URBAN CREEKS MONITORING REPORT

PART B: PESTICIDES & TOXICITY MONITORING IN SAN MATEO COUNTY

Water Year 2022 (October 2021 – September 2022)



Submitted in Compliance with
NPDES Permit No. CAS612008 (Order No. R2-2022-0018)
Provision C.8.h.iii.

SAN MATEO COUNTYWIDE
Water Pollution
Prevention Program

A Program of the City/County Association of Governments of San Mateo County

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CREDITS

This report is submitted by the participating agencies in the

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List of Acronyms

ACCWP	Alameda Countywide Clean Water Program
BAMSC	Bay Area Municipal Stormwater Collaborative
BASMAA	Bay Area Stormwater Management Agencies Association
CCCWP	Contra Costa Clean Water Program
CEDEN	California Environmental Data Exchange Network
DF	Detection Frequency
DPR	(California) Department of Pesticide Regulation
IMR	Integrated Monitoring Report
IPM	Integrated Pest Management
MDL	Method Detection Limit
MPC	Monitoring and Pollutants of Concern
MRP	Municipal Regional Permit
NPDES	National Pollutant Discharge Elimination System
PAH	Polycyclic Aromatic Hydrocarbons
PCBs	Polychlorinated Biphenyls
PEC	Probable Effects Concentrations
QAPP	Quality Assurance Project Plan
QAPrP	Quality Assurance Program Plan
QA/QC	Quality Assurance/Quality Control
RMC	Regional Monitoring Coalition
SCCWRP	Southern California Coastal Water Research Project
SCVURPPP	Santa Clara Valley Urban Runoff Pollution Prevention Program
SFBRWQCB	San Francisco Bay Regional Water Quality Control Board
SMCWPPP	San Mateo Countywide Water Pollution Prevention Program
SOP	Standard Operating Procedures
SPoT	Stream Pollution Trends Program
SWAMP	Surface Water Ambient Monitoring Program
SWPP	Surface Water Protection Program
TEC	Threshold Effects Concentrations
TOC	Total Organic Carbon
TST	Test of Significant Toxicity
TU	Toxic Unit
UCMR	Urban Creeks Monitoring Report
USEPA	Environmental Protection Agency
WQO	Water Quality Objective
WY	Water Year

1.0 Introduction

This *Urban Creeks Monitoring Report (UCMR) Part B: Pesticides & Toxicity Monitoring Status, Water Year[1] (WY) 2022* was prepared by the San Mateo Countywide Water Pollution Prevention Program (SMCWPPP). SMCWPPP is a program of the City/County Association of Governments (C/CAG) of San Mateo County. Each incorporated city and town in the county, OneShoreline, and the County of San Mateo share a common National Pollutant Discharge Elimination System (NPDES) stormwater permit for Bay Area municipalities referred to as the Municipal Regional Permit (MRP).

The MRP was first adopted by the San Francisco Bay Regional Water Quality Control Board (SFBRWQCB or Regional Water Board) on October 14, 2009 as Order R2-2009-0074 (SFBRWQCB 2009; referred to as MRP 1.0). On November 19, 2015, the Regional Water Board updated and reissued the MRP as Order R2-2015-0049 (SFBRWQCB 2015; referred to as MRP 2.0). The current, and third, version of the MRP (i.e., MRP 3.0, SFBRWQCB 2022) was issued by the Regional Water Board as Order R2-2022-0018 and became effective July 1, 2022. The monitoring requirements in MRP 3.0 (SFBRWQCB 2022) are similar to MRP 2.0 (SFBRWQCB 2009) requirements, with minor differences in analytes and reporting structure.

This report fulfills the requirements of provision C.8.h.iii.(3) of MRP 3.0 for interpreting and reporting all Pesticides & Toxicity monitoring data collected during WY 2022 by SMCWPPP. This report builds on the interpretation and reporting of Pesticides & Toxicity monitoring data that were provided in the UCMRs from WYs 2016 through 2021 (SMCWPPP 2017, 2018, 2019, 2021, 2022) and the March 2020 Integrated Monitoring Report (IMR) (SMCWPPP 2020).[2]

Data presented in this report were collected pursuant to water quality monitoring requirements in provision C.8.g (Pesticides & Toxicity Monitoring) of the MRP.[3] Data presented in this report were submitted electronically to the Regional Water Board by SMCWPPP and may be obtained via the California Environmental Data Exchange Network (CEDEN).

1.1 Report Organization

This report is organized into the following sections:

- **Section 1.0** provides the relevant background information and regulatory requirements for Pesticides & Toxicity monitoring pursuant to the MRP.
- **Section 2.0** describes the methods used to generate and analyze data.
- **Section 3.0** presents the results of Pesticides & Toxicity monitoring conducted by the Program in WY 2022, including brief descriptions of sampling protocols and analytical methods and a statement of data quality.

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[1] Most hydrologic monitoring occurs for a period defined as a Water Year, which begins on October 1 and ends on September 30 of the named year. For example, Water Year 2022 (WY 2021) began on October 1, 2021 and concluded on September 30, 2022.

[2] Prior monitoring reports prepared by SMCWPPP are available at https://www.flowstobay.org/data-resources/reports/urban-creek-monitoring-reports/

[3] Monitoring data collected pursuant to other C.8 provisions (e.g., Pollutants of Concern Monitoring, LID Monitoring, and Trash Monitoring) are reported in other Reports of the SMCWPPP Urban Creeks Monitoring Reporting series (UCMR) for WY 2022.

- **Section 4.0** describes conclusions and recommendations based on WY 2022 monitoring data.

  Section 5.0 provides all the references cited with the report.

1.2 Monitoring Requirements

Toxicity testing provides a tool for assessing the toxic effects (acute and chronic) of all chemicals in samples of receiving waters or sediments and allows the cumulative effect of the pollutant present in the sample to be evaluated. Because different test organisms are sensitive to different classes of chemicals and pollutants, several different organisms are monitored. Sediment and water chemistry monitoring for a variety of potential pollutants is conducted synoptically with toxicity monitoring to provide preliminary insight into the possible causes of toxicity should it be observed.

Provision C.8.g of the MRP requires Permittees to conduct wet and dry weather monitoring of pesticides and toxicity in urban creeks.

1.2.1 Dry Weather

Provision C.8.g.ii. of MRP 3.0 requires SMCWPPP to sample one site each year during dry weather for toxicity and sediment chemistry analysis. The permit provides examples of possible monitoring location types, including sites with suspected or past toxicity results, existing bioassessment sites. MRP 3.0 dry weather monitoring includes:

- Toxicity testing in water using five species: *Ceriodaphnia* dubia (chronic survival and reproduction), *Pimephales promelas* (larval survival and growth), *Selenastrum capricornutum* (growth), *Hyalella azteca* (survival) and *Chironomus dilutus* (survival).
- Toxicity testing in sediment using two species: *Hyalella azteca* (survival) and *Chironomus dilutus* (survival).
- Sediment chemistry analysis for pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin), fipronil and it degradates (fipronil-sulfone, fipronil-desulfinyl, fipronil sulfide), total polycyclic aromatic hydrocarbons (PAHs), metals (arsenic, cadmium, chromium, copper, lead, nickel, zinc), total organic carbon (TOC), and sediment grain size.

1.2.2 Wet Weather

Provision C.8.g.iii. of MRP 3.0 requires Permittees to collect samples from the water column during storm events for toxicity and pesticide analysis. Sample locations must be representative of urban watersheds (i.e., bottom of watershed locations). MRP 3.0 wet weather monitoring includes:

- Toxicity testing in water using five species: *Ceriodaphnia* dubia (chronic survival and reproduction), *Pimephales promelas* (larval survival and growth), *Selenastrum capricornutum* (growth), *Hyalella azteca* (survival) and *Chironomus dilutus* (survival).

- Water chemistry analysis for pyrethroids (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin), fipronil and it degradates (fipronil-sulfone, fipronil-desulfinyl, fipronil sulfide)[4], and imidacloprid[5].

If provision C.8.g.iii. sampling is conducted by the Bay Area Municipal Stormwater Collaborative (BAMSC)[6] Regional Monitoring Coalition (RMC) on behalf of all Permittees, a collective total of ten wet weather samples is required, with a minimum of six samples collected by the end of the third water year of the permit term (i.e., WY 2024). If provision C.8.g.iii. sampling is conducted by SMCWPPP, at least one wet weather sample is required per year. Members of the RMC have agreed to coordinate on wet weather Pesticides & Toxicity monitoring in WY 2023.

1.2.3 Follow-up

Provision C.8.g.iv. of MRP 3.0 requires Permittees to provide notification in the next UCMR when analytical results indicate any of the following:

- A toxicity test of growth, reproduction, or survival of any test organism that is reported as "fail" in the both the initial sampling and a second, follow-up sampling, and both have Percent Effect;
- A pollutant is present at a concentration exceeding its water quality objective (WQO) in the Basin Plan; or
- For pollutants without WQOs, results exceed Probable Effects Concentrations (PECs) or Threshold Effects Concentrations (TECs) as defined in MacDonald et al. (2000).

1.3 Regional Monitoring Coalition

Provision C.8.a. (Compliance Options) of the MRP allows Permittees to address monitoring requirements through a regional collaborative effort, their Stormwater Program, and/or individually[7]. The RMC was formed in early 2010 as a collaboration among several Bay Area Stormwater Management Agencies Association (BASMAA) members and MRP Permittees[8] to develop and implement regionally coordinated water quality monitoring programs to improve stormwater management in the region and address water quality monitoring required by the MRP. BAMSC RMC collaboration allows Permittees and the Regional Water Board to improve their ability to collectively answer core management questions in a cost-effective and scientifically rigorous way. Participation in the RMC is facilitated through the BAMSC Monitoring and Pollutants of Concern (MPC) Subcommittee.

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[4] Fipronil amide is optional.

[5] Imidacloprid must be analyzed using a method that achieves a reporting level of 0.01 ppb.

[6] The BAMSC was organized by the Bay Area Stormwater Management Agencies Association (BASMAA) Board of Directors to continue the information sharing and permittee advocacy functions of BASMAA in an informal manner after BASMAA's dissolution in 2021.

[7] Provision C.8.g of MRP 3.0 also encourages Permittees to collaborate with the California Department of Pesticide Regulation for data collection and analysis.

[8] BAMSC RMC partners include Santa Clara Valley Urban Runoff Pollution Prevention Program (SCVURPPP), Alameda Countywide Clean Water Program (ACCWP), Contra Costa Clean Water Program (CCCWP), SMCWPPP, and the Solano Stormwater Alliance (SSA).

The goals of the RMC are to:

1. Assist Permittees in complying with requirements in MRP provision C.8 (Water Quality Monitoring);
2. Develop and implement regionally consistent monitoring approaches and designs in the Bay Area, through the improved coordination among RMC participants and other agencies (e.g., Regional Water Board) that share common goals; and
3. Stabilize the costs of creek monitoring by reducing duplication of effort and streamlining reporting.

2.0 Methods

Water quality data were collected and reviewed in accordance with California Surface Water Ambient Monitoring Program (SWAMP) comparable methods and procedures described in the RMC SOPs (BASMAA 2016) and the associated Quality Assurance Project Plan (QAPP; BASMAA 2020). These documents are updated as needed to optimize applicability. Where applicable, monitoring data were collected using methods comparable to those specified by the SWAMP Quality Assurance Program Plan (QAPrP)[9], and were submitted in SWAMP-compatible format to the Regional Water Board. The SOPs were developed using a standard format that describes health and safety cautions and considerations, relevant training, site selection, and sampling methods/procedures, including pre-fieldwork mobilization activities to prepare equipment, sample collection, and de-mobilization activities to preserve and transport samples.

2.1 Monitoring Methods

Water and sediment samples for pesticides and toxicity monitoring were collected in accordance with SWAMP-comparable methods and procedures described in the RMC SOPs (BASMAA 2016) and the associated QAPP (BASMAA 2020). Before sampling, field personnel conduct a qualitative assessment of the proposed sampling site to identify appropriate sampling locations. This is particularly necessary for sediment sampling, which requires the presence of fine-sediment depositional areas that can support at least five sub-sites within a 100-meter reach.

Water samples were collected using standard grab sampling methods. The required number of labeled amber glass bottles were filled and placed on ice to cool to < 6˚C. The laboratory was notified of the impending sampling delivery to allow for preparation to meet sample hold times. Procedures used for sampling and transporting water samples are described in SOP FS-2 (BASMAA 2016).

Sediment samples were collected after any water samples were collected. Sediment samples were collected from the top 2 cm at each sub-site beginning at the downstream-most location and continuing upstream. Field staff walk in an upstream direction, carefully avoiding disturbance of sediment at collection sub-sites. Sediment samples were placed in a compositing container, thoroughly homogenized, and then aliquoted into separate jars for chemical or toxicological analysis using standard clean sampling techniques (see SOP FS-6, BASMAA 2016).

Samples were submitted to respective laboratories under RMC SOP FS-9 Chain of Custody procedures and field data sheets were reviewed per SOP FS-13 (BASMAA 2016).

2.2 Laboratory Analysis Methods

RMC participants, including SMCWPPP, agreed to use the same laboratories for individual parameters (except pathogen indicators), developed standards for contracting with the labs, and coordinated quality assurance samples. All samples collected by RMC participants that were sent to laboratories for analysis were analyzed and reported per SWAMP-comparable methods as described in the QAPP (BASMAA 2020). Analytical laboratory methods, reporting limits, and

[9]The current SWAMP QAPrP is available at: https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/swamp-qaprp-2022.pdf

holding times for chemical water quality parameters are also described in the QAPP (2020). Analytical laboratory contractors in WY 2022 included:

- CalTest, Inc. – Sediment chemistry
- Pacific EcoRisk, Inc. – Water and sediment toxicity

2.3 Data Evaluation

2.3.1 Water and Sediment Toxicity

Toxicity data evaluation required by the MRP involves first assessing whether the samples are toxic to the test organisms relative to the laboratory control treatment via statistical comparison. MRP 3.0 specifies using the Test of Significant Toxicity (TST) statistical approach to compare the sample to the laboratory control. For samples with toxicity (i.e., those that “failed” the TST), the Percent Effect is evaluated. The Percent Effect compares sample endpoints (survival, reproduction, growth) to the laboratory control endpoints. Both the statistical comparison (e.g., TST) and the comparison of the sample results to the laboratory control (e.g., Percent Effect) are determined by the laboratory. If both the initial and follow-up sample are reported as “fail” with ≥ 50% Percent Effect, the Regional Water Board is notified in the next UCMR.

2.3.2 Sediment Chemistry

In compliance with MRP provision C.8.g.iv., sediment sample results are compared to Probable Effects Concentrations (PECs) and Threshold Effects Concentrations (TECs) as defined by MacDonald et al. (2000). PEC and TEC quotients are calculated as the ratio of the measured concentration to the respective PEC and TEC values from MacDonald et al. (2000). All results where a PEC or TEC quotient is equal to or greater than 1.0 are reported in the next UCMR.

PECs and TECs are listed in MacDonald et al. (2000) for total PAHs, rather than the individual PAHs that are reported by the laboratory. Total PAH concentrations were calculated by summing the concentrations of the 24 individual PAHs that were measured by SMCWPPP. Concentrations equal to one-half of the respective laboratory method detection limits (MDLs) were substituted for non-detect data so that calculations and statistics could be computed. Therefore, some of the TEC and PEC quotients may be artificially elevated due to the method used to account for filling in non-detect data.

The TECs for bedded sediments are very conservative values that do not consider site specific background conditions and are therefore may not be very useful in identifying real water quality concerns in receiving waters. All sites in San Mateo County are likely to have at least one TEC quotient equal to or greater than 1.0. This is due to high levels of naturally occurring chromium and nickel in geologic formations (i.e., serpentinite) and soils that contribute to TEC and PEC quotients. These conditions are considered when making decisions about follow-up investigations.

The current MRP does specify follow-up actions for pyrethroid or fipronil sediment chemistry data, perhaps because pyrethroids are ubiquitous in the urban environment and little is known about fipronil distribution. However, SMCWPPP computed toxic unit (TU) equivalents for individual pyrethroid results based on available literature values for pyrethroids in sediment

LC50 values.[10,11] Because organic carbon mitigates the toxicity of pyrethroid pesticides in sediments, the LC50 values were derived on the basis of TOC-normalized concentrations. Therefore, the pesticide concentrations as reported by the lab were divided by the measured total organic carbon (TOC) concentration at each site, and the TOC-normalized concentrations were then used to compute TU equivalents for each constituent. Concentrations equal to one-half of the respective laboratory MDLs were substituted for non-detect data so that these statistics could be computed, potentially resulting in artificially elevated results.

2.3.3 Water Chemistry

Provision C.8.g.iv. of MRP 3.0 requires that chemical pollutant data from water and sediment monitoring be compared to the corresponding WQOs in the Basin Plan for each analyte sampled. If concentrations in the samples exceed their WQOs, then the Regional Water Board is notified in the next UCMR. However, the Basin Plan does not contain numeric WQOs for the chemical analytes encompassed within the wet weather pesticide monitoring.

2.4 Statement of Data Quality

A comprehensive Quality Assurance/Quality Control (QA/QC) program was implemented by SMCWPPP covering all aspects of Pesticides & Toxicity Monitoring. In general, QA/QC procedures were implemented as specified in the RMC QAPP (BASMAA 2020) and monitoring was performed according to protocols specified in the RMC SOPs (BASMAA 2016). Both documents were adapted from the methods detailed in the SWAMP QAPrP.

Overall, the results of the QA/QC review suggests that the Creek Status and Pesticides & Toxicity Monitoring data generated during WY 2022 were of sufficient quality for the purposes of this monitoring program, in comparison to objectives outlined in the QAPP. No data were rejected nor were there any data discrepancies; however, some data were flagged in accordance with QA/QC protocols. A Detailed QA/AC report for WY 2022 pesticides and toxicity data is included as Attachment 1.

[10] The LC50 is the concentration of a given chemical that is lethal on average to 50% of test organisms.

[11] No LC50 is published for carbaryl in sediment.

3.0 Results and Discussion

This section describes the results of toxicity testing and sediment chemistry monitoring (collectively referred to as pesticides and toxicity monitoring) conducted during WY 2022 in compliance with provision C.8.g. of the MRP. The following discussion includes historical data from SMCWPPP as well as local pesticides and toxicity monitoring results from projects external to SMCWPPP to inform management efforts for San Mateo County urban creeks with respect to achievement of WQOs and support of beneficial uses.

3.1 Site Selection

Throughout the terms of the previous two MRPs (i.e., MRP 1.0 and MRP 2.0; WY 2012 through 2021), sites were selected to represent mixed-land use in urban watersheds not already being monitored for toxicity or pesticides by other programs, such as the SWAMP Stream Pollution Trends (SPoT) Program. A different watershed was targeted each year with the goal of eventually developing a geographically diverse dataset. Specific monitoring locations within the identified creeks were based on the likelihood that they would contain fine depositional sediments during the dry season and would be safe to access during wet weather sampling, if relevant. During WY 2022, Pescadero Creek at the Stage Road bridge adjacent to the Community Church in the Town of Pescadero was selected for monitoring (37.2549, -122.383369). Photographs of this site are provided in Figure 3.1. As described in the *UCMR Part A: Creek Status Monitoring* for WY 2022, Pescadero Creek was also targeted for bioassessment surveys and chlorine monitoring at locations upstream of the pesticide and toxicity monitoring site.

Figure 3.2 shows the WY 2022 pesticides and toxicity monitoring station (in red), stations monitored by SMCWPPP in prior years, and the SPoT monitoring station. In WYs 2012 and 2015, during MRP 1.0, a total of eight sites (two sites per year) were monitored for water and sediment toxicity and sediment chemistry during the wet and dry seasons. The monitoring sites were selected from a list of locations where bioassessment surveys had been conducted and include sites in Atherton, Belmont, Corte Madera, Laurel (204R01288 and 204R02056), Milagra, Pilarcitos, and Redwood Creeks (Figure and Table 3.2). The results of these monitoring efforts were compared to MRP 1.0 trigger thresholds. In WYs 2016 through 2021, during MRP 2.0, one site per year was monitored for water and sediment toxicity and sediment chemistry during the dry season. The monitoring sites were located in varying watersheds throughout San Mateo County to collect data on spatial variations in water quality. The monitored sites from WY 2016 through WY 2021 were located in Laurel Creek, San Pedro Creek, Cordilleras Creek, Pulgas Creek, Bear Creek, and San Gregorio Creek respectively. In WY 2018, wet weather toxicity and water chemistry monitoring was conducted in San Pedro Creek and Cordilleras Creek to satisfy provision C.8.g.iii. of MRP 2.0. WY 2016 through WY 2021 dry weather water and sediment toxicity and sediment chemistry monitoring was conducted at one SMCWPPP site to satisfy the requirements specified in MRP 2.0. Dry weather monitoring took place at one site per year and was located in varying watersheds throughout San Mateo County to collect data on spatial variations in water quality.

Figure 3.1. Pescadero Creek (202-PESCA-11) on July 12, 2022. Left to right: downstream and upstream.

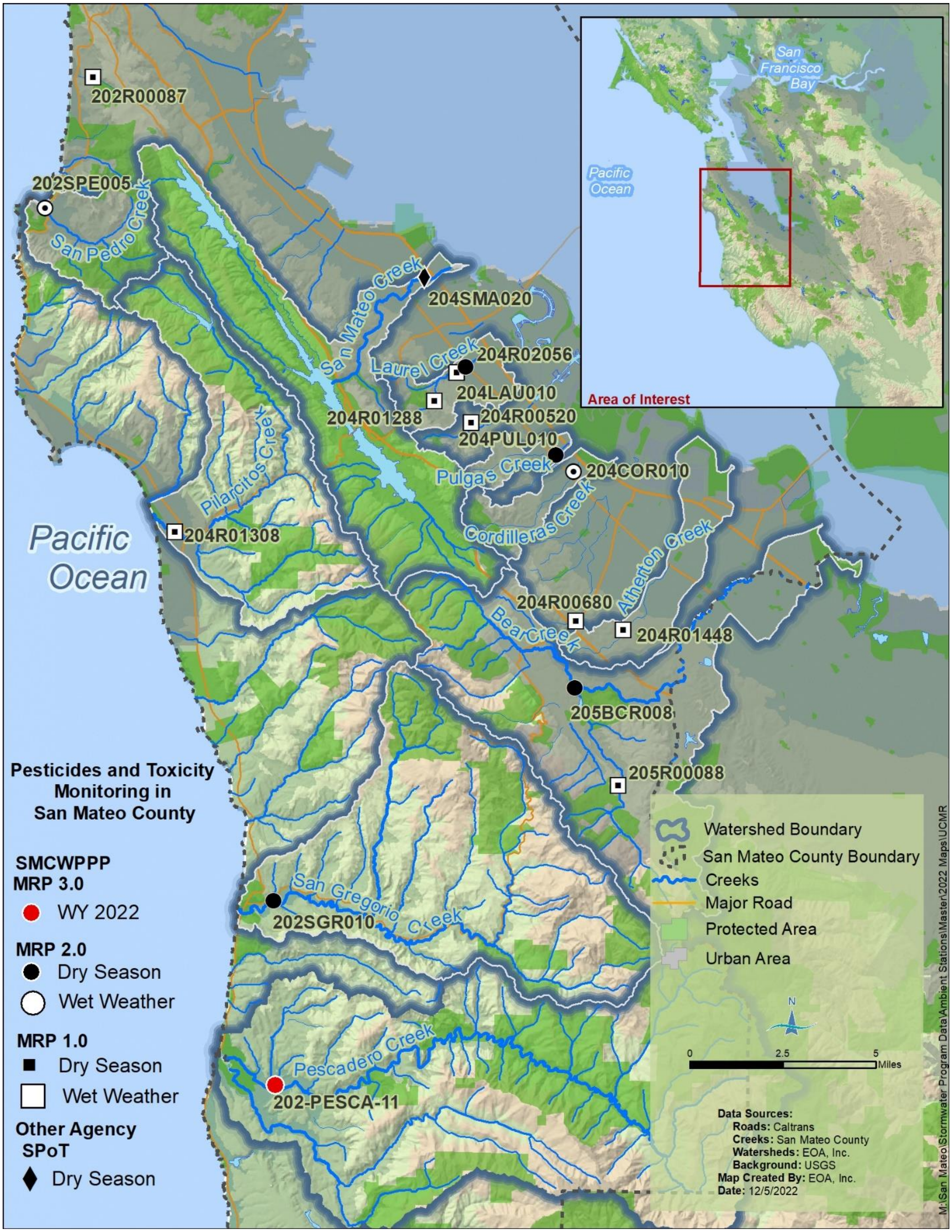

Figure 3.2. SMCWPPP Program Area, major creeks, and monitored sites as of WY 2022.

3.2 Toxicity

3.2.1 WY 2022 Results

Details of the WY 2022 toxicity tests are listed in Table 3.1. There were no test organisms that exhibited significant toxic responses to water and sediment samples (Table 3.1). Likewise, the sediment chemistry, described in more detail in Section 3.3, did not result in any exceedances of MRP 3.0 thresholds for follow-up action (i.e., TEC or PEC ≥ 1.0). The sediment chemistry findings are consistent with the lack of toxicity in the water and sediment samples.

Table 3.1. Summary of SMCWPPP dry weather water and sediment toxicity results, Pescadero Creek, WY 2022.

Site	Organism	Test Type	Unit	Results		% Effect	TST Value	Follow up needed (TST "Fail" and ≥50%)
				Lab Control	Organism Test			
202-PESCA-11 (Pescadero Creek) July 12, 2022	**Water**							
	Ceriodaphnia dubia	Survival	%	100	100	0%	NA [a] (Pass)	No
		Reproduction	Num/ Rep	42	43.1	-2.6%	Pass	No
	Pimephales promelas	Survival	%	95	95	0%	Pass	No
		Growth	mg/ind	0.85	1.00	-17.9%	Pass	No
	Chironomus dilutus	Survival	%	100	100	0%	Pass	No
	Hyalella azteca	Survival	%	94	96	-2.1%	Pass	No
	Selenastrum capricornutum	Growth	cells/ ml	3418000	8195000	-140%	Pass	No
	Sediment							
	Chironomus dilutus	Survival	%	86.3	85.0	1.4%	Pass	No
	Hyalella azteca	Survival	%	97.5	97.5	0%	Pass	No

[a] TST analysis is not performed for survival endpoint - a percent effect <25% is considered a "Pass", and a percent effect ≥25% is considered a "Fail".

3.2.2 WY 2012 – WY 2022 Toxicity Summary

Toxicity results for WYs 2012 through WY 2022 are summarized in Table 3.2. Details of the toxicity tests for WYs 2014 to 2021 can be found in the UCMR for each year (SMCWPPP 2022, 2021, 2019a, 2018, 2017, 2016, 2015). Details of the WY 2019 toxicity test results are compiled with prior years in the IMR (SMCWPPP 2020). An IMR is also available for WYs 2012 and 2013 (SMCWPPP 2014).

During WYs 2012 through WY 2022, there were a total of 185 toxicity tests. Five of these toxicity tests had sample results with significant toxicity relative to the laboratory control *and* a Percent Effect exceeding the MRP trigger threshold (see Section 2.3.1 and Table 3.2). Three of these tests with threshold exceedances were conducted on sediment samples in WYs 2014 and

2015 for the growth (chronic) endpoint of *H. azteca*, a test that was not required by the MRP but was reported by the analytical laboratory prior to WY 2016. With two exceptions, where the Percent Effect was below the MRP trigger threshold, the associated tests for the survival (acute) endpoint did not cause toxicity to *H. azteca. H. azteca* is known to be sensitive to pyrethroid pesticides and these pesticides are commonly detected in urban creek sediment samples throughout San Mateo County. Long-term monitoring of San Mateo Creek by the SPoT program suggests that pyrethroid concentrations in sediment have decreased since 2011/2012 (SMCWPPP 2019b), which may explain why no MRP 2.0 sediment samples were acutely toxic to *H. azteca*.

Overall, 25 of the 185 test results had significant toxicity, but with a Percent Effect that did not exceed the MRP trigger threshold. Two samples found evidence of mortality due to the presence of pathogens in the samples. Most toxicity results were found in water samples and were associated with either *C. dubia* reproduction (10 samples), a chronic toxicity endpoint, or *H. azteca* survival (eight samples), an acute toxicity endpoint. Seven of the eight water samples with toxicity to *H. azteca* were collected during wet season sampling events, suggesting that stormwater runoff is affecting *H. azteca*. The water samples with toxicity to *C. dubia* were more evenly dispersed between wet and dry season sampling events.

C. dubia Toxicity Analysis

As indicated in Table 3.2, chronic (reproductive) *C. dubia* toxicity was observed in 10 of the 25 water samples analyzed by SMCWPPP from WY 2012 – WY 2022, with one test demonstrating a Percent Effect threshold for follow-up sampling. *C. dubia* is a water flea that is sensitive to a broad range of aquatic contaminants. However, the specific cause of the chronic *C. dubia* toxicity in the San Mateo County samples is unknown, not seemingly explained by the synoptic sediment chemistry results. It is possible that these toxicity results are erroneous artifacts of laboratory QA/QC procedures.

In preparation for reissuance of the SWAMP QAPrP in 2013, the SWAMP Toxicity Work Group examined conductivity tolerance in freshwater toxicity test species with respect to the relationship between sample water conductivity and observed toxicity. It was determined that *C. dubia* survival and reproduction are negatively affected at high and low conductivities (SWAMP 2013). The SWAMP Toxicity Work Group (2013) recommended "appropriate controls" when sample water has high (>1900 µS/cm) or low (<100 µS/cm) conductivities because the *C. dubia* test organisms cultivated in the laboratory under standard laboratory conditions (e.g., 310 to 360 µS/cm) may perish or experience reduced reproduction when exposed to the sample water. In light of these findings, SMCWPPP compiled the results of conductivity measurements taken from sample water associated with toxicity monitoring from WY 2012 through WY 2020 to compare with the laboratory water used in these toxicity tests and the results of the tests themselves. In almost all cases, it was found that the sample water conductivity was higher or lower by several hundred µS/cm compared to the laboratory control samples (a mean difference of 433 µS/cm). However, no correlation was found between *C. dubia* toxicity and sample water/laboratory control water conductivity differences.

Statewide, there have been other reports of unexplained chronic *C. dubia* toxicity, within and between laboratory variability in the magnitude of toxicity, and suspicion of false positives. Recent analysis by SWAMP in conjunction with the Statewide Toxicity provisions adopted by the State Water Board on December 1, 2020 indicates that *C. dubia* toxicity variability could arise from inconsistencies in QA procedures used by laboratories. A two-year Special Study requested by the State Water Board is currently underway, with a work plan developed by the

Southern California Coastal Water Research Project (SCCWRP) and a final recommendations report anticipated in June 2023. This study will contain recommendations for improvements to laboratory QA procedures associated with the *C. dubia* toxicity tests and may also yield related findings pertaining to the causes of spurious *C. dubia* toxicity (SWRCB 2020).

Table 3.2. Toxicity test result summary, WY 2012 – WY 2022, for SMCWPPP. The Percent Effect is indicated for test results with toxicity relative to the lab control. Test results with toxicity exceeding the MRP 1.0 (WYs 2012 – 2015), MRP 2.0 (WYs 2016 – 2021), and MRP 3.0 (WY 2022) Percent Effect trigger thresholds are highlighted.

Station ID	Creek	Date	MRP	Sediment			Water						
				C. dilutus [b]	*H. azteca*		*C. dubia*		*P. promelas*		*C. dilutus* [b]	*H. azteca*	*S. capricornutum*
				Survival	Survival	Growth [b]	Survival	Reproduction	Survival	Growth	Survival	Survival	Growth
Dry Season Samples (WY 2012 – WY 2022)													
202R00087	Milagra Cr	7/25/2012	1.0	--	No	No	No	No	No	No	--	No	No
202R00088	Corte Madera Cr	7/25/2012	1.0	--	No	No	No	No	No	No	--	No	No
204R00520	Belmont Cr	7/9/2013	1.0	--	--	--	No	No	**Yes** [c]	--	--	No	No
204R00680	Redwood Cr	7/9/2013	1.0	--	--	--	No	No	No	No	--	No	No
204R00520	Belmont Cr	7/14/2013	1.0	--	**Yes** (15%)	--	--	--	--	--	--	--	--
204R00680	Redwood Cr	7/14/2013	1.0	--	No	No	--	--	--	--	--	--	--
204R01288	Laurel Cr	6/4/2014	1.0	--	**Yes** (18%)	**Yes** (50%)	No	No	No	No	--	No	No
204R01308	Pilarcitos Cr	6/4/2014	1.0	--	No	**Yes** (43%)	No	**Yes** (33%) [a]	No	No	--	No	No
204R01448	Atherton Cr	7/7/2015	1.0	--	No	No	No	No	No	No	--	No	No
204R02056	Laurel Cr	7/7/2015	1.0	--	No	**Yes** (31%)	No	No	No	No	--	No	No
205LAU010	Laurel Cr	7/11/2016	2.0	**Yes** (14%)	No	--	No	**Yes** (31%)	No	No	**Yes** (10%)	**Yes** (29%)	No
202SPE005	San Pedro Cr	7/13/2017	2.0	No	No	--	No	**Yes** (46%)	**Yes** (18%)	No	No	No	No
204COR010	Cordilleras Cr	7/17/2018	2.0	No	No	--	No	No	No	No	**Yes** (11%)	No	No
204PUL010	Pulgas Cr	7/23/2019	2.0	No	No	--	No	**Yes** (20%)	No	No	No	No	No
205BCR008	Bear Cr	7/22/2020	2.0	No	No	--	No	No	No	No	No	No	No
202SGR010	San Gregorio Cr	6/23/2021	2.0	**Yes** (21%)	No	--	No	**Yes** (24%)	No	No	No	No	No
202-PESCA-11	Pescadero Cr	7/12/2022	3.0	No	No	--	No	No	No	No	No	No	No
Wet Weather Samples (WY 2012 – WY 2015, and WY 2018)													
202R00087	Milagra Cr	3/17/2012	1.0	--	--	--	No	No	No	**Yes** (14%)	--	No	No
202R00088	Corte Madera Cr	3/17/2012	1.0	--	--	--	No	**Yes** (51%)	No	No	--	No	No
204R00520	Belmont Cr	3/5/2013	1.0	--	--	--	No	**Yes** (20%)	No	No	--	**Yes** (82%)	No

Station ID	Creek	Date	MRP	Sediment			Water						
				C. dilutus [b]	*H. azteca*		*C. dubia*		*P. promelas*		*C. dilutus* [b]	*H. azteca*	*S. capricornutum*
				Survival	Survival	Growth [b]	Survival	Reproduction	Survival	Growth	Survival	Survival	Growth
204R00680	Redwood Cr	3/5/2013	1.0	--	--	--	No	**Yes** (24%)	**Yes** [c]	No	--	**Yes** (35%)	No
204R01288	Laurel Cr	2/8/2014	1.0	--	--	--	No	No	No	No	--	**Yes** (16%)	No
204R01308	Pilarcitos Cr	2/8/2014	1.0	--	--	--	No	No	No	No	--	No	No
204R01448	Atherton Cr	2/6/2015	1.0	--	--	--	No	**Yes** (30%)	No	No	--	**Yes** (24%)	No
204R02056	Laurel Cr	2/6/2015	1.0	--	--	--	No	**Yes** (22%)	No	No	--	**Yes** (45%)	No
202SPE005	San Pedro Cr	1/20/2018	2.0	--	--	--	No	No	No	**Yes** (23%)	No	**Yes** (16%)	No
204COR010	Cordilleras Cr	1/18/2018	2.0	--	--	--	No	No	No	No	No	**Yes** (20%)	No

Notes:
a. The test response in one of the replicates for this test treatment was determined to be a statistical outlier; the results reported above are for the analysis of the data excluding the outlier.
b. *Chironomus dilutus* testing was not required by MRP 1.0. *Hyalella azteca* growth was not required by either permit but is included here when reported by the lab.
c. Pathogen-related mortality observed in sample.

3.3 Sediment Chemistry

3.3.1 WY 2022 Results

Sediment chemistry results from WY 2022 were evaluated based on TEC and PEC quotients (see Section 2.3.2). SMCWPPP also evaluated TU equivalents of pyrethroids and fipronil.

Table 3.3 lists concentrations and TEC quotients for sediment chemistry constituents (metals and total PAHs) collected in WY 2022 from Pescadero Creek. TEC quotients are calculated as the measured concentration divided by the highly conservative TEC value, per MacDonald et al. (2000)[12]. TECs are extremely conservative and are intended to identify concentrations below which harmful effects on sediment-dwelling organisms are unlikely to be observed. Nickel was the only analyte from the Pescadero Creek sample with a TEC quotient greater than 1.0. Nickel and chromium are expected in watersheds draining hillsides underlain by serpentine formations, which is a common geological feature in San Mateo County.

Table 3.3 also lists PEC quotients for sediment chemistry constituents collected in WY 2022 from Pescadero Creek. PECs are intended to identify concentrations above which toxicity to benthic-dwelling organisms are predicted to be probable. There were no PEC quotients greater than 1.0. Individual PAHs had 23 measurements below the detection limit and one measurement below the reporting limit.

Table 3.3. TEC and PEC quotients for WY 2022 sediment chemistry constituents, Pescadero Creek.

Constituent	202SGR010	TEC		PEC	
Metals (mg/kg DW)	Sample Concentration	TEC Threshold	TEC Quotient	PEC Threshold	PEC Quotient
Arsenic	3	9.79	0.31	33	0.09
Cadmium	0.27	0.99	0.27	4.98	0.05
Chromium	14	43.4	0.32	111	0.13
Copper	8.8	31.6	0.28	149	0.06
Lead	3.7	35.8	0.10	128	0.03
Nickel	23	22.7	**1.01**	48.6	0.47
Zinc	38	121	0.31	459	0.08
PAHs (ug/kg DW)					
Total PAHs	Non-Detect [a]	1610	NA [a]	22800	NA [a]

a. All 24 PAHs were below the detection or reporting limits. Therefore, the PEC and TEC quotients were not calculated.

[12] MacDonald et al. (2000) does not provide TEC or PEC values for pyrethroids, fipronil, or carbaryl. Pesticides are compared to LC50 values in Table 3.4.

Table 3.4 lists the concentrations of pesticides measured in the sediment sample collected from Pescadero Creek in WY 2022 and the published LC50 values. All pesticides were measured at concentrations below the MDL of the analyte, therefore, neither TOC-normalized concentrations nor TU equivalents were calculated.

Table 3.4. Pescadero Creek pesticide concentrations and associated LC50 values, WY 2022.

202SGR010 Pescadero Creek	Unit	LC50 [a]	Measured Concentration [b]
Total Organic Carbon	%	NA	0.56
Pyrethroids			
Bifenthrin	µg/g dw	0.52	< 0.00021
Cyfluthrin, total	µg/g dw	1.08	< 0.000082
Cypermethrin, total	µg/g dw	0.38	< 0.00012
Deltamethrin/Tralomethrin	µg/g dw	0.79	< 0.00021
Esfenvalerate/Fenvalerate, total	µg/g dw	1.54	< 0.00033
Cyhalothrin, Total lambda-	µg/g dw	0.45	< 0.000082
Permethrin, Total	µg/g dw	10.83	< 0.00074
Other MRP Pesticides of Concern			
Carbaryl [c]	mg/Kg dw	NA	< 0.021
Fipronil	ng/g dw	306	< 0.12
Fipronil Desulfinyl	ng/g dw	NA	< 0.16
Fipronil Sulfide	ng/g dw	435	< 0.16
Fipronil Sulfone	ng/g dw	158	< 0.41

a. Sources: Amweg et al. 2005 and Maund et al. 2002 for pyrethroids; Maul et al. 2008 for fipronil compounds; no available LC50 value for Carbaryl or Fipronil Desulfinyl.

b. All pesticide concentrations were below the method detection limit (MDL).

c. Carbaryl is not listed as an analyte in MRP 3.0.

In compliance with the MRP, a grain size analysis was conducted on the sediment sample (Table 3.5). The sample was 27.16% fines (i.e., 9.86% clay and 17.3% silt).

Table 3.5. Summary of grain size for site 202-PESCA-11 in San Mateo County, WY 2022.

Grain Size (%)		202-PESCA-11
		Pescadero Creek
Clay	<0.0039 mm	7.32%
Silt	0.0039 to <0.0625 mm	7.19%
Sand	V. Fine 0.0625 to <0.125 mm	6.74%
	Fine 0.125 to <0.25 mm	16.03%
	Medium 0.25 to <0.5 mm	40.04%
	Coarse 0.5 to <1.0 mm	16.5%
	V. Coarse 1.0 to <2.0 mm	6.17%
Granule	2.0 to <4.0 mm	5.63%
Pebble	Small 4 to <8 mm	1.43%
	Medium 8 to <16 mm	0%
	Large 16 to <32 mm	0%
	V. Large 32 to <64 mm	0%

Note: Sum of grain size values for both sites is greater than 100% due to the laboratory analytical methods used.

3.3.2 WY 2012 – WY 2022 Summary

Between WY 2012 and WY 2022, there were no PEC quotients calculated for the SMCWPPP sediment chemistry dataset that were ≥ 1.0 for analytes other than chromium and nickel. Chromium and nickel are excluded from this PEC/TEC analysis because they are contributed primarily by serpentine formations present in the watersheds where monitoring occurred.

Excluding chromium and nickel, there were 18 samples with TEC quotients ≥ 1.0; the more conservative of the two evaluation criteria. TECs calculated for WY 2012 to WY 2013 made up approximately 78% of all TEC exceedances, mostly because of elevated PAH concentrations measured in Redwood Creek (204R00680) during WY 2013.

The constituents and locations with TEC quotients ≥ 1.0 included:

- Legacy insecticide DDT compounds, which were monitored under MRP 1.0 but not under MRP 2.0 and MRP 3.0, exceeded the TEC in Milagra and Corte Madera Creeks in WY 2012, Laurel Creek in WYs 2014 and 2015, and in Atherton Creek in WY 2015;
- Individual PAHs, pyrene and chlordane, in Atherton Creek in WY 2015 and chlordane in Laurel Creek in WY 2015;
    - Redwood Creek in WY 2013 had seven individual PAHs and total PAHs exceed the TEC quotient ≥ 1.0;
- Copper in Milagra Creek in WY 2012, Belmont Creek in WY 2013, and both copper and zinc in Pulgas Creek in WY 2019.

Table 3.6 lists TU equivalents for pesticides with LC50s available in the literature and concentrations for pesticides without LC50s for sediment samples collected in WY 2012 – WY 2022. The sum-of-pyrethroids TU equivalents ranged from 0.08 (San Pedro Creek in WY 2017) to 7.9 (station 204R01288 on Laurel Creek in WY 2014). The Laurel Creek sediment sample with the high pyrethroid TU equivalent was collected from a location relatively high in the watershed. Subsequent sampling at stations near the bottom of the Laurel Creek watershed in WY 2015 and WY 2016 had lower TU equivalents of 0.7 and 2.6, respectively. All three of these Laurel Creek sediment samples also had sediment toxicity (Table 3.2). The WY 2014 and WY 2015 samples had chronic (growth) toxicity to the pyrethroid-sensitive test organism, *H. azteca,* with Percent Effects exceeding the MRP 1.0 trigger threshold. The WY 2016 Laurel Creek sample was not toxic to *H. azteca* but was toxic to *C. dilutus* with a Percent Effect that did not exceed the MRP 2.0 trigger threshold. Four samples had sum-of-pyrethroid TU equivalents that exceeded the MRP 1.0 trigger threshold of 1.0: Pilarcitos Creek in WY 2014, Laurel Creek in WY 2014 and WY 2015, and Pulgas Creek in WY 2019. In WY 2020, the calculated TU equivalent for pyrethroids (0.2) was based on just one detected pyrethroid (permethrin) and ½ MDL for all others. In WY 2021, the TU equivalent for pyrethroids was not calculated because all were below the MDL. TU equivalents for WY 2022 were also not calculated for pyrethroids because all were below the MDL.

Sampling for fipronil and carbaryl pesticides began in WY 2016 with the adoption of MRP 2.0; fipronil degradates were added to the list of analytes in WY 2017[13]. Carbaryl has not been detected in any of the sediment samples (Table 3.6) and has been excluded from analysis in MRP 3.0 under provision C.8.g. Fipronil and/or fipronil sulfone were detected in San Pedro Creek and Pulgas Creek at TOC-normalized concentrations below the LC50.

[13] Fipronil degrades via UV exposure, oxidation, and hydrolysis to form four principal degradates: fipronil desulfinyl, fipronil sulfide, fipronil sulfone, and fipronil amide. The degradates tend to be more stable and persistent than the parent compound; therefore, SMCWPPP added the first three of the degradates to the monitoring program in WY 2017.

Table 3.6. Toxic Unit (TU) equivalent summary for San Mateo County sediment samples, WY 2012 – WY 2022.

Analyte			Pyrethroids								Other MRP Pesticides of Concern				
			Bifenthrin	Cyfluthrin	Cypermethrin	Deltamethrin	Esfenvalerate	Lambda-cyhalothrin	Permethrin	**Sum Pyrethroids**	Carbaryl	Fipronil	Fipronil desulfinyl	Fipronil sulfide	Fipronil sulfone
		LC50 [c]	0.52 µg/g dw	1.08 µg/g dw	0.38 µg/g dw	0.79 µg/g dw	1.54 µg/g dw	0.45 µg/g dw	10.83 µg/g dw	-	NA [d]	306 ng/g dw	NA [d]	435 ng/g dw	158 ng/g dw
Station ID	**Creek**	**Date**													
MRP 1.0															
205R00088	Corte Madera	7/25/2012	0.04 [b]	0.02 [b]	0.06 [b]	0.04 [b]	0.02 [b]	0.02 [b]	0.02	**0.23**	-	-	-	-	-
202R00087	Milagra	7/25/2012	0.24 [b]	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	**0.54** [a]	-	-	-	-	-
204R00520	Belmont	7/9/2013	0.66	0.18	<MDL	<MDL	<MDL	<MDL	0.02	**0.98** [a]	-	-	-	-	-
204R00680	Redwood	7/9/2013	0.12	0.02 [a]	<MDL	0.18	<MDL	<MDL	0.06	**0.53** [a]	-	-	-	-	-
202R01308	Pilarcitos	6/4/2014	1.06	0.24	<MDL	0.22 [b]	<MDL	<MDL	0.15	**1.9** [a]	-	-	-	-	-
204R01288	Laurel	6/4/2014	5.19	1.02	0.58	0.66	<MDL	<MDL	0.32	**7.9** [a]	-	-	-	-	-
204R01448	Atherton	7/7/2015	0.56	0.06	<MDL	<MDL	<MDL	<MDL	0.03	**0.7** [a]	-	-	-	-	-
204R02056	Laurel	7/7/2015	0.51	0.07	<MDL	<MDL	<MDL	<MDL	<MDL	**0.7** [a]	-	-	-	-	-
MRP 2.0															
204LAU010	Laurel	7/11/2016	1.37	0.36	0.23 [b]	0.51	<MDL	0.09 [b]	0.05	**2.6** [a]	<MDL	<MDL	-	-	-
202SPE005	San Pedro	7/13/2017	0.04	<MDL	<MDL	<MDL	<MDL	<MDL	0.001 [b]	**0.08** [a]	<MDL	0.02 [b]	<MDL	<MDL	0.08 [b]
204COR010	Cordilleras	7/17/2018	0.25 [b]	<MDL	<MDL	0.10 [b]	<MDL	<MDL	0.08 [b]	**0.52** [a]	<MDL	<MDL	<MDL	<MDL	<MDL
204PUL010	Pulgas	7/23/2019	0.56	0.07 [b]	<MDL	0.42	<MDL	<MDL	0.02	**1.2** [a]	<MDL	<MDL	<MDL	<MDL	0.33 [b]
205BCR008	Bear	7/22/2020	0.10	<MDL	<MDL	<MDL	<MDL	<MDL	0.02	**0.2** [a]	<MDL	<MDL	<MDL	<MDL	<MDL
202SGR010	San Gregorio	6/23/2021	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	**NA**	<MDL	<MDL	<MDL	<MDL	<MDL
MRP 3.0															
202-PESCA-11	Pescadero	7/12/2022	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	<MDL	**NA**	<MDL	<MDL	<MDL	<MDL	<MDL

a. TU equivalent calculated using 1/2 MDL and total calculated using 1/2 MDLs for some individual pyrethroids.
b. TU equivalents calculated from concentration below the reporting limit (J-flagged).
c. Sources: Amweg et al. 2005 and Maund et al. 2002 for pyrethroids; Maul et al. 2008 for fipronil compounds
d. No available LC50 value for carbaryl or fipronil desulfinyl.

3.4 Pesticides in Wet Weather Water Samples

Although wet weather sampling was conducted from WY 2012 through WY 2015 in compliance with MRP 1.0, sample analysis was focused on toxicity endpoints; thus the samples were not analyzed for pesticides.

During WY 2018, in compliance with provision C.8.g.iii.(3) of MRP 2.0, wet weather water samples were collected for pesticide analysis at two sites in San Mateo County (San Pedro Creek and Cordilleras Creek). Results were reported in the WY 2018 UCMR (SMCWPPP 2019a). The concentrations of most pesticides analyzed were below the MDL, meaning that these analytes were reported as non-detects. Imidacloprid, a neonicotinoid, was found at detectable levels at one of the two sites (Cordilleras Creek). Additionally, detectable levels of fipronil and its degradation products were found at both sites. However, the WY 2018 wet weather water samples were not toxic to *C. dilutus*, the test organism sensitive to neonicotinoids and fipronil. There are no WQOs specified in the San Francisco Bay Basin Plan for the water column pesticide analytes. As a result, WQO or MRP trigger threshold exceedance analysis was not performed on wet weather pesticide data. Wet weather sampling in compliance with MRP 3.0 will likely be conducted during WY 2023.

3.5 Additional Monitoring Efforts

Throughout the monitoring period associated with the sampling results described in this report, several additional programs external to SMCWPPP and the RMC conducted similar pesticides and toxicity studies within California. These studies provide valuable data for comparison against SMCWPPP findings to view regional water quality in a broader spatial and temporal context.

3.5.1 DPR Surface Water Protection Program Monitoring

The California Department of Pesticide Regulation (DPR) Surface Water Protection Program (SWPP) is one of the largest pesticide monitoring and management efforts currently being undertaken in California. Pesticide studies conducted by the DPR SWPP evaluate the frequency of pesticide detections at any concentration and make use of USEPA aquatic benchmarks for many pesticide compounds (USEPA 2016). DPR provides web access to a number of their monitoring reports which contain detailed analyses of USEPA aquatic benchmark exceedance rates. DPR also maintains the Surface Water Database (SURF) to provide public access to quantitative pesticide data from a wide array of surface water monitoring studies. This database could be queried in the future to allow for the leverage of DPR monitoring data in more complex analyses of MRP pesticide data. The following paragraphs summarize recent DPR studies in urban areas of California.

WY 2017: DPR conducted two studies in Northern and Southern California that involved pesticides and toxicity monitoring at urban sites in Alameda, Contra Costa, Placer, Sacramento, Santa Clara (Guadalupe River), Los Angeles, Orange, and San Diego Counties. Both water and sediment samples were collected and analyzed for a wide range of pesticide compounds. In both the Northern and Southern California studies, bifenthrin and fipronil were among the most frequently detected pesticides. Additionally, pyrethroid concentrations were above their USEPA minimum benchmarks for toxicity to aquatic life for the majority of samples with the exception of cyfluthrin. The study reports also state that the detection frequencies of most pyrethroids have remained consistent over recent years (Budd 2018 and Ensminger 2017).

WY 2018: DPR conducted two urban monitoring studies in Northern and Southern California that collected water and sediment samples in the same counties sampled during WY 2017. Similar to WY 2017, bifenthrin was among the most frequently detected insecticides in water samples from both the Northern and Southern California WY 2018 studies. In the Northern California study, bifenthrin was the most frequently detected insecticide and second most frequently detected compound in water samples with a detection frequency (DF) of 76%. In the Southern California study, bifenthrin was the most frequently detected pyrethroid insecticide and the fifth most frequently detected compound in water samples with a DF of 72%. Fipronil and its degradates were also detected at high rates in water samples from the Northern and Southern California studies. While fipronil itself only had a DF of 48% in the Northern California study, fipronil and its degradates collectively had a DF of 72%. Out of these compounds, fipronil sulfone was found at the highest rate with a DF of 70%. Fipronil was also found at a high rate during the Southern California study with a DF of 76%. Its degradates were also found in a large portion of samples, with fipronil sulfone again being the most found with a DF of 67%. Sediment samples from Northern and Southern California were collected and analyzed for bifenthrin and eight other pyrethroids, but concentrations of fipronil and its degradates were not measured. In both studies, bifenthrin was detected in all samples and was also responsible for the greatest magnitude of TUs (Budd 2019 and Ensminger 2019).

WY 2019: DPR collected water and sediment samples in the same Northern Californian counties targeted during WY 2018. Bifenthrin and fipronil were the most detected insecticides with 41% DF and 37% DF, respectively. Three of fipronil's five degradates were observed and collectively accounted for 61% DF; when combined with the fipronil DF, fipronil and its degradates had an aggregate DF of 98%. Bifenthrin and fipronil both exceeded their lowest USEPA aquatic benchmarks in 34% of all detections. There were no benchmark exceedances for fipronil degradates, yet fipronil sulfone had a 32% DF. Perhaps the biggest conclusion from this DPR study was the observed differences between outfall and stream monitoring and between wet and dry weather monitoring. Bifenthrin and fipronil detections at storm drain outfalls had 73-91% DFs compared to 23-37% in waterways. There was little observed difference between dry and wet events in storm drain outfalls for bifenthrin and fipronil, yet waterways that lacked bifenthrin detections during dry events demonstrated a large increase in bifenthrin (up to 70% DF) during rain events. Likewise, fipronil had 10% DF in waterways during dry events but increased to 50% DF during rain events. Fipronil degradates also exhibited differences in dry weather and storm event monitoring concentrations. While fipronil desulfinyl had equal detection during dry and wet monitoring events, fipronil amide and sulfone had a 36 and 34 percentage point increase in DF, respectively (Ensminger 2020).

In WY 2020: DPR collected water and sediment samples in the same Northern Californian counties targeted during WY 2019. Bifenthrin was the second most detected insecticide at 60% DF and fipronil with a 33% DF. Both bifenthrin and fipronil were observed to exceed their USEPA aquatic benchmarks in 53% and 27% of all detections, respectively. Three of fipronil's degradates were measured. Fipronil sulfone had a 29% DF and exceeded its benchmark 2% of the time. Fipronil amide was measured at 11% DF and fipronil desulfinyl had 7% DF. Fipronil degradates collectively amounted to 47% DF and when combined with fipronil reflect an aggregate 80% DF (Ensminger 2021).

WY 2017-WY 2020: Findings from the DPR studies generally corroborate the results garnered from SMCWPPP pesticides monitoring. For example, bifenthrin has been the most frequently detected pesticide in samples collected by SMCWPPP from WYs 2014 through WY 2022, and the second most detected insecticide in DPR samples. However, although fipronil and its degradates were frequently detected during the DPR studies, they were seldom found at detectable concentrations in SMCWPPP samples.

3.5.2 SPoT Monitoring Program

The SPoT Monitoring Program conducts annual dry season monitoring (subject to funding constraints) of sediments collected from a statewide network of large rivers. The goal of the SPoT Program is to investigate long-term trends in water quality. Sites are targeted in bottom-of-the-watershed locations with slow water flow and appropriate micromorphology to allow deposition and accumulation of sediments, including a station near the mouth of San Mateo Creek (Figure 3.1). In most years, sediments are analyzed for toxicity, pesticides, metals, polychlorinated biphenyls (PCBs), mercury, and organic pollutants (Phillips et al. 2014). The most recent technical report prepared by SPoT program staff was published in 2020 and describes ten-year trends from the initiation of the program in 2008 through 2017 (Phillips et al. 2020).

Toxicity testing was conducted by SPoT in sediment samples collected from San Mateo Creek using indicator organisms *H. azteca*, which is sensitive to pyrethroids, and *C. dilutus*, added in 2015 to assess neonicotinoid and fipronil impacts. Toxicity samples were evaluated using the TST statistical approach (Phillips et al. 2020).

Acute and chronic toxicity to *H. azteca* has been observed; however, the percent effect was less than 20%. Furthermore, there is a statistically significant decreasing trend in acute *H. azteca* toxicity in San Mateo Creek. Neither acute nor chronic *C. dilutus* toxicity have been observed since monitoring for this organism began in 2015. The SPoT findings are consistent with the SMCWPPP toxicity dataset summarized in Table 2.2.

The SPoT sediment chemistry results from San Mateo Creek do not show a statistically significant trend in sum-of-pyrethroid concentrations but do show a decreasing trend in sum-of-fipronil-and-its-degradates concentrations over the 2008 – 2017 dataset reviewed by Philips et al. (2020). A review of SPoT data from 2008 to 2020 downloaded from CEDEN suggests the following:

- **Pyrethroids.** Pyrethroid concentrations in San Mateo Creek peaked in 2011 (88.2 ng/g). This concentration was driven by a relatively high permethrin concentration that year (58 ng/g). In other years, the individual pyrethroid with the highest was bifenthrin, although permethrin was measured at roughly double (9.3 ng/g) the concentration of bifenthrin in 2018.
- **Fipronil.** Fipronil has been detected three times (2014, 2019, and 2020) in the years it was monitored (2013-2018). Three of its degradates (fipronil desulfinyl, fipronil sulfide, and fipronil sulfone) have been found at increasingly measurable concentrations more recently from 2017-2020, suggesting a consistent degradation of fipronil.

4.0 Conclusions and Recommendations

This section presents conclusions and recommendations from review of the WY 2022 Pesticides & Toxicity Monitoring data that were generated in compliance with provision C.8.g. of the MRP and which are presented in the preceding chapters of this report.

All monitoring and data validation were conducted using methods consistent with the BAMSC RMC QAPP (BASMAA 2020) and SOPs (BASMAA 2016). Recommendations for future monitoring are described in Section 4.3.

4.1 Conclusions

Toxicity testing of water and sediment samples and sediment chemistry monitoring, collectively referred to as pesticides and toxicity monitoring, was conducted during WY 2022 in compliance with provision C.8.g. of the MRP. Samples were collected from a novel site on Pescadero Creek to broaden the program's spatial representation of urban (i.e., bottom of watershed locations) creeks.

4.1.1 Data Evaluation Summary

Five toxicity test species are analyzed in water samples and two test species in sediment samples. The test organism *H. azteca*, required for water and sediment samples is known to be sensitive to pyrethroid pesticides and the test organism *C. dilutus*, is known to be sensitive to neonicotinoids. A two-tiered approach is applied to assess toxicity. First, organism responses from ambient samples are compared to responses from appropriate laboratory control samples using a statistical comparison. This is followed by a comparison to a "threshold value" or "Percent Effect" that indicates the magnitude of the difference in response. If the MRP 3.0 threshold of 50 Percent Effect is exceeded, a follow-up sample is collected.

Sediment chemistry data for metals, PAHs, and legacy pesticides (MRP 1.0 only) are compared to Threshold Effect Concentrations (TECs) and Probable Effect Concentrations (PECs) published by MacDonald et al. (2000). Most samples in San Mateo County have chromium and nickel concentrations that exceed the more conservative TEC and many exceed the PEC. These metals are naturally occurring in the serpentine formations that underly mountains and hills in the region, and therefore are not prioritized for follow-up management actions. Sediment chemistry data for pyrethroid and fipronil pesticides are compared to TOC-normalized LC50s, calculated as Toxic Unit (TU) equivalents.

Under MRP 1.0 (WY 2014 and WY 2015), pesticides and toxicity monitoring stations were selected from the list of bioassessment stations surveyed those years. Under MRP 2.0 (WY 2016 – WY 2021), bottom-of-the-watershed stations in different creeks were monitored each year with the goal of eventually developing a geographically diverse dataset. The MRP 2.0 method of selecting monitoring sites will continue for MRP 3.0 monitoring efforts.

4.1.2 WY 2022 Results

In WY 2022, SMCWPPP conducted dry season pesticides and toxicity monitoring at one station on Pescadero Creek at the Stage Road bridge. Statistically significant toxicity to any of the analyzed test organisms was not observed. Pesticide concentrations in the WY 2022 Pescadero Creek sediment sample were all very low, with all values reported below the method detection limit. Nickel was the only analyte from the creek sediment chemistry sample with a TEC quotient ≥ 1.0, and was likely the result naturally occurring nickel deposits originating from geologic features common in the region. These results did not show any evidence that pesticides are causing impairments to aquatic life in Pescadero Creek.

In compliance with provision C.9 of the MRP, SMCWPPP permittees are implementing pesticide toxicity control programs that focus on source control and pollution prevention measures. The control measure programs include the implementation of integrated pest management (IPM) policies/ordinances, public education and outreach programs, pesticide disposal programs, and sustainable landscaping requirements for new and redevelopment projects. California's Pesticide Use Reporting Program (PUR) contains extensive data for nearly all types of registered pesticides and their associated applications. Ongoing evaluations of pesticides and their uses through PUR inform DPR, Permittees, and the public about potential emerging trends with registered pesticide usage. These efforts will eventually be supplemented by the statewide Urban Pesticides Amendments (UPAs) which will seek to improve considerations of surface water quality during the registration process overseen by state and federal pesticide regulatory authorities such as DPR and USEPA. The anticipated result of the UPAs will be reduction in pyrethroids and other pesticides in urban stormwater runoff and the eventual elimination of pesticide-related toxicity in local urban creeks. The UPAs would also likely establish a statewide monitoring program that may substitute for pesticides and toxicity monitoring requirements in MS4 permits, such as the MRP. The goal of this statewide coordinated monitoring program is to generate useful data at minimal cost and standardize information at the statewide level to support the objectives of the UPAs. At this time, the mechanism for implementing the statewide monitoring program is uncertain, but will likely be developed over the next few years.

4.1.3 WY 2012 – WY 2022 Data Summary

Toxicity and chemistry data from WY 2012 through 2022 were reviewed for overall findings and evidence of trends. These data provide a reference to inform management decisions regarding water quality improvement in San Mateo County watersheds and may inform planning of future monitoring in the area.

Toxicity. Overall, there were 25 test results indicating significant toxicity, but with a Percent Effect that did not exceed the MRP trigger thresholds. A majority of these toxicity results were found in water samples and were associated with either *C. dubia* reproduction (ten samples), a chronic toxicity endpoint, or *H. azteca* survival (eight samples), an acute toxicity endpoint. Seven of the eight water samples with toxicity to *H. azteca* were collected during wet weather sampling events, suggesting that stormwater runoff is affecting *H. azteca*. The water samples with toxicity to *C. dubia* were more evenly dispersed between wet and dry season sampling events. It is possible that the chronic *C. dubia* toxicity observed in San Mateo water samples are false positives resulting from inconsistencies in QA procedures used by the laboratory. Statewide, there have been other reports of unexplained chronic *C. dubia* toxicity, and the State Water Board is currently carrying out a special study to examine the issue.

Sediment Chemistry. Between WY 2012 and 2022, PEC quotients calculated for the SMCWPPP sediment chemistry dataset were not ≥ 1.0 for analytes other than chromium and nickel. Excluding these naturally occurring metals, four samples had TEC quotients ≥ 1.0, the more conservative of the two evaluation criteria. These included legacy insecticide DDT compounds measured during MRP 1.0, individual PAHs in in WYs 2014 and 2015, copper in WYs 2012, 2013, and 2019, and zinc in WY 2019. Overall, detection frequencies for bifenthrin and fipronil were on par with results from the DPR Northern California study (Ensminger 2021) and *H. azteca* toxicity responses were similar to SPoT monitoring in San Mateo Creek (Phillips et al. 2020).

4.2 Recommendations

The following recommendations are based on findings from eleven years (WY 2012 through WY 2022) of Pesticides & Toxicity monitoring conducted by SMCWPPP, as well as reflections on other monitoring, data analysis, and policy development projects being conducted in the region and statewide.

- SMCWPPP will coordinate with the RMC to complete the MRP 3.0 wet weather Pesticides & Toxicity Monitoring requirements in WY 2023. SMCWPPP will collect two of the required ten regional samples. One sample will be collected from a new station on Colma Creek downstream of the newly constructed regional stormwater capture facility at Orange Memorial Park. The second sample will be collected at the SPoT monitoring station on San Mateo Creek to provide wet weather data for comparison with the dry season data collected through the SPoT program.
- Pesticides and Toxicity Monitoring will be conducted during the dry season at a bottom-of-the-watershed station. In order to continue expanding the geographic extent of these data, a new station will be selected in WY 2023. If enough fine sediment is present, this station could be located at the Colma Creek wet weather station.

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ATTACHMENTS

Attachment 1

QA/QC Report

Urban Creeks Monitoring Report - Pesticides & Toxicity Monitoring

Quality Assurance/Quality Control Report

Water Year 2022

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San Mateo Countywide Water Pollution Prevention Program

March 31, 2023

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LIST OF ACRONYMS

BAMSC	Bay Area Municipal Stormwater Collaborative
BASMAA	Bay Area Stormwater Management Agencies Association
CDFW	California Department of Fish and Wildlife
DQO	Data Quality Objective
EDDs	Electronic data deliverables
KEI	Kinnetic Environmental, Inc.
LCS	Laboratory Control Sample
LCSD	Laboratory Control Sample Duplicate
MDL	Method Detection Limit
MQO	Measurement Quality Objective
MRP	Municipal Regional Permit
MS	Matrix Spike
MSD	Matrix Spike Duplicate
MV	Measured Value
ND	Non-detect
NIST	National Institute of Standards and Technology
NPDES	National Pollution Discharge Elimination System
NV	Native Value
PAH	Polycyclic Aromatic Hydrocarbon
PR	Percent Recovery
QA	Quality Assurance
QAPP	Quality Assurance Project Plan
QC	Quality Control
RL	Reporting Limit
RMC	Regional Monitoring Coalition
RPD	Relative Percent Difference
SAFIT	Southwest Association of Freshwater Invertebrate Taxonomists
SFRWQCB	San Francisco Regional Water Quality Control Board
SMCWPPP	San Mateo County Urban Pollution Prevention Program
SOP	Standard Operating Procedures
SV	Spike Value
SWAMP	Surface Water Ambient Monitoring Program
WY	Water Year

1. INTRODUCTION

In Water Year 2022 (WY 2022; October 1, 2021 through September 30, 2022), the San Mateo County Water Pollution Prevention Program (SMCWPPP or Program) conducted Pesticide & Toxicity Monitoring in compliance with Provision C.8.g of the National Pollutant Discharge Elimination System (NPDES) stormwater permit for Bay Area municipalities, referred to as the Municipal Regional Permit (MRP; SFBRWQCB 2022). The monitoring strategy includes local “targeted” monitoring as described in the Bay Area Stormwater Management Agencies Association (BASMAA[1]) Regional Monitoring Coalition (RMC) Creek Status and Long-Term Trends Monitoring Plan (BASMAA 2012). The Program implemented a comprehensive data quality assurance and quality control (QA/QC) program, covering all aspects of Pesticides & Toxicity monitoring. QA/QC for the data collected was performed according to procedures detailed in the BASMAA RMC Quality Assurance Project Plan (QAPP) (BASMAA 2020) and the BASMAA RMC Standard Operating Procedures (SOP; BASMAA 2016), SOP FS-13 (Standard Operating Procedures for QA/QC Data Review). The BASMAA RMC QAPP and SOP are based on the QA program developed by the California Surface Water Ambient Monitoring Program (SWAMP 2022).

Based on the QA/QC review, WY 2022 data met overall QA/QC objectives. Some additional data were flagged, but not rejected. Details are provided in the sections below.

1.1. Data Types Evaluated

During pesticide and toxicity monitoring (MRP Provision C.8.g), several data types were collected and evaluated for quality assurance and quality control. These data types include the following:

1. Water Toxicity (dry weather; MRP Provision C.8.g.i)
2. Sediment Toxicity (dry weather; MRP Provision C.8.g.ii)
3. Sediment Chemistry (dry weather; MRP Provision C.8.g.ii)

1.2. Laboratories

Laboratories that provided analytical and taxonomic identification support to SMCWPPP and the RMC were selected based on the demonstrated capability to adhere to specified protocols. Laboratories are certified and are as follows:

- Caltest Analytical Laboratory (chemistry)
- Pacific EcoRisk, Inc. (toxicity)

1.3. QA/QC Attributes

The RMC SOP and QAPP identify seven data quality attributes that are used to assess data QA/QC. They include (1) Representativeness, (2) Comparability, (3) Completeness, (4) Sensitivity, (5) Precision, (6) Accuracy, and (7) Contamination. These seven attributes are compared to Data Quality Objectives (DQOs), which were established to ensure that data collected are of adequate quality and sufficient for the intended uses. DQOs address both quantitative and qualitative assessment of the acceptability of data – representativeness and comparability are qualitative while completeness, sensitivity, precision, accuracy, and contamination are quantitative assessments.

Specific DQOs are based on Measurement Quality Objectives (MQOs) for each analyte. Chemical analysis relies on repeatable physical and chemical properties of target constituents to assess accuracy and precision.

[1] BASMAA was dissolved in January 2021 and was replaced by the Bay Area Municipal Stormwater Collaborative (BAMSC)

1.3.1. Representativeness

Data representativeness assesses whether the data were collected in a manner that is representative of actual conditions at each monitoring location. For this project, all samples and field measurements are assumed to be representative if they are performed according to protocols specified in the RMC QAPP and SOPs.

1.3.2. Comparability

The QA/QC officer ensures that the data may be reasonably compared to data from other programs producing similar types of data. For MRP C.8 monitoring, individual countywide stormwater programs try to maintain comparability within the RMC. The key measure of comparability for all RMC data is the California Surface Water Ambient Monitoring Program.

1.3.3. Completeness

Completeness is the degree to which all data were produced as planned; this covers both sample collection and analysis. For chemical data and field measurements, an overall completeness of greater than 90% is considered acceptable for RMC chemical data and field measurements.

1.3.4. Sensitivity

Sensitivity analysis determines whether the methods can identify and/or quantify results at low enough levels. For the chemical analyses in this project, sensitivity is considered to be adequate if the reporting limits (RLs) comply with the specifications in RMC QAPP Appendix E: RMC Target Method Reporting Limits.

1.3.5. Accuracy

Accuracy is assessed as the percent recovery of samples spiked with a known amount of a specific chemical constituent. Chemistry laboratories routinely analyze a series of spiked samples. The results of these analyses are reported by the laboratories and evaluated using the RMC Database QA/QC Testing Tool. Acceptable levels of accuracy are specified for chemical analytes and toxicity test parameters in RMC QAPP Appendix A: Measurement Quality Objectives for RMC Analytes.

1.3.6. Precision

Precision is nominally assessed as the degree to which replicate measurements agree and determined by calculation of the relative percent difference (RPD) between duplicate measurements. Chemistry laboratories routinely analyze a series of duplicate samples that are generated internally. The RMC QAPP also requires the collection and analysis of field duplicate samples at a rate of 5% of all samples for all parameters. The results of the duplicate analyses are reported by the laboratories and evaluated using RMC Database QA/QC Testing Tool. Results of the Tool are confirmed manually. Acceptable levels of precision are specified for chemical analytes and toxicity test parameters in RMC QAPP Appendix A: Measurement Quality Objectives for RMC Analytes.

1.3.7. Contamination

For chemical data, contamination is assessed as the presence of analytical constituents in blank samples, including laboratory, field, and equipment blanks.

2. METHODS

2.1. REPRESENTATIVENESS

To ensure representativeness, each member of the SMCWPPP field crew received and reviewed all applicable SOPs and the QAPP. As a result, each field crew member was knowledgeable of, and performed data collection according to the protocols in the RMC QAPP and SOPs, ensuring that all samples and field measurements are representative of conditions in San Mateo County urban creeks.

2.2. COMPARABILITY

SMCWPPP staff maintain close communication with other stormwater program staff to ensure comparable data collection across the region, including timing of sample collection and use of the same contract laboratories. Sub-contractors collecting samples and the laboratories performing analyses received copies of the RMC SOP and QAPP and have acknowledged reviewing the documents. Data collection and analysis by these parties adhered to the RMC protocols and was included in their operating contracts.

Following completion of the field and laboratory work, the field data sheets and laboratory reports were reviewed by the SMCWPPP Program Quality Assurance staff and were compared against the methods and protocols specified in the SOPs and QAPP. Specifically, staff checked for conformance with field and laboratory methods as specified in SOPs and QAPP, including sample collection and analytical methods, sample preservation, sample holding times, etc.

Electronic data deliverables (EDDs) were submitted to the San Francisco Regional Water Quality Control Board (SFRWQCB) in Microsoft Excel templates developed by SWAMP, to ensure data comparability with the SWAMP program. In addition, data entry followed SWAMP documentation specific to each data type, including the exclusion of qualitative values that do not appear on SWAMP's look up lists[2] such as field crew member names and site IDs. Completed templates were reviewed using SWAMP's online data checker[3], further ensuring SWAMP-comparability.

2.3. COMPLETENESS

2.3.1. Data Collection

All efforts were made to collect 100% of planned samples and follow-up samples as required by the MRP. Upon receipt of the toxicity results, program staff evaluate the need for a follow-up sample and plan accordingly.

2.3.2. Field Sheets

Following the completion of each sampling event, the local monitoring coordinator reviewed any field generated documents for completion, and any missing values were entered. Once field sheets were returned to the office or shared electronically, a SMCWPPP QA staff member reviewed the field sheets again and noted any missing data.

2.3.3. Laboratory Results

SCVURPPP QA staff review laboratory reports and EDDs to ensure all analytes and test organisms were included in the laboratory analysis and results.

[2] Look up lists available online at https://swamp.waterboards.ca.gov/swamp_checker/LookUpLists.aspx
[3] Checker available online at https://swamp.waterboards.ca.gov/swamp_checker/SWAMPUpload.aspx

2.4. SENSITIVITY

The reporting limits for chemical analytes were compared to the target reporting limits in Appendix E (RMC Target Method Reporting Limits) of the RMC QAPP. Results with reporting limits that exceeded the target reporting limit were flagged.

2.5. ACCURACY

For sediment chemistry (pesticides) analysis, Caltest evaluated and reported the percent recovery (PR) of laboratory control samples (LCS; in lieu of reference materials) and matrix spikes (MS), which were recalculated and compared to the applicable MQOs set by Appendix A (Measurement Quality Objectives for RMC Analytes) of the RMC QAPP MQOs. If a QA sample did not meet MQOs, all samples in that batch for that particular analyte were flagged.

For reference materials, percent recovery was calculated as:

PR = MV / EV x 100%

Where: MV = the measured value
EV = the expected (reference) value

For matrix spikes, percent recovery was calculated as:

PR = [(MV – NV) / SV] x 100%

Where: MV = the measured value of the spiked sample
NV = the native, unspiked result
SV = the spike concentration added

2.6. PRECISION

2.6.1. Laboratory Duplicates

Caltest evaluated and reported the RPD for laboratory duplicates, laboratory control sample duplicates (LCSD), and matrix spike duplicates (MSD). The RPDs for all duplicate samples were recalculated and compared to the applicable MQO set by Appendix A of the RMC QAPP. If a laboratory duplicate sample did not meet MQOs, all samples in that batch for that particular analyte were flagged.

2.6.2. Field Duplicates

The RMC QAPP requires collection and analysis of duplicate sediment chemistry and toxicity samples at a rate of 5% of total samples collected for the project. Responsibility for the collection of the field duplicate rotates each year amongst Alameda County Clean Water Program (ACCWP), Contra Costa Clean Water Program (CCCWP), Santa Clara Valley Urban Runoff Pollution Prevention Program (SCVURPPP), and SMCWPPP.

The sediment sample and field duplicate were collected together using the Sediment Scoop Method described in the RMC SOP, homogenized, and then distributed to two separate containers. For sediment chemistry field duplicates, the RPD was calculated for each analyte and compared to the MQOs (RPD < 25%) set by Tables 26-7 through 26-11 in Appendix A of the RMC QAPP. For sediment and water toxicity field duplicates, the RPD of the batch mean was calculated and compared to the recommended acceptable RPD (< 20%) set by Tables 26-12 and 26-13 in Appendix A. If the RPD of the field duplicates did not meet the MQO, the results were flagged.

The RPD is calculated as:

RPD = ABS ([X1-X2] / [(X1+X2) / 2])

Where: X1 = the first sample result
X2 = the duplicate sample result

2.7. Contamination

Blank samples were analyzed for contamination, and results were compared to MQOs set by Appendix A of the RMC QAPP. The RMC QAPP requires all blanks (laboratory, equipment, and field) to be less than the analyte reporting limits. If a blank sample did not meet this MQO, all samples in that batch for that analyte were flagged.

3. RESULTS

3.1. Overall Project Representativeness

The SMCWPPP staff and subcontractor field crew members were trained in SWAMP and RMC protocols and received significant supervision from the local monitoring coordinator and QA officer. As a result, pesticides and toxicity monitoring data are considered to be representative of conditions in San Mateo County Creeks.

3.2. Overall Project Comparability

SMCWPPP pesticides and toxicity monitoring data are considered to be comparable to other countywide stormwater agencies subject to the MRP and to SWAMP due to a shared QAPP and SOP, trainings, use of the same electronic data templates, and close communication.

3.3. Sediment Chemistry

The dry season sediment chemistry sample was collected by Kinnetic Environmental, Inc (KEI) in tandem with the dry season toxicity sample on July 12, 2022. Caltest analyzed samples for inorganic compounds, synthetic organic compounds, and grain size distribution. The laboratory conducted all QA/QC requirements as specified in the RMC QAPP and reported their findings to the RMC. Key sediment chemistry MQOs are listed in RMC QAPP Tables A-7 through A-11.

3.3.1. Completeness

The MRP requires a sediment chemistry sample to be collected at one location in San Mateo County each year. In WY 2022, SMCWPPP collected the sediment chemistry sample at one site and the laboratory reported 100% of the required analytes.

3.3.2. Sensitivity

For sediment chemistry analysis conducted in WY 2022, laboratory RLs were higher than RMC QAPP target RLs for metals, pyrethroid pesticides, fipronil and its degradates, and total organic carbon. A comparison of target and actual reporting limits for these parameters is shown in Table 1. Since RLs for an individual sample are dependent on the percent solids of that sample, it is likely that the amount of solids in the sample caused these exceedances. Additionally, the pyrethroid and fipronil samples required a dilution. As a result of this dilution, the RL for these analytes (1 ng/g) was greater than the target RL (0.33 ng/g) listed in the RMC QAPP. If dilutions had not been necessary, the analytical RLs would have met the target RL.

Table 1. Comparison of target and actual reporting limits (RLs) for sediment analytes where analytical reporting limits exceeded target limits.

Analyte	Target RL	Actual RL	Unit
Arsenic	0.3	0.51	mg/Kg
Cadmium	0.01	0.04	mg/Kg
Chromium	0.1	0.51	mg/Kg
Copper	0.01	0.2	mg/Kg
Lead	0.01	0.04	mg/Kg
Nickel	0.02	0.08	mg/Kg
Zinc	0.1	0.4	mg/Kg
Bifenthrin	0.33[a]	1 [b]	ng/g
Cyfluthrin	0.33 [a]	1 [b]	ng/g
Total Lambda-cyhalothrin	0.33 [a]	1 [b]	ng/g
Total Cypermethrin	0.33 [a]	1 [b]	ng/g
Total Deltamethrin	0.33 [a]	1 [b]	ng/g
Total Esfenvalerate/Fenvalerate	0.33 [a]	1 [b]	ng/g
Permethrin	0.33 [a]	1 [b]	ng/g
Fipronil	0.33 [a]	1 [b]	ng/g
Fipronil Desulfinyl	0.33 [a]	1 [b]	ng/g
Fipronil Sulfide	0.33 [a]	1 [b]	ng/g
Fipronil Sulfone	0.33 [a]	1 [b]	ng/g
Total Organic Carbon	0.01	0.074	% dw

[a] There is no appropriate SWAMP targets for pyrethroids or for fipronil and its degradates. For these analytes, the RMC target RLs are based on current lab capabilities.

[b] These samples were diluted, which raised the RL. If dilutions had not been necessary, the samples' RL would have been less than the target RL.

3.3.3. Accuracy

Inorganic Analytes

In the RMC QAPP, the PR MQO for LCS and MS samples is 75-125% for inorganic analytes. One of the chromium MS samples exceeded the MQO listed in the RMC QAPP. The result was flagged by a QA officer.

Synthetic Organic Compounds

The MQO specified in the RMC QAPP for the recovery of synthetic organic compounds in sediment is 50-150% for both LCS and MS samples. None of the LCS samples exceeded the RMC MQO range, but a MS/MSD pair for benzo(g,h,i)perylene was below the MQO range and total permethrin exceeded the MQO for both the MS and MSD. The constituents were flagged accordingly.

3.3.4. Precision

Inorganic Analytes

The RMC QAPP lists the maximum RPD for inorganic analytes (metals) as 25%. All MS/MSD pairs for metals were below this maximum threshold. The RMC QAPP does not require the analysis of LCS duplicates for inorganic compounds.

Laboratory duplicates were collected and analyzed for grain sizes and total organic carbon. All RPDs were below the MQO limits (25%) except for total organic carbon, and small and medium pebbles; the associated samples were flagged.

Synthetic Organic Compounds
The maximum RPD for synthetic organics listed in the sediment laboratory report ranges from 30 to 50% for most analytes. However, the RMC QAPP lists the MQO as < 25% RPD for most synthetic organics, < 35% for pyrethroids and fipronil, and < 40% for carbaryl. All MS/MSD pairs met their RPD MQO.

Field Duplicates
A sediment sample field duplicate was collected in San Mateo County on July 12, 2022 and evaluated for precision. The field duplicate sample and corresponding RPDs are shown in Table 2. Due to the variability in reporting limits, values less than the RL were not evaluated for RPD. The measured concentrations of many of the analytes from the original and duplicate samples were below the method detection limit and therefore reported as non-detect (ND). Three analytes had either a duplicate or original sample that was above the method detection limit (MDL) but below the RL (Detected but Not Quantified; EPA “J” flag), resulting in incalculable RPDs. Small pebbles (4 to <8 mm) and total organic carbon were flagged were due to exceeding their MQOs. This list is comparable to past years’ results.

Given the inherent variability associated with sediment sample field duplicates, the number of analytes with RPDs outside of the MQO limits is acceptable. The method used to collect sediment field duplicates provides more insight to laboratory precision than precision of field methods; however, the results do suggest that field methods are precise.

Table 2. Sediment chemistry duplicate field results for site 202-PESCA-11 collected on July 12, 2022 in San Mateo County. Data in highlighted rows exceed monitoring quality objectives in RMC QAPP.

Analyte		Unit	Original	Duplicate	RPD (%)	Exceeds MQO? (<25%)[a]
Grain Size Distribution	Clay: <0.0039 mm	%	7.32	7.14	2.49	No
	Silt: 0.0039 to <0.0625 mm	%	7.19	6.97	3.12	No
	Sand: V. Fine 0.0625 to <0.125 mm	%	6.74	7.53	11.07	No
	Sand: Fine 0.125 to <0.25 mm	%	16.03	14.7	8.66	No
	Sand: Medium 0.25 to <0.5 mm	%	40.04	41.01	2.39	No
	Sand: Coarse 0.5 to <1.0 mm	%	16.5	17.62	6.57	No
	Sand: V. Coarse 1.0 to <2.0 mm	%	6.17	5.02	20.55	No
	Granule: 2.0 to <4.0 mm	%	5.63	4.73	17.37	No
	Pebble: Small 4 to <8 mm	%	1.43	0.86	49.78	Yes
	Pebble: Medium 8 to <16 mm	%	ND	ND	NA	NA
	Pebble: Large 16 to <32 mm	%	ND	ND	NA	NA
	Pebble: V. Large 32 to <64 mm	%	ND	ND	NA	NA
Metals	Arsenic	mg/Kg dw	3	3.3	9.52	No
	Cadmium	mg/Kg dw	0.27	0.29	7.14	No
	Chromium	mg/Kg dw	14	15	6.9	No
	Copper	mg/Kg dw	8.8	9.5	7.65	No
	Lead	mg/Kg dw	3.7	3.5	5.56	No
	Nickel	mg/Kg dw	23	25	8.33	No
	Zinc	mg/Kg dw	38	43	12.35	No
	Total Organic Carbon	%	0.56	0.74	27.69	Yes
Pyrethroids (MQO <35%)	Bifenthrin	ng/g dw	ND	ND	NA	NA
	Cyfluthrin	ng/g dw	ND	ND	NA	NA
	Lambda-Cyhalothrin	ng/g dew	ND	ND	NA	NA
	Cypermethrin	ng/g dw	ND	ND	NA	NA

Table 2. Sediment chemistry duplicate field results for site 202-PESCA-11 collected on July 12, 2022 in San Mateo County. Data in highlighted rows exceed monitoring quality objectives in RMC QAPP.

Analyte		Unit	Original	Duplicate	RPD (%)	Exceeds MQO? (<25%)[a]
	Deltamethrin/Tralomethrin	ng/g dw	ND	J 0.29	NA	NA
	Esfenvalerate/Fenvalerate	ng/g dw	ND	ND	NA	NA
	Permethrin	ng/g dw	ND	ND	NA	NA
	Carbaryl	mg/Kg dw	ND	ND	NA	NA
	Fipronil	ng/g dw	ND	ND	NA	NA
Polycyclic Aromatic Hydrocarbons	Acenaphthene	ng/g dw	ND	ND	NA	NA
	Acenaphthylene	ng/g dw	ND	ND	NA	NA
	Anthracene	ng/g dw	ND	ND	NA	NA
	Benz(a)anthracene	ng/g dw	ND	ND	NA	NA
	Benzo(a)pyrene	ng/g dw	ND	ND	NA	NA
	Benzo(b)fluoranthene	ng/g dw	ND	ND	NA	NA
	Benzo(e)pyrene	ng/g dw	ND	ND	NA	NA
	Benzo(g,h,i)perylene	ng/g dw	ND	ND	NA	NA
	Benzo(k)fluoranthene	ng/g dw	ND	ND	NA	NA
	Biphenyl	ng/g dw	ND	ND	NA	NA
	Chrysene	ng/g dw	ND	ND	NA	NA
	Dibenz(a,h)anthracene	ng/g dw	ND	ND	NA	NA
	Dibenzothiophene	ng/g dw	ND	ND	NA	NA
	Dimethylnaphthalene, 2,6-	ng/g dw	ND	ND	NA	NA
	Fluoranthene	ng/g dw	ND	ND	NA	NA
	Fluorene	ng/g dw	ND	ND	NA	NA
	Indeno(1,2,3-c,d)pyrene	ng/g dw	ND	ND	NA	NA
	Methylnaphthalene, 1-	ng/g dw	ND	ND	NA	NA
	Methylnaphthalene, 2-	ng/g dw	J 1	ND	NA	NA
	Methylphenanthrene, 1-	ng/g dw	ND	ND	NA	NA
	Naphthalene	ng/g dw	ND	ND	NA	NA
	Perylene	ng/g dw	ND	ND	NA	NA
	Phenanthrene	ng/g dw	ND	J 3.1	NA	NA
	Pyrene	ng/g dw	ND	ND	NA	NA

[a] MQO for pyrethroids is <35%. In accordance with the RMC QAPP, if the native concentration of either sample is less than the reporting limit, the RPD is not applicable

J – Detected not quantified; results detected above the MDL but below RL

3.3.5. Contamination

The RMC QAPP requires all blanks (laboratory and field) to be less than the analyte reporting limits. All laboratory blanks for all inorganic and synthetic analytes were below their respective MDL, and thus no contamination was detected.

3.4. TOXICITY TESTING

Dry season water and sediment toxicity samples were collected by KEI concurrently with dry season sediment chemistry samples at one San Mateo County site on July 12, 2022. All toxicity tests were performed by Pacific EcoRisk. In accordance with the MRP, the water samples were analyzed for toxicity to five organisms (*Selenastrum capricornutum, Ceriodaphnia dubia, Pimephales promelas, Hyalella azteca, and Chironomus dilutus*) and the sediment samples were analyzed for toxicity to *Hyalella azteca* and *Chironomus dilutus.*

3.4.1. Completeness

The MRP requires the collection of dry season water and sediment toxicity samples at one site per year in San Mateo County. Pacific EcoRisk tested the required organisms for toxicity, and 100% of results were reported.

3.4.2. Sensitivity and Accuracy

Internal laboratory procedures that align with the RMC QAPP were performed and submitted to SMCWPPP. Four measures of quality control are assessed, including maintenance of acceptable test conditions, negative control testing, positive control (i.e., reference toxicant testing), and Concentration Response Relationship assessment. The laboratory data QC checks found that all conditions and responses were acceptable. A copy of the laboratory QC report is available upon request.

3.4.3. Precision

Field duplicates for water and sediment toxicity are not required by the RMC QAPP. Subsequently, precision could not be evaluated.

3.4.4. Contamination

There are no QA/QC procedures for contamination of toxicity samples, but staff followed applicable RMC SOPs to limit possible contamination of samples.

4. SUMMARY

In WY 2022, sample collection and analysis followed MRP and RMC QAPP requirements and no data were rejected. A summary of the QA/QC analysis is provided below.

- The chromium MS and permethrin MS and MSD samples were flagged due to their MS/MSDs exceeding the PR MQO. The MS sample for benzo(g,h,i)perylene was also flagged because it was found to be below the MQO range.

- Total organic carbon and small (4 to <8 mm) and medium pebbles (8 to <16 mm) were flagged due to the laboratory duplicate exceeding the RPD MQO.

- Small pebbles and total organic carbon were flagged for exceeding field duplicate MQOs.

5. REFERENCES

Bay Area Stormwater Management Agency Association (BASMAA). 2012. Regional Monitoring Coalition Final Creek Status and Long-Term Trends Monitoring Plan. Prepared By EOA, Inc. Oakland, CA. 23 pp.

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