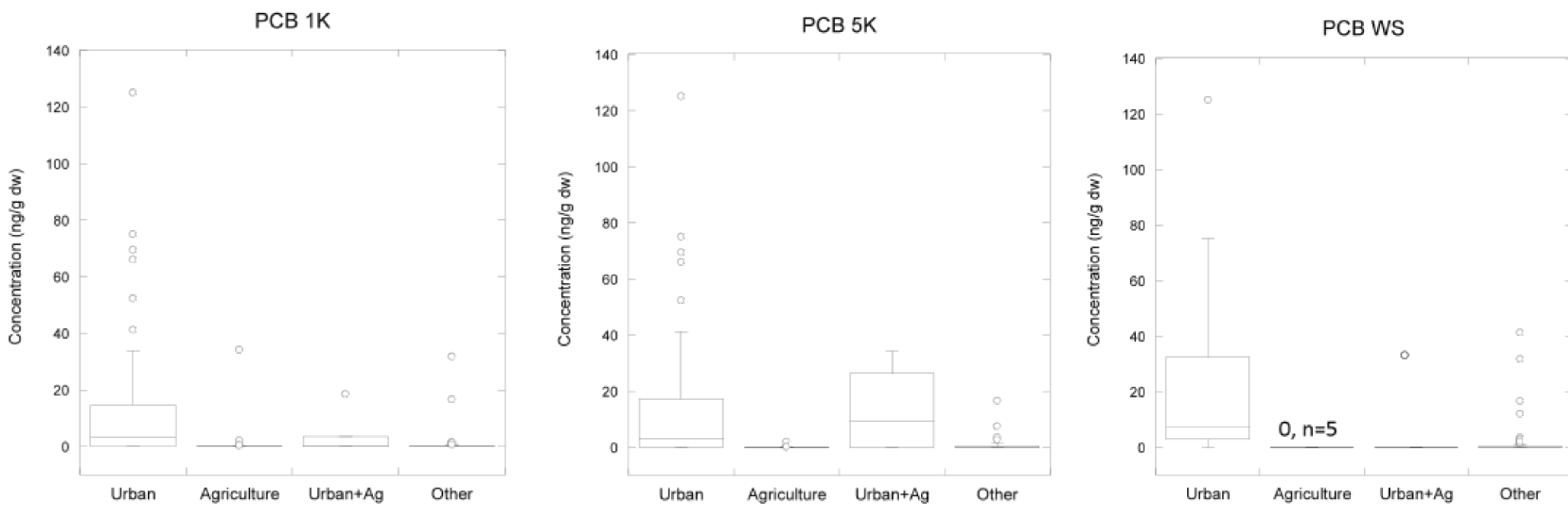

Figure 34. Sediment concentrations of PCBs by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

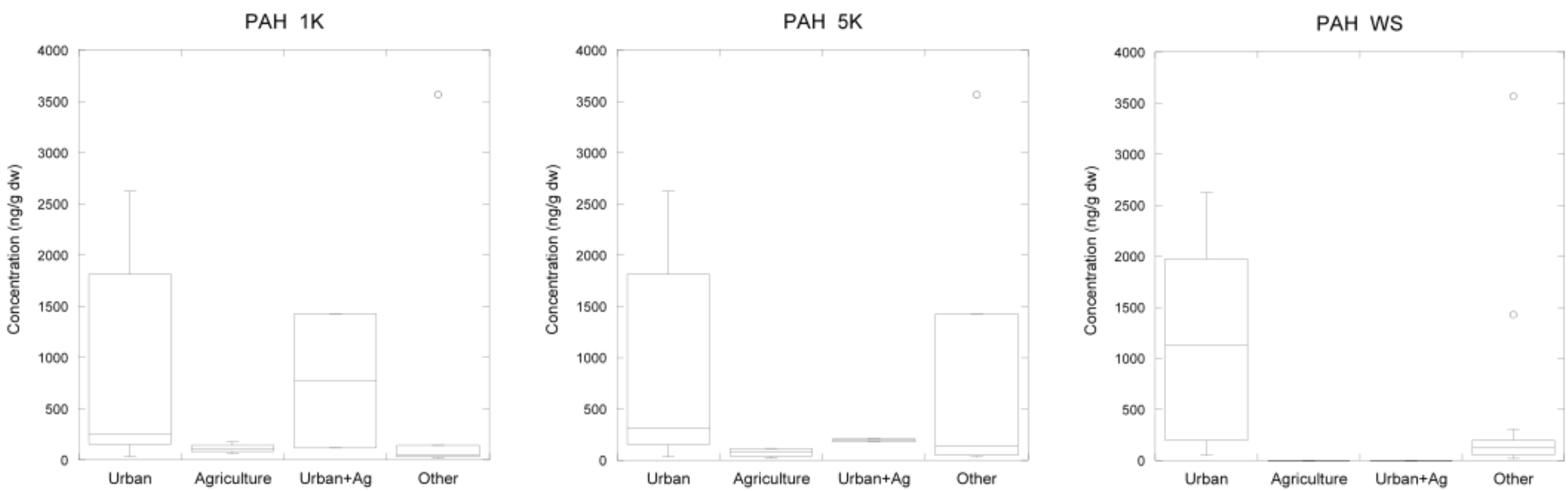

Figure 35. Sediment concentrations of PAHs by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

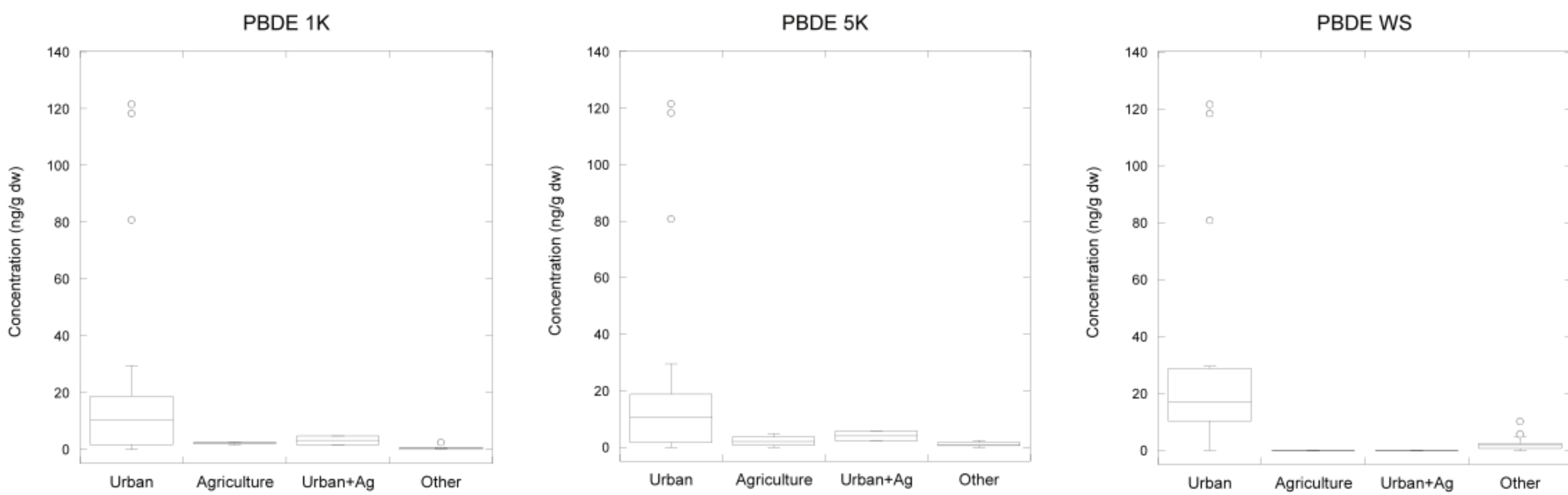

Figure 36. Sediment concentrations of PBDEs by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

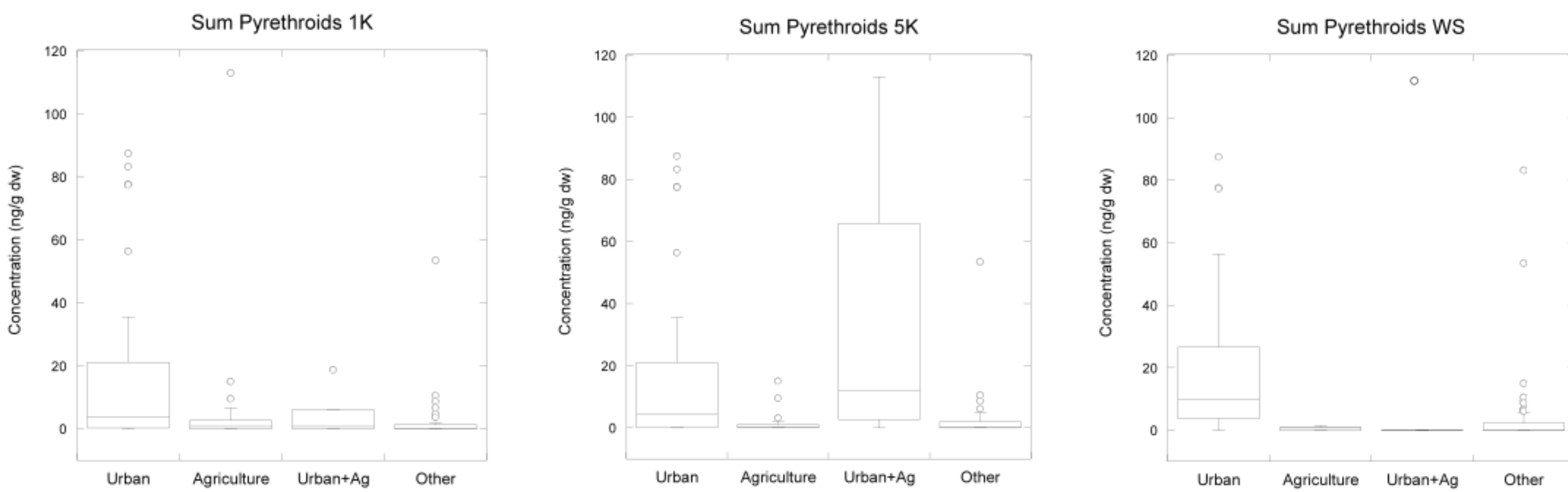

Figure 37. Sediment concentrations of pyrethroids by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

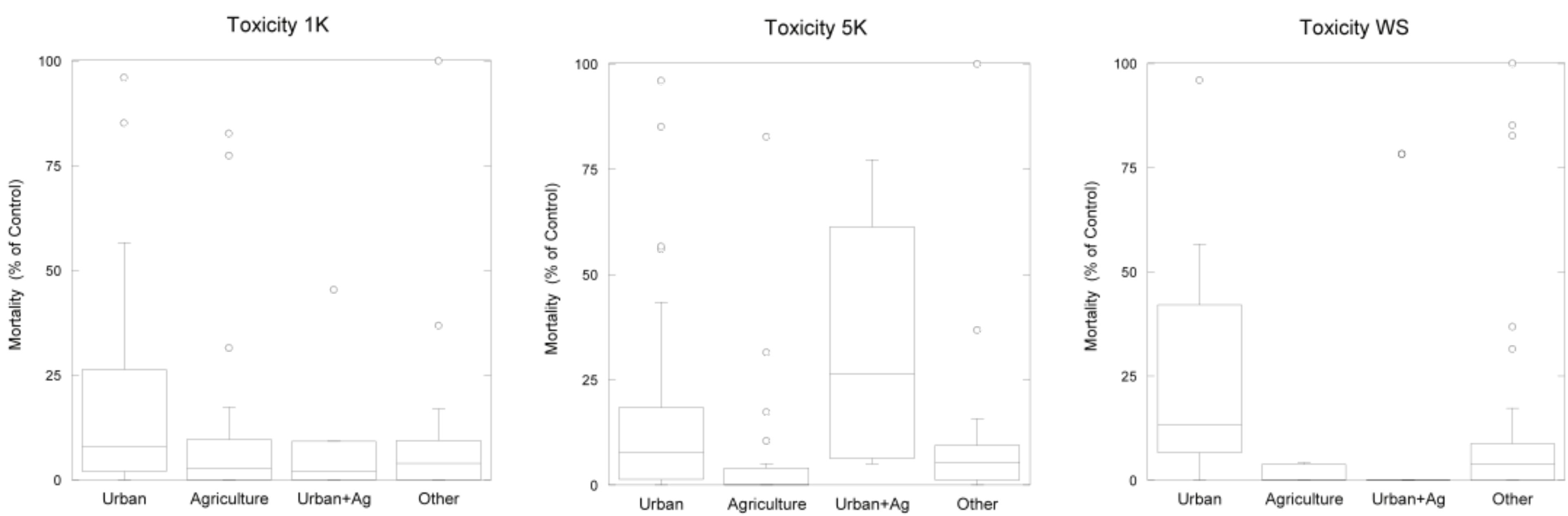

Figure 38. Observed sediment toxicity by land cover category. Box and whiskers represent mean, quartiles, and 95% confidence limits.

sample was 25% (± 36% sd), with a RPD range of -125% to +163%. In the two cases where the sum of eight metals had a significant positive correlation with a land cover type, sieved sediments correlated more strongly (Table 3). The same was true for all five cases in which the sum of four metals had significant positive correlations with a land cover type.

TOXICITY

Sediment toxicity was significantly correlated with the proportion of urban land cover at all three watersheds scales (Table 3). Toxicity was greater in samples from urban and urban/agricultural watersheds than in samples from agricultural or other watersheds (Fig. 38). Toxicity was significantly correlated with PCBs, pyrethroids, TOC, PBDEs, DDTs, PAHs and with some metals (Table 5). Toxicity did correlate significantly with sediment TOC, a common result in sediment assessments, because organic pollutants accumulate with TOC in stream depositional areas. The correlation between toxicity and grain size was not significant ($\alpha = 0.05$).

Table 5
Probability values for multivariate Spearman rank correlations of observed toxicity and measured pollutant concentrations. Asterisks indicate statistically significant correlations at the $\alpha = 0.05$ level.

Total PCBs	< 0.0001*
Sum Pyrerthroid	< 0.0001*
Total Organic Carbon	< 0.0001*
Total PBDEs	0014*
Total DDTs	0.021*
Cd+Cu+Pb+Zn sieved	0.031*
Cd+Cu+Pb+Zn unsieved	0.036*
Sum PAH	0.040*
% Fines	0.052
Total 8 Metals unsieved	0.055
Total 8 Metals sieved	0.065
Total Phosphorus	0.067

PHOSPHORUS

Phosphorus is more abundant in some geologic formations than others, which confounds correlation with human activities linked to transport into streams. Phosphate, along with nitrate, is a primary ingredient in fertilizers applied to agricultural, residential, and other watershed areas, and can be mobilized by grading and other soil disturbance related to land development.

In this survey, total phosphorus did not correlate significantly with any land cover type, grain size, TOC, or pollutant. For most of the State, there was no obvious pattern in the spatial distribution of total phosphorus, with low concentrations adjacent to higher concentrations in many areas (Fig. 39). However, concentrations were consistently high in the Los Angeles area, and moderately high in the Sierra and southern mountain ranges.

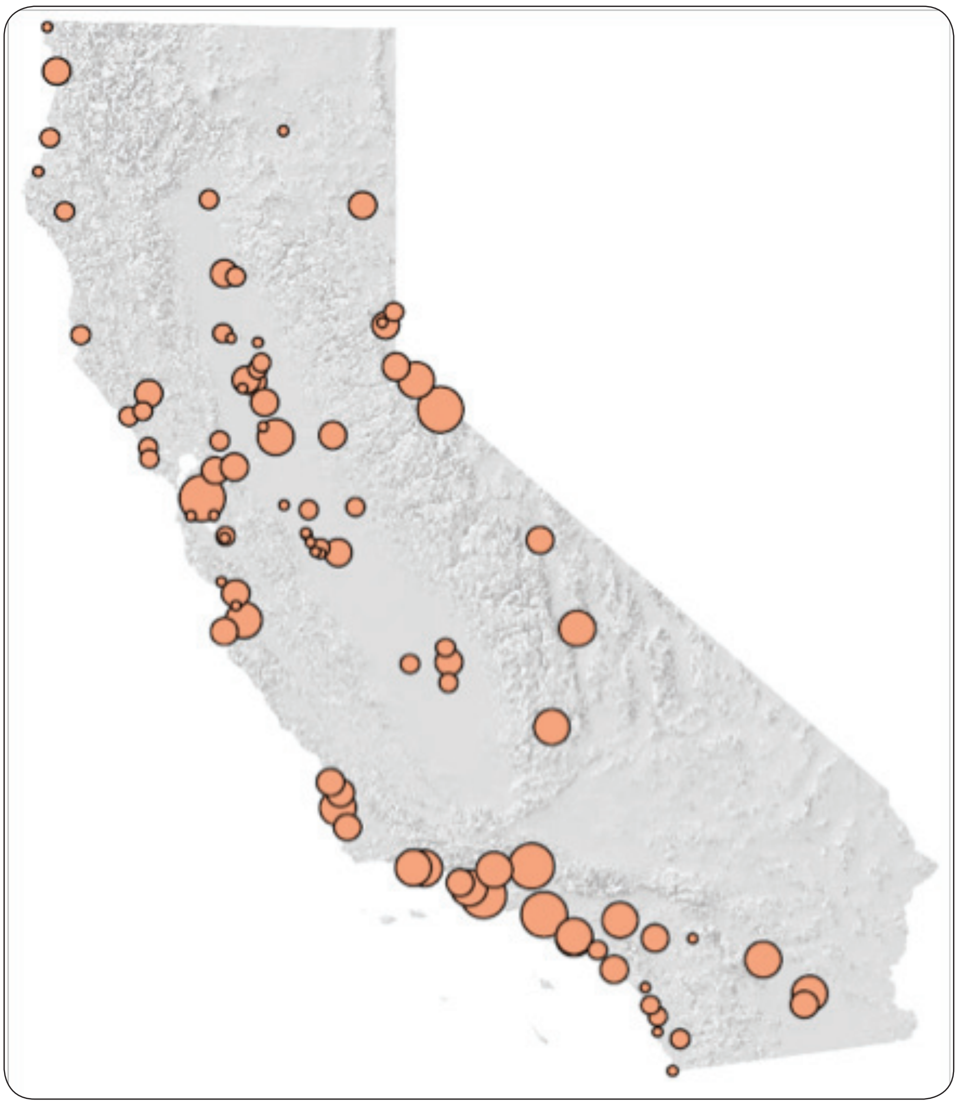

Figure 39. Distribution of total phosphorus, with concentrations ranging from 0 to 1900 mg/kg.

SECTION 5
DISCUSSION

One of the SPoT program's primary goals is to provide statewide perspective for local and regional monitoring, and the SPoT program staff coordinates with many of these programs to make data available across scales to address a number of assessment questions. From the statewide perspective, a number of patterns emerge from this first year of SPoT monitoring. Primary among these themes are that stream sediment pollutant concentrations and toxicity were greatest at sites draining urban watersheds, many SPoT sites across the state yielded elevated concentrations of a number of pollutants, and pyrethroid pesticides frequently exceeded concentrations previously linked directly to acute toxicity to amphipods.

Most elevated pyrethroid concentrations were in samples from watersheds classified as urban (> 10% urban land cover). This general result differs from results of a recent SWAMP report summarizing nine years of SWAMP toxicity data statewide. That report was a summary of results from many different studies with different monitoring designs, and the combined results did not indicate a significant difference in sediment toxicity between urban and agriculturally-influenced sites (Anderson et al. 2011).

In considering results presented here, it is important to note that the sampling sites and survey timing were specifically targeted to low watershed depositional sites during base flow conditions following seasonal high water. This targeted approach was implemented in order to most efficiently address the SPoT assessment objectives of characterizing long-term trends and understanding linkages between land cover and stream pollution. The sites and times were not selected probabilistically. With probabilistic designs, it is possible to make inferences about un-sampled areas, which is a major advantage when addressing questions about the overall condition of areas too large or sites too numerous to sample completely. Therefore, the data from targeted sites presented here should not be extrapolated to draw conclusions about un-sampled watersheds, or generalized to make assumptions about larger regional patterns. However, the consistent base-of-the-watershed targeted sampling approach allows for improved understanding of the relationships between land use and stream condition as these change over time.

It should also be noted that the potential for toxic effects in these sediments is likely greater than estimated by these results, for two reasons. First, amphipod toxicity tests employed standard 10-day exposures, whereas the persistence in sediment of most of the measured pollutants is much longer. Second, the toxicity tests were conducted at the standard temperature of 23°. Most of the streams sampled run at temperatures closer to 15° (unpublished data). Subsequent SPoT analyses (data forthcoming) measured greater toxicity in 15° tests than in 23° tests, a likely result of pyrethroid effects.

CHEMICALS OF CONCERN

Previous studies have shown that statistically significant toxicity to amphipods generally occurs in sediments with greater than 0.4 toxic units of pyrethroid pesticides (Trimble et al. 2010, Holmes et al. 2008). In this survey, 28% of all samples (26 of 92) exceeded 0.4 toxic units of pyrethroid pesticides, which were detected in samples from 55% of the streams. On a statewide basis, pyrethroids were more strongly associated with urban areas than with agricultural or other areas. Pyrethroids are used in commercial and residential pest extermination (Spurlock and Lee 2008), and the high impervious surface cover in urban areas likely facilitates transport to streams. The use restrictions on pyrethroid pesticides are currently being re-evaluated in California, and the results of this study should add to the body of knowledge upon which management decisions are based. The SPoT program is designed to evaluate stream pollution trends as new pyrethroid labeling restrictions take effect.

Organophosphate pesticides, particularly diazinon and chlorpyrifos, have been linked to water column toxicity in many California waterways (deVlaming et al. 2000, Hunt et a. 2003), and chlorpyrifos has also been linked to sediment toxicity (Anderson et al. 2006, Phillips et al. 2010). These compounds were seldom detected in the present study, however, and were not measured at known toxic concentrations in any of the samples. Chlorpyrifos has been found in elevated sediment concentrations in California streams in previous studies (e.g., Anderson et al. 2006, 2011). Had SPoT program sampling occurred over the past decade, it may have been possible to document a decline in chlorpyrifos concentrations in urban stream sediments as regulatory programs implemented additional restrictions on non-agricultural use of this pesticide.

It is perhaps expected but still of concern to find DDTs and PCBs widely distributed in California streams nearly 40 years after their usage was banned by law. DDTs in particular were found in a number of stream samples above threshold effects concentrations (TECs; MacDonald et al., 2000). While strict usage regulations are in place, enhanced measures may be necessary to restrict mobilization of contaminated soils through activities such as grading of old agricultural lands for development.

PBDEs and PAHs were measured only at Tier II SPoT sites, which were mostly in urban areas. Both chemical classes were widely detected. In sea otters, liver concentrations of PBDE 028 have been significantly correlated with the presence of specific infectious diseases, as well as traumatic death (Miller et al. 2007). PBDEs are expected to be an important trend indicator for the SPoT program because recent regulation is expected to decrease use of certain PBDE compounds.

Probable effect concentrations (PECs) were exceeded for arsenic (Lower Owens River), lead (San Gabriel River), mercury (two San Francisco Bay area watersheds), and zinc (San Leandro Creek).

TEC and PEC values are shown in Appendix 3, Table 14.

POLLUTANT ASSOCIATIONS WITH TOXICITY

Concentrations of many chemicals, especially organic compounds, co-varied across samples analyzed in this survey, and these also co-varied with TOC. The strongest correlations between pollutants and toxicity were observed for PCBs and pyrethroids, with pyrethroids having the better established basis for asserting causality. Numerous recent studies have linked pyrethroids with sediment toxicity to amphipods (e.g., Holmes et al. 2008.). In addition, subsequent SPoT surveys have shown increased sediment toxicity with decreased test temperature, a result consistent with the non-metabolically influenced mode of action for these compounds (Harwood et al. 2009, Holmes et al. 2008.; SPoT data forthcoming in second program report).

Because trend monitoring will focus on contaminant concentrations, the biological effects to be measured are the responses of a contaminant-sensitive, representative, benthic invertebrate species (Hyalella azteca) that has been the subject of numerous studies linking its response to the composition of in situ benthic communities (e.g., Anderson et al. 2003a, 2003b, 2006; Kedwards et al. 1999; Phillips et al. 2004; Schulz 2004; Tucker and Burton 1999).

POLLUTANT ASSOCIATIONS WITH LAND COVER

Two analytical approaches were taken to investigate relationships between stream pollution and land cover in the watersheds surveyed. Correlation analyses indicated statistically significant relationships between increasing concentrations of most pollutants and increasing levels of both urban land cover and impervious surfaces (e.g., Fig. 26-27). Multiple comparisons among results grouped by land cover classification showed significantly higher pollutants concentrations in urban watersheds than in agricultural or other watersheds (Tables 3-4; Figs. 30–38). On a statewide basis, both approaches indicated higher stream pollution in watersheds with more urban land cover.

It is important to note two potential confounding factors that were not included in the land cover analyses: the effects of dams on sediment transport and the contributions of point sources to measured pollutant concentrations. The great majority of rivers in California have dams, often many dams, and these are very effective at impeding downstream sediment transport, essentially breaking the hydrologic-sediment connectivity to large watershed areas upstream of sampled sites. Dam locations were frequently considered in selecting SPoT site locations, but the effect of dams was not accounted for in GIS analyses of drainage areas to sites. That is, land cover from all areas upstream was considered equally, whether there was an intervening dam or not. The effect of this factor is most likely to influence analyses at the whole watershed scale (as opposed to the 1 km and 5 km drainage area scales). It was not within the scope of this study to identify and assess the sediment transport effects of dams in 92 watersheds, especially because of the many small dams with uncertain hydrologic impacts, particularly with fine sediment during high flows. Many point sources discharge to streams, and many data are available about chemical concentrations in their effluents; but accurately assessing all these data was again beyond the scope of this analysis.

SPACE FOR TIME SWAPS

While there is substantial scatter in correlation analyses relating land cover to pollutant concentrations, significant relationships were detected for many pollutants. These relationships indicate that, all other factors remaining equal, the expected trend of increasingly developed land cover in California watersheds will result in increased pollutant concentrations and toxicity in streams (Figs. 26-29). Corroboration of this finding with subsequent SPoT survey results will better establish whether these relationships are seen repeatedly, and whether temporal trend analyses yield results that support the link between increasing urbanization and stream pollution.

SECTION 6 RECOMMENDATIONS

This report covers results from one statewide survey comprising the first year of a long-term trends monitoring program. Field experience has already led to some adjustments in site location and timing. Based on program objectives and first year results, the following recommendations are made to maximize the value of this statewide stream pollution trends monitoring program:

(1) Continue the annual SPoT surveys to develop time-series data to investigate trends in stream pollution. Social, economic, technical, and resource management activities evolve and change unpredictably, with uncertain ramifications for the sustainability of California's most important natural resource. Trend monitoring is the only way to evaluate whether human activities and natural events lead to further impairment or to preservation and restoration of water quality.

(2) Continue to build SPoT partnerships with stormwater, agricultural and other monitoring programs, as well as with regulatory agency priority programs. Communicate SPoT trend data from Measure W priority watersheds to US EPA for use in the Measure W program.

(3) Compare trends over time with relationships between land cover and stream pollution. Analysis of data from continued surveys will indicate whether currently observed relationships with urban land cover reflect changes concomitant with urbanization over time.

(4) Evaluate spatial and temporal variability in pollution indicators around SPoT sites. The primary program design is limited to collecting one sediment sample from one site once a year in the target watersheds. To understand how well that sample represents the stream and its watershed, measure samples from additional low watershed locations, each collected at different times of the year, to characterize variance in space and time and provide estimates of confidence in statistical results.

(5) Improve tracking of management activities through General Permit language and alignment of grant projects. Many conservation practices are currently being implemented in urban, residential, and agricultural areas to improve water quality. To evaluate the effectiveness of this substantial effort, specific and standardized information must be collected to record the number of projects per watershed, the area affected, the water volume treated, chemical load reductions achieved, and continuity of practices. Resource Conservation Districts along the California central coast are developing standardized reporting formats in cooperation with the Agricultural Water Quality Alliance (AWQA: http://www.awqa.org/), and this effort should be expanded.

(6) Implement SPoT-type monitoring in smaller watersheds with more homogeneous land cover to better understand causal relationships between human activities and stream pollution. The SPoT watersheds were selected to represent large, mixed-use areas to better characterize general conditions in California. While this is good for understanding the overall situation, the heterogeneity in land use and economic activity adds noise to the analysis of relationships with water quality. A suite of small drainage areas dominated by similar human activities (e.g., row crops or high density residential) could be studied to more specifically understand the causes of water quality impairments.

(7) Conduct sediment toxicity tests at two temperatures: 15° C as well as the standard 23° C. This would better cover the range of ambient temperatures at study sites (which are generally closer to 15° C), and also provide compelling data to evaluate the biological effects of pyrethroids, which are among the few classes of compounds exhibiting greater toxicity at lower temperatures.

(8) Use data from this and future SPoT surveys to inform regulatory review of pyrethroid pesticide usage and the long-term effectiveness of labeling changes.

(9) Use Hyalella azteca amphipod tests in water column monitoring. Commonly used *Ceriodaphnia dubia* test organisms are sensitive to and useful for detecting toxicity due to organophosphate pesticides. As OP pesticide use decreases and pyrethroids become more pervasive, H. azteca will likely better detect the potential for toxic effects on aquatic invertebrates.

(10) Continue to participate in and promote coordination efforts and data sharing through the California Environmental Data Exchange Network (CEDEN) to link local, regional, and statewide monitoring programs to address assessment questions at multiple scales.

(11) Continue to develop cross-program monitoring designs that optimally leverage data from California's statewide monitoring programs and address broadly applicable assessment questions. Encourage use of ecological endpoints and probabilistic monitoring designs to determine the status of large upstream areas and high quality streams. These data can be used to test hypotheses about the upstream extent of impairments that are identified by targeted studies focused on pollution causes and sources.

(12) Encourage Regional SWAMP programs to take advantage of SPOT sites by adding water column toxicity testing, chemical analysis or measurement of other regionally valuable parameters.

REFERENCES R

Amweg, E.L.,Weston, D.P., Ureda, N.M., 2005. Use and toxicity of pyrethroid pesticides in the Central Valley, CA, USA. Environ. Toxicol. and Chem. 24: 966-972 (erratum 24, 1300-1301).

Anderson, B.S., Hunt, J.W., Phillips, B.M., Nicely, P.A., de Vlaming, V., Connor, V., Richard, N., Tjeerdema, R.S., 2003a. Integrated assessment of the impacts of agricultural drainwater in the Salinas River (California, USA). Environmental Pollution 124, 523-532.

Anderson, B.S., Hunt, J.W., Phillips, B.M., Nicely, P.A., Gilbert, K.D., De Vlaming, V., Connor, V., Richard, N., Tjeerdema, R.S., 2003b. Ecotoxicologic impacts of agricultural drain water in the Salinas River, California, USA. Environmental Toxicology and Chemistry 22, 2375-2384.

Anderson B, Hunt, J, Markiewicz, D, Larsen, K. 2011. Toxicity in California Waters. Surface Water Ambient Monitoring Program. California State Water Resources Control Board. Sacramento, CA. (http://www.swrcb.ca.gov/water_issues/programs/swamp/docs/txcty_rprt.pdf)

Anderson, BS, Phillips, BM, Hunt, JW, Richard, N, Connor, V., Tjeerdema, RS. 2006 Evidence of pesticide impacts in the Santa Maria River watershed (California, USA). Environ. Toxicol. Chem 25: 1160 – 1170.

Bernstein B. 2010. SWAMP Assessment Framework. http://www.swrcb.ca.gov/water_issues/programs/swamp/docs/reports/app_c_assess_frmwrk.pdf

Bonifacio E, Falsone G, Piazza S. 2010. Linking Ni and Cr concentrations to soil mineralogy: does it help to assess metal contamination when the natural background is high? Journal of Soils and Sediments 10: 1475-1486.

Brown, R.P., Landre, A.M., Miller, J.A., Kirk, H.D., Hugo, J.M., 1997. Toxicity of sediment-associated chlorpyrifos with the freshwater invertebrates Hyalella azteca (amphipod) and Chironomus tentans (midge). Health and Environmental Research Laboratories, Dow Chemical, Midland, MI, USA.

CRWQCB-SFR. 2011. Municipal Regional Stormwater NPDES Permit Order R2-2009-0074; NPDES Permit No. CAS612008. California Regional Water Quality Control Board- San Francisco Bay Region. Adopted October 14, 2009; Revised November 28, 2011.

Davis J.A., A.R. Melwani, S.N. Bezalel, J.A. Hunt, G. Ichikawa, A. Bonnema, W.A. Heim, D. Crane, S. Swenson, C. Lamerdin, and M. Stephenson. 2010. Contaminants in Fish from California Lakes and Reservoirs, 2007-2008: Summary Report on a Two-Year Screening Survey. A Report of the Surface Water Ambient Monitoring Program (SWAMP). California State Water Resources Control Board, Sacramento, CA. http://www.waterboards.ca.gov/water_issues/programs/swamp/docs/lakes_study/lake_survey_yr2_no_app.pdf

DiToro, D.M., et al. 1991. Technical basis for establishing sediment quality criteria for nonionic organic chemicals by using equilibrium partitioning. Environ. Toxicol. Chem. 10:1541–1583.

Foster, IDL, Charlesworth, SM. 1996. Heavy metals in the hydrological cycle: Trends and explanation. Hydrological Processes 10(2): 227-261.

Hall, L. W. Jr., R. D. Anderson, and W. D. Killen. in press. Mapping the spatial extent of depositional areas in agricultural, urban and residential California streams: Implications for pyrethroid toxicity. Human and Ecological Risk Assessment.

Hall, L. W. Jr., R. D. Anderson, and W. D. Killen. 2010. Mapping the Spatial Extent of Depositional Areas in Agricultural, Urban and Residential California Streams with Suspected Pyrethroid Toxicity. Abstract: SETAC North America 2010 Annual Meeting, Portland, OR.

Harwood A, You J, Lydy M. 2009. Temperature as a toxicity identification evaluation tool for pyrethroid insecticides: Toxicokinetic confirmation. Environ. Toxicol. and Chem. 28: 1051–1058.

Holmes R, Anderson B, Phillips B, Hunt J, Crane D, Mekebri A, Connor V. 2008. Statewide Investigation of the Role of Pyrethroid Pesticides in Sediment Toxicity in California's Urban Waterways. Environ. Sci. Technol. 2008, 42: 7003–7009.

Hunt, J.W., Anderson, B.S., Phillips, B.M., Nicely, P.N., Tjeerdema, R.S., Puckett, H.M., Stephenson, M., Worcester, K., De Vlaming, V., 2003. Ambient toxicity due to chlorpyrifos and diazinon in a central California coastal watershed. Environmental Monitoring and Assessment 82, 83-112.

Karickhoff, SW. 1984. Organic pollutant sorption in aquatic systems. J Hydraulic Engineering 110: 707-736

Kedwards, T.J., Maund, S.J., Chapman, P.F., 1999. Community level analysis of ecotoxicological field studies: I. Biological monitoring. Environmental Toxicology and Chemistry 18, 149-157.

Macdonald, D.D., Ingersoll, C.G., Berger, T.A., 2000. Development and evaluation of consensus-based sediment quality guidelines for freshwater ecosystems. Arch Environ Contam Toxicol 39, 20-31.

Mahler B, Van Metre P, Callender E. 2006. Trends in metals in urban and reference lake sediments across the United States, 1970 to 2001. Environ. Toxicol. and Chem. 25: 1698–1709.

Miller M, Dodd E, Ziccardi M, Jessup D, Crane D, Dominik C, Spies R, Hardin D. 2007. Persistent organic pollutant concentrations in southern sea otters (Enhydra lutris nereis): patterns with respect to environmental risk factors and major causes of mortality. Report to the California Regional Water Quality Control Board, Region 3. http://www.cclean.org/ftp/CCLEAN_Final_Prop13.pdf

NRC. 2002. Opportunities to Improve the U.S. Geological Survey National Water Quality Assessment Program. National Research Council. National Academy Press. Washington, DC. 238 pp.

Perneger, TV. 1998. What's wrong with Bonferroni adjustments. BMJ British Medical Journal 316: 1230-1232. Shelton, L.R. and Capel, P.D. 1994, Guidelines for collecting and processing samples of streambed sediment for analysis of trace elements and organic contaminants for the National Water-Quality Assessment Program: U.S. Geological Survey Open File Report 94-458, 20 p.

Phillips, B.M., Anderson, B.A., Hunt, J.W., Siegler, K., Voorhees, J.P., McNeill, K., 2010. Santa Maria River Watershed and Oso Flaco Creek Watershed TMDL Monitoring Study – Final Report. Central Coast Regional Water Quality Control Board, San Luis Obispo, CA.

Phillips, B.M., Anderson, B.S., Hunt, J.W., Nicely, P.A., Kosaka, R.A., Tjeerdema, R.S., de Vlaming, V., Richard, N., 2004. In situ water and sediment toxicity in an agricultural watershed. Environmental Toxicology and Chemistry 23, 435-442.

Schueler, T.R., 1994. The importance of imperviousness, Watershed Protection Techniques, 1(3):100–111.

Schulz, R., 2004. Field studies on exposure, effects, and risk mitigation of aquatic nonpoint-source insecticide pollution: A review. Journal of Environmental Quality 33, 419-448.

Spurlock F and Lee M. 2008. Synthetic pyrethroid use patterns, properties, and environmental effects. In Gan JY, Superlock F, Hendley P, Weston D, eds, Synthetic Pyrethroids Occurrence and Behavior in Aquatic Environments, Section One: Overview and Occurrence. American Chemical Society, Washington, DC, pp 6–9.

SWAMP. 2010. Update of the Comprehensive Monitoring and Assessment Strategy to Protect and Restore California's Water Quality. SWRCB. Sacramento, CA

Swartz, R.C., 1999. Consensus sediment quality guidelines for polycyclic aromatic hydrocarbon mixtures. Environmental Toxicology and Chemistry 18, 780-787.

USEPA. 2011. Pesticide registration fact sheet: oxadiazon. http://www.epa.gov/oppsrrd1/REDs/factsheets/oxadiazon_fs.htm.

Trimble A, Weston D, Belden J, Lydy M. 2010. Identification and evaluation of pyrethroid insecticide mixtures in urban sediments. Environ. Toxicol. and Chem. 28: 1687–1695.

Tucker, K.A., Burton, G.A., 1999. Assessment of nonpoint-source runoff in a stream using in situ and laboratory approaches. Environmental Toxicology and Chemistry 18, 2797-2803.

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