RMP
REGIONAL MONITORING PROGRAM FOR WATER QUALITY IN SAN FRANCISCO BAY

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Current-Use Pesticides, Fragrance Ingredients, and Other Emerging Contaminants in San Francisco Bay Margin Sediment and Water

Prepared by:

Matthew Heberger, Rebecca Sutton, Nina Buzby, Jennifer Sun, Diana Lin, and Miguel Mendez
San Francisco Estuary Institute

Michelle Hladik, James Orlando, and Corey Sanders
U.S. Geological Survey, California Water Science Center

Edward T. Furlong
U.S. Geological Survey, National Water Quality Laboratory

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U.S. Geological Survey, California Water Science Center

Edward T. Furlong
U.S. Geological Survey, National Water Quality Laboratory

San Francisco Estuary Institute
Richmond, CA
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Acronyms and Abbreviations

CAS	Chemical Abstracts Service
CASRN	Chemical Abstracts Service Registry Number
CAWSC	USGS California Water Science Center
CD3	Contaminant Data, Display and Download Tool
CEC	Contaminant of emerging concern
CEDEN	California Environmental Data Exchange Network
CGA	Chlorogenic acid
CHN	Carbon Hydrogen Nitrogen
CRM	Certified reference material
CUP	Current-use pesticide
DDE	Dichlorodiphenyldichloroethylene, a chemical that results from the breakdown of DDT
DDT	Dichlorodiphenyltrichloroethane, a legacy pesticide
DEET	N,N-Diethyl-meta-toluamide, or diethyltoluamide
DEHP	Bis(2-ethylhexyl) phthalate
DEP	Diethyl phthalate
DPR	California Department of Pesticide Regulation
dw	Dry weight
ECHA	European Chemicals Agency
EC_{10}	Effect concentration where 10% of a population exhibit a response
EC_{50}	Median effective concentration, or effect concentration where 50% of a population exhibit a response
f_{OC}	fraction of the sediment that is organic carbon, expressed as a percentage or unitless ratio
GC-MS	Gas chromatography-mass spectrometry
HHCB	Galaxolide (HHCB is an abbreviation of the chemical name 1,3,4,6,7,8-hexahydro-4,6,6,7,8,8,-hexamethyl-cyclopenta[g]benzopyran)
HLB	Hydrophobic Lipophilic Balance
IP	A quality assurance flag, indicating an analyte was detected in a field or lab blank
K_{ow}	Octanol-Water partition coefficient
LC_{50}	Lethal concentration that kills 50% of a population of organisms
LC-MS/MS	Liquid chromatography-tandem mass spectrometry
LEB	Likely effect benchmark
LOEC	Lowest-observed-effect concentration
MDL	Method detection limit
MGD	Million gallons per day
MTL	Monitoring trigger level
ND	Non-detect
NOA	(2-Naphthalenyloxy)acetic acid

NOEC	No observed effect concentration
NWQA	National Water Quality Assessment
NWQL	National Water Quality Laboratory, a USGS lab in Denver
OC	Organic carbon
OCRL	Organic Chemistry Research Laboratory, a USGS lab in Sacramento
OPE	Organophosphate ester
ORP	Oxygen reduction potential
PAH	Polycyclic aromatic hydrocarbon
PBDE	Polybrominated diphenyl ethers
PCB	Polychlorinated biphenyl
PCS	Permit compliance system
PNEC	Predicted no-effect concentration
POTW	Publicly-owned treatment works
PUR	Pesticide Use Reporting database, maintained by the California Department of Pesticide Regulation
QA	Quality assurance
QAPP	Quality Assurance Project Plan
QC	Quality control
RMP	Regional Monitoring Program for Water Quality in San Francisco Bay
RSD	Relative standard deviation
SAP	Sampling and analysis plan
SFEI	San Francisco Estuary Institute
SOSL	Southern sloughs (southern portion of San Francisco Bay)
SRM	Standard reference material
SURF	Surface Water Database, maintained by the California Department of Pesticide Regulation
TEB	Threshold effect benchmark
TOC	Total organic carbon
TRC	Technical Review Committee
USGS	U.S. Geological Survey
USEPA	U.S. Environmental Protection Agency
WHO	World Health Organization
WWTP	Wastewater treatment plant

Executive Summary

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has recently focused attention on better characterization of contaminants in nearshore "margin" areas of San Francisco Bay. The margins of the Lower South Bay are mudflats and shallow regions that receive direct discharges of stormwater and wastewater; as a result, they may have higher levels of urban contaminants than the open Bay. In the summer of 2017, the RMP collected samples of margin sediment in the South and Lower South Bay for analysis of legacy contaminants. The study described here leveraged that sampling effort by adding monitoring of sediment and water for two additional sets of emerging contaminants: 1) current-use pesticides; and 2) fragrance ingredients including the polycyclic musk galaxolide, as well as a range of other commonly detected emerging contaminants linked to toxicity concerns such as endocrine disruption.

A number of current-use pesticides were observed in margin samples. Bifenthrin, a current-use pesticide commonly detected in freshwater sediments at concentrations associated with aquatic invertebrate toxicity, was present in 3 of 12 sites at concentrations ranging from 1.3 to 1.7 µg/kg dry weight (dw). Eighteen pesticides were detected in filtered water samples, and none were detected in suspended sediment. Three of these pesticides—carbendazim, fipronil, and imidacloprid—were detected in some samples at concentrations greater than U.S. Environmental Protection Agency (USEPA) aquatic life benchmarks for freshwater settings.

Among fragrance ingredients and other emerging contaminants, a total of 16 compounds were detected in bed sediment, with five compounds detected in at least half of the samples. Four compounds were detected at concentrations comparable to or greater than available ecotoxicology thresholds, including the fragrance ingredients indole and camphor, as well as 4-methylphenol and 4-n-nonylphenol. A total of 18 distinct compounds were detected in water samples, with one, an organophosphate ester (OPE) known as tris(1,3-dichloroisopropyl) phosphate or TDCPP, exceeding a protective ecotoxicity threshold.

Evaluation of the results for individual contaminants relative to available toxicity thresholds generally supported existing classifications within the RMP's Tiered Risk-based Framework for emerging contaminants. Among pesticides, findings were consistent with fipronil and imidacloprid as Moderate Concerns for the Bay, pyrethroids as Low Concern for the Bay (this class is considered a High Concern in tributaries), and other current-use pesticides as Possible Concerns for the Bay. Fragrance ingredients were generally found at levels indicative of minimal or Low Concern. One exception, indole, a fragrance ingredient that is also produced naturally and used as a fecal indicator, is considered a Possible Concern for the Bay. Another emerging contaminant with natural and anthropogenic sources, 4-methylphenol, may also be considered a Possible Concern. Detections of TDCPP and other OPEs, used as flame retardants and plastic additives, were consistent with classification of this class as a Moderate Concern for the Bay. Likewise, detections of 4-n-nonylphenol were consistent with the current designation of alkylphenols and alkylphenol ethoxylates as a Moderate Concern for the Bay.

Periodic monitoring of current-use pesticides and fragrance ingredients is recommended for the future, because many of these contaminants are derived from consumer products that may be used in increasing quantities as the Bay Area population continues to undergo rapid growth, and because a number of them are toxic to aquatic life.

Introduction

The Regional Monitoring Program for Water Quality in San Francisco Bay (RMP) has recently focused attention on characterizing contaminants in nearshore "margin" areas of San Francisco Bay. The margins are intertidal, less-accessible (to boats) regions that have not been previously included in the study design for Status and Trends monitoring (Figure 1). The margins—consisting of mudflats and adjacent shallow areas—are important habitats for fish, waterfowl, and other wildlife that may be exposed to contaminants.

The margins receive direct discharges of stormwater and, in some locations, wastewater, and may be more contaminated by some types of urban pollution than the open Bay (Yee et al. 2018; 2019). The margins are also more likely to be a depositional sediment environment relative to the open Bay, so sediment-bound contaminants may build up in these areas. For example, a 2018 RMP study of Central Bay margins found that the margins, which account for only 5% of the area of the Central Bay, contained about 20% of the PCB mass (Yee et al. 2018).

The water in the southern portion of the Bay experiences longer residence times and less tidal flushing by seawater relative to other embayments, and therefore contaminants in water and sediment may pose a relatively greater risk to wildlife. In the summer of 2017, the RMP collected samples of margin sediment in the South Bay for analysis of legacy contaminants. The study described here leveraged that sampling effort by adding monitoring for two additional sets of emerging contaminants in margin sediment and water.

The first class of emerging contaminants analyzed was current-use pesticides. Pesticide analyses can inform Bay water quality managers as well as the California Department of Pesticides Regulation (DPR). Fipronil, a phenylpyrazole insecticide used to control ants, fleas, and termites, is considered an emerging contaminant of "Moderate Concern" for the Bay within the RMP's Tiered Risk-based Framework for emerging contaminants (Sutton et al. 2017). Fipronil degradates have been detected in Bay sediments at levels comparable to toxicity thresholds. More recently, RMP monitoring of imidacloprid in Bay water has provided support for classification of this widely used neonicotinoid insecticide as a Moderate Concern for the Bay as well (Buzby, Lin, and Sutton in prep.).

In contrast, another class of common insecticides, pyrethroids, are considered "Low Concern" for the Bay. Previous RMP monitoring of several pyrethroids in Bay sediment found concentrations well below levels of concern (Sutton et al. 2017). Pyrethroids have been found in sediments in Bay Area creeks (Ensminger et al. 2013) and in wastewater effluent, although removal by secondary wastewater treatment may be as high as 90% (Weston, Ramil, and Lydy 2013).

There are little to no monitoring data for many other current-use pesticides in the Bay. As a result, this class of contaminants (all current-use pesticides other than fipronil and pyrethroids) has been classified as a "Possible Concern" for the Bay in the RMP's Tiered Risk-based Framework, indicating uncertainty as to the presence and potential for impacts (Sutton et al. 2017).

The second class of emerging contaminants analyzed was fragrance ingredients, including galaxolide, and other emerging contaminants linked to toxicity concerns such as endocrine disruption. A driver for this study was the lack of Bay data on presence and levels of widely used fragrance ingredients. Fragrances are complex chemical mixtures often added to personal care and cleaning products that are typically disposed of down the drain. Fragrance ingredients may therefore make their way through wastewater treatment plants and into receiving waters.
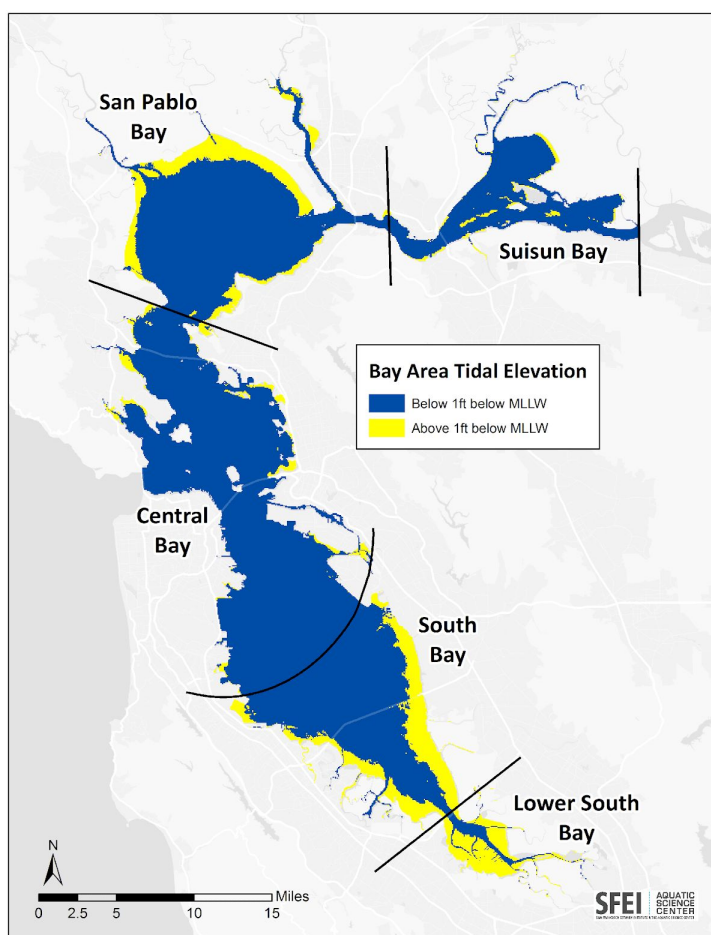
Figure 1. San Francisco Bay regions, with margins in yellow.

Of particular concern among fragrance ingredients is the polycyclic musk galaxolide.[1] A study that evaluated the impacts of subchronic exposure on larval development of the marine copepod *Nitocra*

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[1] Galaxolide is also referred to as HHCB or
1,3,4,6,7,8-hexahydro-4,6,6,7,8,8,-hexamethyl-cyclopenta[g]benzopyran.

spinipes established a no observed effect concentration (NOEC) of 7,000 nanograms per liter (ng/L) (Breitholtz, Wollenberger, and Dinan 2003). Based on this study, a monitoring trigger level (MTL) of 70 ng/L was established for California estuarine waters (P. D. Anderson et al. 2012).

Monitoring of galaxolide and other common fragrance ingredients in the Bay informs Bay water quality managers. This limited screening effort is not intended to provide a definitive characterization, but rather a preliminary evaluation of occurrence and potential concerns associated with both current-use pesticides and fragrance ingredients like galaxolide in the Bay.

Methods
Selection of Target Analytes and Analytical Laboratories

Current-Use Pesticides

Target analytes included several current-use pesticides that were identified primarily using DPR's Surface Water Monitoring Prioritization Model (Luo et al. 2014; 2013; Luo and Deng 2015), a watershed-specific pesticide prioritization algorithm that uses pesticide application data from the State of California's Pesticide Use Reporting (PUR) database and pesticide toxicity benchmarks from USEPA. Because the PUR database does not include information on use of pesticides marketed to consumers, DPR has conducted marketplace surveys to assess relative availability of different active ingredients to supplement the model-based prioritization.

A synthesis of these exercises specific to the study area (the South and Lower South Bay region detailed below) suggested the need to monitor a number of current-use pesticides in margin sediment, including:

- eight pyrethroid insecticides (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, lambda-cyhalothrin, permethrin, tetramethrin);
- etofenprox (pyrethroid ether insecticide);
- fipronil (and degradates; insecticide);
- oxyfluorfen (herbicide);
- pendimethalin (herbicide); and
- pyriproxyfen (hormone mimic).

Pesticides identified as priorities for water monitoring included:

- five organophosphate insecticides (dichlorvos [DDVP], malathion, diazinon, naled, chlorpyrifos);
- eight pyrethroid insecticides (bifenthrin, cyfluthrin, cypermethrin, deltamethrin, esfenvalerate, fenpropathrin, lambda-cyhalothrin, permethrin);
- atrazine (herbicide);
- diquat dibromide (herbicide);
- diuron (herbicide);

- etofenprox (pyrethroid ether insecticide);
- fipronil (and degradates; insecticide);
- flumioxazin (herbicide);
- imidacloprid (insecticide);
- mancozeb (fungicide, target degradate ethylene thiourea);
- oxyfluorfen (herbicide);
- pendimethalin (herbicide);
- pyriproxyfen (hormone mimic); and
- sulfometuron-methyl (herbicide).

The USGS Organic Chemistry Research Laboratory (OCRL; Sacramento, California) has developed methods to analyze 139 pesticides and related compounds in sediment samples and 172 compounds in water samples (dissolved and particulate phases). The list of analytes (Table A1) includes the active ingredients in current-use and legacy insecticides, fungicides, and herbicides, in addition to pesticide degradates and other chemicals in pesticide formulations such as carriers and adjuvants.

The only compounds identified by the DPR monitoring prioritization model that were not included in the OCRL analyses were pyriproxyfen in bed sediment and diquat dibromide, ethylene thiourea (a degradate of mancozeb), flumioxazin, naled, and sulfometuron-methyl in water. Pyriproxyfen was analyzed in water samples (dissolved and particulate phases). Further, the insecticide naled breaks down quickly into DDVP (dichlorvos), which we analyzed in water.

Fragrance Ingredients and Other Emerging Contaminants

As described previously, the polycyclic musk galaxolide (or HHCB), a fragrance ingredient, has significant ecotoxicity concerns (Breitholtz, Wollenberger, and Dinan 2003). The USGS National Water Quality Laboratory (NWQL; Denver, Colorado) developed standardized methods to analyze sediment and water (total) for galaxolide and additional fragrance compounds, including the related polycyclic musk tonalide, as well as acetophenone, benzophenone, camphor, diethyl phthalate, indole, isoborneol, d-limonene (also a registered pesticide), menthol, skatole (or 3-methylindole), methyl salicylate, and triethyl citrate (IFRA 2016). These fragrance ingredients are among a suite of emerging contaminants identified due to their potential to cause endocrine disruption or other ecotoxicity concerns in aquatic ecosystems. Other contaminants included in the analyses were several pharmaceuticals, some industrial chemicals, polycyclic aromatic hydrocarbons (PAHs), and natural compounds such as cholesterol and the fecal indicator beta-3-coprostanol.

Analysis of Bay margin samples using this standard USGS method provided data to complement an ongoing USGS National Water Quality Assessment (NWQA) program study of northern and central California, part of a series of studies taking place in regions across the nation (https://txpub.usgs.gov/RSQA/). Because the scope of this federal monitoring effort focuses on freshwater streams and specifically excludes the Bay, the RMP helped fill this important data gap and will gain insights from independent USGS monitoring being conducted on Bay Area streams.

Geographic Setting and Site Selection

This study is focused on the South Bay. For purposes of this report, the southern portion of San Francisco Bay is collectively referred to as the "South Bay," and is made up of three regions (see [Figure 2](#)):

1) the Upper South Bay as described in (Yee et al. 2019), more commonly termed the South Bay in RMP reports;
2) the Lower South Bay; and
3) the Extreme Lower South Bay as described in (Yee et al. 2019), consisting of locations further south that have been previously referred to in RMP reports as the "Southern Sloughs" (sampling locations include the prefix "SOSL").

In this report, the southernmost portion of the Bay is described as the "Extreme Lower South Bay," to reflect the fact that samples from these sites are part of the Bay and not in narrow channels such as sloughs or creeks.

The South Bay is generally south of Bay Farm Island in the east and Coyote Point in the west. The drainage area to the South Bay is heavily urbanized. Shoreline cities include Hayward, Union City, Fremont, Milpitas, San Jose, Santa Clara, Mountain View, Palo Alto, Redwood City, and San Mateo.

Contaminants enter the Upper South, Lower South, and Extreme Lower South Bays via stormwater runoff from urban areas surrounding the Bay and via effluent discharged by municipal wastewater treatment plants ([Figure 2](#)). San José-Santa Clara, Sunnyvale, and Palo Alto wastewater treatment plants discharge treated effluent via shallow water outfalls in this part of the Bay. In general, wastewater treatment plants are designed to remove organic matter, other solids, and bacteria. They are not specifically designed to remove the wide array of organic compounds that are present in today's wastewater, such as pesticides or fragrance ingredients in personal care and cleaning products.
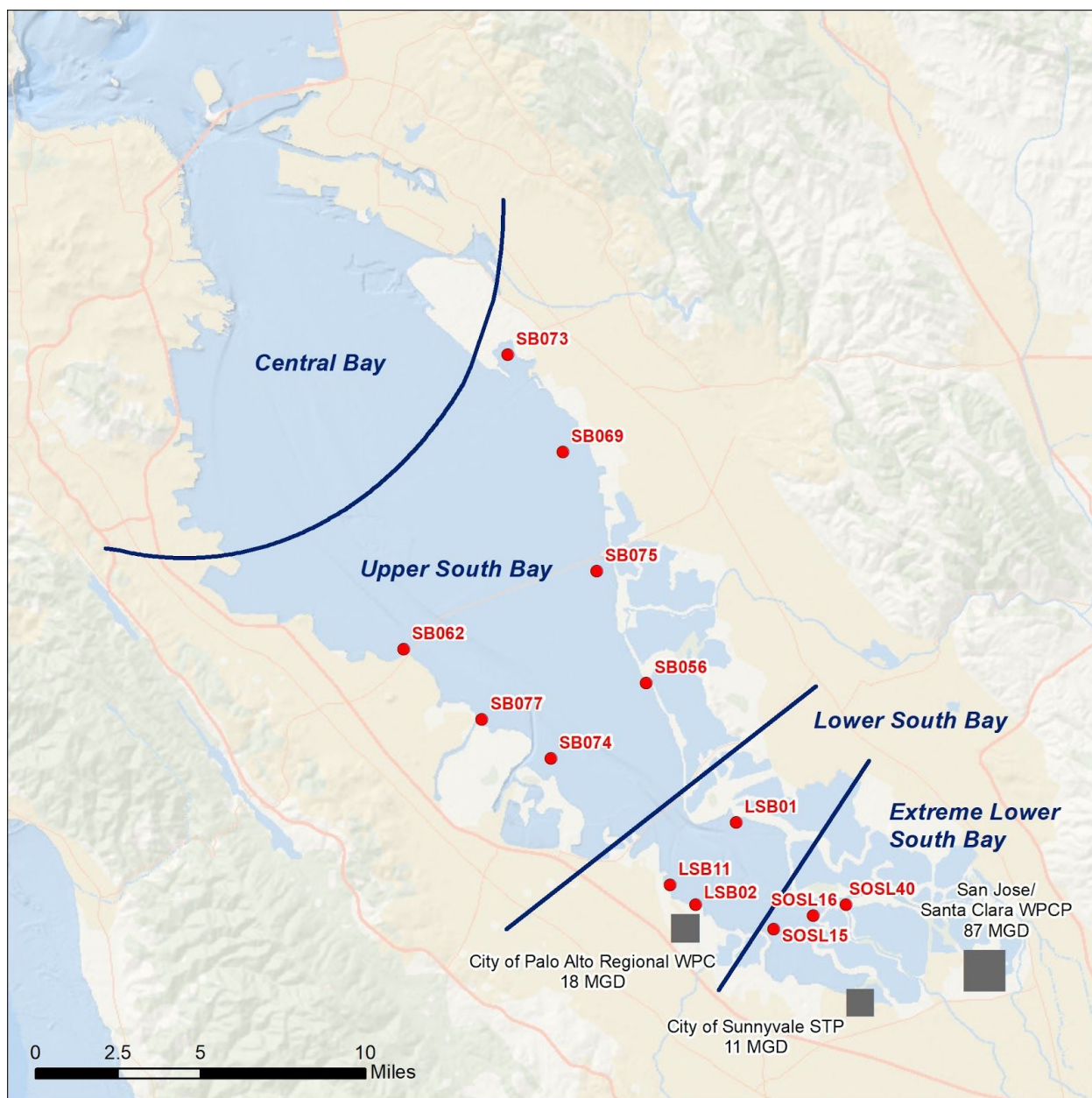
Figure 2. Bay margin sampling locations for pesticides, fragrance ingredients, and other emerging contaminants (red dots). Grey squares depict wastewater treatment plants that discharge to the margins. Annual average effluent flow is shown in million gallons per day (MGD).*

*Effluent flow data is from Bay Area Clean Water Agencies' *Nutrient Watershed Permit Annual Report* (2018), Table 4-1 on page 13.

Sampling locations were chosen in the "margins" of Upper South, Lower South, and Extreme Lower South Bays, defined by the RMP as areas one foot below mean lower low water (MLLW) up to the vegetated marsh edge (or constructed hardscape in some areas), roughly the mean higher high water (MHHW) line. Most of the margins are in the intertidal zone—areas exposed to the air at low tide and submerged at high tide—or in the littoral zone—submerged areas where light penetrates to the sediment surface.

This emerging contaminants study leveraged a larger study of legacy contaminants in Bay margin sediments. The larger study covered more sites and analyzed sediment physical characteristics, as well as legacy pollutants. Methods and rationale for the selection of margin sampling locations are described in more detail by Yee et al. (2019). Briefly, sampling locations were randomly selected using the Generalized Random-Tessellation Stratified (GRTS) method in the statistical software R (NPS 2017).

While the GRTS design is unbiased, meaning that every location in the target area has an equal probability of being sampled, the subset of sites for emerging contaminants analysis was specifically selected to be near stormwater and wastewater discharges (Figure 2; Table 1). Twelve sites were selected for analysis; however, the water sample containers for one site (LSB11) were damaged during shipment to the USGS NWQL, so an additional water sample was collected at a thirteenth site (SB073). Water samples from 11 of the 12 stations were analyzed for *both* current-use pesticides and fragrance ingredients and other emerging contaminants. The water sample from LSB11 was analyzed only for current-use pesticides (OCRL), and the water sample from SB073 was analyzed only for fragrance ingredients and other emerging contaminants (NWQL). The sediment sample from LSB11 survived shipping and was analyzed for the full suite of analytes.

Samples were collected during the dry summer months when wastewater is likely to have the largest impact on local water quality conditions, as there are minimal inflows from other, natural sources, such as local runoff or flow from rivers and creeks. Sampling in the dry summer months may result in an underestimate of contaminants from stormwater runoff, particularly for water-soluble or readily degradable contaminants.

Table 1. Planned and actual sampling locations.

Station Code	Embayment	Sample Date	Sample Time	Target Latitude	Target Longitude	Actual Latitude	Actual Longitude	Deviation from planned location (meters)
LSB01	Lower South Bay	2017-06-06	11:50	37.49878	-122.082	37.498767	-122.082	1.4
LSB02	Lower South Bay	2017-06-05	11:45	37.46282	-122.105	37.4629	-122.105033	9.3
LSB11* pesticides	Lower South Bay	2017-06-05	10:45	37.47164	-122.119	37.4716	-122.11915	14
SOSL15	Extreme Lower South Bay	2017-06-07	6:15	37.45178	-122.062	37.4518	-122.06195	5
SOSL16	Extreme Lower South Bay	2017-06-07	8:00	37.45758	-122.04	37.4576	-122.03995	4.9
SOSL40	Extreme Lower South Bay	2017-06-06	6:45	37.46212	-122.022	37.462083	-122.022217	20
SB056	Upper South Bay	2017-07-17	8:15	37.56052	-122.131	37.560516	-122.130917	7.3
SB062	Upper South Bay	2017-07-19	6:45	37.57639	-122.265	37.576433	-122.265	4.8
SB069	Upper South Bay	2017-07-18	10:10	37.66252	-122.176	37.6625	-122.175967	3.7
SB073* galaxolide & others, water only	Upper South Bay	2017-07-18	7:55	37.70561	-122.206	37.705683	-122.206017	8.2
SB074	Upper South Bay	2017-07-17	11:35	37.52771	-122.184	37.52775	-122.184	4.4
SB075	Upper South Bay	2017-07-19	12:35	37.60993	-122.158	37.60995	-122.15805	4.9
SB077	Upper South Bay	2017-07-19	14:15	37.54515	-122.222	37.545117	-122.222117	11

*Note: SB073 was not planned as a sampling site for this study. However, the sample bottle of water from LSB11 was broken in shipment to NWQL in Denver. Therefore, the project team collected an extra sample from SB073 to make up for this and bring the number of samples up to 12 for both analytical laboratories.

Sample Collection

Sediment and water samples were collected by boat at 13 sites in the Upper South, Lower South, and Extreme Lower South Bays in June and July 2017. The sampling plan is described in the 2017 RMP Margins Sediment Cruise Plan (Trowbridge et al. 2017). Further documentation is provided in a cruise report by Coastal Conservation & Research (2017) and the 2017 RMP Field Sampling Report (Shimabuku, Sun, and Trowbridge 2017).

All sampling and handling was conducted using clean techniques to avoid sample contamination during collection. All equipment used at different sampling stations was re-cleaned in the field between uses.

Sediment was collected using a stainless steel, Kynar (polymer)-covered modified Van Veen grab (0.1 m^2 area) penetrating 8 to 10 cm into the sediment. Sediment (top 5 cm) from at least three separate grabs per site was collected using an acetone-washed, stainless steel scoop (one per site) and placed into a 2-liter glass jar. All jars filled on the boat were placed on wet ice. Jars were picked up by SFEI staff each evening, chilled on wet ice overnight, and taken to SFEI the following day for homogenization using acetone-washed, stainless steel spoons and subsampling into glass sample containers. Sediment sample containers were frozen until overnight shipment to laboratories.

Water samples were collected in a 1-liter amber glass jar by submerging the closed jar under water about 0.1 meters, uncapping the jar to fill to the neck, and then re-capping the jar under water before pulling it out and onto the boat. Water samples were chilled to 4ºC and shipped overnight as soon as possible to laboratories.

Additional samples collected include field duplicates, field blanks, and samples to be used for matrix spikes and matrix spike duplicates. For the sediment field blank for pesticides, an open jar was placed on the boat console while sampling was conducted. For the sediment field blank for fragrance ingredients and other emerging contaminants, baked Ottawa sand provided by the USGS NWQL was used. Clean sand was handled with field equipment in the same way that typical samples were handled. For both types of sediment field blanks, jars were reopened at SFEI during sample homogenization. Field blanks for water were collected by pouring trace-clean water supplied by USGS NWQL directly into amber glass jars. In some cases field blanks, field duplicates, and material for matrix spikes and matrix spike duplicates were collected at alternate sites than specified in the original plan.

At each sampling location, field measurements, including sediment pH, ORP (Oxygen Reduction Potential or E_h measured in millivolts), color, composition (e.g., sand, mud), and anoxic transition depth were made, along with field observations for each site (e.g., wind speed, wave height, weather). In addition, latitude and longitude coordinates were recorded using a handheld GPS unit.

Laboratory Analyses

A brief overview of the analytical methods is provided below. In sum, the two labs analyzed 234 distinct compounds. Eight pesticides were analyzed by both laboratories (atrazine, carbaryl, chlorpyrifos, diazinon, dichlorvos, metalaxyl, metolachlor, and prometon), though method detection and reporting limits varied. None of the eight compounds analyzed by both labs were detected in study samples.

For the pesticide analyses at OCRL, water samples were filtered, and the dissolved and particulate fractions were analyzed separately. NQWL used methods for analyzing whole water and did not filter samples. Table 2 summarizes the number of compounds analyzed in each matrix by each laboratory.

Table 2. Number of distinct compounds analyzed by each lab and for each matrix.

	Whole water (unfiltered)	Water (filtered, dissolved fraction)	Suspended sediment (particulate fraction from filtered water)	Bed sediment	Total distinct compounds
OCRL Pesticides	-	172	139	118	**174**
NWQL Emerging Contaminants	68	-	-	56	**68**
Total distinct compounds	**68**	**172**	**139**	**169**	**234**

Current-Use Pesticides

The OCRL has developed multiple broad screening analyses for pesticides in sediment and water. The first method uses gas chromatography mass spectrometry (GC-MS) to analyze bed sediment as well as filtered water and suspended sediment (Hladik, Smalling, and Kuivila 2008; 2009; Hladik and McWayne 2012). Briefly, filtered water samples were subjected to solid-phase extraction (SPE) using an Oasis Hydrophobic Lipophilic Balance (HLB) cartridge with no additional cleanup steps. Sediment and particulate samples were extracted using an accelerated solvent extraction system, and the compounds of interest were separated from co-extracted matrix interferences (including sulfur) by passing the extracts through high performance liquid chromatography (HPLC) with gel-permeation chromatography (GPC), along with the use of either stacked graphitized carbon and alumina SPE cartridges or packed Florisil®. The sample extracts were stored at -20°C until analysis (up to 30 days). Chromatographic separation, detection, and quantification of the pesticides from the extracts were then accomplished via an Agilent Technologies 7890A GC coupled to an Agilent 5975C MS operated in electron ionization (EI) mode (instrument details in Hladik and McWayne 2012).

The second method uses liquid chromatography tandem mass spectrometry (LC-MS/MS) to analyze filtered water samples, or the dissolved fraction (Hladik and Calhoun 2012). Solid phase extraction is accomplished using an Oasis HLB cartridge. The sample extracts were stored at -20°C until analysis (up to 30 days). Chromatographic separation, detection, and quantification of the pesticides from the extracts were then performed via an Agilent 1260 LC coupled to a 6430 tandem MS operated in positive mode electrospray ionization (ESI+; instrument details in Hladik and Calhoun 2012).

Table A1 lists the pesticide analytes, methods, and matrices for compounds analyzed by OCRL. In total the OCRL lab analyzed:

- 172 compounds in (filtered) water samples;
- 139 analytes in suspended sediment (the particulate fraction filtered from water samples);
- 118 compounds in bed sediment.

In addition, OCRL analyzed the total organic carbon (TOC) in bed sediment, reported as the percent of the sample mass. This ancillary parameter is important because sediment ecotoxicity thresholds for contaminants are often reported in units of micrograms per gram of organic carbon (µg/g OC). TOC was analyzed by USEPA Method 440 (Zimmerman, Keefe, and Bashe 1997), and the method detection limit was 0.01%.

Galaxolide, Fragrances Ingredients, and Other Emerging Contaminants

The NWQL developed GC-MS methods for sediment and total water screenings of galaxolide and other emerging contaminants. Table A2 lists the analytes, methods, and matrices for compounds analyzed by NWQL.

An important caveat in broad screening methods like these is that, for some contaminants, the method detection and reporting limits will be higher than for a method specifically optimized for the individual contaminants. For example, the reporting limits for bisphenol A and triclosan in the NWQL total water screening method are 20 and 160 ng/L, respectively; methods targeted to those individual compounds can achieve reporting limits at least an order of magnitude lower. Compounds like these may be observed at levels below the NWQL reporting limits if more optimized methods are used.

The NWQL analyzed sediment samples for 56 compounds as described in USGS Techniques and Methods 5-B2 (Burkhardt et al. 2006). Sediment samples were extracted using a pressurized solvent extraction system. The compounds of interest were extracted from interfering matrix components by high-pressure water/isopropyl alcohol extraction, then isolated using disposable SPE cartridges containing chemically modified polystyrene-divinylbenzene resin. The cartridges were dried with nitrogen gas, and then sorbed compounds were eluted with methylene chloride (80%)-diethyl ether (20%) through a Florisil®/sodium sulfate SPE cartridge, and then analyzed. Compounds in sample extracts were determined using gas chromatography coupled to electron-impact ionization full-scan mass spectrometry (GC-MS) employing a single quadrupole mass analyzer. An Agilent Technologies

Model 5975 bench top GC-MS system was used for all analyses (instrument details in Burkhardt et al. 2006).

The NWQL analyzed water samples for 68 compounds as described in USGS Techniques and Methods 5-B4 (Zaugg, Smith, and Schroeder 2006). Whole-water samples were extracted using continuous liquid-liquid extractors and methylene chloride solvent, and then analyzed by GC-MS as with sediment (instrument details in Zaugg, Smith, and Schroeder 2006).

All samples collected for analysis at NWQL were extracted and preserved by freezing following the methods described above within 24 hours of arrival at OCRL prior to shipment on ice to NWQL.

Quality Assurance Methods

SFEI staff performed a quality assurance review of the dataset for completeness, accuracy, precision, and lack of contamination following methods described in the RMP Quality Assurance Project Plan (Yee et al. 2017). A summary of this review is provided in Appendix B. Data were flagged with a qualifying code if accuracy and precision did not meet RMP criteria. We did this by independently calculating reported precision (as relative percent difference, RPD, or relative standard deviation, RSD) for lab replicates, and percent recovery for samples of a known concentration. In some cases, records were already flagged by the reporting laboratory. Qualifiers added by SFEI or the laboratory indicate that there has been a deviation from the project's quality criteria and are meant to warn data users that certain records may be inaccurate or imprecise. Summary statistics were calculated excluding the results of field duplicates, as duplicates are quality assurance samples intended to evaluate the accuracy of the field samples.

To verify that contamination of samples had not occurred in sampling or lab analysis, we compared the results for blank samples (field and lab blanks) to method detection limits (MDL; OCRL) or reporting (quantitation) limits (RL; NWQL) provided by the laboratories. In cases where an analyte was detected in a blank, we compared the measured concentration in the blank sample to concentrations measured in field samples; RMP criteria specify censoring field sample measurements that are within three times the method blank level. However, for this project, all data were reportable, as we did not find serious violations with respect to accuracy, precision, or sample contamination that would lead to the rejection of data.

The dataset from the USGS analytical labs contains several results that are below the MDL (OCRL) or RL (NWQL). For example, in the water sample collected at LSB02 on June 5, 2017, the lab reported a concentration galaxolide of 10 ng/L while the RL is 20 ng/L. USGS scientists occasionally report results below the MDL or RL when they believe they have likely detected the compound in the sample. Nevertheless, the result is less certain, and a qualifier is attached to these values in publicly available databases (CD3 and CEDEN) to indicate that the result is estimated. For results below the MDL, the qualifying flag of "JDL" is used, and for results below the RL, the qualifying flags of "JA" or "J" are used to indicate that they are estimates, with uncertainty in their

quantification. This practice of listing values despite lack of certainty in their quantification is viewed by many chemists and statisticians as the best way of dealing with results below or near the detection or quantitation limit. If results below the MDL or RL are left unreported, it can result in bias if, for example, these observations are left out or substituted with an arbitrary value such as half the MDL or RL when calculating a mean. The project team chose to show results below the quantitation limit. In instances where results have a "J" flag or its equivalent, data users should interpret this as follows: "An estimated concentration for the compound was provided, but below the specified detection or reporting quantification limit. Any such amount shown should be considered an estimate."

Aquatic Toxicity Thresholds

To determine whether contaminants were present in concentrations that are ecologically relevant, i.e., those which may cause harm to aquatic biota, we compared observed concentrations with thresholds for aquatic toxicity gathered from several sources. The presence of a compound above a threshold is not necessarily evidence that harm is taking place, but rather it is a first step in a process for interpreting the data and evaluating relative ecological risk.

Sediment toxicity benchmarks for pesticides and degradates were obtained from recent work by USGS scientists (Nowell et al. 2016). This work contains two sets of thresholds:

> **Likely Effect Benchmark (LEB)** - pesticide concentration in whole sediment above which there is a high probability of adverse effects on benthic invertebrates; and

> **Threshold Effect Benchmark (TEB)** - concentration below which adverse effects to benthic invertebrates are unlikely.

These thresholds were determined for two species of freshwater invertebrates, *Hyalella azteca* (an amphipod) and *Chironomus dilutus* (midge larvae), and an "integrated benchmark" was calculated based on the lower of the two. These benchmarks were developed for freshwater environments; similar benchmarks for marine or estuarine environments are not available.

The benchmarks are reported in units of micrograms per gram of organic carbon (μg/g OC). The lab measurements for this study reported contaminants on a dry weight basis. The analytical results were converted to an organic carbon-normalized sediment concentration ($C_{sed\text{-}TOC}$) according to this equation:

$$C_{sed\text{-}TOC} = \frac{C_{sed\text{-}dw}}{f_{OC}}$$

where $C_{sed\text{-}dw}$ is the concentration of a compound in sediment on a dry weight basis (μg/g dw) and f_{OC} is the fraction of the sediment that is organic carbon, expressed as a percentage or unitless ratio.

To determine whether pesticides or their degradates in water may pose a threat to aquatic life, we compared observed concentrations to aquatic life benchmarks published by the USEPA's Office of Pesticide Programs (USEPA 2017). These comparisons should be interpreted with caution, however. The benchmarks published by USEPA were developed for freshwater environments; similar benchmarks for marine or estuarine environments are not available. Where aquatic life benchmarks were not available, we compared observed levels of contaminants with aquatic toxicity thresholds drawn from the scientific literature or developed by the European Chemicals Agency (ECHA).

For fragrance ingredients and other emerging contaminants in sediment and water, levels were compared to available marine predicted no effect concentrations (PNECs) from the literature and the ECHA. When PNEC values were not found, the lowest available concentration was used, such as a median effective concentration (EC_{50}) or the no observed effect concentration (NOEC). For example, for the disinfection byproduct bromoform, we compared observations against the EC_{50} for fish from a report by the Battelle Corporation's Marine Research Lab (Gibson et al. 1979). For the nicotine metabolite cotinine, we obtained a more recent PNEC calculated by French scientists (Gosset et al. 2017). These values are shown in Table 6.

For a limited number of compounds, water and sediment results could also be compared to monitoring trigger levels (MTLs) recommended by California's Ambient Ecosystems CECs Advisory Panel (B. Anderson et al. 2012; Dodder, Mehinto, and Maruya 2015), which are protective benchmarks based on potential ecological and human health risks. MTL exceedances can indicate a need for additional monitoring but do not necessarily indicate a toxicity concern.

Results and Discussion

Complete analytical results and ancillary data are publicly available via the Contaminant Data, Display and Download Tool (CD3, https://cd3.sfei.org/) and the California Environmental Data Exchange Network (CEDEN, http://ceden.org/). Key information for water quality managers is summarized below. See Appendix C for instructions on how to download the data from this study.

Water Quality Conditions

Samples were collected in June and July 2017, a time in which freshwater inflows to the Bay are at their minimum. Figure 3 shows the tide elevation in South San Francisco Bay, measured at NOAA tide station 9414523 in Redwood City. Red dots on Figure 3 show the tidal elevation at the time of sampling. Samples were collected during a variety of tidal conditions on June 5, 6, and 7 and on July 17, 18, and 19. June samples were collected during slack tide at higher low water. July samples were collected on the rising phase of the higher high tide when water is generally flowing toward the shore.
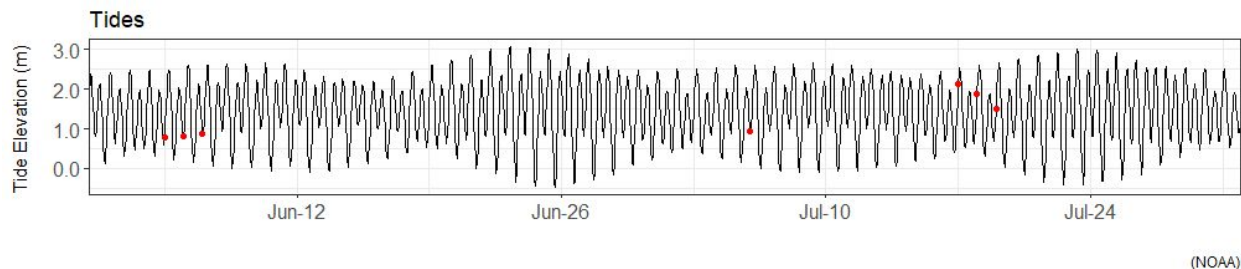
Figure 3. Tidal elevation during sampling events (red dots) in June and July 2017.

All sampling occurred during the summer dry period, with no measurable precipitation for two months prior to sampling (Figure 4). In June, the San Jose Santa Clara Regional Wastewater Facility discharges an average of 100 MGD to the Extreme Lower South Bay, with other nearby plants discharging smaller inflows (Figure 2).

During the June sampling events, salinity averaged between 18 to 20 parts per thousand (ppt) and in July between 22 to 24 ppt (Figure 4). This gives a rough indication of the source of water in the region. Pacific Ocean water has a salinity of about 35 ppt, while river water is generally less than 1 ppt. We can roughly estimate that in June, about 50 to 60% of the water is from the ocean, while the remaining water is from rivers and wastewater discharge. In July, South Bay water is closer to 60% to 70% ocean water. Salinity also varied tidally, with higher conductivity measured on the incoming tide as saltier seawater moved further into the South Bay, and lower conductivity during outgoing tides when fresher water is pulled out of the South Bay.
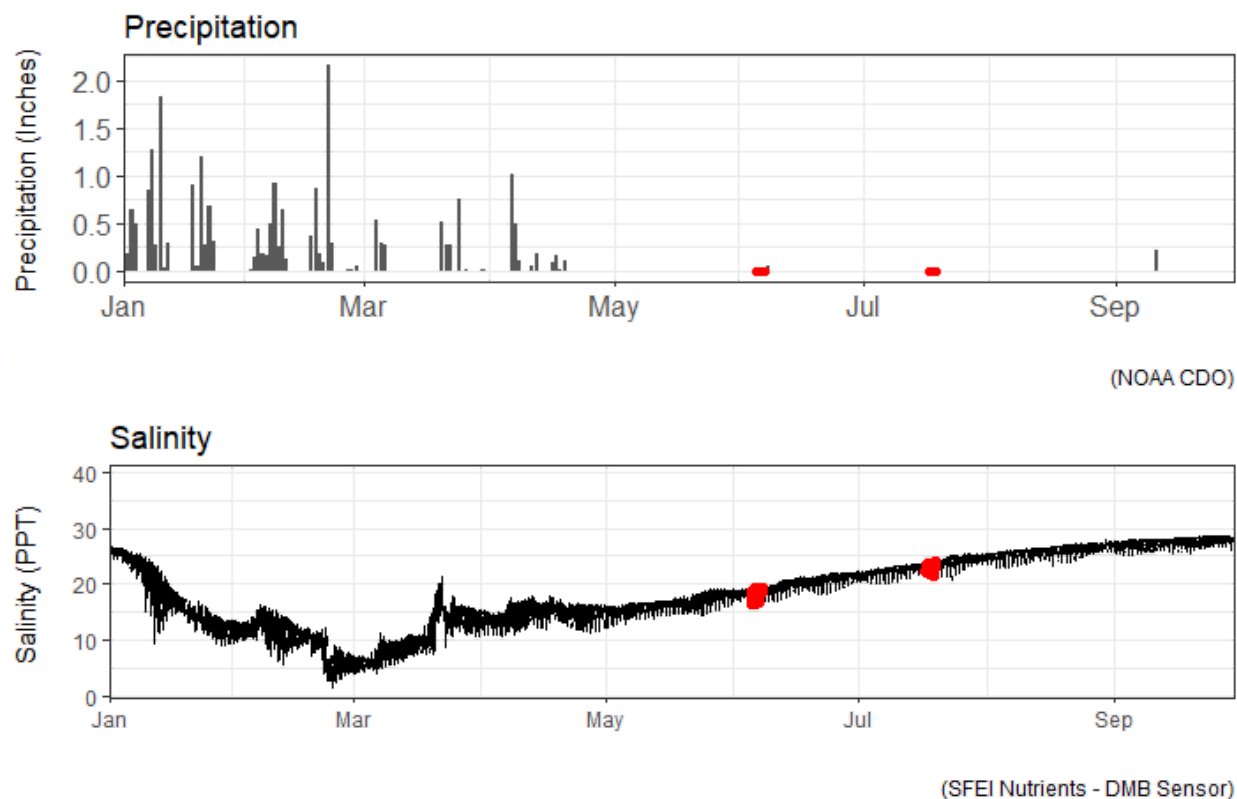
Figure 4. Hydrologic conditions during the sampling period: Precipitation (top) and salinity measured at the Dumbarton Bridge (bottom).

Daily precipitation totals as measured at NOAA weather station at San Francisco Airport, https://www.ncdc.noaa.gov/cdo-web/datasets/GHCND/stations/GHCND:USW00023234/detail

Salinity measured at SFEI sensor at the Dumbarton Bridge, https://www.enviz.org/nutviz/

Pesticides in Sediment

Bifenthrin was the only current-use pesticide detected in bed sediment samples (Table 3). This insecticide was present in the bed sediment at 3 of 12 sites, in concentrations ranging from 1.3 to 1.7 µg/kg dw. Expressed as a ratio of organic carbon in the sediment sample, bifenthrin concentrations ranged from 0.098 to 0.13 µg/g OC.

Bifenthrin is a pyrethroid insecticide that is widely used on crops and around homes to control a variety of insect pests. It has a low water solubility and therefore is more likely to be found in sediment. Bifenthrin is the most frequently detected pesticide in freshwater aquatic sediment in California (Ensminger et al. 2013) and is toxic to aquatic invertebrates at very low concentrations. The EC_{50} for bifenthrin for the invertebrate *Hyalella azteca* has been calculated at 3.3 ng/L (Weston

and Jackson 2009). Further, a study of urban creeks draining to northern San Francisco Bay linked bifenthrin in water samples with paralysis of the *Hyalella azteca* (Weston, Chen, and Lydy 2015).

Measurements of bifenthrin in South Bay margin bed sediment did not exceed ecotoxicology thresholds for sediment. The highest measured concentration of bifenthrin in bed sediment was 0.13 μg/g OC, just below the threshold effect benchmark (TEB) of 0.17 μg/g OC (Nowell et al. 2016). However, bifenthrin concentrations measured in the Bay margin sediment, on a dry-weight basis, ranged from 1.3 to 1.7 μg/kg dw, about 25 to 30 times greater than California's monitoring trigger level (MTL) of 0.052 μg/kg dw for bifenthrin in coastal embayment sediments (P. D. Anderson et al. 2012). MTL exceedances can indicate a need for additional monitoring, but do not necessarily indicate a toxicity concern.

Bifenthrin has been detected in sediment samples in other recent studies conducted in the Bay and California. Previous monitoring of open Bay sediment detected bifenthrin in 23 of 77 samples, with a maximum concentration of 1.0 μg/kg dw, slightly lower than the concentrations measured in this study (summarized in Klosterhaus, Yee, et al. 2013). In addition, recent monitoring of the Russian River found bifenthrin in bed sediment at a maximum concentration of 1.4 μg/kg dw (Maruya et al. 2018). This is similar to the maximum sediment concentration found in the South Bay margins of 1.7 μg/kg dw. In contrast, monitoring in southern California coastal sediments detected concentrations up to 65 μg/kg dw, with the highest concentrations reported near urban stormwater discharges (Lao et al. 2012; Maruya et al. 2016; Ensminger et al. 2013; Taylor et al. 2019).

Table 3. Pesticides and degradates detected in bed sediment in South and Lower South San Francisco Bay margins, summer 2017.

Pesticide or Degradate	CAS Number	Use	Number of Detections (n=12)	Detection Frequency (%)	Median Concentration (µg/kg dw)	Maximum Concentration (µg/kg dw)	Maximum Concentration (µg/g OC)	Likely Effect Benchmark, LEB* (µg/g OC)	Threshold Effect Benchmark, TEB* (µg/g OC)	Number of Samples Exceeding TEB (n=12)
Bifenthrin	82657-04-03	Insecticide	3	25%	<0.7	1.7	0.13	0.6	0.17	0
DDD(p,p')	72-54-8	DDT degradate	10	83%	1.9	5.1	0.39	200.	33.	0
DDE(p,p')	72-55-9	DDT degradate	12	100%	2.4	6.3	0.46	240.	66.	0
DDT(p,p')	50-29-3	Legacy Insecticide	10	83%	2.3	6.9	0.39	550.	55.	0

*Benchmarks from Nowell et al. 2016

Other pesticides and related compounds identified by the DPR monitoring prioritization model were not detected in the South Bay margin samples. While fipronil and its degradates have been observed in open Bay sediment (Sutton et al. 2017), they were not detected in the margin sediment samples. This lack of detection may be due to the higher method detection limits for fipronil and degradates in the present study. Broad screening methods for large numbers of analytes, such as the pesticide methods employed in this study, are not always able to achieve the lowest method detection limits for each individual analyte.

Unfortunately, we were not able to analyze for the presence of pyriproxyfen in bed sediment. This compound was not detected in water, but its low water solubility suggests it may accumulate in sediment. Pyriproxyfen mimics juvenile hormones in insects and is used to control a variety of pests. Pyriproxyfen is toxic to benthic organisms at the relatively low concentration of 0.07 μg/kg dw sediment (ECHA 2012). Therefore, future analyses of sediment in the Bay and Delta should strive to include this compound.

Legacy (not current-use) organochlorine pesticides were not the focus of this study, but the laboratory included results for DDT and its degradates as part of its schedule of pesticides analytes. The legacy pesticide DDT was found in 10 of 12 bed sediment samples, or at a detection frequency of 83%. Two DDT degradates, DDD(p,p') and DDE(p,p') were found in 83% and 100% of sediment samples, respectively. This is not a surprising result, as these organochlorine pesticides were once widely used and are highly persistent. While DDT has been banned for about 40 years, it has been consistently found in Bay sediment since then. A 1998 review of Bay sediment quality found that organochlorine pesticides "persist in soils that wash into the Bay, and are still commonly detected at elevated concentrations in sediments and tissue from throughout the estuary" (Hunt et al. 1998). More recent observations in bird eggs collected from San Francisco Bay nesting sites between 2002 and 2012 indicate DDT remains present in the region, with declining concentrations observed at some sites (Ross et al. 2016).

Pesticides in Water

Table 4 summarizes the results for those pesticides and pesticide degradates that were detected in South Bay margin water samples. Of the 172 pesticide analytes, 18 were detected in filtered water samples, and none were detected in suspended sediment. Ten analytes were detected in more than half of the samples. Below, we briefly discuss the noteworthy results for several individual analytes. Three analytes, carbendazim, fipronil, and imidacloprid, were detected at levels greater than USEPA aquatic life benchmarks.

Table 4. Pesticides and degradates detected in water in South and Lower South San Francisco Bay margins, summer 2017. Those in bold were detected at concentrations greater than benchmarks.

Pesticide or Degradate	CAS Number	Description	Method Detection Limit (ng/L)	Number of Detections (n=12)	Detection Frequency (%)	Median Concentration (ng/L)	Maximum Concentration (ng/L)	Lowest USEPA Aquatic Life Benchmark (ng/L)	Most Sensitive Ecotoxicity Data Considered	Number of Samples Exceeding Benchmark (n=12)	Frequency of Samples Exceeding Benchmark (%)
Azoxystrobin	131860-33-8	Fungicide	3.1	5	42%	<3.1	17.	44,000	Invertebrates - Chronic	-	0%
Boscalid	188425-85-6	Fungicide	2.8	6	50%	<2.8	15.	116,000	Fish - Chronic	-	0%
Carbendazim	**10605-21-7**	**Fungicide**	**4.2**	**10**	**83%**	**160.**	**1000.**	**990**	**Fish - Chronic**	**1**	**8%**
Dichlorobenzenamine, 3,4-	95-76-1	Diuron degradate	3.2	10	83%	3.7	58.	none		na	na
Dichlorophenyl Urea, 3,4-	4300-43-0	Diuron degradate	3.4	3	25%	<3.4	4.6	none		na	na
Dichlorophenyl-3-methyl Urea, 3,4-	3567-62-2	Diuron degradate	3.5	6	50%	<3.5	6.8	none		na	na
Dinotefuran	165252-70-0	Insecticide	4.5	1	8%	<4.5	7.4	6,360,000	Fish - Chronic	-	0%
Dithiopyr	97886-45-8	Herbicide	1.6	1	8%	<1.6	5.1	20,000	Nonvascular plants - Acute	-	0%
Diuron	330-54-1	Herbicide	3.2	10	83%	4.4	26.	2,400	Nonvascular plants - Acute	-	0%
Fipronil	**120068-37-3**	**Insecticide**	**2.9**	**5**	**42%**	**<2.9**	**12.**	**11**	**Invertebrates - Chronic**	**1**	**8%**
Fipronil Desulfinyl	205650-65-3	Fipronil degradate	1.6	6	50%	<1.6	6.	540	Fish - Chronic	-	0%
Fipronil Sulfide	120067-83-6	Fipronil degradate	1.8	1	8%	<1.8	4.3	100	Invertebrates - Chronic	-	0%
Fipronil Sulfone	120068-36-2	Fipronil degradate	3.5	3	25%	<3.5	6.8	37	Invertebrates - Chronic	-	0%
Fluridone	59756-60-4	Herbicide	3.7	10	83%	11.	14.	480,000	Fish - Chronic	-	0%
Hexazinone	51235-04-02	Herbicide	8.4	12	100%	12.	15.	7,000	Nonvascular plants - Acute	-	0%
Imidacloprid	**138261-41-3**	**Insecticide**	**3.8**	**4**	**33%**	**<3.8**	**11.**	**10**	**Invertebrates - Chronic**	**1**	**8%**
Simazine	122-34-9	Herbicide	5.0	6	50%	<5	13.	6,000	Nonvascular plants - Acute	-	0%
Thiabendazole	148-79-8	Fungicide	3.6	3	25%	<3.6	8.2	42,000	Invertebrates - Chronic	-	0%

The fungicide carbendazim was found at 10 of 12 sites. Measured concentrations were highest in the Extreme Lower South Bay (Figure 5). A single sample, with a concentration of 1,000 ng/L, exceeding the USEPA aquatic life benchmark of 990 ng/L for chronic toxicity to fish. All other observations were below this threshold, with a median concentration of 170 ng/L.

Carbendazim is currently used as a biocide in paints and coatings. It is also a degradate of the fungicide thiophanate-methyl (CAS #23564-05-8), which is used on a variety of fruit, nut, and root crops, and in turf and landscaping products in California. Carbendazim, as an active ingredient, has not been registered for use in California since 1989 (DPR 1999). Another of carbendazim's parent compounds, the fungicide benomyl, is also no longer in use since manufacturers voluntarily withdrew its USEPA registration in 2001.

Carbendazim has not been previously monitored in the Bay but has been frequently detected by monitoring studies elsewhere. It was detected in four of five Russian River monitoring locations at levels up to 200 ng/L (Maruya et al. 2018). Concentrations of up to 750 ng/L were reported among urban freshwater streams in California examined by the USGS; in contrast, one agricultural stream had carbendazim concentrations of up to 4,900 ng/L (Sanders, Orlando, and Hladik 2018). In a broader survey of surface waters in 11 midwestern states, USGS scientists found that carbendazim was among the most commonly detected pesticides (Nowell et al. 2018).
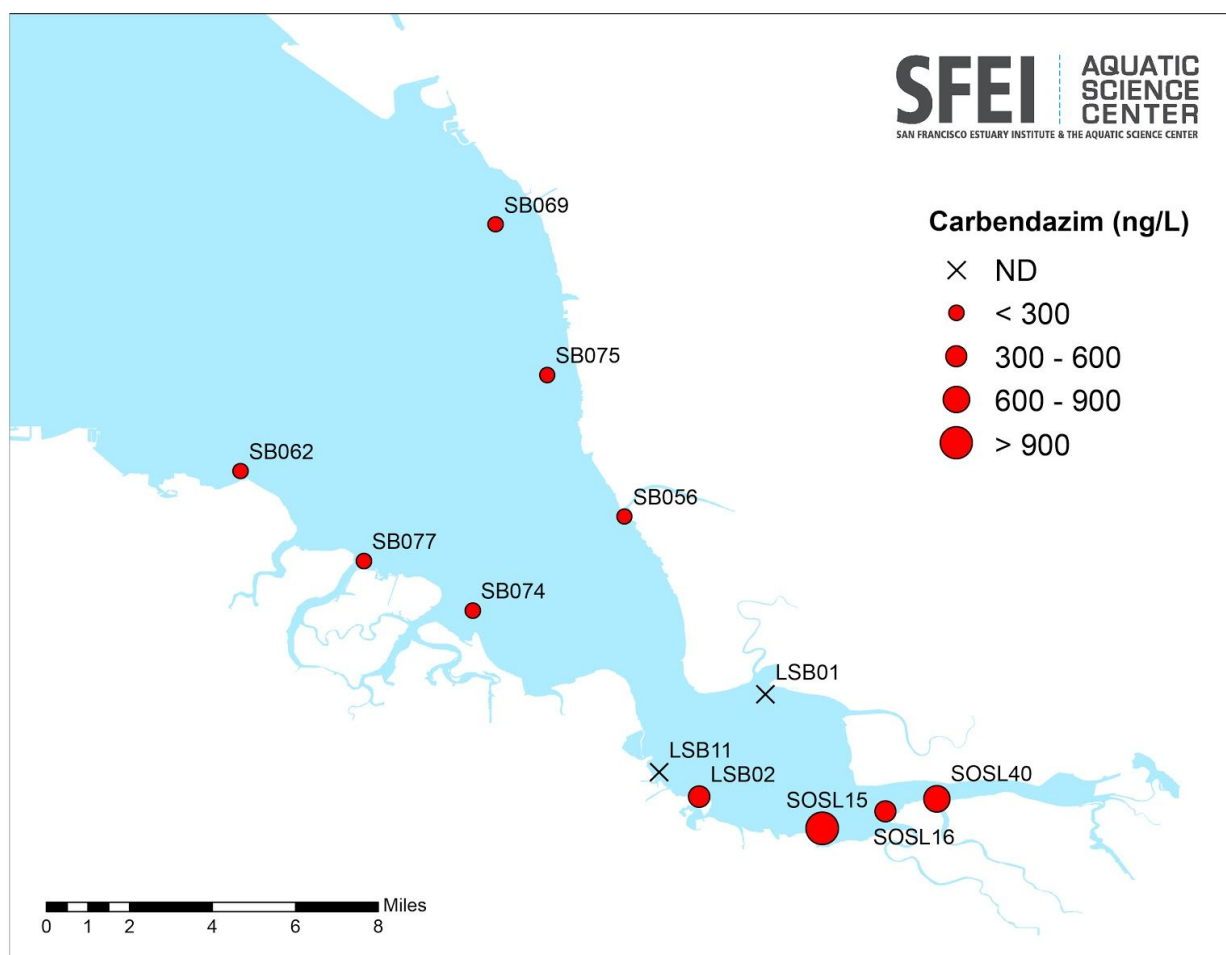
Figure 5. Measured concentrations of the pesticide carbendazim in South and Lower South Bay margin water samples. Method detection limit = 4.2 ng/L.

The insecticide fipronil was found in 5 out of 12 water samples (Figure 6). Fipronil has become a widely used replacement for urban uses of organophosphate insecticides, and is the active ingredient in many products to control fleas, ants, and termites. In California, its main uses are in products for pets and in and around structures. Outside of the state, fipronil is used on some crops, however, these uses are not permitted in California (DPR 2017). Globally, concern over the effects of fipronil on aquatic life and honeybees has led to product bans in China, France, and Italy (Parsons 2011). Fipronil in water has been linked to toxicity in benthic invertebrates. A 2013 study linked fipronil and its sulfone degradate to toxic effects (paralysis) in the freshwater midge larvae *Chironomus dilutus* (Weston, Chen, and Lydy 2015). In our study, the highest concentration of fipronil in South Bay water samples was 12 ng/L, exceeding the USEPA aquatic life benchmark of 11 ng/L for chronic toxicity to freshwater invertebrates. The median concentration of fipronil was 5.1 ng/L. Three fipronil degradates were also found in water, but they did not exceed USEPA aquatic life benchmarks or more recently published ecotoxicity thresholds (Weston and Lydy 2014). Neither fipronil nor its degradates were found in sediment.

Previous open Bay monitoring did not detect fipronil in water (dissolved phase; reporting limit 2 ng/L) but did find these compounds in sediment, with concentrations up to 0.56 µg/kg dw for fipronil sulfone (Klosterhaus, Yee, et al. 2013). Fipronil and its degradates have been detected in Bay tributaries in concentrations that exceed the USEPA aquatic life benchmark for chronic toxicity to freshwater invertebrates (Ensminger et al. 2013). Recently, fipronil was also detected in wastewater effluent from eight plants discharging to the Bay (Sadaria et al. 2017).
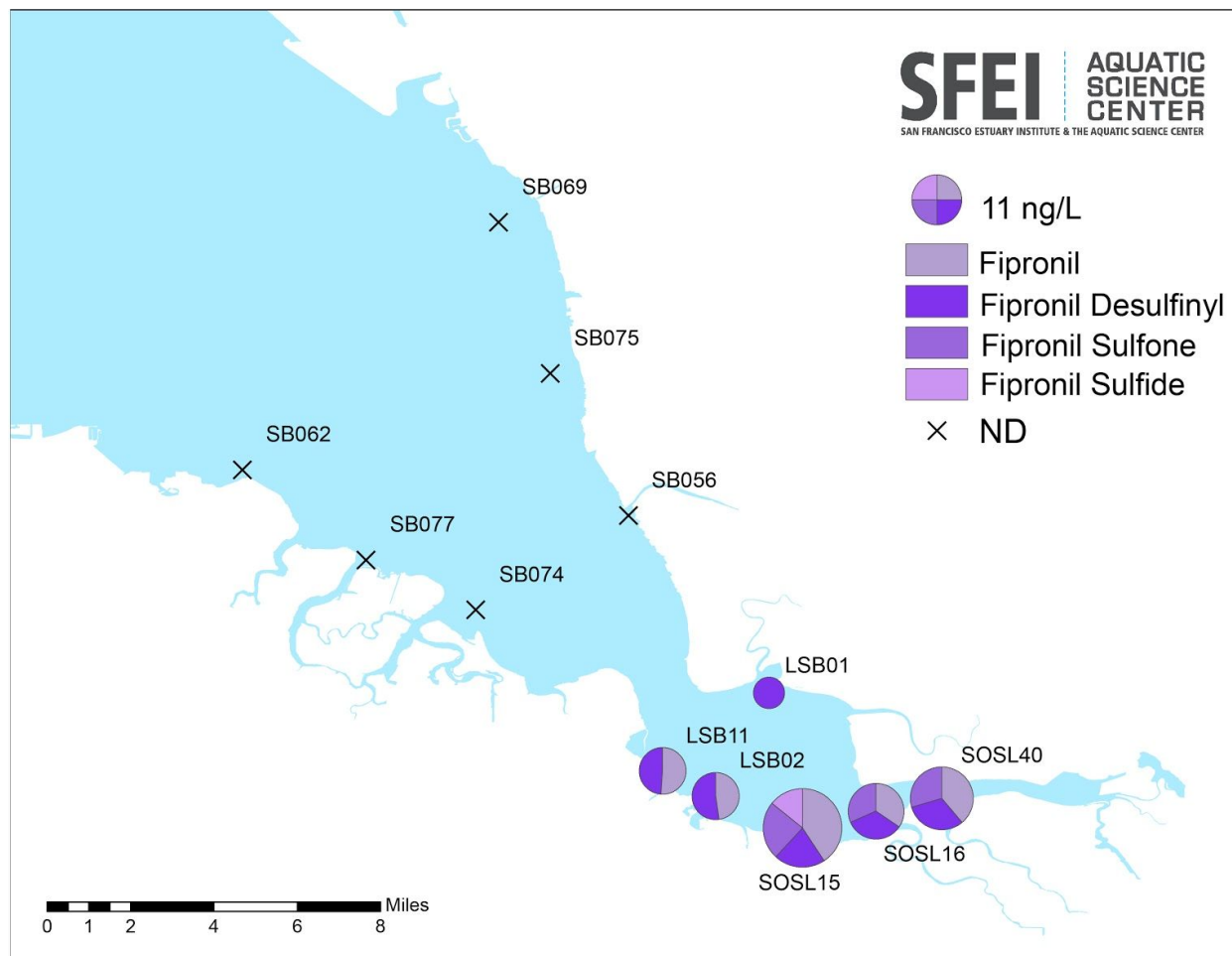
Figure 6. Measured concentrations of the pesticide fipronil and degradates fipronil desulfinyl, fipronil sulfone, and fipronil sulfide in South and Lower South Bay margin water samples.

In California, fipronil has been detected in surface water samples from around the state. DPR reviewed monitoring results from 2008 to 2013 and found that 46% of the urban California streams that were sampled had fipronil concentrations above USEPA aquatic life chronic benchmark values (Budd et al. 2015). The recent USGS study of 12 freshwater California streams frequently found fipronil and degradates during repeat water sampling at four of six urban sites, though rarely at agricultural sites; fipronil was often detected at levels exceeding the USEPA aquatic life benchmark (Sanders, Orlando, and Hladik 2018).

The insecticide imidacloprid was found in 4 of 12 South Bay margins water samples (Figure 7). A single sample contained 11 ng/L imidacloprid, greater than the USEPA aquatic life benchmark of 10 ng/L for chronic toxicity to invertebrates. An additional measurement exceeded a PNEC for imidacloprid of 4.8 ng/L developed by the European Union (European Commission 2015). Imidacloprid is a neonicotinoid insecticide that has entered into widespread use in both agricultural and urban settings. Imidacloprid is effective against a variety of insects, and is used to treat seeds, soil, crops, building materials, and to control ants, fleas, and termites.
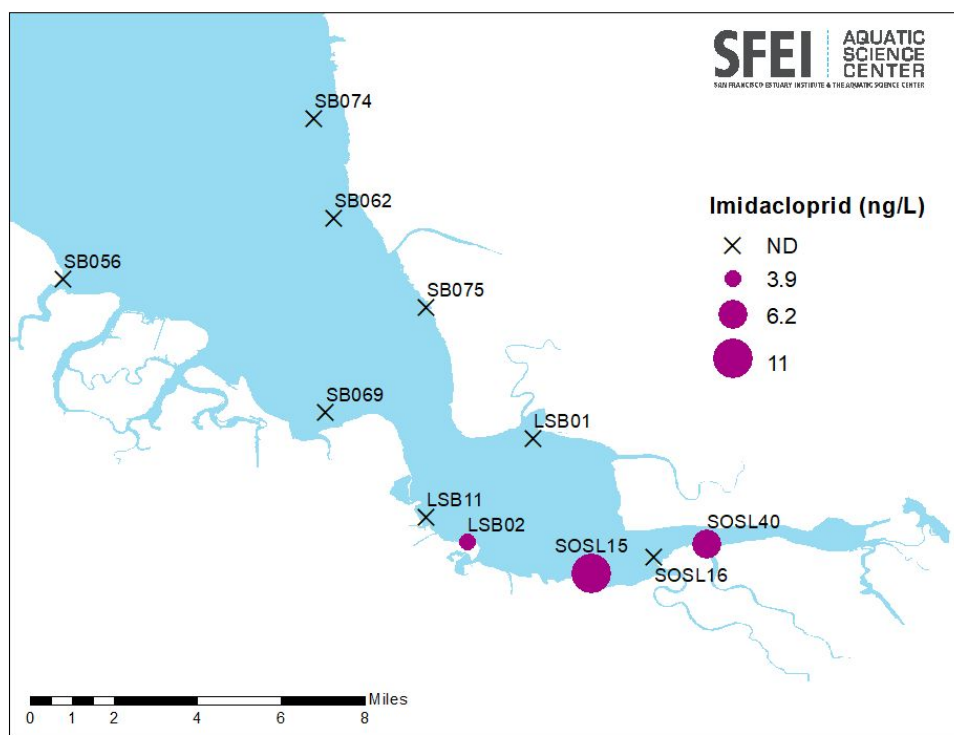

Figure 7. Measured concentrations of the pesticide imidacloprid in South and Lower South Bay margin water samples. Method detection limit = 3.8 ng/L.

Urban creeks draining to north San Francisco Bay have been found to have concentrations of imidacloprid up to 1,462 ng/L (Weston, Chen, and Lydy 2015). Imidacloprid has also been found in samples of wastewater effluent discharged to the Bay (Sadaria et al. 2017). However, recent open Bay water monitoring found little to no imidacloprid in San Francisco Bay (Buzby, Lin, and Sutton in prep.).

Imidacloprid has been widely found in California surface waters. A concentration of 11 ng/L was detected at one site in the Russian River (Maruya et al. 2018). The recent USGS study of 12 freshwater California streams frequently detected imidacloprid at levels exceeding the USEPA aquatic life benchmark of 10 ng/L (Sanders, Orlando, and Hladik 2018).

Among the remaining current-use pesticides monitored, the herbicide diuron and three of its degradates were found in water. Observed concentrations of diuron did not exceed aquatic life benchmarks. USEPA has not published benchmarks for the three degradates of diuron that were

detected in samples. The lowest ecotoxicological threshold reported for one degradate, 3,4-dichlorobenzenamine (or 3,4-dichloroaniline), is a NOEC of 3,200 ng/L for reproductive effects in the marine worm *Ophryotrocha diadema* (summarized in Crossland 1990). Crossland also reported a chronic toxicity study finding sublethal effects (length and weight reduction) in juvenile *Pimephales promelas* (fathead minnow, a freshwater fish) following exposure to concentrations of 7,100 ng/L or more of this compound.

Other compounds identified by the DPR monitoring prioritization model and included in this analysis were not detected in water samples collected from the margins. In contrast, recent sampling in the Sacramento-San Joaquin Delta, which receives significant agricultural as well as urban discharges, detected a number of these priority compounds, including atrazine (detection frequency 20%), oxyfluorfen (20%), pendimethalin (15%), bifenthrin (10%), and diazinon (10%) (Jabusch et al. 2018).

As noted previously, the laboratories did not analyze several of the compounds identified by the DPR monitoring prioritization model, namely diquat dibromide, ethylene thiourea (degradate of mancozeb), flumioxazin, naled, and sulfometuron-methyl. Therefore, we were not able to determine whether these five compounds are present in South Bay margin water or sediments, or may be causing harm to Bay wildlife. An additional caveat, sample collection during the dry season may not fully capture contamination derived from stormwater discharges during the wet season, particularly for water-soluble or less persistent pesticides used outdoors in urban settings.

Fragrance Ingredients and Other Emerging Contaminants in Sediment

Table 5 summarizes fragrance ingredients and other emerging contaminants detected in bed sediment in South Bay margin samples. A total of 16 distinct compounds were detected (excluding PAHs). It is important to note that some target analytes not detected by the present analysis might have been observed using different methods specifically optimized for their detection. Among the compounds detected in this analysis, five were observed in at least half of the samples. Four compounds were detected at levels that were comparable to or greater than available ecotoxicology thresholds: camphor, indole, 4-methylphenol, and 4-n-nonylphenol.

Table 5. Fragrance ingredients and other emerging contaminants detected in sediment in South and Lower South San Francisco Bay margins, summer 2017. Those in bold were detected at concentrations similar to or greater than PNECs.

Chemical	CAS Number	Description or Use	Reporting Limit (µg/kg dw)*	Median Concentration (µg/kg dw)	Maximum Concentration (µg/kg dw)	Number of Detections (n=12)	Detection Frequency (%)	Marine Sediment Predicted No Effect Concentration (PNEC, µg/kg dw)	Number of Samples Exceeding PNEC (if PNEC exists)	PNEC Source URL
Bisphenol A	80-05-7	Plastic additive	50 - 100	<50	71	1	8%	240.	0	https://echa.europa.eu/brief-profile/-/briefprofile/100.001.133
Camphor	**76-22-2**	**Fragrance, personal care product ingredient**	**50 - 100**	**<50**	**15**	**2**	**17%**	**17.4**	**0**	https://echa.europa.eu/brief-profile/-/briefprofile/100.000.860
Carbazole	86-74-8	Dye production intermediate, combustion byproduct, component of tobacco smoke	50 - 100	<50	9.8	3	25%	none	na	https://echa.europa.eu/brief-profile/-/briefprofile/100.001.542
Cholesterol	57-88-5	Natural sterol	250 - 500	3,700	16,000	12	100%	none	na	
Coprostanol, beta-3-	360-68-9	Carnivore fecal indicator	500 - 1,000	<500	410	1	8%	none	na	
Dichlorobenzene, 1,4-	106-46-7	Moth repellent, fumigant, deodorant	50 - 100	<50	6.4	2	17%	98.	0	https://echa.europa.eu/brief-profile/-/briefprofile/100.003.092
Galaxolide	1222-05-5	Fragrance ingredient	50 - 100	<50	12	2	17%	394.	0	https://echa.europa.eu/brief-profile/-/briefprofile/100.013.588
Indole	**120-72-9**	**Natural compound, fragrance ingredient, fecal biomarker**	**100 - 200**	**230**	**410**	**11**	**92%**	**5.66**	**11**	https://echa.europa.eu/brief-profile/-/briefprofile/100.004.019
Isophorone	78-59-1	Solvent, plastic ingredient	50 - 100	<50	5.1	1	8%	83.9	0	https://echa.europa.eu/brief-profile/-/briefprofile/100.001.024
Limonene, d-	5989-27-5	Fragrance ingredient, solvent	50 - 100	<50	130	1	8%	385.	0	https://echa.europa.eu/brief-profile/-/briefprofile/100.025.284
Methylindole, 3-	83-34-1	Natural compound, fragrance ingredient, fecal biomarker	50 - 100	20	39	12	100%	none	na	
Methylphenol, 4-	**106-44-5**	**Natural compound, used in antioxidants, preservatives, other materials**	**250 - 500**	**40**	**150**	**7**	**58%**	**85.**	**4**	https://echa.europa.eu/brief-profile/-/briefprofile/100.003.090
Nonylphenol, 4-n-	**104-40-5**	**Detergent, surfactant, plastic additive**	**750 - 1,500**	**<750**	**200**	**2**	**17%**	**39.**	**2**	https://www.who.int/ipcs/methods/Nonylphenol.pdf
Octylphenol, tert-4-	140-66-9	Detergent, surfactant, plastic additive	50 - 100	<50	11	1	8%	1230.	0	https://echa.europa.eu/brief-profile/-/briefprofile/100.004.934
Sitosterol, beta-	83-46-5	Plant sterol	500 - 1,000	1,200	3,700	7	58%	none	na	
Stigmastanol, beta	83-45-4	Plant sterol	500 - 1,000	<500	1,200	4	33%	none	na	

*Method detection limit varied due to differing sample dilutions.

Among fragrance ingredients, indole was detected in 11 of 12, or 92% of sediment samples (Figure 8). Indole is both manufactured and naturally occurring, and therefore has a number of sources. It is widely used as a fecal biomarker as it is produced by gut microbiota in both humans and animals. Further, over 85 known bacterial species can biosynthesize indole (Ma, Zhang, and Qu 2018). It can also be found in coal tar and cigarette smoke as well as wastewater from petroleum processing. Every detection in South Bay sediment was above the marine sediment PNEC of 5.66 μg/kg dw. The median concentration of indole in bed sediment was 230 μg/kg dw, 40 times greater than the PNEC. The maximum observed concentration of indole was 405 μg/kg dw, which exceeds the PNEC by a factor of 70.

German scientists flagged indole as a potential problem in a study of marine water and sediment off the northern coast of Germany (Reineke et al. 2006). The authors linked one case of observed toxicity to a combination of brominated phenols and indoles, and noted that these compounds, "which are assumed to be of biogenic origin, have rarely been discussed so far in the context of ecotoxicologic effects in marine ecosystems."

Camphor was detected at 2 of 12 sites. Camphor is a naturally occuring compound and is used as a medicinal agent, as well as a fragrance ingredient in personal care and cleaning products. The maximum concentration of camphor in bed sediment was estimated at 15 μg/kg dw (below the reporting limit of 50 μg/kg dw). This concentration is just below the PNEC of 17.4 μg/kg dw. However, this result is considered highly uncertain and an estimate only, as it is below the laboratory reporting limit.

Other fragrance ingredients included in this analysis that were detected in margin sediment include:

- galaxolide (maximum concentration 12 μg/kg dw [est.]; PNEC 394 μg/kg dw)
- d-limonene (maximum concentration 129 μg/kg dw; PNEC 385 μg/kg dw),
- 3-methylindole (or skatole; maximum concentration 39 μg/kg dw [est.]; no PNEC available).

Fragrance ingredients *not* detected in sediment included acetophenone, benzophenone, diethyl phthalate, isoborneol, menthol, methyl salicylate, tonalide, and triethyl citrate.

A study of fragrance ingredients and other compounds in bed sediment from six stream sites in the Potomac River basin found somewhat similar levels of contamination (Kolpin et al. 2013). Indole was detected in all samples in the Potomac Basin, with a maximum concentration of 197 μg/kg dw, well above the freshwater PNEC of 56.6 μg/kg dw. Skatole, or 3-methylindole, was detected in 57% of samples, and diethyl phthalate was detected in 14% of sites. Acetophenone, benzophenone, camphor, d-limonene, galaxolide, isoborneol, menthol, and tonalide were not detected; methyl salicylate and triethyl citrate were not analyzed.

In addition, research on fragrance ingredients and other contaminants in bed sediment from twenty locations (nine stream sites, nine lake sites, and two wetland sites) in remote Rocky Mountain National Park (RMNP) demonstrated higher levels of contamination (Battaglin et al. 2018). All sediment samples in RMNP contained indole with a maximum concentration of 1,150 μg/kg dw,

which is significantly greater than the freshwater PNEC (56.6 μg/kg dw). Skatole, or 3-methylindole, was found in 98% of samples, with a maximum concentration of 212 μg/kg dw. Camphor and d-limonene were detected at similar frequencies (44% and 40%, respectively). The estimated maximum concentrations of camphor and d-limonene were 9,010 and 1,690 μg/kg dw, which are both well above their respective PNECs of 17.4 and 385 μg/kg dw. Finally, acetophenone was observed in 16% of samples, and benzophenone in 9% of samples. Diethyl phthalate, galaxolide, isoborneol, menthol, tonalide, 4-methylphenol, methyl salicylate, and triethyl citrate were not analyzed.
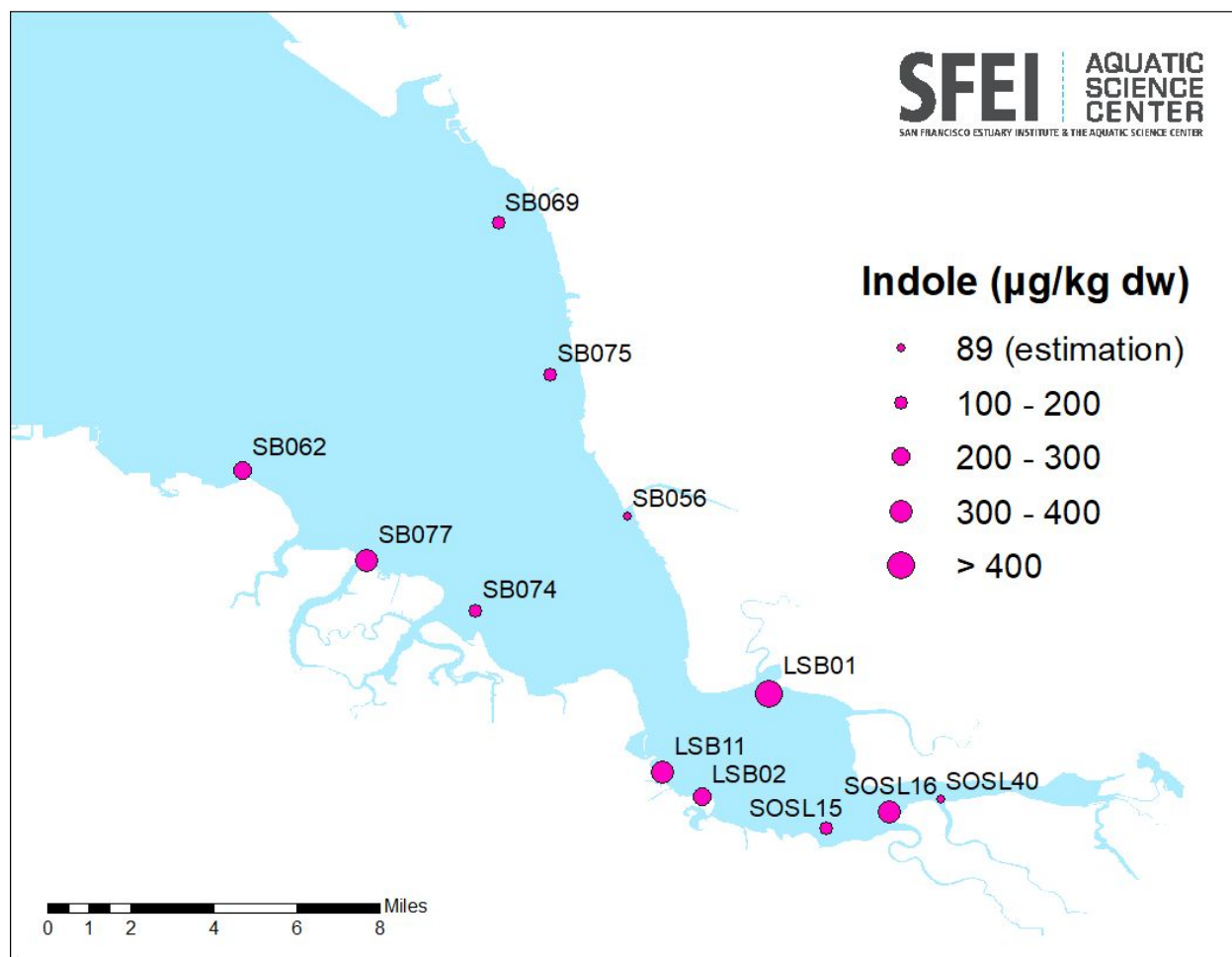
Figure 8. Measured concentrations of the fragrance ingredient indole in South and Lower South Bay margin sediment samples. Reporting limit = 100-200 μg/kg dw; values reported below the limits are generally considered estimates only.

Among other emerging contaminants, 4-methylphenol (or para-cresol) was detected in 7 of 12 monitoring locations, or 58% of South Bay margin sediment samples (Figure 9). 4-Methylphenol is a naturally occurring compound and is also used in preservatives (e.g., creosote), antioxidants, and

other materials. Creosote-treated pilings and other wooden structures present in the Bay are one source of this compound; however, extensive mapping has identified relatively few pilings in the South Bay (Werme et al. 2010).

The concentrations of 4-methylphenol in 33% of samples exceeded the marine PNEC of 85 µg/kg dw. The median concentration was 40 ng/L, and the highest observed concentration was 150 µg/kg dw, nearly double the marine PNEC. However, all reported values are below the reporting limit, and are therefore considered estimates only. In the study of Potomac River basin stream sites, 4-methylphenol was found in all sediment samples, with a maximum concentration of 396 µg/kg dw (Kolpin et al. 2013).

The compound 4-n-nonylphenol—an estrogenic degradation product of ethoxylated nonylphenols used in detergents, surfactants, and as plastic additives—was found in two samples (detection frequency 17%). The concentration of 4-n-nonylphenol in 10 of 12 bed sediment samples was below the reporting limit, which varied among samples between 750 and 1,500 µg/kg dw. The highest observed concentration, 200 µg/kg dw (estimated), was five times higher than the marine PNEC of 39 µg/kg dw. A related compound, 4-tert-octylphenol, was detected in a single sample (estimated concentration of 11 µg/kg dw) at a concentration significantly below its marine PNEC (1,230 µg/kg dw). Nonylphenol and octylphenol mono- and diethoxylates were not detected, but reporting limits for some of these compounds were relatively high compared to reporting limits for other contaminants (ranging from 500 - 2000 µg/kg dw for nonylphenol and its derivatives and 50 - 500 µg/kg dw for octylphenol and its derivatives).
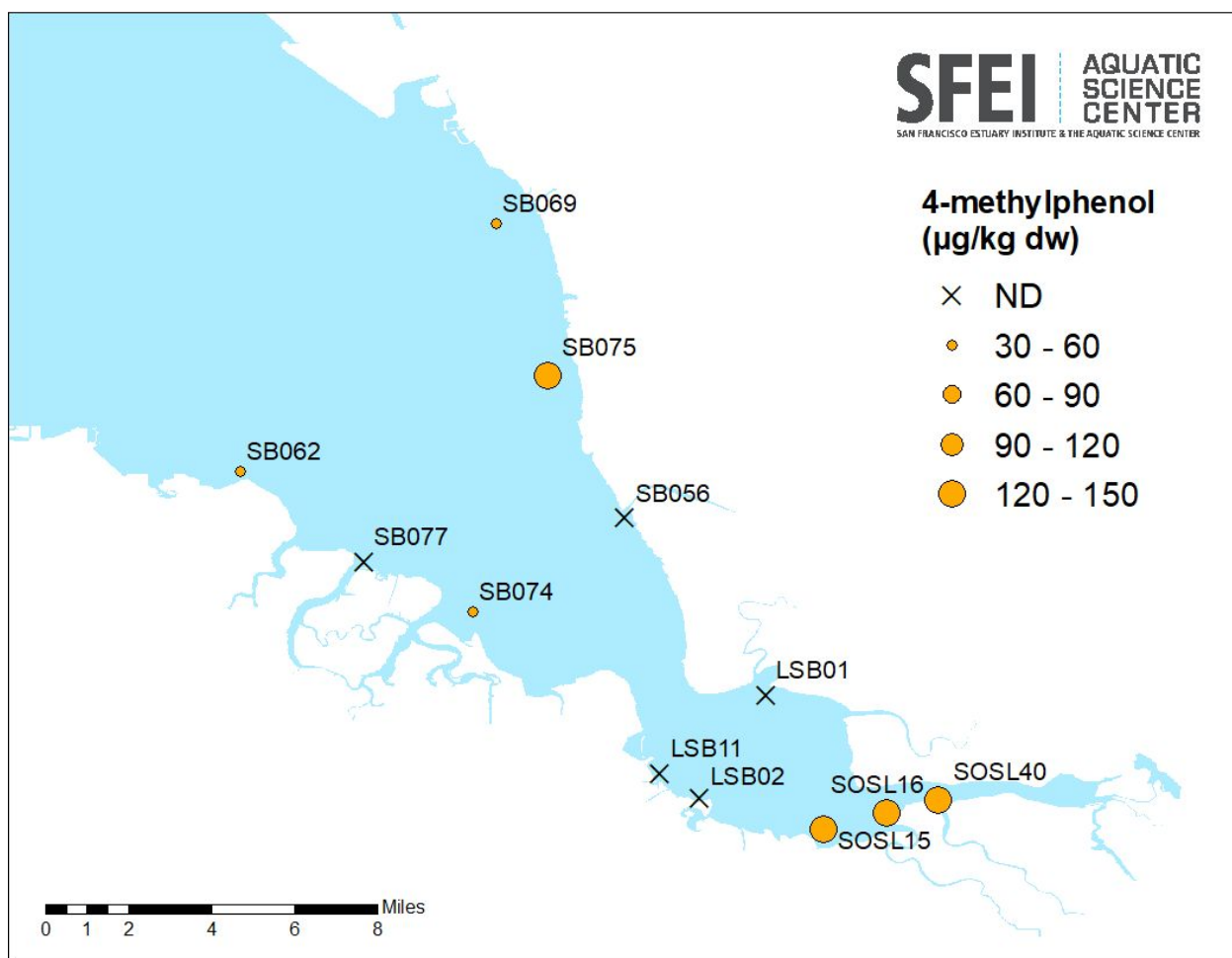
Figure 9. Measured concentrations of 4-methylphenol in South and Lower South Bay margin sediment samples. Reporting limit 250-500 µg/kg dw; all values shown are considered estimates only.

Previous monitoring of nearshore Bay sediment found 4-n-nonylphenol at concentrations of 22 to 86 µg/kg dw (Klosterhaus, Yee, et al. 2013). Nonylphenol mono- and diethoxylates were also observed in Bay sediments in the 2013 study at concentrations of < 1 to 40 µg/kg dw. A study of nearshore sediment in southern California coastal embayments detected 4-n-nonylphenol in about half of samples, with a maximum concentration reported of 490 µg/kg dw (Maruya et al. 2016). Within Rocky Mountain National Park (Colorado) lake and stream sediment, 4-n-nonylphenol was detected in 2 out of 57 samples at levels below the reporting limit (1,500 µg/kg dw), with estimated maximum concentrations of 253 and 974 µg/kg dw (Battaglin et al. 2018). Nonylphenol diethoxylate was discovered in a single sample at 1,134 µg/kg dw, below its reporting limit of 1,500 µg/kg dw. 4-tert-octylphenol was also found in 12% of samples at an estimated maximum concentration of 33.9 µg/kg dw. The diethoxylate derivative was determined to be in 7% of samples at estimated concentrations between 5.93 to 61.1 µg/kg dw. In contrast, sediment in the Potomac River basin did not contain detectable levels of nonylphenol, octylphenol, or related compounds (Kolpin et al. 2013).

PAHs were not the focus of this study, but the laboratory included results for PAHs as part of its schedule of analytes related to wastewater. While we did not perform a detailed analysis of these compounds, Table D1 summarizes the results for PAHs in water samples and Table D2 summarizes the results for PAHs in bed sediment.

Fragrance Ingredients and Other Emerging Contaminants in Water

Table 6 summarizes the 18 distinct fragrance ingredients and other emerging contaminants (excluding PAHs) detected in South San Francisco Bay margin water samples. It is important to note that some target analytes not detected by the present analysis might have been observed using different methods specifically optimized for their detection. For example, bisphenol A was not detected in margin water samples via the present screening method (reporting limit 20 ng/L), while it was widely observed in a more sensitive, targeted bisphenols analysis of open Bay waters, at a median concentration of 10 ng/L (Shimabuku et al. 2020).

Two compounds were detected in more than half of the samples. The insect repellent DEET (Diethyl-3-methyl-benzamide, N,N-) was detected in 92% of samples. Previous monitoring of open Bay water detected this compound in 100% of samples (Klosterhaus, Grace, et al. 2013). Tributyl phosphate (a flame retardant, plastic additive, and solvent) was detected in 83% of samples. This compound has also been widely detected in open Bay water samples (Sutton et al. 2019; Shimabuku et al. 2020).

The most frequently detected fragrance ingredient was the polycyclic musk galaxolide (or HHCB), which was detected in 25% of South Bay margins water samples (Figure 10). This study was motivated in part by a desire to learn whether galaxolide was present at levels of concern in Bay waters. Previously, California's Ambient Ecosystems CECs Advisory Panel set the monitoring trigger level (MTL) for galaxolide at 70 ng/L for estuarine water bodies (P.D. Anderson et al. 2012). The median concentration of galaxolide in South Bay margin water samples was less than the reporting limit (RL) of 20 ng/L. The maximum observed concentration was 30 ng/L, below the MTL, as well as the European Chemicals Agency PNEC for marine waters of 440 ng/L.

Table 6. Fragrance ingredients and other emerging contaminants detected in water in South and Lower South San Francisco Bay margins samples, summer 2017. Those in bold were detected at concentrations greater than PNECs.

Chemical	CAS Number	Use	Reporting Limit (ng/L)	Median Observed Concentration (ng/L)	Maximum Observed Concentration (ng/L)	Number of Detections (n=12)	Detection Frequency (%)	Ecotoxicity Threshold (ng/L)	Threshold Type	Samples Exceeding Threshold (n=12)	Percent of samples exceeding threshold	Reference	Ecotoxicology Threshold Source
Benzophenone	119-61-9	Fragrance ingredient, UV stabilizer	40	<40	30	2	17%	2,000	PNEC, Marine	-	-	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.003.943
Bromoform	75-25-2	Disinfection byproduct	80	<80	50	4	33%	12,000,000	LC50, Fish	-	-	Gibson et al. 1979	http://www.ukmarinesac.org.uk/activities/water-quality/wq8_28.htm#a4
Cholesterol	57-88-5	Natural sterol	800	<800	510	5	42%	none		na	na		
Coprostanol, beta-3-	360-68-9	Natural compound, biomarker of fecal matter and/or wastewater	800	<800	230	1	8%	none		na	na		
Cotinine	486-56-6	Nicotine metabolite	40	<40	21	1	8%	1,000	PNEC	-	-	Gosset et al. 2017	https://pubs.rsc.org/en/content/articlelanding/2017/em/c7em00159b/
Dichlorophenyl isocyanate, 3,4-	102-36-3	Starting material and intermediate in organic synthesis, degradate of the pesticide diuron	160	<160	19	1	8%	65,000	NOEC (21 days), Invertebrates	-	-	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.002.752
Diethyl phthalate	84-66-2	Plastic additive, fragrance and cosmetic ingredient	200	<200	50	1	8%	1,200	PNEC, Marine	-	-	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.001.409
Diethyl-3-methyl-benzamide, N,N-	134-62-3	Insect repellant (DEET)	20	10	30	11	92%	37,500,000	Fish - Acute	-	-	USEPA 2017	https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ecological-risk
Galaxolide	1222-05-5	Fragrance ingredient	20	<20	30	3	25%	440	PNEC, Marine	-	-	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.013.588
Methyl-1H-benzotriazole, 5-	29385-43-1	Corrosion inhibitor, UV stabilizer	160	<160	200	3	25%	8,000	PNEC, Marine	-	-	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.045.073
Tributylphosphate	126-73-8	Flame retardant, plastic additive, solvent	32	14	20	10	83%	35,000	PNEC, Marine	-	-	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.004.365
Triethyl citrate	77-93-0	Food additive, pharmaceutical and cosmetic ingredient	20	<20	20	4	33%	2,450,000	EC50 (4 days), Non-vascular plants	-	-	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.000.974
Tris(1,3-dichloroisopropyl) phosphate	**13674-87-8**	**Flame retardant, plastic additive**	**160**	**<160**	**90**	**4**	**33%**	**20**	**PNEC, Marine**	**3**	**25%**	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.033.767
Tris(2-chloroethyl)phosphate	115-96-8	Flame retardant, plastic additive	80	<80	50	4	33%	72,000,000	NOEC (72 h), Aquatic algae, cyanobacteria	-	-	ECHA	https://echa.europa.eu/brief-profile/-/briefprofile/100.003.744

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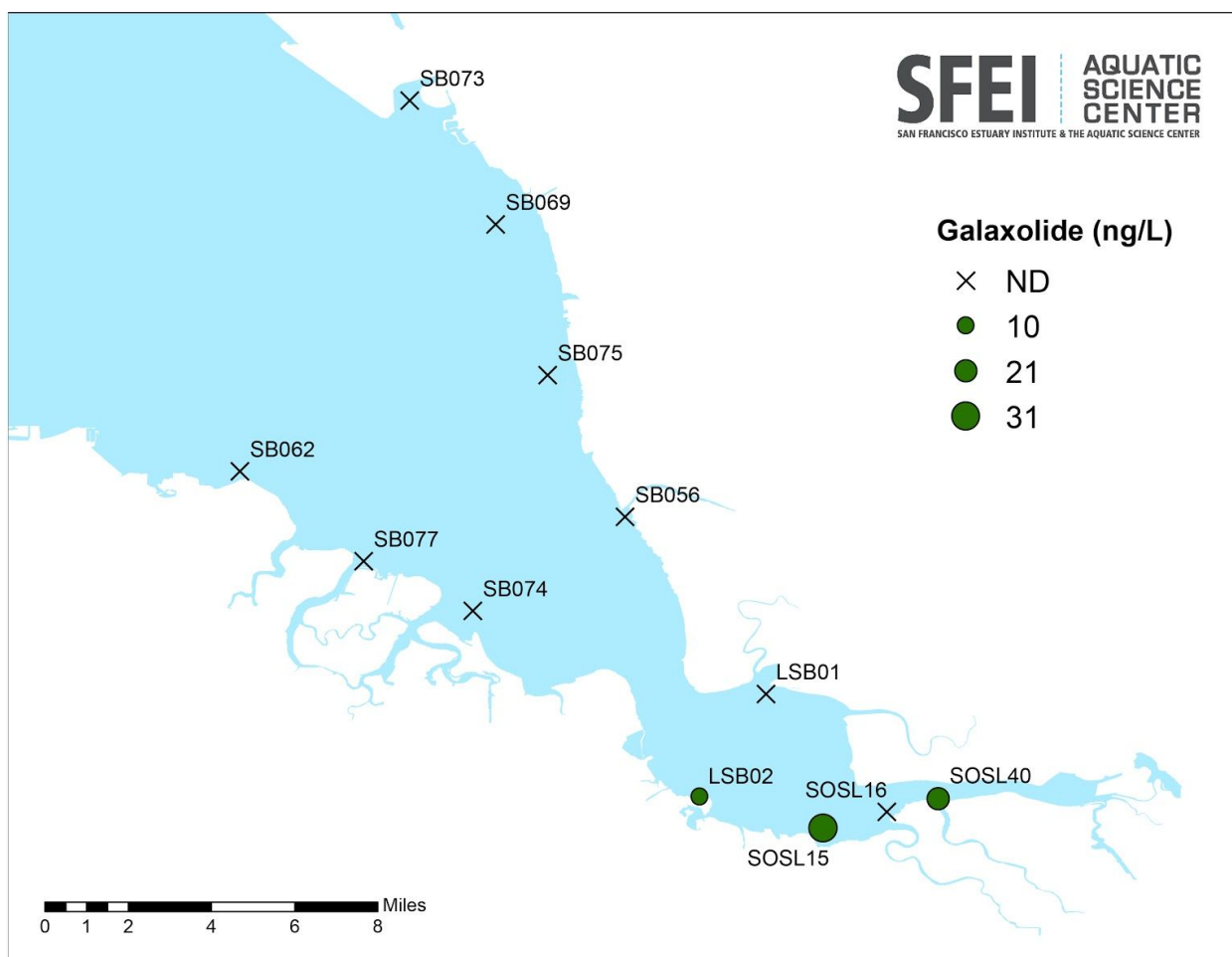
Figure 10. Measured concentrations of the polycyclic musk galaxolide in South and Lower South Bay margin water samples. Reporting limit = 20 ng/L; values reported below 20 ng/L are considered estimates only.

In contrast, a recent study of effluent-dominated rivers in southern California reported average galaxolide levels of 2,260 and 2,410 ng/L for the Los Angeles and San Gabriel Rivers, respectively (Sengupta et al. 2014). Water samples from the Russian River contained up to 370 ng/L galaxolide (Maruya et al. 2018). However, laboratory blank contamination of 120 ng/L galaxolide was also reported in the Russian River study. Other studies of galaxolide in US water bodies include sites along the Potomac River basin (detection frequency 57%, maximum concentration 27 ng/L; Kolpin et al. 2013) and source waters for drinking water treatment facilities (detection frequency 36%, maximum concentration 110 ng/L) (Glassmeyer et al. 2017).

Other fragrance ingredients that were detected in South Bay margin water samples include:

- benzophenone (maximum concentration 30 ng/L; PNEC 2,000 ng/L),
- diethyl phthalate (maximum concentration 50 ng/L; PNEC 1,200 ng/L), and
- triethyl citrate (maximum concentration 20 ng/L; PNEC 2,450,000 ng/L).

Fragrance ingredients *not* detected in water samples included acetophenone, camphor, d-limonene, diethyl phthalate, indole, isoborneol, menthol, and tonalide.

Similarly, surface water samples from lakes and streams in the remote Rocky Mountain National Park found detectable concentrations of various fragrance ingredients including benzophenone, camphor, d-limonene, indole, and skatole, though most concentrations are below method reporting limits (Battaglin et al. 2018). Camphor was found in nearly 45% of samples, and was the only compound to have a maximum concentration (131 ng/L) above its reporting limit (80 ng/L). Indole was detected in 12% of samples at concentrations between 2.6 to 18 ng/L (reporting limit 40 ng/L). The remaining contaminants (benzophenone, d-limonene, and skatole) were found in four or less samples at estimated concentrations 50% or lower than reporting limits.

Among other emerging contaminants, a single analyte was observed in water samples at levels exceeding relevant ecotoxicological thresholds. Tris(1,3-dichloroisopropyl)phosphate or TDCPP was detected in 4 of 12 water samples, or at a frequency of 33% (Figure 11). TDCPP is a chlorinated organophosphate ester (OPE) used in many applications, including as a flame retardant and plastic additive. Three samples had concentrations exceeding the marine PNEC of 20 ng/L. The maximum observed concentration was 90 ng/L (estimated; reporting limit 160 ng/L) at SOSL15 in the Extreme Lower South Bay. TDCPP has been linked to human health impacts and is listed under California Proposition 65 as a chemical determined by the California Environmental Protection Agency "to cause cancer, birth defects or other reproductive harm" (Cal EPA 2017).
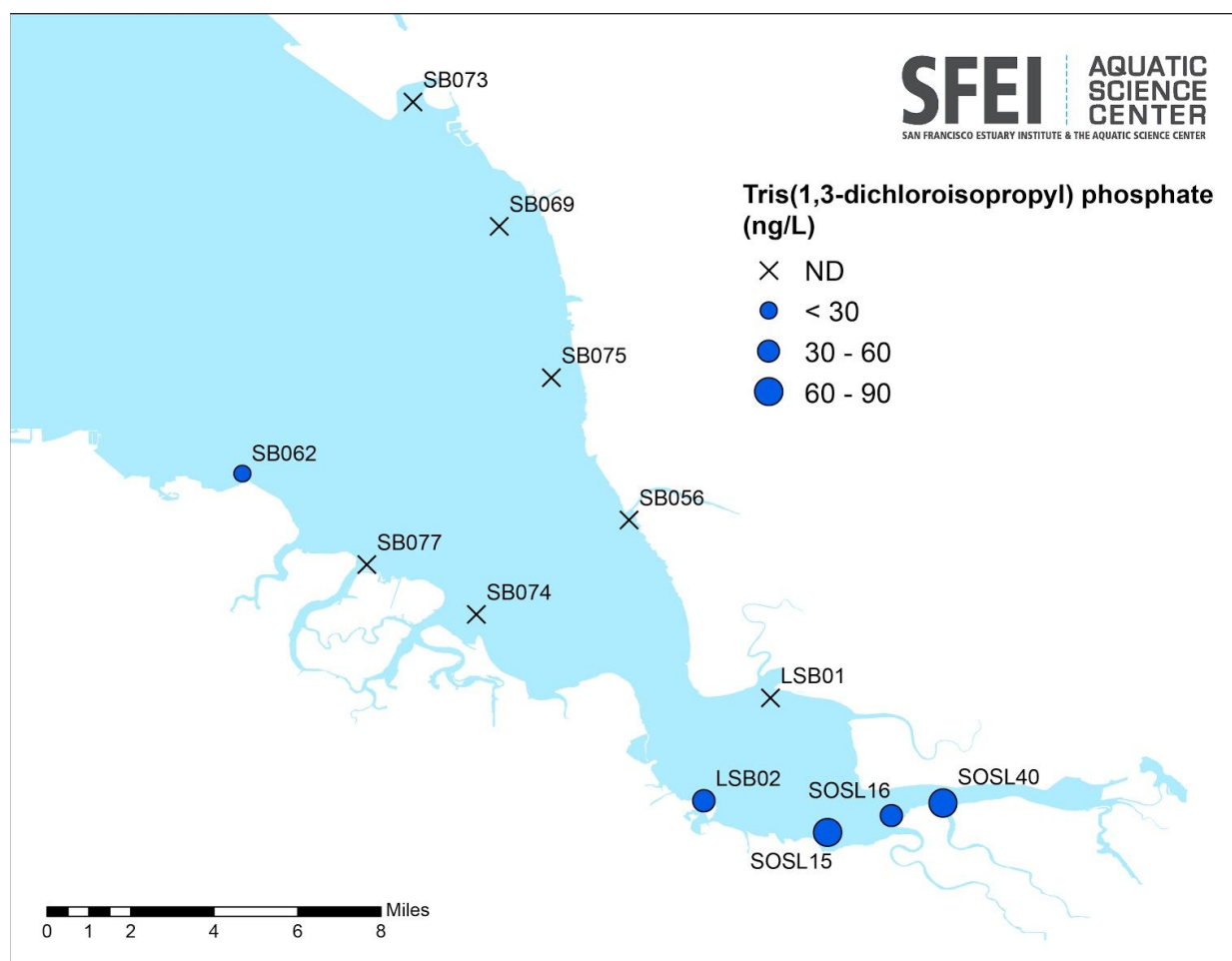
Figure 11. Measured concentrations of tris(1,3-dichloroisopropyl)phosphate) in South and Lower South Bay margin water samples. Reporting limit = 160 ng/L; values shown are considered estimates only.

TDCPP has previously been widely detected at similar concentrations in open Bay water samples (Sutton et al. 2019; Shimabuku et al. 2020). Levels of up to 1,345 ng/L have been reported for effluent-dominated streams in southern California (Sengupta et al. 2014).

Nonylphenol, octylphenol, and related compounds were not detected in margin water samples, but reporting limits for some of these compounds were relatively high. Nonylphenol was detected in previous open Bay water monitoring, at a maximum concentration of 73 ng/L (Klosterhaus, Grace, et al. 2013). Related compounds were not detected in open Bay samples.

Risk Evaluation for San Francisco Bay

The RMP assigns emerging contaminants monitored in Bay water, sediment, and wildlife to tiers in the program's Tiered Risk-based Framework (Sutton et al. 2017). The degree of concern associated with a particular chemical or chemical class guides both RMP monitoring activities and water quality management actions. The criteria listed below were used for placement in each tier:

- **High Concern** – Bay occurrence data suggest a high probability of a moderate or high level effect on Bay wildlife (e.g., frequent detection at concentrations greater than the EC_{10}, the effect concentration where 10% of the population exhibit a response).
- **Moderate Concern** – Bay occurrence data suggest a high probability of a low level effect on Bay wildlife (e.g., frequent detection at concentrations greater than the PNEC or NOEC but less than the EC_{10} or another low level effects threshold).
- **Low Concern** – Bay occurrence data suggest a high probability of minimal effect on Bay wildlife (i.e., Bay concentrations are well below toxicity thresholds and potential toxicity to wildlife is sufficiently characterized).
- **Possible Concern** – Uncertainty in toxicity thresholds suggests uncertainty in the level of effect on Bay wildlife. Bay occurrence data exist; in some cases, they may be constrained by analytical methods with insufficient sensitivity.

Secondary factors that may impact tier assignments include trends in use of the chemical or trends in Bay concentrations, as well as the potential for cumulative impacts.

Fipronil: Moderate Concern

Findings from this study provide a limited amount of additional support for the RMP's current designation of fipronil as a Moderate Concern contaminant for San Francisco Bay (Sutton et al. 2017). The concentration of fipronil in water exceeded a USEPA aquatic life benchmark for chronic invertebrate toxicity at a single site among the 12 examined. Fipronil degradates were also detected in water samples, though at concentrations below available toxicity thresholds.

Neither fipronil nor degradates were detected in sediment. However, the method detection limits for these compounds (Table 3) were higher within this broad pesticide screening method than levels measured in previous studies of open Bay sediment using fipronil-specific analytical methods (Sutton et al. 2017). The detection of fipronil and degradates in margin water samples, previous detections in open Bay sediment samples, along with the high toxicity of the compounds are sufficient to justify the Moderate Concern classification for the Bay. Continued monitoring of fipronil concentrations in Bay sediment to evaluate status and trends requires use of analytical methods with detection limits well below available toxicity thresholds.

Imidacloprid: Moderate Concern

Findings from this study provided critical support to the recent classification of imidacloprid as a Moderate Concern for the Bay (Buzby, Lin, and Sutton in prep.). Imidacloprid exceeded its USEPA aquatic life benchmark in a single margin water sample. While a single measurement greater than an ecotoxicity threshold is not typically considered sufficient to support a Moderate Concern designation, when evaluated against a European Union PNEC for imidacloprid of 4.8 ng/L, an additional sample exceeded the limit.

An additional, low-level detection in an open Bay water sample collected in the Lower South Bay in summer 2017, along with widespread detection in Bay Area wastewater and stormwater, are documented in a synthesis of Bay-wide data that supports classification of this pesticide as Moderate Concern for the Bay (Buzby, Lin, and Sutton in prep.).

Pyrethroids: Low Concern

As with previous monitoring efforts in the ambient Bay, concentrations of pyrethroids in margin sediment were significantly lower than available benchmarks, suggesting minimal impacts to wildlife. While pyrethroids remain classified as High Concern for Bay tributaries, they are considered Low Concern for the Bay itself.

Carbendazim and Other Current-Use Pesticides: Possible Concern

Other current-use pesticides have been classified as a Possible Concern for the Bay (Sutton et al. 2017). Findings from this study were generally consistent with this classification.

Carbendazim exceeded its USEPA aquatic life benchmark in a single water sample. A single measurement greater than an ecotoxicity threshold is not typically considered sufficient evidence for a Moderate Concern designation within the RMP's Tiered Risk-based Framework. For the other pesticides included in the margin sediment and water analyses, they were either not detected or observed at levels significantly below available thresholds. However, these results do not guarantee that these pesticides pose minimal risks to Bay wildlife (Low Concern), as this screening covers a discrete span with respect to both season and geography.

Because sampling occurred during the dry season, when inflows to the South Bay were dominated by wastewater effluent, it is possible that pesticides discharged via stormwater were not adequately observed via this study design, particularly in water samples. Likewise, pesticides entering the Bay via Delta inflows or agricultural runoff from northern portions of the Bay would not be adequately monitored. A full evaluation of the risks posed by these pesticides would need to account for the seasonal and geographic diversity of pesticide inputs.

The present dataset for carbendazim and other current-use pesticides, while not suggesting significant risks at this time, does not adequately address uncertainties relating to the potential for pesticide pollution during the wet season or in other regions of the Bay. The data are consistent with the current classification of current-use pesticides (other than fipronil, imidacloprid, and pyrethroids) as a Possible Concern for the Bay. Periodic screening of this class of contaminants is recommended to provide a more comprehensive evaluation of risks posed, and to assess the potential impacts of new pesticides, products, and changing use patterns. Wet season or stormwater sampling may be more appropriate for those pesticides used outdoors.

Galaxolide and Other Fragrance Ingredients: Low Concern

Fragrance ingredients are considered part of the larger class of personal care and cleaning product ingredients. Thousands of chemicals are used in personal care and cleaning products, and the RMP has only monitored the Bay for a small subset of these compounds. Those that have been monitored have been classified as Low Concern for the Bay, with minimal impacts to wildlife anticipated (Sutton et al. 2017). However, given the growing urban population around the Bay, use of these products is anticipated to grow, with corresponding increases in Bay contamination possible. Periodic screening is therefore recommended.

Levels of the polycyclic musk galaxolide observed in the margin samples were consistent with placement in the Low Concern tier. The maximum observed concentration of galaxolide in South Bay margin water samples was 30 ng/L, below the state MTL for estuarine settings, as well as the European Chemicals Agency PNEC for marine waters of 440 ng/L. Galaxolide was also detected in sediment at levels well below the available PNEC. Previous monitoring by the RMP found detectable levels of galaxolide in bivalves (855 μg/kg dw) and bird eggs (1 μg/kg wet weight) collected in 2002 through 2004 (Klosterhaus, Yee, et al. 2013).

Apart from indole, levels of most other fragrance ingredients examined via this study were generally well below available toxicity thresholds. Minor exceptions include camphor, with just two detections in sediment that were both slightly lower than the marine PNEC, and d-limonene, with a maximum detection in sediment less than half the marine PNEC. As a result, the dataset is generally considered consistent with a classification of fragrance ingredients and other personal care and cleaning product ingredients as Low Concern for the Bay. However, periodic screening is merited, given the potential for increased use and associated contamination due to a growing Bay Area population.

Indole: Possible Concern

Indole, a natural compound also used as a fragrance ingredient, was not detected in water samples (reporting limit 20 ng/L), but was detected in 92% of sediment samples. Every detection in

sediment was above the marine sediment PNEC of 5.66 µg/kg dw. The maximum observed concentration was 405 µg/kg dw, which exceeds the PNEC by a factor of 70.

Interestingly, lake and stream bed sediment samples collected within the relatively pristine Rocky Mountain National Park (Battaglin et al. 2018) contained higher concentrations of indole (maximum concentration 1,150 µg/kg dw) and more frequent detections (100%) relative to South Bay margins. ndole was detected in just 12% of Rocky Mountain surface water samples, at an estimated maximum concentration of 18 ng/L, which is lower than the reporting limit for the present screening (20 ng/L). It is possible that indole was present in Bay water samples at levels lower than could be quantified using the present screening method. While the compound is water soluble, it is known to be transformed and degraded by many bacterial species in the environment (Ma, Zhang, and Qu 2018), which could explain the lack of detection in water samples.

Closer examination of the marine sediment PNEC for indole revealed that it was developed in the absence of any ecotoxicity data relevant to sediment-dwelling organisms, and was instead provisionally calculated using sparse freshwater aquatic ecotoxicity thresholds and a standardized equilibrium partitioning method. The higher level of uncertainty associated with this PNEC suggests the need for further testing in benthic species. An examination of the scientific literature revealed only one additional aquatic ecotoxicity study (Eisentraeger et al. 2008) and no sediment ecotoxicity studies.

Given the uncertainties associated with the potential for indole to pose risks to Bay wildlife, the present evidence is consistent with a classification of Possible Concern for the Bay.

4-Methylphenol: Possible Concern

Like indole, 4-methylphenol (or para-cresol), detected at 7 of 12 margin sediment sites, has both natural and anthropogenic sources. Creosote-treated pilings and other wooden structures in the Bay are one of the anthropogenic sources of this compound; however, previous mapping has identified relatively few pilings in the South Bay (Werme et al. 2010). Methylphenol was not detected in water samples.

The concentrations of methylphenol in 4 of 12 sediment samples exceeded the marine PNEC of 85 µg/kg dw. However, all values were below the reporting limit, and are therefore considered estimates only. As with indole, the ECHA marine sediment PNEC for methylphenol was provisionally calculated using freshwater aquatic ecotoxicity data rather than data relevant to sediment-dwelling organisms. Likewise, a Canadian screening assessment for methylphenols (including 2-, 3-, and 4-methylphenol) lacked sediment ecotoxicity data, and instead derived a PNEC relevant to sediment using water-only toxicity testing of a sediment-dwelling amphipod (*Gammarus pulex*). The resulting PNEC was 2.1 milligrams/L (Environment and Climate Change Canada and Health Canada 2016). Concentrations in this range would undoubtedly have been detected in water samples using the present screening method (reporting limit 40 ng/L); however, 4-methylphenol was

not detected in any margin water samples. Clearly, testing in benthic species is needed to establish a more robust sediment toxicity threshold.

Due to uncertainties in the quantification of methylphenol (concentrations below reporting limits) as well as its toxicity, the present evidence supports a classification of Possible Concern for the Bay.

Organophosphate Esters: Moderate Concern

Among other emerging contaminants, the organophosphate ester (OPE) flame retardant and plastic additive tributyl phosphate was one of the most commonly detected in water samples (detection frequency 83%). Concentrations of another OPE, TDCPP (detection frequency 33%), exceeded the marine PNEC of 20 ng/L at 3 of 4 sites where it was detected in the margins. Observed levels of these contaminants were consistent with those of two previous studies of open Bay water samples (Sutton et al. 2019; Shimabuku et al. 2020). Three other OPEs were not detected in the margin samples, possibly due to higher reporting limits associated with this broad screening method.

A report on 2017 open Bay water monitoring for OPEs provides evidence to support designation of this contaminant class as a Moderate Concern for the Bay (Shimabuku et al. 2020). While only a single member of this class, TDCPP, exceeded toxicity thresholds, concerns about cumulative exposure and combined effects, particularly with respect to endocrine disruption, indicate risks may be posed by the class as a whole. Future Bay monitoring would be best served by analytical methods specific to OPEs, with method detection limits well below available toxicity thresholds.

Alkylphenols and Alkylphenol Ethoxylates: Moderate Concern

Alkylphenol ethoxylates, widely used in surfactants, plastics, and detergents and cleaning products, degrade in the environment to form estrogenic alkylphenols. Two alkylphenols, 4-n-nonylphenol and 4-tert-octylphenol, were detected in a small number of margin sediment samples. The highest observed concentration of nonylphenol, 200 μg/kg dw (estimated), was five times higher than the marine PNEC of 39 μg/kg dw. The two analytes were not detected in water samples; nonylphenol and octylphenol mono- and diethoxylates were not detected in either matrix.

Alkylphenols and alkylphenol ethoxylates as a class are considered a Moderate Concern for the Bay based on prior detections in sediment and water at levels of concern, as well as the potential for additive or synergistic estrogenicity or toxicity (Sutton et al. 2017). While the detection frequencies for these compounds are relatively low in the present study, this is likely due to the relatively high reporting limits for the screening method employed. For example, the mean reporting limit for the previous, targeted study of 4-n-nonylphenol in Bay sediment was 0.482 μg/kg dw (Klosterhaus, Grace, et al. 2013), while for the present study, the reporting limit ranged between 750 and 1,500 μg/kg dw. The estimated concentrations of nonylphenol that were observed in the present study of Bay margin sediment are comparable to prior observations (up to 86 μg/kg dw). As a result, these

new data are consistent with the prior findings that supported the designation of this class of emerging contaminants as a Moderate Concern for the Bay.

Conclusions

This study was intended to fill key monitoring data gaps for current-use pesticides, fragrance ingredients, and other emerging contaminants in water and sediment in the near-shore environment of the South Bay. Our hypothesis was that contaminants found in stormwater and wastewater are concentrated in the South Bay margins. Because the region has a heavily urban watershed and is subject to less dilution by relatively clean ocean water, contaminant levels measured here may represent a worst-case scenario for the Bay as a whole.

In general, levels of contaminants detected in the South Bay margins were comparable to or lower than those measured in other freshwater and marine settings in California and the US. Of particular interest are the pesticides fipronil, imidacloprid, and carbendazim, as each of these compounds exceeded USEPA aquatic life benchmarks at one or more sites. Among non-pesticide emerging contaminants, indole, 4-methylphenol, 4-n-nonylphenol, and TDCPP exceeded available marine PNECs. In contrast, the fragrance ingredient galaxolide was observed at levels well below thresholds of concern.

This pilot study filled in gaps in our knowledge of the occurrence of pesticides and emerging contaminants in the near-shore areas of South San Francisco Bay. However, this relatively small study does not tell us how contaminant levels may change over time. A rapidly growing Bay Area population suggests that contamination derived from common consumer products and pesticides could increase in the future.

Periodic monitoring is recommended in order to determine if levels of contaminants of more focused concern are increasing or decreasing over time. If future monitoring indicates that specific contaminants may be having an adverse impact on Bay wildlife, followup monitoring is recommended to better understand the sources and pathways by which contaminants enter the Bay. Urban pesticides and other contaminants with significant outdoor applications may be best examined in stormwater, or in samples collected from the Bay during the wet season, when stormwater discharges are more influential. In contrast, contaminants likely derived primarily from wastewater discharges, such as fragrance ingredients, may be best examined in effluent or in samples collected from the Bay during the dry season.

References

Anderson, Brian, Bryn Phillips, Dan Markiewicz, and Marie Stillway. 2012. "Toxicity in California Waters: San Francisco Bay Region." California State Water Resources Control Board.

Anderson, Paul D., Nancy D. Denslow, Jörg E. Drewes, Adam W. Olivieri, Daniel Schlenk, Geoffrey I. Scott, and Shane A. Snyder. 2012. "Monitoring Strategies for Contaminants of Emerging Concern (CECs) in California's Aquatic Ecosystems: Recommendations of a Science Advisory Panel." Technical Report 692. Costa Mesa, CA: Southern California Coastal Water Research Project. https://www.waterboards.ca.gov/water_issues/programs/swamp/cec_aquatic/docs/cec_ecosystems_rpt.pdf.

BACWA. 2018. "Bay Area Clean Water Agencies Nutrient Reduction Study Group Annual Report Nutrient Watershed Permit Annual Report." Oakland, California: Bay Area Clean Water Agencies. https://bacwa.org/wp-content/uploads/2018/10/Group-Annual-Report-2018-Final_wAppendices_Reduced.pdf.

Battaglin, William A., Paul M. Bradley, Luke Iwanowicz, Celeste A. Journey, Heather L. Walsh, and Vicki S. Blazer. 2018. "Pharmaceuticals, Hormones, Pesticides, and Other Bioactive Contaminants in Water, Sediment, and Tissue from Rocky Mountain National Park, 2012–2013." *Science of The Total Environment* 643 (December): 651–73. https://doi.org/10.1016/j.scitotenv.2018.06.150.

Breitholtz, Magnus, Leah Wollenberger, and Laurence Dinan. 2003. "Effects of Four Synthetic Musks on the Life Cycle of the Harpacticoid Copepod Nitocra Spinipes." *Aquatic Toxicology* 63 (2): 103–118.

Budd, Robert, Michael Ensminger, Dan Wang, and Kean S. Goh. 2015. "Monitoring Fipronil and Degradates in California Surface Waters, 2008–2013." *Journal of Environment Quality* 44 (4): 1233. https://doi.org/10.2134/jeq2015.01.0018.

Burkhardt, Mark R., Steven D. Zaugg, Steven G. Smith, and Rhiannon C. ReVello. 2006. "Determination of Wastewater Compounds in Sediment and Soil by Pressurized Solvent Extraction, Solid-Phase Extraction, and Capillary-Column Gas Chromatography/Mass Spectrometry." Report 5-B2. Techniques and Methods. USGS Publications Warehouse. https://pubs.usgs.gov/tm/2006/tm5b2/.

Buzby, Nina, Diana Lin, and Rebecca Sutton. in prep. "Neonicotinoid Pesticides and Degradates in San Francisco Bay."

Cal EPA. 2017. "Chemicals Known to the State to Cause Cancer or Reproductive Toxicityp65122917.Pdf." State of California, Environmental Protection Agency, Office of Environmental Health Hazard Assessment. https://oehha.ca.gov/media/downloads/proposition-65/p65122917.pdf.

Coastal Conservation & Research. 2017. "2017 Cruise Report: Contaminant and Microplastic Concentrations In San Francisco Bay and Tomales Bay Water, Sediment, and Fish." San Francisco Estuary Institute. https://www.sfei.org/sites/default/files/biblio_files/CCR%20Margins%20Microplastics%20Cruise%20Report.pdf.

Crossland, N. O. 1990. "A Review of the Fate and Toxicity of 3,4-Dichloroaniline in Aquatic Environments." *Chemosphere* 21 (12): 1489–97. https://doi.org/10.1016/0045-6535(90)90054-W.

Dodder, Nathan G, Alvine C Mehinto, and Keith A Maruya. 2015. "Monitoring of Constituents of Emerging Concern (CECs) in California's Aquatic Ecosystems – Pilot Study Design and QA/QC Guidance." Technical Report 854. Costa Mesa, CA: Southern California Coastal Water Research Project. ftp://ftp.sccwrp.org/pub/download/DOCUMENTS/TechnicalReports/854_CaliforniaCEC_PilotStudy_040315.pdf.

DPR. 1999. "Benomyl Risk Characterization Document." RCD 99-01. Sacramento, California: California Department of Pesticide Regulation. https://www.cdpr.ca.gov/docs/risk/rcd/benomyl.pdf.

DPR. 2017. "Problem Formulation Document - Fipronil." California Department of Pesticide Regulation. https://www.cdpr.ca.gov/docs/risk/rcd/fipronil.pdf.

ECHA. 2012. "Pyriproxyfen Assessment Report." The Netherlands: European Chemicals Agency. http://dissemination.echa.europa.eu/Biocides/ActiveSubstances/0061-18/0061-18_Assessment_Report.pdf.

Eisentraeger, Adolf, Corinna Brinkmann, Henner Hollert, Anne Sagner, Andreas Tiehm, and Judith Neuwoehner. 2008. "Heterocyclic Compounds: Toxic Effects Using Algae, Daphnids, and the Salmonella/Microsome Test Taking Methodical Quantitative Aspects into Account." *Environmental Toxicology and Chemistry* 27 (7): 1590–1596.

Ensminger, Michael P., Robert Budd, Kevin C. Kelley, and Kean S. Goh. 2013. "Pesticide Occurrence and Aquatic Benchmark Exceedances in Urban Surface Waters and Sediments in Three Urban Areas of California, USA, 2008–2011." *Environmental Monitoring and Assessment* 185 (5): 3697–3710. https://doi.org/10.1007/s10661-012-2821-8.

Environment and Climate Change Canada, and Health Canada. 2016. "Screening Assessment: Internationally Classified Substance Grouping, Cresol (Phenol, Methyl-) Substances." https://www.ec.gc.ca/ese-ees/default.asp?lang=En&n=6ED0027C-1#toc95.

European Commission. 2015. "Directive 98/8/EC of the European Parliament and of the Council of 16 February 1998 Concerning the Placing of Biocidal Products on the Market." http://data.europa.eu/eli/dir/1998/8/oj/eng.

Gibson, Charles I., Frederick C. Tone, Peter Wilkinson, and J. W. Blaylock. 1979. "Toxicity and Effects of Bromoform on Five Marine Species."

Glassmeyer, Susan T., Edward T. Furlong, Dana W. Kolpin, Angela L. Batt, Robert Benson, J. Scott Boone, Octavia Conerly, et al. 2017. "Nationwide Reconnaissance of Contaminants of Emerging Concern in Source and Treated Drinking Waters of the United States." *Science of The Total Environment* 581–582 (March): 909–22. https://doi.org/10.1016/j.scitotenv.2016.12.004.

Gosset, Antoine, Claude Durrieu, Frédéric Orias, Rémy Bayard, and Yves Perrodin. 2017. "Identification and Assessment of Ecotoxicological Hazards Attributable to Pollutants in Urban Wet Weather Discharges." *Environmental Science: Processes & Impacts* 19 (9): 1150–1168.

Hladik, Michelle L., and Daniel L. Calhoun. 2012. "Analysis of the Herbicide Diuron, Three Diuron Degradates, and Six Neonicotinoid Insecticides in Water-Method Details and Application to Two Georgia Streams." Scientific Investigations Report 2012–5206. US Geological Survey. https://pubs.usgs.gov/sir/2012/5206/pdf/sir20125206.pdf.

Hladik, Michelle L., and Megan M. McWayne. 2012. "Methods of Analysis—Determination of Pesticides in Sediment Using Gas Chromatography/Mass Spectrometry." Techniques and Methods 5–C3. US Geological Survey. http://pubs.usgs.gov/tm/tm5c3.

Hladik, Michelle L., Kelly L. Smalling, and Kathryn Kuivila. 2009. "Methods of Analysis-Determination of Pyrethroid Insecticides in Water and Sediment Using Gas Chromatography/Mass Spectrometry." US Geological Survey. https://pubs.usgs.gov/tm/tm5c2/tm5c2.pdf.

Hladik, Michelle L., Kelly L. Smalling, and Kathryn M. Kuivila. 2008. "A Multi-Residue Method for the Analysis of Pesticides and Pesticide Degradates in Water Using HLB Solid-Phase Extraction and Gas Chromatography–Ion Trap Mass Spectrometry." *Bulletin of Environmental Contamination and Toxicology* 80 (2): 139–144.

Hunt, John W., Brian S. Anderson, Bryn M. Phillips, John Newman, Ron S. Tjeerdema, Karen Taberski, Craig J. Wilson, et al. 1998. "Sediment Quality and Biological Effects in San Francisco Bay: Bay Protection and Toxic Cleanup Program Final Technical Report." 1998: California State Water Resources Control Board. https://www.waterboards.ca.gov/water_issues/programs/bptcp/docs/reg2report.pdf.

IFRA. 2016. "IFRA Volume of Use Survey 2016: Transparency List." International Fragrance Association. http://www.ifraorg.org/en-us/ingredients#.XG1qMOhKjIU.

Jabusch, Thomas, Philip Trowbridge, Matthew Heberger, James Orlando, Matthew De Parsia, and Marie

Stillway. 2018. "Delta Regional Monitoring Program Annual Monitoring Report for Fiscal Year 2015–16: Pesticides and Toxicity." Richmond, CA: Aquatic Science Center. http://www.sfei.org/documents/delta-pesticides-2016.

Klosterhaus, Susan, Richard Grace, M. Coreen Hamilton, and Don Yee. 2013. "Method Validation and Reconnaissance of Pharmaceuticals, Personal Care Products, and Alkylphenols in Surface Waters, Sediments, and Mussels in an Urban Estuary." *Environment International* 54 (April): 92–99. https://doi.org/10.1016/j.envint.2013.01.009.

Klosterhaus, Susan, Don Yee, Meg Sedlak, Adam Wong, and Rebecca Sutton. 2013. "Contaminants of Emerging Concern in San Francisco Bay: A Summary of Occurrence Data and Identification of Data Gaps." Contribution No. 698. Richmond, CA: San Francisco Estuary Institute. https://www.sfei.org/documents/contaminants-emerging-concern-san-francisco-bay-summary-occurrence-data-and-identification.

Kolpin, Dana W., Vicki S. Blazer, James L. Gray, Michael J. Focazio, John A. Young, David A. Alvarez, Luke R. Iwanowicz, et al. 2013. "Chemical Contaminants in Water and Sediment near Fish Nesting Sites in the Potomac River Basin: Determining Potential Exposures to Smallmouth Bass (Micropterus Dolomieu)." *The Science of the Total Environment* 443 (January): 700–716. https://doi.org/10.1016/j.scitotenv.2012.09.063.

Lao, Wenjian, Liesl Tiefenthaler, Darrin J. Greenstein, Keith A. Maruya, Steven M. Bay, Kerry Ritter, and Kenneth Schiff. 2012. "Pyrethroids in Southern California Coastal Sediments." *Environmental Toxicology and Chemistry* 31 (7): 1649–56. https://doi.org/10.1002/etc.1867.

Luo, Yuzhou, and Xin Deng. 2015. "Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas III: Watershed-Based Prioritization." Sacramento: California Department of Pesticide Regulation.

Luo, Yuzhou, Xin Deng, Robert Budd, Keith Starner, and Michael Ensminger. 2013. "Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas." Sacramento, California: California Department of Pesticide Regulation. https://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prioritization_report.pdf.

Luo, Yuzhou, Michael Ensminger, Robert Budd, Xin Deng, and April DaSilva. 2014. "Methodology for Prioritizing Pesticides for Surface Water Monitoring in Agricultural and Urban Areas II: Refined Priority List." Sacramento, California: California Department of Pesticide Regulation. http://www.cdpr.ca.gov/docs/emon/pubs/ehapreps/analysis_memos/prioritization_report_2.pdf.

Ma, Qiao, Xuwang Zhang, and Yuanyuan Qu. 2018. "Biodegradation and Biotransformation of Indole: Advances and Perspectives." *Frontiers in Microbiology* 9 (November). https://doi.org/10.3389/fmicb.2018.02625.

Maruya, Keith A., Nathan G. Dodder, Ashmita Sengupta, Deborah J. Smith, J. Michael Lyons, Ann T. Heil, and Jörg E. Drewes. 2016. "Multimedia Screening of Contaminants of Emerging Concern (CECS) in Coastal Urban Watersheds in Southern California (USA)." *Environmental Toxicology and Chemistry* 35 (8): 1986–94. https://doi.org/10.1002/etc.3348.

Maruya, Keith A., Alvine C. Mehinto, Wenjian Lao, Rebecca Sutton, Thomas Jabusch, Jennifer Sun, Diana Lin, Jay Davis, and Rich Fadness. 2018. "Pilot Monitoring of Constituents of Emerging Concern (CECs) in the Russian River Watershed (Region 1)." SCCWRP Technical Report 1020. Richmond, California: Southern California Coastal Water Research Project Authority, San Francisco Estuary Institute, and North Coast Regional Water Quality Control Board. https://www.waterboards.ca.gov/water_issues/programs/swamp/docs/reglrpts/cecspilotstudyinreg1.pdf.

Nowell, Lisa H., Patrick W. Moran, Travis S. Schmidt, Julia E. Norman, Naomi Nakagaki, Megan E. Shoda, Barbara J. Mahler, et al. 2018. "Complex Mixtures of Dissolved Pesticides Show Potential Aquatic Toxicity in a Synoptic Study of Midwestern U.S. Streams." *Science of The Total Environment* 613–614

(February): 1469–88. https://doi.org/10.1016/j.scitotenv.2017.06.156.

Nowell, Lisa H., Julia E. Norman, Christopher G. Ingersoll, and Patrick W. Moran. 2016. "Development and Application of Freshwater Sediment-Toxicity Benchmarks for Currently Used Pesticides." *Science of The Total Environment* 550 (April): 835–50. https://doi.org/10.1016/j.scitotenv.2016.01.081.

NPS. 2017. "GRTS Spatial Sampling (for Monitoring)." National Park Service, Inventory & Monitoring. 2017. https://science.nature.nps.gov/im/datamgmt/statistics/r/advanced/grts.cfm.

Parsons, Wayne. 2011. "What Should Consumers Know about Termidor Aka Fipronil." Website of Honolulu personal injury lawyer. The Legal Examiner. 2011. https://honolulu.legalexaminer.com/health/toxic-substances/what-should-consumers-know-about-termidor-aka-fipronil/.

Reineke, N., S. Biselli, S. Franke, W. Francke, N. Heinzel, H. Hühnerfuss, H. Iznaguen, et al. 2006. "Brominated Indoles and Phenols in Marine Sediment and Water Extracts from the North and Baltic Seas–Concentrations and Effects." *Archives of Environmental Contamination and Toxicology* 51 (2): 186–96. https://doi.org/10.1007/s00244-005-0135-3.

Ross, J.R.M, J. A. Davis, P. Trowbridge, J. Sun, J. T. Ackerman, T. Adelsbach, C. A. Eagles-Smith, et al. 2016. "Contaminant Concentrations in Eggs of Double-Crested Cormorants and Forster's Terns from San Francisco Bay: 2002-2012." 2016.

Sadaria, Akash M., Rebecca Sutton, Kelly D. Moran, Jennifer Teerlink, Jackson Vanfleet Brown, and Rolf U. Halden. 2017. "Passage of Fiproles and Imidacloprid from Urban Pest Control Uses through Wastewater Treatment Plants in Northern California, USA." *Environmental Toxicology and Chemistry* 36 (6): 1473–1482.

Sanders, Corey J., James L. Orlando, and Michelle L. Hladik. 2018. "Detections of Current-Use Pesticides at 12 Surface Water Sites in California during a 2-Year Period Beginning in 2015." USGS Numbered Series 1088. Data Series. Reston, VA: U.S. Geological Survey. http://pubs.er.usgs.gov/publication/ds1088.

Sengupta, Ashmita, J. Michael Lyons, Deborah J. Smith, Jörg E. Drewes, Shane A. Snyder, Ann Heil, and Keith A. Maruya. 2014. "The Occurrence and Fate of Chemicals of Emerging Concern in Coastal Urban Rivers Receiving Discharge of Treated Municipal Wastewater Effluent." *Environmental Toxicology and Chemistry* 33 (2): 350–58. https://doi.org/10.1002/etc.2457.

Shimabuku, Ila, Da Chen, Yan Wu, Jennifer Sun, and Rebecca Sutton. 2020. "Flame Retardants and Plastic Additives in San Francisco Bay: A Targeted Monitoring of Organophosphate Esters and Bisphenols." Contribution No. 925. https://www.sfei.org/documents/flame-retardants-and-plastic-additives-san-francisco-bay-targeted-monitoring.

Shimabuku, Ila, Jennifer Sun, and Phil Trowbridge. 2017. "2017 RMP Field Sampling Report." Contribution No. 849. Richmond, California: San Francisco Estuary Institute. https://www.sfei.org/documents/bay-2017-bay-rmp-field-sampling-report.

Sutton, Rebecca, Da Chen, Jennifer Sun, Denise J. Greig, and Yan Wu. 2019. "Characterization of Brominated, Chlorinated, and Phosphate Flame Retardants in San Francisco Bay, an Urban Estuary." *Science of the Total Environment* 652 (February): 212–23. https://doi.org/10.1016/j.scitotenv.2018.10.096.

Sutton, Rebecca, Meg Sedlak, Jennifer Sun, and Diana Lin. 2017. "Contaminants of Emerging Concern in San Francisco Bay: A Strategy for Future Investigations. 2017 Revision." Richmond, CA: San Francisco Estuary Institute. https://www.sfei.org/documents/contaminants-emerging-concern-san-francisco-bay-strategy-future-investigations-2017.

Taylor, Allison R., Jun Li, Jie Wang, Daniel Schlenk, and Jay Gan. 2019. "Occurrence and Probable Sources of Urban-Use Insecticides in Marine Sediments off the Coast of Los Angeles." *Environmental Science*

& Technology 53 (16): 9584–93. https://doi.org/10.1021/acs.est.9b02825.

Trowbridge, Phil, Jennifer Sun, Amy Franz, and Don Yee. 2017. "2017 Margins Sediment Cruise Plan."
    Contribution No. 847. Richmond, CA: San Francisco Estuary Institute.
    https://www.sfei.org/documents/2017-margins-microplastics-cruise-plan.

USEPA. 2017. "Aquatic Life Benchmarks and Ecological Risk Assessments for Registered Pesticides." Data
    and Tools. US Environmental Protection Agency. 2017.
    https://www.epa.gov/pesticide-science-and-assessing-pesticide-risks/aquatic-life-benchmarks-and-ec
    ological-risk.

Werme, Christine, Jennifer Hunt, Erin Beller, Kristen Cayce, Marcus Klatt, Aroon Melwani, Eric Polson, and
    Robin M. Grossinger. 2010. "Removal of Creosote-Treated Pilings and Structures from San
    Francisco Bay." Contribution No. 605. Oakland, CA: San Francisco Estuary Institute.
    https://www.sfei.org/SFBayCreosoteAssessment.

Weston, Donald P., Da Chen, and Michael J. Lydy. 2015. "Stormwater-Related Transport of the Insecticides
    Bifenthrin, Fipronil, Imidacloprid, and Chlorpyrifos into a Tidal Wetland, San Francisco Bay,
    California." *Science of The Total Environment* 527–528 (September): 18–25.
    https://doi.org/10.1016/j.scitotenv.2015.04.095.

Weston, Donald P., and Colin J. Jackson. 2009. "Use of Engineered Enzymes to Identify Organophosphate
    and Pyrethroid-Related Toxicity in Toxicity Identification Evaluations." *Environmental Science &*
    Technology 43 (14): 5514–20. https://doi.org/10.1021/es900434z.

Weston, Donald P., and Michael J. Lydy. 2014. "Toxicity of the Insecticide Fipronil and Its Degradates to
    Benthic Macroinvertebrates of Urban Streams." *Environmental Science & Technology* 48 (2): 1290–97.
    https://doi.org/10.1021/es4045874.

Weston, Donald P., Heather L. Ramil, and Michael J. Lydy. 2013. "Pyrethroid Insecticides in Municipal
    Wastewater." *Environmental Toxicology and Chemistry* 32 (11): 2460–68.
    https://doi.org/10.1002/etc.2338.

Yee, Don, Amy Franz, Adam Wong, John Ross, and Philip Trowbridge. 2017. "2017 Quality Assurance
    Program Plan for the Regional Monitoring Program for Water Quality in San Francisco Bay." San
    Francisco Estuary Institute.
    https://www.sfei.org/documents/2017-quality-assurance-program-plan-regional-monitoring-progra
    m-water-quality-san-francisco-bay.

Yee, Don, Adam Wong, Nina Buzby, and Philip Trowbridge. 2019. "Characterization of Sediment
    Contamination in South Bay Margin Areas." Contribution No. 962. Richmond, CA: San Francisco
    Estuary Institute.
    https://www.sfei.org/documents/characterization-sediment-contamination-south-bay-margin-areas.

Yee, Don, Adam Wong, Ila Shimabuku, and Philip Trowbridge. 2018. "Characterization of Sediment
    Contamination in Central Bay Margin Areas." Contribution #829. Richmond, CA: San Francisco
    Estuary Institute.
    https://www.sfei.org/documents/characterization-sediment-contamination-central-bay-margin-areas
    -0.

Zaugg, Steven D., Steven G. Smith, and Michael P. Schroeder. 2006. "Determination of Wastewater
    Compounds in Whole Water by Continuous Liquid-Liquid Extraction and Capillary-Column Gas
    Chromatography/Mass Spectrometry." Report 5-B4. Techniques and Methods.
    https://pubs.usgs.gov/tm/2006/05B04/.

Zimmerman, C. F., C. W. Keefe, and J. Bashe. 1997. "Method 440.0 Determination of Carbon and Nitrogen
    in Sediments and Particulates of Estuarine/Coastal Waters Using Elemental Analysis." US
    Environmental Protection Agency.
    https://cfpub.epa.gov/si/si_public_record_report.cfm?dirEntryId=309418.

Appendix A Laboratory Analytical Method Detection and Reporting Limits

Table A1. List of analytes, methods, and method detection limits for pesticides analyzed by USGS Organic Chemistry Research Laboratory (OCRL; Sacramento).

CASRN	Analyte Name	Type	Filtered Water (Dissolved Fraction) Analyzed	Suspended Sediment (Particulate Fraction) Analyzed	Bed Sediment Analyzed	Analysis Method	Method Detection Limit in water (ng/L)	Method Detection Limit in Sediment (µg/kg dry weight)
135410-20-7	Acetamiprid	Insecticide	●	-	-	LC/MS/MS	3.3	-
135158-54-2	Acibenzolar-S-methyl	Fungicide	●	●	-	GC/MS	3.0	-
15972-60-8	Alachlor	Herbicide	●	●	●	GC/MS	1.7	0.57
584-79-2	Allethrin	Insecticide	●	●	●	GC/MS	1.0	1.7
1912-24-9	Atrazine	Herbicide	●	●	●	GC/MS	2.3	1.5
86-50-0	Azinphos Methyl	Insecticide	●	●	●	GC/MS	9.4	1.7
961-22-8	Azinphos-methyl oxygen analog	Degradate	●	●	-	GC/MS	9.4	-
131860-33-8	Azoxystrobin	Fungicide	●	●	●	GC/MS	3.1	0.93
1861-40-1	Benfluralin	Herbicide	●	●	●	GC/MS	2.0	1.7
1072957-71-1	Benzovindiflupyr	Fungicide	●	●	-	GC/MS	3.4	-
82657-04-3	Bifenthrin	Insecticide	●	●	●	GC/MS	0.7	0.61
188425-85-6	Boscalid	Fungicide	●	●	●	GC/MS	2.8	1.2
116255-48-2	Bromoconazole	fungicide	●	●	-	GC/MS	3.2	-
33629-47-9	Butralin	Herbicide	●	●	●	GC/MS	2.6	1.6
2008-41-5	Butylate	Herbicide	●	●	●	GC/MS	1.8	1.3
133-06-2	Captan	Fungicide	●	●	●	GC/MS	10.2	3.1
63-25-2	Carbaryl	Insecticide	●	●	●	GC/MS	6.5	1.2
10605-21-7	Carbendazim	Fungicide	●	-	-	LC/MS/MS	4.2	-
1563-66-2	Carbofuran	Insecticide	●	●	●	GC/MS	3.1	1.2
5234-68-4	Carboxin	Fungicide	●	-	-	LC/MS/MS	4.5	-
500008-45-7	Chlorantraniliprole	Insecticide	●	-	-	LC/MS/MS	4.0	-
122453-73-0	Chlorfenapyr	Insecticide	●	●	-	GC/MS	3.3	-
6967-29-9	Chloro-N-(2,6-diethylphenyl) acetamide, 2-	Degradate	-	-	●		-	1.3
32428-71-0	Chloro-N-(ethoxymethyl)-N-(2-ethyl-6-methylphenyl)acetamide, 2-	Degradate	●	●	-	GC/MS	1.5	-
1897-45-6	Chlorothalonil	Fungicide	●	●	●	GC/MS	4.1	1.1
2921-88-2	Chlorpyrifos	Insecticide	●	●	●	GC/MS	2.1	0.89
5598-15-2	Chlorpyrifos Oxon	Insecticide	●	●	-	GC/MS	5.0	-
81777-89-1	Clomazone	Herbicide	●	●	●	GC/MS	2.5	2.0
210880-92-5	Clothianidin	Insecticide	●	-	-	LC/MS/MS	3.9	-
56-72-4	Coumaphos	Insecticide	●	●	●	GC/MS	3.1	1.2
736994-63-1	Cyantraniliprole	Insecticide	●	-	-	LC/MS/MS	4.2	-
120116-88-3	Cyazofamid	Fungicide	●	-	-	LC/MS/MS	4.1	-
1134-23-2	Cycloate	Herbicide	●	●	●	GC/MS	1.1	0.8
68359-37-5	Cyfluthrin, Total	Insecticide	●	●	●	GC/MS	1.0	1.3
122008-85-9	Cyhalofop-butyl	Herbicide	●	●	●	GC/MS	1.9	0.8
91465-08-6	Cyhalothrin	Insecticide	●	●	●	GC/MS	0.5	0.69
57966-95-7	Cymoxanil	Fungicide	●	-	-	LC/MS/MS	3.9	-
52315-07-8	Cypermethrin, Total	Insecticide	●	●	●	GC/MS	1.0	1.2
94361-06-5	Cyproconazole	Fungicide	●	●	●	GC/MS	4.7	1.0
121552-61-2	Cyprodinil	Fungicide	●	●	●	GC/MS	7.4	1.7
1861-32-1	Dacthal	Herbicide	●	●	●	GC/MS	2.0	1.7
72-54-8	DDD(p,p')	Insecticide	●	●	●	GC/MS	4.1	0.98
72-55-9	DDE(p,p')	Insecticide	●	●	●	GC/MS	3.6	0.97
50-29-3	DDT(p,p')	Insecticide	●	●	●	GC/MS	4.0	0.84
52918-63-5	Deltamethrin	Insecticide	●	●	●	GC/MS	0.6	1.3
120983-64-4	Desthio-prothioconazole	Fungicide	●	-	-	LC/MS/MS	3.0	-
333-41-5	Diazinon	Insecticide	●	●	●	GC/MS	0.9	1.6
962-58-3	Diazoxon	Insecticide	●	●	-	GC/MS	5.0	-
626-43-7	Dichloroaniline, 3,5-	Herbicide	●	●	●	GC/MS	7.6	1.5
95-76-1	Dichlorobenzenamine, 3,4-	Herbicide	●	●	●	LC/MS/MS	3.2	1.3
2327-02-8	Dichlorophenyl Urea, 3,4-	Degradate	●	-	-	LC/MS/MS	3.4	-

Table A1. List of analytes, methods, and method detection limits for pesticides analyzed by USGS Organic Chemistry Research Laboratory (OCRL; Sacramento).

CASRN	Analyte Name	Type	Filtered Water (Dissolved Fraction) Analyzed	Suspended Sediment (Particulate Fraction) Analyzed	Bed Sediment Analyzed	Analysis Method	Method Detection Limit in water (ng/L)	Method Detection Limit in Sediment (µg/kg dry weight)
3567-62-2	Dichlorophenyl-3-methyl Urea, 3,4-	Herbicide	●	-	-	LC/MS/MS	3.5	-
62-73-7	Dichlorvos	Insecticide	●	●	-	GC/MS	5.1	-
119446-68-3	Difenoconazole	Fungicide	●	●	●	GC/MS	10.5	1.0
110488-70-5	Dimethomorph	Fungicide	●	●	●	GC/MS	6.0	1.5
165252-70-0	Dinotefuran	Insecticide	●	-	-	LC/MS/MS	4.5	-
97886-45-8	Dithiopyr	Herbicide	●	●	●	GC/MS	1.6	1.3
330-54-1	Diuron	Herbicide	●	-	-	LC/MS/MS	3.2	-
759-94-4	EPTC	Herbicide	●	●	●	GC/MS	1.5	0.79
66230-04-4	Esfenvalerate	Insecticide	●	●	●	GC/MS	0.5	0.98
162650-77-3	Ethaboxam	Fungicide	●	-	-	LC/MS/MS	3.8	-
55283-68-6	Ethalfluralin	Herbicide	●	●	●	GC/MS	3.0	1.2
80844-07-1	Etofenprox	Insecticide	●	●	●	GC/MS	2.2	1.0
153233-91-1	Etoxazole	Insecticide	●	●	-	GC/MS	4.2	-
131807-57-3	Famoxadone	Fungicide	●	●	●	GC/MS	2.5	1.7
161326-34-7	Fenamidone	Fungicide	●	●	-	GC/MS	5.1	-
60168-88-9	Fenarimol	Fungicide	●	●	●	GC/MS	6.5	1.4
114369-43-6	Fenbuconazole	Fungicide	●	●	●	GC/MS	5.2	1.8
126833-17-8	Fenhexamid	Fungicide	●	●	●	GC/MS	7.6	2.5
39515-41-8	Fenpropathrin	Insecticide	●	●	●	GC/MS	0.6	1.0
134098-61-6	Fenpyroximate	Insecticide	●	●	●	GC/MS	5.2	1.9
55-38-9	Fenthion	Insecticide	●	●	●	GC/MS	5.5	2.0
120068-37-3	Fipronil	Insecticide	●	●	●	GC/MS	2.9	1.6
205650-65-3	Fipronil Desulfinyl	Insecticide	●	●	●	GC/MS	1.6	1.8
205650-69-7	Fipronil Desulfinyl Amide	Insecticide	●	●	●	GC/MS	3.2	2.0
120067-83-6	Fipronil Sulfide	Insecticide	●	●	●	GC/MS	1.8	1.5
120068-36-2	Fipronil Sulfone	Insecticide	●	●	●	GC/MS	3.5	0.96
158062-67-0	Flonicamid	Insecticide	●	-	-	LC/MS/MS	3.4	-
79622-59-6	Fluazinam	Fungicide	●	●	●	GC/MS	4.4	2.1
272451-65-7	Flubendiamide	Insecticide	●	●	-	GC/MS	6.2	-
131341-86-1	Fludioxonil	Fungicide	●	●	●	GC/MS	7.3	2.5
142459-58-3	Flufenacet	Herbicide	●	●	●	GC/MS	4.7	1.0
62924-70-3	Flumetralin	Plant growth regulator	●	●	●	GC/MS	5.8	1.2
239110-15-7	Fluopicolide	Fungicide	●	●	-	GC/MS	3.9	-
658066-35-4	Fluopyram	Fungicide	●	●	-	GC/MS	3.8	-
361377-29-9	Fluoxastrobin	Fungicide	●	●	●	GC/MS	9.5	1.2
951659-40-8	Flupyradifurone	Insecticide	●	-	-	LC/MS/MS	3.0	-
59756-60-4	Fluridone	Herbicide	●	-	-	LC/MS/MS	3.7	-
85509-19-9	Flusilazole	Fungicide	●	●	●	GC/MS	4.5	2.2
66332-96-5	Flutolanil	Fungicide	●	●	●	GC/MS	4.4	2.1
76674-21-0	Flutriafol	Fungicide	●	●	●	GC/MS	4.2	1.1
907204-31-3	Fluxapyroxad	Fungicide	●	●	-	GC/MS	4.8	-
51235-04-2	Hexazinone	Herbicide	●	●	●	GC/MS	8.4	0.92
35554-44-0	Imazalil	Fungicide	●	●	●	GC/MS	10.5	1.8
138261-41-3	Imidacloprid	Insecticide	●	-	-	LC/MS/MS	3.8	-
120868-66-8	Imidacloprid urea	Insecticide	●	-	-	LC/MS/MS	4.0	-
173584-44-6	Indoxacarb	Insecticide	●	●	●	GC/MS	4.9	2.4
125225-28-7	Ipconazole	Fungicide	●	●	-	GC/MS	7.8	-
36734-19-7	Iprodione	Fungicide	●	●	●	GC/MS	4.4	0.87
875915-78-9	Isofetamid	Fungicide	●	●	-	GC/MS	2.0	-
143390-89-0	Kresoxim-methyl	Fungicide	●	●	●	GC/MS	4.0	0.51
1634-78-2	Malaoxon	Insecticide	●	●	-	GC/MS	5.0	-
121-75-5	Malathion	Insecticide	●	●	●	GC/MS	3.7	0.98
374726-62-2	Mandipropamid	Fungicide	●	-	-	LC/MS/MS	3.3	-

Table A1. List of analytes, methods, and method detection limits for pesticides analyzed by USGS Organic Chemistry Research Laboratory (OCRL; Sacramento).

CASRN	Analyte Name	Type	Filtered Water (Dissolved Fraction) Analyzed	Suspended Sediment (Particulate Fraction) Analyzed	Bed Sediment Analyzed	Analysis Method	Method Detection Limit in water (ng/L)	Method Detection Limit in Sediment (µg/kg dry weight)
57837-19-1	Metalaxyl	Fungicide	●	●	●	GC/MS	5.1	1.9
125116-23-6	Metconazole	Fungicide	●	●	●	GC/MS	5.2	1.2
950-37-8	Methidathion	Insecticide	●	●	●	GC/MS	7.2	1.8
40596-69-8	Methoprene	Insecticide	●	●	●	GC/MS	6.4	1.6
161050-58-4	Methoxyfenozide	Insecticide	●	-	-	LC/MS/MS	2.7	-
51218-45-2	Metolachlor	Herbicide	●	●	●	GC/MS	1.5	0.73
2212-67-1	Molinate	Herbicide	●	●	●	GC/MS	3.2	0.98
88671-89-0	Myclobutanil	Fungicide	●	●	●	GC/MS	6.0	1.7
15299-99-7	Napropamide	Herbicide	●	●	●	GC/MS	8.2	0.87
116714-46-6	Novaluron	Insecticide	●	●	●	GC/MS	2.9	1.1
19044-88-3	Oryzalin	Herbicide	●	-	●	LC/MS/MS	5.0	1.4
19666-30-9	Oxadiazon	Herbicide	●	●	-	GC/MS	2.1	-
1003318-67-9	Oxathiapiprolin	Fungicide	●	-	-	LC/MS/MS	3.2	-
42874-03-3	Oxyfluorfen	Herbicide	●	●	●	GC/MS	3.1	1.9
76738-62-0	Paclobutrazol	Fungicide	●	●	-	GC/MS	6.2	-
298-00-0	Parathion, Methyl	Insecticide	●	●	●	GC/MS	3.4	1.1
1114-71-2	Pebulate	Herbicide	●	●	●	GC/MS	2.3	0.9
40487-42-1	Pendimethalin	Herbicide	●	●	●	GC/MS	2.3	0.81
219714-96-2	Penoxsulam	Herbicide	●	-	-	LC/MS/MS	3.5	-
1825-21-4	Pentachloroanisole	Insecticide	●	●	●	GC/MS	2.3	1.1
82-68-8	Pentachloronitrobenzene	Fungicide	●	●	●	GC/MS	3.5	1.1
183675-82-3	Penthiopyrad	Fungicide	●	-	-	LC/MS/MS	0.6	-
52645-53-1	Permethrin, Total	Insecticide	●	●	●	GC/MS	0.6	0.93
26002-80-2	Phenothrin	Insecticide	●	●	●	GC/MS	1.0	0.89
732-11-6	Phosmet	Insecticide	●	●	●	GC/MS	4.4	0.93
117428-22-5	Picoxystrobin	Fungicide	●	●	-	GC/MS	4.2	-
51-03-6	Piperonyl Butoxide	Synergist	●	●	●	GC/MS	2.3	1.2
29091-21-2	Prodiamine	Herbicide	●	●	●	GC/MS	5.2	1.4
1610-18-0	Prometon	Herbicide	●	●	●	GC/MS	2.5	2.7
7287-19-6	Prometryn	Herbicide	●	●	●	GC/MS	1.8	1.3
709-98-8	Propanil	Herbicide	●	●	●	GC/MS	10.1	2.2
2312-35-8	Propargite	Insecticide	●	●	●	GC/MS	6.1	2.2
60207-90-1	Propiconazole	Fungicide	●	●	●	GC/MS	5.0	1.1
23950-58-5	Propyzamide	Herbicide	●	●	●	GC/MS	5.0	1.5
175013-18-0	Pyraclostrobin	Fungicide	●	●	●	GC/MS	2.9	1.1
96489-71-3	Pyridaben	Insecticide	●	●	●	GC/MS	5.4	1.2
53112-28-0	Pyrimethanil	Fungicide	●	●	●	GC/MS	4.1	1.1
95737-68-1	Pyriproxifen	Insect growth regulator	●	●	-	GC/MS	5.2	-
124495-18-7	Quinoxyfen	Fungicide	●	●	-	GC/MS	3.3	-
10453-86-8	Resmethrin	Insecticide	●	●	●	GC/MS	1.0	1.3
874967-67-6	Sedaxane	Fungicide	●	●	-	GC/MS	5.2	-
122-34-9	Simazine	Herbicide	●	●	●	GC/MS	5.0	1.3
946578-00-3	Sulfoxaflor	Insecticide	●	-	-	LC/MS/MS	4.4	-
107534-96-3	Tebuconazole	Fungicide	●	●	●	GC/MS	3.7	1.2
112410-23-8	Tebufenozide	Insecticide	●	-	-	LC/MS/MS	3.0	-
96182-53-5	Tebupirimfos	Insecticide	●	●	●	GC/MS	1.9	2.0
none	Tebupirimfos oxon	Degradate	●	●	●	GC/MS	2.8	1.5
79538-32-2	Tefluthrin	Insecticide	●	●	●	GC/MS	0.6	0.66
112281-77-3	Tetraconazole	Fungicide	●	●	●	GC/MS	5.6	1.1
116-29-0	Tetradifon	Insecticide	●	●	●	GC/MS	3.8	2.0
7696-12-0	Tetramethrin	Insecticide	●	●	●	GC/MS	0.5	0.94
102851-06-9	T-Fluvalinate	Insecticide	●	●	●	GC/MS	0.7	1.2

Table A1. List of analytes, methods, and method detection limits for pesticides analyzed by USGS Organic Chemistry Research Laboratory (OCRL; Sacramento).

CASRN	Analyte Name	Type	Filtered Water (Dissolved Fraction) Analyzed	Suspended Sediment (Particulate Fraction) Analyzed	Bed Sediment Analyzed	Analysis Method	Method Detection Limit in water (ng/L)	Method Detection Limit in Sediment (µg/kg dry weight)
148-79-8	Thiabendazole	Fungicide	●	-	-	LC/MS/MS	3.6	-
111988-49-9	Thiacloprid	Insecticide	●	-	-	LC/MS/MS	3.2	-
153719-23-4	Thiamethoxam	Insecticide	●	-	-	LC/MS/MS	3.4	-
none	Thiamethoxam Degradate (CGA-355190)	Degradate	●	-	-	LC/MS/MS	3.5	-
117718-60-2	Thiazopyr	Herbicide	●	●	●	GC/MS	4.1	1.9
28249-77-6	Thiobencarb	Herbicide	●	●	●	GC/MS	1.9	0.61
129558-76-5	Tolfenpyrad	Insecticide	●	-	-	LC/MS/MS	2.9	-
43121-43-3	Triadimefon	Fungicide	●	●	●	GC/MS	8.9	1.5
55219-65-3	Triadimenol	Fungicide	●	●	●	GC/MS	8.0	1.5
2303-17-5	Triallate	Herbicide	●	●	●	GC/MS	2.4	1.4
78-48-8	Tributyl Phosphorotrithioate, S,S,S-	Herbicide	●	●	●	GC/MS	3.1	2.2
41814-78-2	Tricyclazole	Fungicide	●	-	-	LC/MS/MS	4.1	-
141517-21-7	Trifloxystrobin	Fungicide	●	●	●	GC/MS	4.7	1.0
68694-11-1	Triflumizole	Fungicide	●	●	●	GC/MS	6.1	1.1
1582-09-8	Trifluralin	Herbicide	●	●	●	GC/MS	2.1	0.88
131983-72-7	Triticonazole	Fungicide	●	●	●	GC/MS	6.9	1.8
50471-44-8	Vinclozalin	Fungicide	-	-	-		-	-
156052-68-5	Zoxamide	Fungicide	●	●	●	GC/MS	3.5	1.1

Table A2. List of analytes, methods, and reporting limits for fragrance ingredients and other emerging contaminants by USGS National Water Quality Laboratory (NWQL; Denver).

CASRN	Analyte Name	Analyzed in whole water (unfiltered)	Analyzed in bed sediment	Reporting Limit in Water (ng/L)	Reporting Limit in Sediment (µg/kg dry weight)	Chemical Source or Use, from Zaugg et al. (2006) and other sources
98-86-2	Acetophenone	●	●	200	150 - 300	Fragrance in detergent and tobacco, flavor in beverages
120-12-7	Anthracene	●	●	10	50 - 100	Component of tar, diesel, or crude oil, combustion product
84-65-1	Anthraquinone	●	●	20	50 - 100	Manufacture of dye/textiles, seed treatment, bird repellent
1912-24-9	Atrazine	●	●	80	100 - 200	Selective triazine herbicide
50-32-8	Benzo(a)pyrene	●	●	10	50 - 100	Regulated PAH, used in cancer research, combustion product
119-61-9	Benzophenone	●	●	40	50 - 100	Fixative for perfumes and soaps
117-81-7	Bis(2-ethylhexyl)phthalate	●	●	1,000	250 - 500	Plasticizer for polymers and resins, pesticide inert
80-05-7	Bisphenol A	●	●	20	50 - 100	Manuf polycarbonate resins, antioxidant, flame retardant
314-40-9	Bromacil	●	●	80	500 - 1,000	herbicide (general use pesticide), >80% noncrop usage on grass/brush
75-25-2	Bromoform	●	-	80	-	Wastewater ozonation byproduct, military/explosives
58-08-2	Caffeine	●	-	40	-	Beverages, diuretic, very mobile/biodegradable
76-22-2	Camphor	●	●	40	50 - 100	Flavor, odorant, ointments
63-25-2	Carbaryl	●	-	30	-	Insecticide, crop and garden uses, low persistence
86-74-8	Carbazole	●	●	10	50 - 100	Insecticide, Manuf dyes, explosives, and lubricants
2921-88-2	Chlorpyrifos	●	●	60	50 - 100	Insecticide, domestic pest and termite control (domestic use restricted as of 2001)
57-88-5	Cholesterol	●	●	800	250 - 500	Often a fecal indicator, also a plant sterol
360-68-9	Coprostanol, beta-3-	●	●	800	500 - 1,000	Carnivore fecal indicator
486-56-6	Cotinine	●	-	40	-	Primary nicotine metabolite
599-64-4	Cumylphenol, 4-	●	●	20	50 - 100	Nonionic detergent or metabolite
333-41-5	Diazinon	●	●	160	50 - 100	Insecticide, >40% nonagricultural usage, ants, flies
106-46-7	Dichlorobenzene, 1,4-	●	●	40	50 - 100	Moth repellent, fumigant, deodorant
102-36-3	Dichlorophenyl isocyanate, 3,4-	●	-	160	-	Degradate of diuron, a noncrop herbicide
62-73-7	Dichlorvos	●	-	40	-	Insecticide, pet collars; naled or trichlofon degradate
84-66-2	Diethyl phthalate	●	●	200	100 - 200	Plasticizer for polymers and resins
134-62-3	Diethyl-3-methyl-benzamide, N,N-	●	●	20	100 - 200	Insecticide, urban uses, mosquito repellent
581-42-0	Dimethylnaphthalene, 2,6-	●	●	20	50 - 100	Present in diesel/kerosene (trace in gasoline)
206-44-0	Fluoranthene	●	●	10	50 - 100	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product

Table A2. List of analytes, methods, and reporting limits for fragrance ingredients and other emerging contaminants by USGS National Water Quality Laboratory (NWQL; Denver).

CASRN	Analyte Name	Analyzed in whole water (unfiltered)	Analyzed in bed sediment	Reporting Limit in Water (ng/L)	Reporting Limit in Sediment (µg/kg dry weight)	Chemical Source or Use, from Zaugg et al. (2006) and other sources
1222-05-5	Galaxolide	●	●	20	50 - 100	Musk fragrance, persistent, widespread in ground water, concern for bioaccumulation and toxicity
120-72-9	Indole	●	●	20	100 - 200	Pesticide inert ingredient, fragrance in coffee
124-76-5	Isoborneol	●	●	45	50 - 100	Fragrance in perfumery, in disinfectants
78-59-1	Isophorone	●	●	25	50 - 100	Solvent for lacquer, plastic, oil, silicon, resin
98-82-8	Isopropylbenzene	●	●	20	100 - 200	Manufacture of phenol, acetone, fuels and paint thinner
119-65-3	Isoquinoline	●	●	400	100 - 200	Flavors and fragrances
5989-27-5	Limonene, d-	●	●	80	50 - 100	Fungicide, antimicrobial, antiviral, fragrance in aerosols
89-78-1	Menthol	●	●	160	50 - 100	Cigarettes, cough drops, liniment, mouthwash
57837-19-1	Metalaxyl	●	-	80	-	Herbicide, Fungicide (general use pesticide), mildew, blight, pathogens, golf/turf
119-36-8	Methyl salicylate	●	-	40	-	Liniment, food, beverage, UV-absorbing lotion
83-34-1	Methylindole, 3-	●	●	20	50 - 100	Fragrance, stench in feces and coal tar
136-85-6	Methyl-1H-benzotriazole, 5-	●	-	160	-	Antioxidant in antifreeze and deicers
90-12-0	Methylnaphthalene, 1-	●	●	20	50 - 100	2–5% of gasoline, diesel fuel, or crude oil
91-57-6	Methylnaphthalene, 2-	●	●	20	50 - 100	2–5% of gasoline, diesel fuel, or crude oil
106-44-5	Methylphenol, 4-	●	●	40	250 - 500	Wood preservative
51218-45-2	Metolachlor	●	●	20	50 - 100	Herbicide (general use pesticide), indicator of agricultural drainage
91-20-3	Naphthalene	●	●	10	50 - 100	Fumigant, moth repellent, major component (about 10%) of gasoline
20427-84-3	Nonylphenol Diethoxylate, 4-	●	●	800	1000 - 2000	Detergents, paints, pesticides, personal care products, and plastics
104-35-8	Nonylphenol Monoethoxylate, 4-	●	●	800	500 - 1,000	Nonionic detergent
84852-15-3	Nonylphenol, tech-	●	●	800	750 - 1,500	Degradate of nonionic surfactants in sewage
27193-28-8	Octylphenol	●	●	10	50 - 100	Production of rubber, pesticides, and paints
2315-61-9	Octylphenol diethoxylate, tert-4-	●	●	100	50 - 100	Nonionic detergent or metabolite
2315-67-5	Octylphenol monoethoxylate, tert-4-	●	●	300	250 - 500	Nonionic detergent or metabolite
140-66-9	Octylphenol, tert-4-	●	●	200	50 - 100	Nonionic detergent or metabolite
5436-43-1	PBDE 047	●	●	20	50 - 100	Widely used brominated flame retardant
87-86-5	Pentachlorophenol	●	-	800	-	Herbicide, fungicide, wood preservative, termite control

Table A2. List of analytes, methods, and reporting limits for fragrance ingredients and other emerging contaminants by USGS National Water Quality Laboratory (NWQL; Denver).

CASRN	Analyte Name	Analyzed in whole water (unfiltered)	Analyzed in bed sediment	Reporting Limit in Water (ng/L)	Reporting Limit in Sediment (µg/kg dry weight)	Chemical Source or Use, from Zaugg et al. (2006) and other sources
85-01-8	Phenanthrene	●	●	10	50 - 100	Used in the manufture of explosives, component of tar, diesel fuel, or crude oil, combustion product
108-95-2	Phenol	●	●	80	50 - 100	Disinfectant, Manuf several products, leachate
1610-18-0	Prometon	●	●	80	50 - 100	Herbicide (noncrop only), applied prior to blacktop
129-00-0	Pyrene	●	●	10	50 - 100	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product
83-46-5	Sitosterol, beta-	●	●	2,400	500 - 1,000	Plant sterol
19466-47-8	Stigmastanol, beta	●	●	1,700	500 - 1,000	Herbivore fecal indicator (digestion of sitosterol)
127-18-4	Tetrachloroethylene	●	-	80	-	Solvent, degreaser, veterinary anthelmintic
21145-77-7	Tonalide	●	●	20	50 - 100	Musk fragrance, persistent, widespread in ground water, concern for bioaccumulation and toxicity
126-73-8	Tributylphosphate	●	●	32	50 - 100	Antifoaming agent, flame retardant
3380-34-5	Triclosan	●	●	160	50 - 100	Disinfectant, antimicrobial (concern for acquired microbial resistance)
77-93-0	Triethyl citrate	●	-	20	-	Cosmetics, pharmaceuticals
115-86-6	Triphenyl Phosphate	●	●	40	50 - 100	Plasticizer, resin, wax, finish, roofing paper, flame retardant
13674-87-8	Tris(1,3-dichloroisopropyl) phosphate	●	●	160	100 - 200	Flame retardant
78-51-3	Tris(2-butoxyethyl) phosphate	●	●	320	150 - 300	Flame retardant
115-96-8	Tris(2-chloroethyl)phosphate	●	●	80	100 - 200	Plasticizer, flame retardant

Appendix B Quality Assurance Summary

Overall, the data were acceptable as a screening level effort. However, because the majority of the results for this study were non-detects, the statistical basis for this determination is somewhat limited. Quality assurance was performed by the SFEI data management team under the direction of QA Officer Dr. Don Yee.

Sediment – Current-Use Pesticides, Fragrance Ingredients, and Other Emerging Contaminants

Overall acceptability

Overall the data were marginally acceptable primarily as a screening level effort. Most analytes were non-detects. Recovery in the matrix spike sample was acceptable for all spiked compounds. Precision on the lab or field replicates (for the few compounds detected at high enough concentrations in replicates) were also acceptable aside from cholesterol and sitosterol, beta-. The lab also flagged many results as "Q" = questionable result, so the quantitativeness of much of this set is suspect and many results should be considered estimates only.

Hold time review

Hold times were all 185 days or less. The Bay RMP Quality Assurance Project Plan (QAPP) does not list hold times for most emerging contaminants. However, internal studies conducted by OCRL scientists have not found measurable degradation or analyte loss for hold times of 90 and 180 days for dissolved and particulate pesticide methods, respectively, so the impact on reported results is likely negligible.

Dataset completeness

Results for 14 grab sediment samples (including 1 lab replicate and 1 field replicate), 1 to 3 lab blanks (depending on analyte), 1 field blank, and 1 matrix spike were reported for 170 analytes, with the majority of analytes being pesticides. TOC and a handful of PAHs, BDE 47, and various legacy pollutant compounds were also reported.

For this study, 26% of sediment samples (5 of 19) were analyzed for quality control purposes.

Blank contamination

Octylphenol diethoxylate, tert-4-, and phenol were detected in lab blanks averaging over the MDL. All the field sample results were <3x the blank and censored (VRIP flags).

Method sensitivity

We analyzed the results to determine whether the analytical methods used were of sufficient sensitivity to achieve the objectives of the study. We concluded that effective study of emerging contaminants in the aquatic environment may benefit from development of methods with lower

detection limits, as all but 16 analytes were non-detect in all samples. Of those, only 10 were detected in more than half the samples; among those 10, 4 were PAHs, and 3 were DDT compounds, rather than emerging contaminants. Nevertheless, these laboratories are among the leading research labs with world-class capabilities, and their detection limits are generally the lowest that can be practically obtained at this time for broad screening methods.

Accuracy

Matrix spikes, where a sample is spiked with a known amount of a contaminant, provide a determination of method accuracy that can account for matrix interferences or other analytical problems. Accuracy was flagged based on the matrix spike with generally good recoveries, and recovery error 26% or better for all analytes, within the 35% target RMP usually uses for flagging organics. The majority of cases were under-recovery, although some analytes were up to 14% higher than their expected values.

Precision

The precision of analysis methods (ability to consistently obtain the same result) is determined by analyzing duplicate samples. The laboratories analyzed lab replicates (split and analyzed in the laboratory) to assess the repeatability of measurements. Field crews also collected one field duplicate (collected in the same place at the same time as the normal sample).

Only TOC and three DDT compounds were detected in the lab replicate and its corresponding field sample at 3x MDL or greater, with relative standard deviation (RSD) 7% or better. For the other compounds, the field replicate was the only sample on which precision could be evaluated for most analytes, as the majority of analytes were 100% non-detects. Of those detected, only cholesterol and sitosterol, beta-, had poor or marginal recovery, with RSD of 109% and 49% respectively (other compounds with RSD of 12% or less). Since field duplicates are expected to have more variation not entirely due to analytical variation, results for those two analytes were flagged VIU (for marginal recovery) but not censored.

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Overall acceptability

Laboratory analytical results were generally acceptable for all analytes. However, because most of the target analytes were not detected in any sample, the quality assurance review is limited. The lab marked several results as JA = estimated. In these cases, the lab is confident that the compound is present in the sample. This indicates that the results are estimates only, and are not fully quantitative. Care should be taken in interpreting these results. The lab flagged other results as Q = questionable.

Some field samples were marked by the lab as IP = blank contaminated. However, the results submitted by the lab do not show any of the target analytes as having been detected in the field blank, and no lab blank was reported by the lab. SFEI's QA Officer kept flags inserted by the lab in the final dataset.

Hold time review

Hold times were all 72 days or less. The QAPP has no hold times for most emerging contaminants.

Dataset completeness

Results for 13 grab water samples (including 1 field replicate), 1 field blank, and 2 matrix spikes were reported for 232 dissolved and 139 particulate analytes, with the majority of analytes being pesticides. Different sites were used as parent samples for matrix spikes for different analyte groups.

Blank contamination

None of the analytes were detected in the field blank, so no blank flags were needed.

However, the lab flagged a number of analytes with "IP" flags (analytes detected in blank); acetophenone, benzophenone, cholesterol, diethyl phthalate, fluoranthene, pyrene, triethyl citrate, yet none of them were detected > MDL in the (field) blank. Those lab added flags were left in the reported data.

Method sensitivity

Many target analytes were not detected, with 100% non-detect (ND) for all particulate analytes, and only 48 analytes were detected in the dissolved phase. Of those, only eight were detected in more than half the samples, with two of the frequently detected compounds being PAHs.

Accuracy

Recovery was evaluated on the matrix spikes. Recoveries on matrix spikes averaged within 27% of the target value or better for all analytes. The majority under-recovered, but for some analytes average over-recovery up to 13% was found.

Precision

No lab replicates were reported by the lab, therefore, we used the results of field replicates to analyze precision. Few analytes were detected in the field replicates, but of the ones found over 3x MDL, RSDs were always < 10%, so no precision flags were needed. Likewise, for the remaining analytes detected only in the paired matrix spike and matrix spike duplicate, RSDs were about 15% or better for all analytes.

Appendix C How to Obtain Study Data

The results from this study can be downloaded from the California Environmental Data Exchange Network (CEDEN).

 To download project data, visit: https://ceden.waterboards.ca.gov/AdvancedQueryTool

Click "Select Programs" and choose "SF Bay Regional Monitoring for Water Quality."

Then click "Select Parent Projects" and choose "Regional Monitoring Program - Margins."

Then click "Retrieve Data."

If you have chosen Excel format, the downloaded file will be a text file with comma-separated values, or a .csv file. However, the file will have the extension .xls. If you open the file, you will get a warning message, "The file and extension of 'ceden_data_###" don't match. The file could be corrupted or unsafe. Unless you trust its source, don't open it. Do you want to open it anyway?" You can safely click "Yes" to open the file.

Appendix D Summary Tables of Results for Polycyclic Aromatic Hydrocarbons (PAHs)

Table D1. Summary of polycyclic aromatic hydrocarbons (PAHs) detected in water in South San Francisco Bay Margin samples, summer 2017.

Chemical Name	CAS Number	Chemical Uses (from Zaugg et al. 2006)	Number of Locations where detected, out of 12	Detection frequency (n = 12)	Reporting Limit (ng/L)	Median Observed Concentration (ng/L)	Maximum Observed Concentration (ng/L)
Anthraquinone	84-65-1	Manufacture of dye/textiles, seed treatment, bird repellent	5	42%	20	<20	15
Benzo(a)pyrene	50-32-8	Regulated PAH, used in cancer research, combustion product, Plant sterol	4	33%	10	<10	13
Fluoranthene	206-44-0	Constituent of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product	11	92%	10	<10	20
Phenanthrene	85-01-8	Manufacture of explosives, component of tar, diesel fuel, or crude oil, combustion product	1	8%	10	<10	12
Pyrene	129-00-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product	11	92%	10	11	24

Table D2. Summary of polycyclic aromatic hydrocarbons (PAHs) detected in bed sediment in South San Francisco Bay Margin samples, summer 2017.

Chemical Name	CAS Number	Chemical Uses (from Zaugg et al. 2006)	Reporting limit (µg/kg dw)*	Number of Locations where detected, out of 12	Detection Frequency (n = 12)	Median Observed Concentration (µg/kg dw)	Maximum Observed Concentration (µg/kg dw)
Anthracene	**0120-12-7**	**Wood preservative, component of tar, diesel, or crude oil, combustion product**	**50 - 100**	**12**	**100%**	**30**	**120**
Anthraquinone	84-65-1	Manufacture of dye/textiles, seed treatment, bird repellent	50 - 100	8	67%	11	23
Benzo(a)pyrene	50-32-8	Used in cancer research, combustion product, Plant sterol	50 - 100	12	100%	140	450
Dimethylnaphthalene, 2,6-	28804-88-8	Present in diesel/kerosene (trace in gasoline)	50 - 100	10	83%	30	49
Fluoranthene	206-44-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product	50 - 100	12	100%	180	530
Methylnaphthalene, 1-	90-12-0	2–5% of gasoline, diesel fuel, or crude oil	50 - 100	7	58%	8	13
Methylnaphthalene, 2-	91-57-6	2–5% of gasoline, diesel fuel, or crude oil	50 - 100	6	50%	8	26
Naphthalene	91-20-3	Fumigant, moth repellent, major component (about 10%) of gasoline	50 - 100	6	50%	20	59
Phenanthrene	85-01-8	Manufacture of explosives, component of tar, diesel fuel, or crude oil, combustion product	50 - 100	12	100%	90	320
Pyrene	129-00-0	Component of coal tar and asphalt (only traces in gasoline or diesel fuel), combustion product	50 - 100	12	100%	210	740

*Method detection limit varied by sample. The laboratory occasionally reported estimated concentrations below the MDL.