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Temporal and spatial trends in sediment contaminants associated with toxicity in California watersheds

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ABSTRACT

California's Stream Pollution Trends program (SPoT) assesses long-term water quality trends, using 100 base-of-the-watershed sampling sites. Annual statewide sediment surveys from 2008 to 2012 identified consistent levels of statewide toxicity (19%), using the freshwater amphipod *Hyalella azteca*. Significant contaminant trends included a decrease in PCBs, stable concentrations of metals and PAHs, and a statewide increase in detections and concentrations of pyrethroid pesticides. The pyrethroid pesticide bifenthrin was detected in 69% of samples (n = 410). Detection of toxicity increased in a subset of samples tested at a more environmentally relevant test temperature (15 °C), and the magnitude of toxicity was much greater, indicating pyrethroid pesticides as a probable cause. Pyrethroid toxicity thresholds (LC50) were exceeded in 83% of samples with high toxicity. Principal components analysis related pyrethroids, metals and total organic carbon to urban land use.

1. Introduction

California represents the seventh largest world economy with highly urbanized cities, intensively cultivated agriculture lands, and open space (Bloomberg, 2015). Surface water monitoring is conducted throughout California as part of numerous state, regional and municipal programs. Monitoring is primarily coordinated by the California State Water Resources Control Board and is designed to meet the State's regulatory requirements for water quality. California's Stream Pollution Trends (SPoT) program is a core component of the state's Surface Water Ambient Monitoring Program (SWAMP). SPoT is a long-term statewide trends assessment program, and data are used to detect changes in contamination and associated biological effects in major watersheds of the state. SPoT is one of four statewide monitoring programs conducted under the SWAMP framework, including the Perennial Streams Assessment Program, the Reference Conditions Management Program and the Bioaccumulation Oversight Group. SPoT is the only statewide monitoring program assessing toxicity in freshwater habitats. The three goals of SPoT 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 efforts; and 3) establish a network of sites throughout the state for collaboration with other monitoring programs.

SPoT is an adaptive monitoring program and strives to incorporate emerging contaminants of concern, as well as to evaluate trends in specific contaminant classes related to implementation of new regulations. The program currently monitors 100 sites annually for sediment toxicity to *Hyalella azteca* (Nebeker et al., 1984) and measures chemical parameters including pesticides, hydrocarbons, organochlorine compounds and metals.

SPoT indicators are measured in stream sediment because this environmental compartment integrates chemical contamination over time. Sediment measurements are appropriate for long-term trend monitoring because contaminants that accumulate in depositional sediment are much more stable over time than dissolved or suspended contaminants that move downstream in highly variable pulses (Apitz, 2005). SPoT surveys are timed to collect sediment in summer after the high water season when most sediment and contaminant transport takes place.

This paper summarizes the first five years of annual surveys and emphasizes preliminary descriptions of trends in chemicals of concern and the watershed land uses associated with their presence in California streams. These comprehensive baseline data are an important starting point for assessing management and regulatory needs in the state, particularly during a time of increasing stress due to drought. Significant trends data reflect the changing

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prevalence of contaminant classes, and when linked to land use, provide guidance on future efforts of contaminant source control, management, increased monitoring needs, and regulatory actions. The paper also describes how this monitoring program will evolve to document changing statewide and regional water quality patterns. Data from California are relevant to a world where population growth and urbanization are impacting water quality.

2. Methods

2.1. Site selection and sampling procedures

SPoT has surveyed 92 to 100 sites in four of the five years covered in this study. Program funding was greatly reduced in 2009 when only 23 sites were sampled. Sites were located in all nine of the regulatory water quality regions of the state, and were selected for a targeted monitoring design based on the US Geological Survey's (USGS) National Water Quality Assessment (Domagalski et al., 1998). Factors considered in SPoT site selection included location in a large watershed with heterogeneous land cover, in most cases on the order of an 8-digit hydrologic unit code (USGS cataloging unit = watershed); location at or near the base of a watershed, defined as the confluence with either an ocean, lake, or another stream of equal or greater stream order; and location where site-specific conditions are appropriate for the indicators selected (e.g., depositional areas, sufficient flow, appropriate channel morphology, substrate). Sites were established near the base (discharge point) of larger, relatively heterogeneous drainages, providing a composite record of contaminants mobilized from throughout the watershed. Availability of previous data on sediment contaminant concentrations, biological impacts, or other relevant water quality data was considered, particularly if sites could be co-located with key sites from cooperative monitoring programs.

Sample collection occurred annually from May to October, in roughly the same order each year, to reduce temporal variation from the sampling regime. Sediment was collected from recent stream bed deposits during base flow periods after the high flow season, when most sediment and contaminant transport and loading take place. Fine depositional sediments were collected as a composite sample, from up to ten areas at a depth of up to 5 cm, along a 100 m reach at each site using polycarbonate core tubes or polyethylene scoops. Samples were collected in glass containers and transported to the laboratory on ice, where they were held at 4 °C for toxicity testing and grain size analysis and at −20 °C for total organic carbon and analytical chemistry. Sample holding times followed SWAMP guidelines, with toxicity testing occurring within 8 weeks of sample collection, and other analyses occurring within one year.

2.2. Toxicity testing

To estimate biological effects of contaminants, sediment toxicity was assessed using the 10-day growth and survival test with the resident freshwater amphipod *H. azteca* (U.S. EPA, 2000). Toxicity of sediment samples was determined using the US EPA's test of significant toxicity-TST (USEPA, 2010). Sites were classified as not toxic, significantly toxic, or highly toxic. Highly toxic sites had lower percent survival than the SWAMP-defined high toxicity threshold for *H. azteca* (38.6% survival) (Anderson et al., 2011). All samples were tested at the standard test temperature of 23 °C. A subset of samples was also tested at 15 °C, as a toxicity identification evaluation (TIE) diagnostic tool for determining the contribution of pyrethroid pesticides to the observed toxicity (Coats et al., 1989).

2.3. Physical parameters and analytical chemistry

Sediment physical parameters including total organic carbon (TOC), sediment grain size, and total phosphorus were measured for all samples. Organic contaminants were analyzed for all samples using US EPA methods (organophosphate (EPA 814M Gas Chromatography − Flame Photometric Detector (GC FPD)), organochlorine (8081 BM Gas Chromatography − Mass Spectrometry (GC-MSMS)), pyrethroid pesticides (EPA 8270M) and polychlorinated biphenyls (PCBs, EPA 8082 GC-MSMS)). A subset of sites with greater than 20% urban land use within 5 km of the site were identified as Tier II sites. These sites were also measured for polycyclic aromatic hydrocarbons (PAHs, 8270M-GC-MS) and polybrominated diphenyl ethers (PBDEs, EPA 8081BM). Trace metals (Ag, Al, As (metalloid), Cd, Cr, Cu, Hg, Mn, Ni, Pb, Zn) were analyzed by inductively coupled plasma mass spectrometry (IC-P-MS).

2.4. Geographic information system analyses

Geographic information system (GIS) analyses were used to evaluate the relationships between human activity in watersheds, as indicated by land cover and contaminant concentrations in recently deposited stream sediment. The entire drainage area specific to each SPoT site was delineated using automated scripts based on digital elevation models (=whole watershed scale). Drainage areas near the site were also delineated with 1 km and 5 km radius buffers to create two additional watershed scales for evaluation, although only the 5 km scale was used for trend analyses. Drainage area shape files were used to extract land cover grids from the National Land Cover Dataset (NLCD). For the purposes of trend analyses by land use, contaminant concentrations were compared to continuous percent land cover data as percent urban, percent agricultural, and percent open space. For analyses based on comparisons among watersheds types, watershed areas were characterized as “urban” if they had greater than 20% urban cover (NLCD categories 22, 23, 24) at the 5 km scale. This characterization is in line with studies indicating stream degradation where impervious surface cover exceeds 10% (Schueler, 1994). Watershed areas were characterized as “agricultural” if they had greater than 20% cultivated crop cover (NLCD 82). Watershed areas were characterized as “open” if they had greater than 50% combined undeveloped space (forest, wetland, shrub, barren and grassland). Thirteen sites were placed in more than one category.

2.5. Data analyses

Due to the large number of sites and analytes, chemicals were grouped into classes for most statistical analyses. DDTs, PCBs, PBDEs, and PAHs were summed, where appropriate, in each analyte class, in accordance with previous studies evaluating sediment quality guidelines (Macdonald 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) (Amweg et al., 2005). Since sediment organic carbon is a primary-binding phase for organic chemicals in sediment, normalizing measured pyrethroid concentrations to total organic carbon content provides a measure of the bioavailable fraction of pyrethroids in sediment. Calculation of organic carbon normalized toxic units were based on previously described methods for relating sediment pyrethroid concentrations to their respective LC50s for *H. azteca* (Amweg et al., 2005). For statistical analyses, the sum of four metals (Cd, Cu, Pb and Zn) was used as an indicator of metal contamination commonly released into the environment by human activity (Mahler et al., 2006).

Multivariate principal components analysis (PCA) was used for