Spatial and Temporal Trends in Toxicity and Chemical Contamination Relative to Land Use in California Watersheds: Stream Pollution Trends (SPoT) Monitoring Program Fifth Report: Ten Year Trends (2008-2017)

Overview

- The State Water Resources Control Board's Surface Water Ambient Monitoring Program (SWAMP) has released the fifth report on results from the Stream Pollution Trends monitoring program (SPoT).
- The report summarizes the results of ten years of annual SPoT surveys, with over 800 sediment samples from 100 diverse California watersheds, and over 900 toxicity tests with sensitive indicator organisms. SPoT surveys assess large watersheds across California to determine how stream pollutant concentrations are affected by land use, with an emphasis on urban and agricultural development.
- SPoT data can be used to support decision making and planning related to stream contamination and toxicity, such as the impacts of land development on water quality, prioritization of waterbodies for water quality management, and evaluation of water quality program/project effectiveness. SPoT data and information provides a statewide perspective on where stream condition has been impacted, how it has changed over time (trends), and how it compares to other watersheds monitored by the program.

About the Survey

- The SPoT Monitoring Program measures contaminant concentrations and toxicity in sediments that accumulate in the lower reaches of large watersheds.
- Sediments are monitored because the majority of contaminants entering streams accumulate in sediments, and this environmental compartment integrates pollution signals over time.
- Samples are analyzed for industrial compounds, legacy and current-use pesticides, and metals, and are tested for toxicity to resident aquatic organisms *Hyalella azteca* (amphipod) and *Chironomus dilutus* (midge).

Relationships among Toxicity, Pyrethroid Pesticide Concentrations, and Urban Land Use

Between 2008 and 2017, **concentrations of many individual pyrethroid insecticides increased in urban land use watersheds, and the number of detections of many pyrethroids increased for all land uses**. These pyrethroids include lambda-cyhalothrin, cypermethrin, deltamethrin, esfenvalerate, and fenpropathrin. **Pyrethroids contribute to much of the observed amphipod**

toxicity, as is evidenced by toxic unit analysis and diagnostic testing at colder temperatures, and both toxicity and pyrethroid concentrations are significantly related to urban land use (Figure 1).

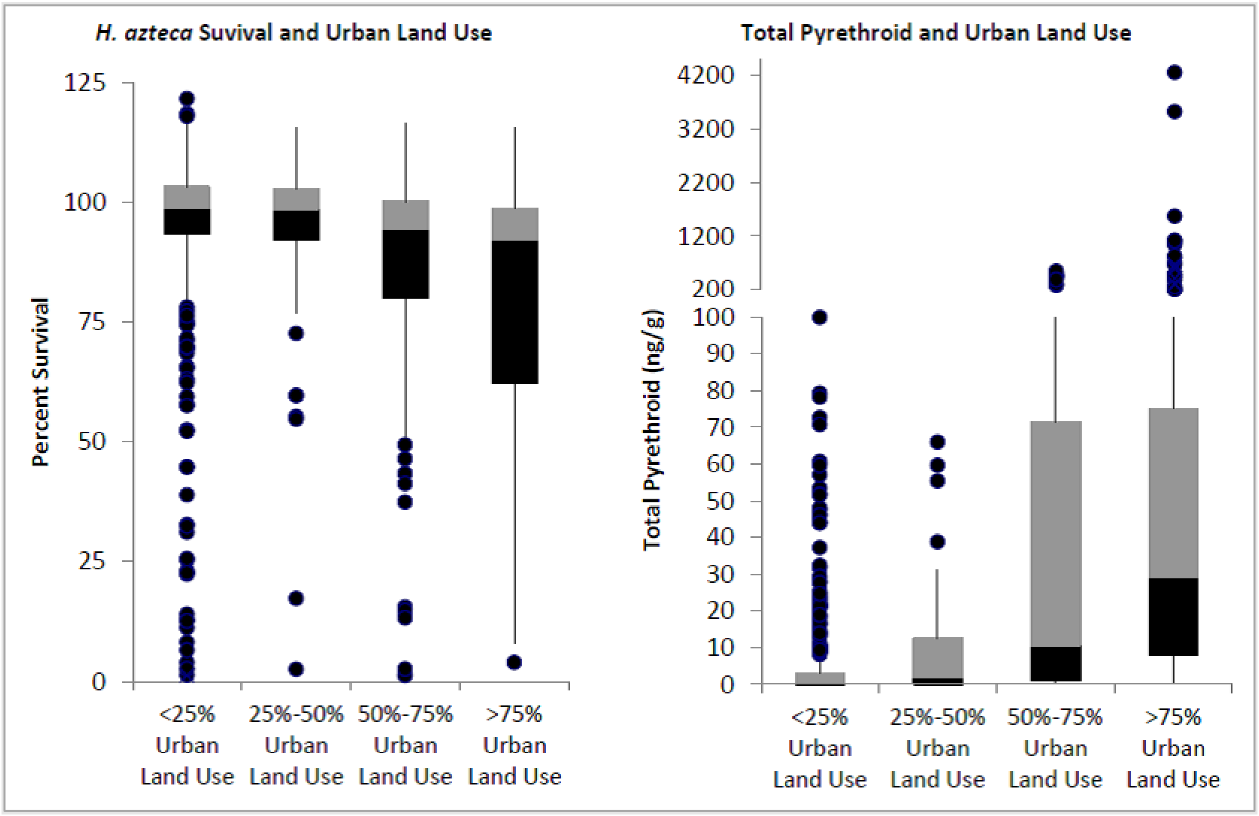

Figure 1. *Hyalella azteca* survival as percent of control (left), and total pyrethroid concentrations in categories of increasing urban land use (right). Data from 2008-2017.

Few other chemical classes are showing significant increasing or decreasing trends.

- From 2013 to 2017, incidents of detection and detected concentrations of the urban-use insecticide fipronil were stable.
- No significant trends for individual polycyclic aromatic hydrocarbons (PAH) or the sum of PAHs.
- Total polybrominated diphenyl ethers (PBDE), which are brominated flame retardants, are significantly increasing.
- Of the chlorinated compounds, the legacy organochlorine pesticide DDT is significantly decreasing in open watersheds, but the legacy industrial chemicals in the polychlorinated biphenyl (PCB) class show no trend.
- Copper concentrations are not showing any trends either, but zinc concentrations are significantly increasing statewide.

Comparing Organism Survival to Pyrethroid Toxicity Thresholds

The relationships between toxicity and sediment pyrethroid concentrations were investigated by comparing organism survival to individual and combined pyrethroid threshold values in the form of toxic units. Toxic units are calculated by dividing the measured concentration of an individual pyrethroid by its toxicity threshold or median lethal concentration (LC50). One toxic unit of pyrethroid would be expected to cause mortality to half of the exposed organisms. Because pyrethroids in a mixture can work additively, toxic units can be summed. **Eighty-eight percent of sediment samples with organic carbon-normalized pyrethroid toxic units greater than five were significantly toxic to the amphipod *H. azteca*, and measured concentrations of pyrethroids explained approximately 25% of the observed *H. azteca* toxicity in the last decade.**

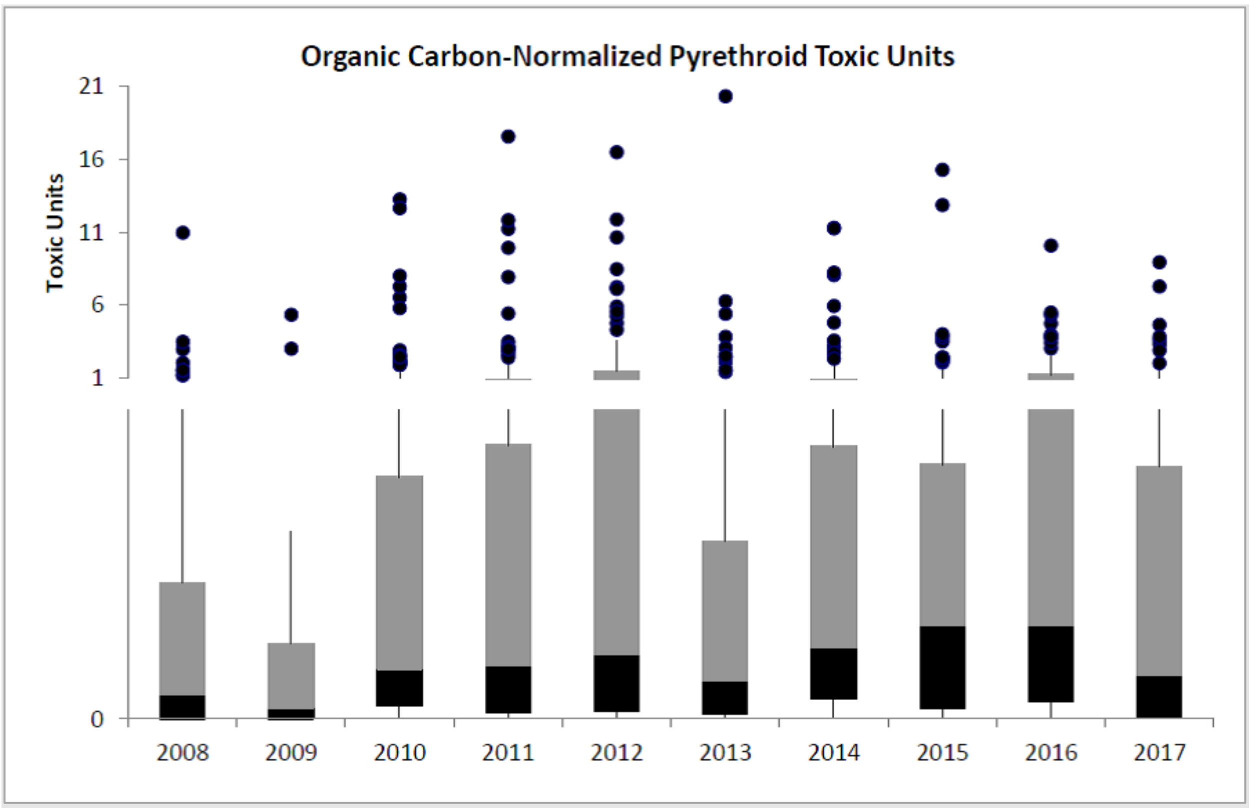

Figure 2. Yearly range of organic carbon-normalized pyrethroid toxic units (2008-2017). Expressed as the potential for a pyrethroid pesticide to cause toxicity to *H. azteca*, concentrations of these compounds continue to significantly increase.

Concentrations of individual pyrethroids at sites representing various land uses are either demonstrating no trend or significantly increasing, but there is a significant upward trend in statewide pyrethroid concentrations when examined as the sum of toxic units (Figure 2).

Use of Multiple Toxicity Test Species and Endpoints

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

Of all the samples tested with both species between 2015 and 2017, 29% were significantly toxic to amphipod survival or growth. An additional 17% of samples were toxic to the midge, revealing the importance of adding the midge testing and confirming that multiple species and endpoints capture a more complete picture of toxicity in SPoT watersheds (Figure 3). B**ased solely on survival, an average of 18% of all the samples tested in the 10-year program were toxic to the amphipod.** There were no significant trends in amphipod toxicity except for a marginal decrease in toxic response observed in watersheds with minimal agricultural or urban land use.

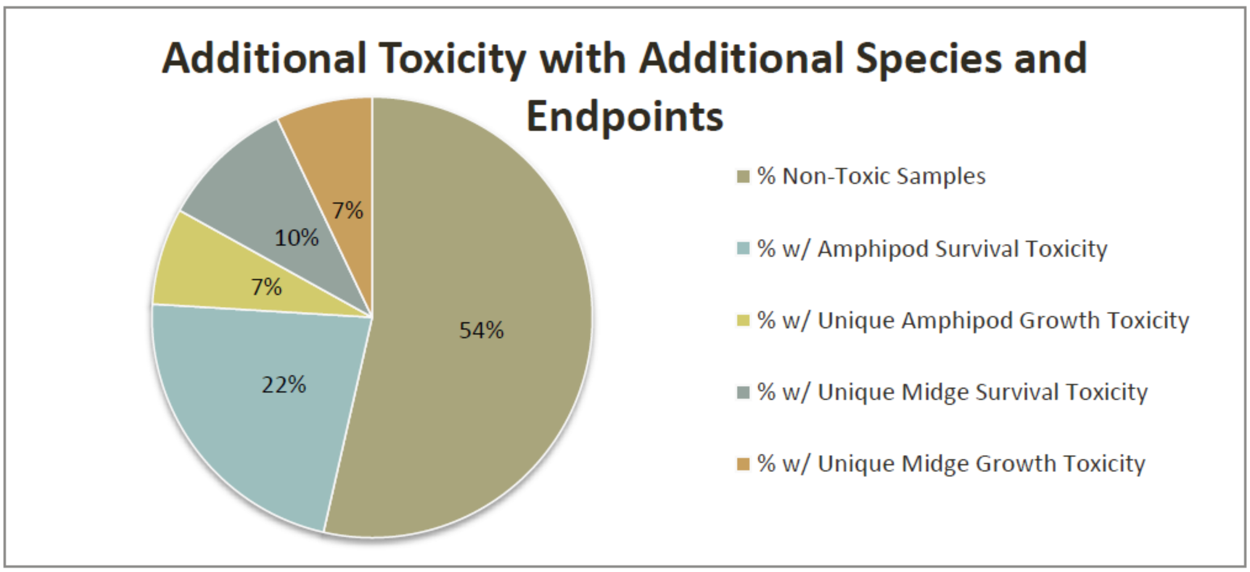

Figure 3. Significant toxicity based on various endpoints in a subset of SPoT samples tested with both *H. azteca* and *C. dilutus* (n=183, 2015-2017).

Collaborative Studies with SPoT

An overarching goal of SPoT is to establish a network of sites throughout the state to serve as a backbone for collaboration with local, regional, and federal monitoring programs and management agencies. Current collaborations include the following:

California Department of Pesticide Regulation

- Intensive Site Study to determine trends in urban pyrethroid and fipronil concentrations after adoption of use restrictions: Significant decreases were observed in three of four monitoring locations.
- Surface Water Monitoring Program Supplemental Toxicity Testing: Sites normally monitored only with chemical analyses showed significant incidences of water column toxicity to amphipods and midges.

California Department of Toxic Substances Control

- Analysis of additional chemicals of concern at SPoT sites provided geographical coverage and filled in data gaps for partner agencies.

State Water Resources Control Board

- Passive sampling project at six SPoT sites provided data on a number of constituents of emerging concern and supported recommended guidance for conducting SWAMP-supported passive sampling projects.

SPoT's Evolving Monitoring Parameters

Although toxicity testing results demonstrate the presence of bioavailable contaminant mixtures in toxic concentrations, the analysis of these chemicals is limited by a static analyte list. Traditional environmental monitoring programs have focused on the targeted analysis of hydrophobic contaminants, but recent advances in chemical analyses have demonstrated the presence of a wide range of polar chemicals in sediments. Many of these chemicals could be contributing to the type of whole organism toxicity that is monitored by SPoT, but could also be contributing to a number of sub-lethal impacts on biota. In 2021, SPoT will be adding certain per- and polyfluoroalkyl substances (PFAS) to the analyte list.

A pilot project using non-targeted chemical analysis and behavioral toxicity endpoints began during the 2020 sampling season. Use of non-targeted analysis will allow for the identification of contaminants of emerging concern, and enable regulators to focus resources on these compounds. Potential risk to biota will be assessed beyond standard acute and chronic endpoints with behavioral endpoints.