Identification of pesticides in vernal pool sediments using suspect screening methods to improve exposure assessment of listed species

Amanda Brennan[1], Leah Oliver[2], Bob Payne[3]

[1]U.S. Environmental Protection Agency, Office of Research and Development, Center for Computational Toxicology and Exposure, Research Triangle Park, NC
[2]U.S. Environmental Protection Agency, Office of Research and Development, Center for Environmental Measurement and Modeling, Gulf Breeze, FL
[3]Oak Ridge Associated Universities, Research Triangle Park, NC

Poster does not reflect Agency policy

Amanda Brennan I brennan.amanda @epa.gov I 919-541-2323

Introduction

- The fairy shrimp, *Branchinecta lynchi* (*B. lynchi*), is listed as threatened under the Endangered Species Act.
- Vernal pools (VP) are ephemeral wetlands that provide critical habitat for *B. lynchi*. VP are often located near agricultural fields and can be impacted by pesticides from runoff and application.
- Paired sediment and water samples were collected from VP in California for exposure assessments for *B. lynchi*.
- A target pesticide analyte list was chosen based on pesticide application and crop data from surrounding agricultural areas including 13 select pyrethroids, organophosphate pesticides (OP), and carbamates.
- Analysis of water and select sediment samples resulted in non-detectable concentrations of the 13 targeted pesticides.
- A suspect screening method was adapted and validated to screen for more than 220 pesticides to potentially identify other unknowns in paired sediments samples and subsequent water analyses.

Methods

Sediment Extraction

- Approximately 10 g sediment (wet weight)
- QuEChERS (Quick, Easy, Cheap, Effective, Rugged, and Safe)
  - Extraction: acidified acetonitrile and 6 g magnesium sulfate ($MgSO_4$) and 1.5 g sodium acetate
  - Clean-up: Dispersive solid-phase extraction with 400 mg primary secondary amines, 1200 mg $MgSO_4$, 400 mg carbon-18, 15 mg graphitized carbon
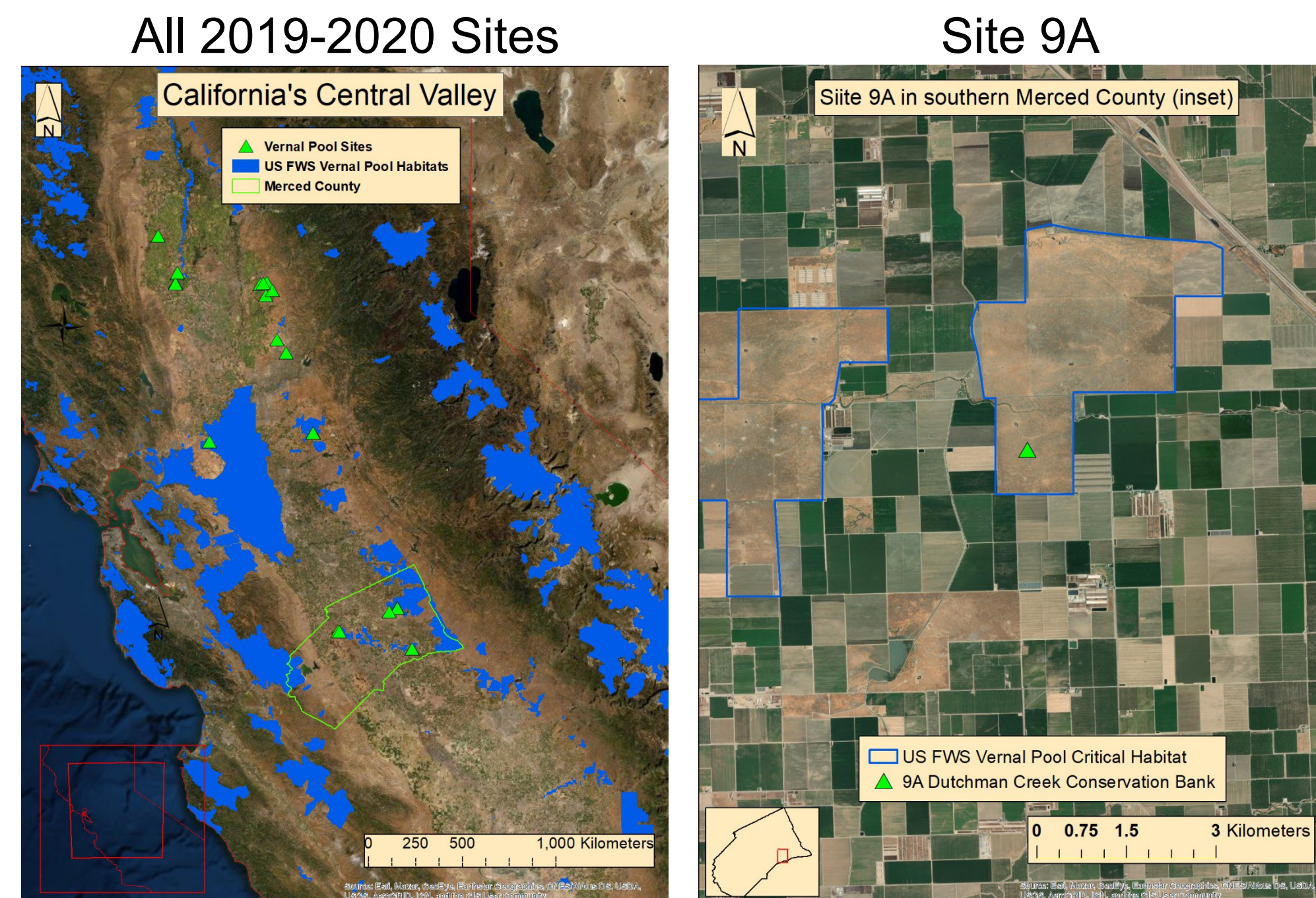
Analytical

- Method adapted from Restek GC Multiresidue Pesticide Kit
- Gas chromatography (GC)- tandem mass spectrometry (MS) in electron ionization with selected reaction monitoring on a Thermo Trace 1300 GC/TSQ 8000
  - 223 pesticides (OP, organochlorines (OC), organonitrogens (ON), pyrethroids, and herbicide methyl esters) and 10 internal standards
  - 3 transitions per pesticide
    - Ion ratios and retention times used for confirmation
  - Minimum 5-point calibration curve per quantified pesticide
  - GC parameters: Oven- 90 °C (1 min), 8.9 °C /min to 330 °C (5 min); Flow- 1.4 mL/min; Column- Restek Rxi-5SIL MS, 30 m × 0.25 mm ID × 0.25 μm
  - MS parameters: Transfer line- 290 °C; Ion source temperature- 325 °C
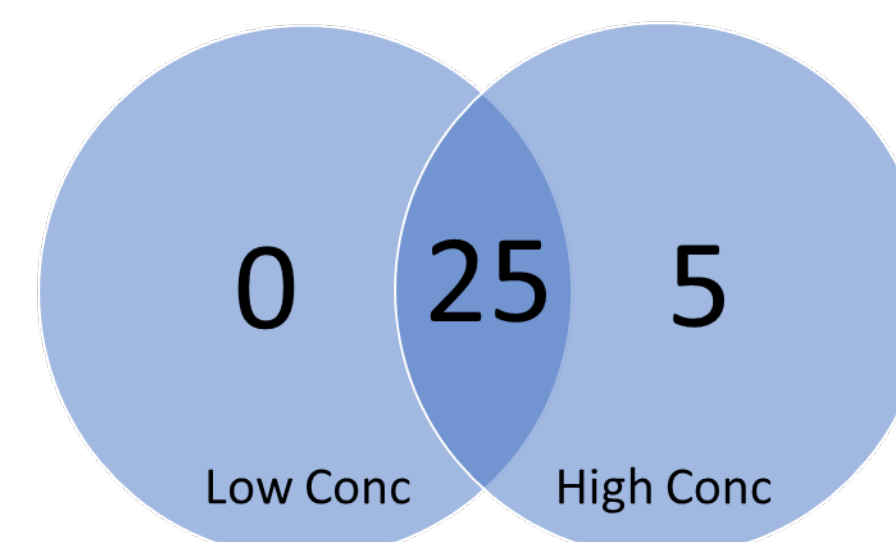
Methods

Sediment Sampling

- Sediment sampled during the 2019 to 2020 rainy season in California with a stainless-steel scoop.
- Results for 2019 sediments, excluding all identified banned pesticides are shown here.
  - More detailed results are shown for Site 9A; 9A is in a conservation bank surrounded by agricultural areas

All 2019-2020 Sites — California's Central Valley

Site 9A — Site 9A in southern Merced County (inset)

Method Validation

- Blind spiked with one of EPA's Non-Targeted Analysis Collaborative Trial mixtures containing 364 analytes.
  - 30 analytes overlapped with suspect screening list.
  - Spiked to be at a low and high concentration in extracts ranging from approximately 1 to 8 ng/mL and 15 to 25 ng/mL, respectively, depending on the molecular weight of the analyte.
- Results: missed identifications (IDs) at low concentrations (conc) were likely due to low analyte response or missing or incorrect ion ratios.

Identified Pesticides During Method Validation: Low Conc 0 — 25 — High Conc 5
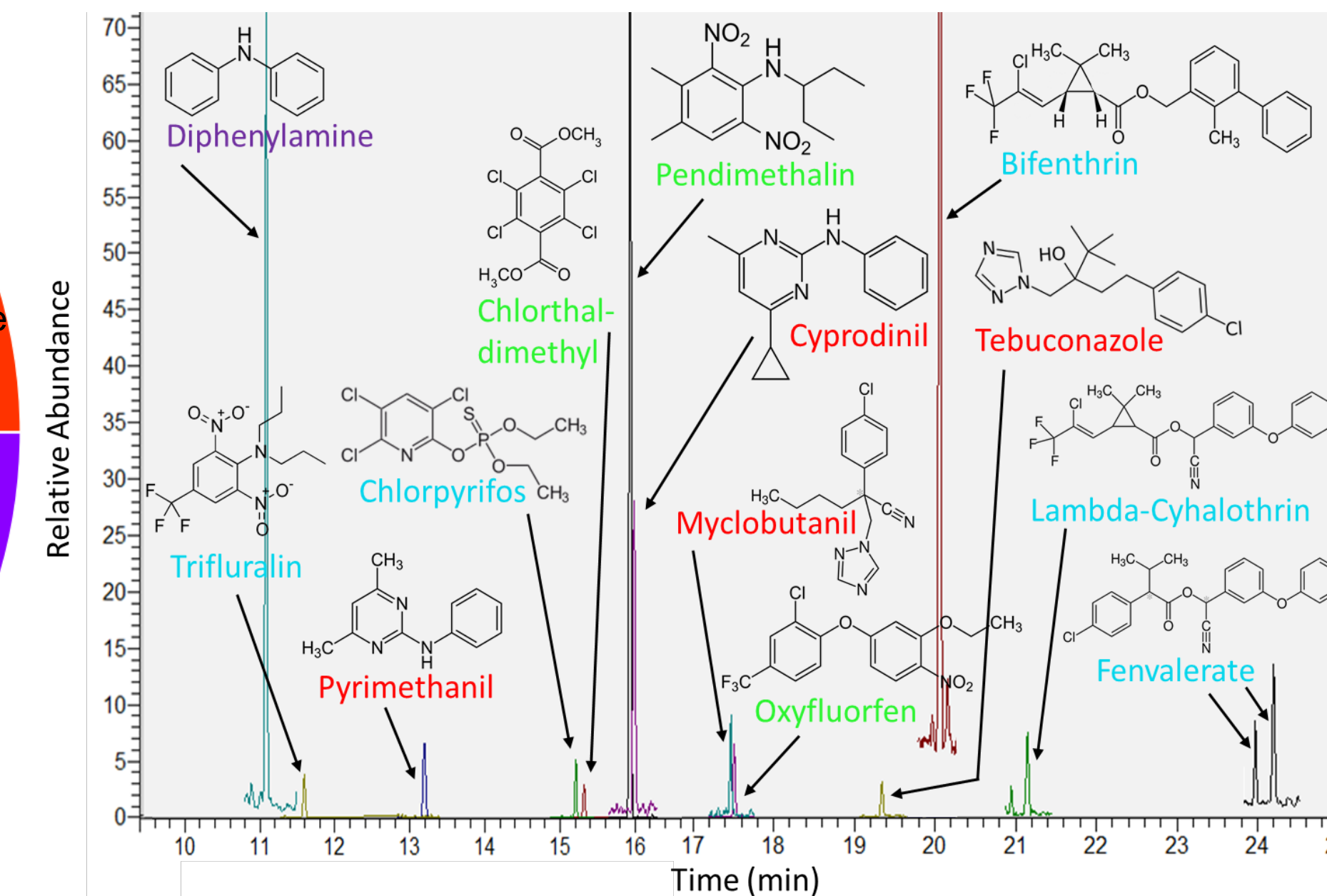
Results- Application of Suspect Screening Method

Total Pesticide Category & Class IDs
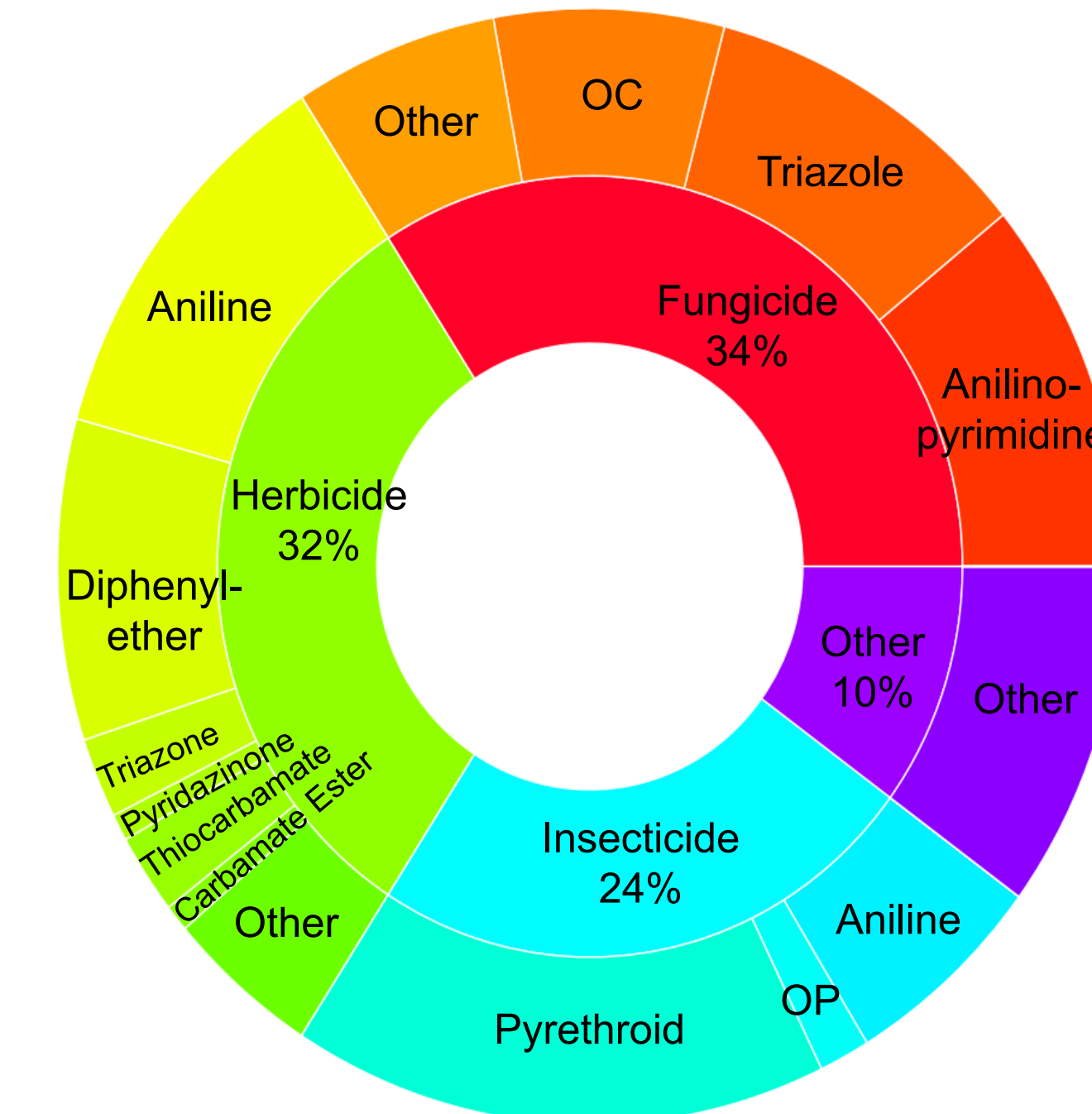
Commonly Identified Pesticides
Chromatogram from Site 9A

- The original 13 target list included mainly insecticides; however, herbicides and fungicides were identified in more sediments.
- Only 20% of total IDs from the suspect screening method were analytes on the original 13 target list.
  - IDs included Bifenthrin, Fenvalerate, Chlorpyrifos, lambda-Cyhalothrin, and Thiobencarb
- Pendimethalin was identified in 83% of sediments, followed by Oxyfluorfen (67%), Bifenthrin (61%), Pyrimethanil (61%), and Tebuconazole (50%).
- Pendimethalin was quantified at the highest concentrations in extracts ranging from approximately 2 to 58 ng/mL.

Future Research

The screening method highlighted the high number of contaminants present in VPs and the potential hazard to fairy shrimp. Future research includes:

- Comparing pesticide IDs with crop and pesticide usage in surrounding agricultural areas for further confirmation.
- Comparing sediment exposure data with lab effects data for surrogate fairy shrimp species.
- Comparing Pesticide in Water Calculations (PWC) modeled concentrations with measured concentrations.
  - PWC is a fate and transport aquatic model used to estimate pesticide concentrations.
- Analyzing extracts on the LCMSMS using the Restek LC Multiresidue Pesticide Kit to screen for additional pesticides.