Pilot Study of Constituents of Emerging Concern in the Sacramento-San Joaquin Delta Year 1 Data Report

Authors:

Michael Weaver and Don Yee: San Francisco Estuary Institute – Aquatic Science Center

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AQUATIC SCIENCE CENTER

Moss Landing Marine Laboratories

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Summary

This report documents the first year results from a pilot study for the monitoring of Constituents of Emerging Concern (CECs) in the Sacramento-San Joaquin River Delta (the Delta). A suite of CECs recommended for monitoring by a State Water Resources Control Board guidance document were analyzed in water, sediment and tissue samples obtained from the Delta. Many of the primary target compounds in the water matrix were frequently not detected, but the few that were measured generally appeared to be in a concentration range similar to those reported in the literature for other water bodies (examples in the text). For the polybrominated diphenyl ethers (PBDEs) and perfluoroalkyl and polyfluoroalkyl substances (PFAS) measured in sediment and tissue, results were also in a similar concentration range to those found in other water bodies such as San Francisco Bay. The relative abundance of individual compounds in these analyte groups also were also similar to data from other studies. In sediment, primary target PBDEs 047 and 099 were detected in all samples, but at <1 ng/g dw, while 209 (the most degradation-resistant, and dominant in the "deca" formulation that was banned last, but a secondary PBDE analyte with high RPDs (125-175%) in replicates that exceed the MQO of <35%) was most abundant in 2 of 3 samples, while tissue samples primarily had PBDE 047 and 099, which have chemical properties conducive to bioaccumulation. Of the PFAS, PFOS was detected at the highest concentrations. These data provide a baseline for comparison to other regions in California and beyond, and to track potential trends in environmental concentrations and exposure, with management restrictions or changing use patterns for these chemicals.

Introduction

A pilot study for the monitoring of Constituents of Emerging Concern (CECs) in the Sacramento-San Joaquin River Delta (the Delta) by the Delta Regional Monitoring Program (Delta RMP) was conducted beginning in 2020. This pilot study (Larry Walker Associates 2018) was designed by Larry Walker Associates, an entity representing Delta RMP stakeholders, based on the State Water Resources Control Board design guidance (Tadesse 2016) to better understand methods of evaluating ambient concentrations and sources of Constituents of Emerging Concern (CECs) in different Central Valley surface water scenarios.

The stated goals for the study in the statewide guidance document from the State Board (Tadesse 2016) are:

> "This statewide pilot study implements the second phase of the recommendation which is to gather data to determine the occurrence and biological impacts of CEC. The result of this pilot study will help the State Water Board to develop a statewide CEC monitoring strategy and control action."
>
> "The objective of the CEC statewide pilot study monitoring plan is to generate statewide data to inform Water Board managers of the status and trends of CECs

in water. The plan is designed to narrow the data gap among regions by producing comparable CEC data throughout the state."

The responsible agency for the first year of the surface water monitoring program was the San Francisco Estuary Institute-Aquatic Science Center (SFEI-ASC), acting as the implementing entity to the Delta RMP. The pilot study's Quality Assurance Project Plan (QAPP), version 1.0 (Heberger et al. 2020), developed by SFEI-ASC, describes how the project was to be managed, organized and implemented in year one. Deviations from the plans and procedures outlined in that QAPP that occurred during the implementation of the project are documented in this report (Appendix 4).

This Report

This data report presents the methods and results for the first year of CEC monitoring by the Delta Regional Monitoring Program. In 2020, the Delta RMP initiated CEC monitoring of water, sediment, fish and bivalves. Fish were collected in September 2020 from four stations and analyzed for PFAS (PFOS and PFOA) and PBDEs. Clams were collected in October 2020 from five stations and analyzed for PBDEs. Sediment was collected in August and September 2020 from three stations and analyzed for PFAS (PFOS and PFOA) and PBDEs (and ancillary parameters). Quarterly sampling of PFAS (PFOS and PFOA), Pharmaceuticals and Personal Care Products (PPCPs) (including estrone, 17-beta-estradiol, ibuprofen, diclofenac, triclosan, and bisphenol A), galaxolide, and ancillary parameters in water, at eight sites, began in September 2020, with further sampling conducted in January, April, and June 2021.

Monitoring Description

Water

Water samples were collected four times between September 2020 and June 2021. There were eight water collection sites (see Figure 1) that were planned to be sampled at each sampling event (three sites by SFEI-ASC and five sites by Department of Water Resources - Municipal Water Quality Investigations (DWR-MWQI)). However, due to COVID-19 related restrictions, DWR-MWQI did not sample during the second sampling event (in January 2021), so samples were only collected at three sites by SFEI-ASC during that event.

SFEI-ASC collected water samples at Sacramento River at Elkhorn Boat Launch Facility (519SUT108), Dry Creek at Roseville Wastewater Treatment Plant (WWTP) (519DRYCRK) and Old Alamo Creek at Lewis Road (511SOL011) during the September, January, April and June sampling events. DWR-MWQI collected water samples at American River at Discovery Park (519AMNDVY), Sacramento River at Freeport (510ST1301), Sacramento River at Hood Monitoring Station Platform (510SACC3A), San Joaquin River at Buckley Cove (544LSAC13) and San Joaquin River at Airport Way near Vernalis (541SJC501), during the September, April and June sampling events. Further details on sampling stations and dates are listed in Table 1.

At each site and event where water sampling occurred, samples were collected for every planned water analysis (PFOS and PFOA, galaxolide, PPCPs, and SSC), field water quality measurements (dissolved oxygen, pH, specific conductivity, temperature, and turbidity) were taken, and habitat observations were recorded. QC samples were also collected as required by the project QAPP (see Appendix 3 for additional details). Details on water sample collection methods are described in the Methods section of this report.

The water sampling monitoring design called for four sampling events on a schedule (listed in QAPP table 10.2) beginning with a summer (dry season) event, followed by a late summer/early fall event, a first flush event and spring storm event. The order of these events was shifted, due to a late start in sampling, so water collections began with an early fall event in 2020 and ended with a dry season event in summer 2021. Additionally, due to a lack of rainfall in spring 2021, the spring sampling event was a dry event rather than a spring storm event.

Some deviations from the StationCodes listed in the QAPP occurred during water sampling due to a) QAPP latitudes and longitudes not matching the CEDEN coordinates for the stations and b) CEDEN stations in the same vicinity sharing near-identical station names (see deviation forms 2020-04 and 2020-05 in Appendix 4 for more details). As a result of this, for the American River at Discovery Park site listed in the QAPP, water was sampled at the station with CEDEN StationCode 519AMNDVY (not 519SWPDCP), for the Dry Creek u/s of WWTP site, water was sampled at 519DRYCRK (not 519LSAC12), and for the Sacramento River at Veterans Bridge site, water was sampled at 519SUT108 (not 519SWPVTB). (The determination of the most appropriate StationCode to use was made by MLJ Environmental, based on which CEDEN station most closely

matched the actual coordinates sampled at, with a preference to have consistent StationCodes used among the different project matrices, wherever possible.)

Sediment

Sediment samples were collected in August and September 2020, concurrently with a State Water Resources Control Board - Surface Water Ambient Monitoring Program - Stream Pollution Trends Monitoring Program (SWRCB-SWAMP-SPoT) sediment cruise and SFEI-ASC's first event of water sampling for this project. Sediment was collected at three locations (two sites by SFEI-ASC and one site by SWRCB-SWAMP-SPoT). These locations were a subset of the water sample collection sites (see Figure 1).

SFEI-ASC collected sediment samples at Dry Creek at Roseville WWTP (519DRYCRK) and Old Alamo Creek at Lewis Road (511SOL011), in September 2020. SWRCB-SWAMP-SPoT collected sediment samples at American River at Discovery Park (519AMNDVY) in August 2020. Further details on sampling stations and dates are listed in Table 1.

At each site where sediment sampling occurred, samples were collected for every planned sediment analysis (PFOS and PFOA, PBDEs, TOC), field water quality measurements (dissolved oxygen, pH, specific conductivity, temperature and turbidity) were taken, and habitat observations were recorded. QC samples were also collected as required by the project QAPP (see Appendix 3 for additional details). Details on sediment sample collection methods are described in the Methods section of this report.

As with water sampling, some deviations from the StationCodes listed in the QAPP occurred during sediment sampling due to a) QAPP latitudes and longitudes not matching the CEDEN coordinates for the stations and b) CEDEN stations in the same vicinity sharing near-identical station names (see deviation forms 2020-04 and 2020-05 in Appendix 4 for more details). As a result of this, for the American River at Discovery Park site listed in the QAPP, sediment was sampled at the station with CEDEN StationCode 519AMNDVY (not 519SWPDCP), and for the Dry Creek u/s of WWTP site, sediment was sampled at 519DRYCRK (not 519LSAC12).

Fish

Fish samples were collected from four stations in the Delta (Figure 1). Fish samples were collected at a subset of the eight water sample collection sites (though in two instances, different stations in the same vicinity of the water collection sites were sampled). Fish collections were completed in September 2020. Details on sampling stations and dates are listed in Table 1 and in greater detail in the cruise report (Appendix 1).

For two fish sampling stations, there were deviations from the Station Codes listed in the QAPP, due to multiple CEDEN stations in the same vicinity sharing near-identical station names (see deviation form 2020-04 in Appendix 4). As a result of this, for the Sacramento River at Veterans Bridge site listed in the QAPP, fish were sampled at 519ST1309 (not 519SWPVTB), and for the Sacramento River at Freeport site, fish were sampled at 510ST1317 (not 510ST1301).

Bivalve

Sampling of *Corbicula fluminea* clams was planned at six sites in the San Francisco Bay-Delta in October 2020. At one site, San Joaquin River at Airport Way near Vernalis, sampling was attempted, but no clams were collected due to the site being inaccessible (see deviation form 2020-08 in Appendix 4), so clam samples were only collected at 5 sites (Figure 1). Details on sampling stations and dates are listed in Table 1 and in greater detail in the cruise report (Appendix 2).

As with water sampling, some deviations from the StationCodes listed in the QAPP occurred during clam sampling due to a) QAPP latitudes and longitudes not matching the CEDEN coordinates for the stations and b) CEDEN stations in the same vicinity sharing near-identical station names (see deviation forms 2020-04 and 2020-05 in Appendix 4 for more details). As a result of this, for the American River at Discovery Park site listed in the QAPP, clams were sampled at the station with CEDEN StationCode 519AMNDVY (not 519SWPDCP), and for the Sacramento River at Veterans Bridge site, clams were sampled at 519SUT108 (not 519SWPVTB).

Table 1 Sampling station code, name, latitude, longitude, and collection dates.

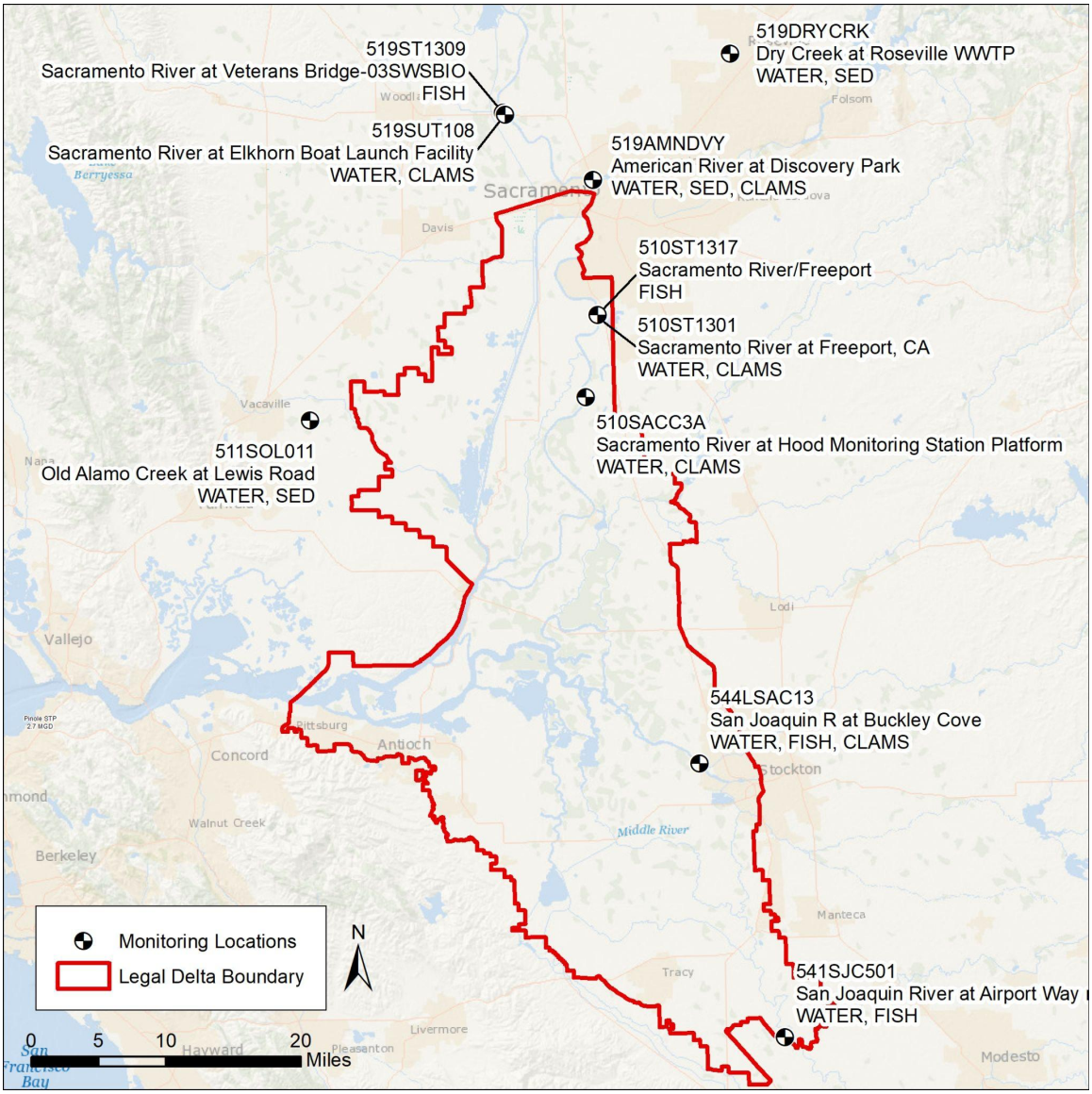
CEDEN Station Code	CEDEN Station Name	CEDEN Target Latitude	CEDEN Target Longitude	Fish Collection Dates	Bivalve Collection Dates	Sediment Collection Dates	Water Collection Dates
510SACC3A	Sacramento River at Hood Monitoring Station Platform	38.36771	-121.5205	-	10/15/2020	-	9/29/2020, 4/13/2021, 6/15/2021
510ST1301	Sacramento River at Freeport, CA	38.45555	-121.50194	-	10/15/2020	-	9/29/2020, 4/13/2021, 6/15/2021
510ST1317	Sacramento River/Freeport	38.4556	-121.5019	9/9/2020	-	-	-
511SOL011	Old Alamo Creek at Lewis Road	38.34643	-121.89702	-	-	9/30/2020	9/30/2020, 1/27/2021, 4/14/2021, 6/16/2021
519AMNDVY[1]	American River at Discovery Park	38.60094	-121.5055	-	10/15/2020	8/19/2020	9/29/2020, 4/13/2021, 6/15/2021
519DRYCRK[2]	Dry Creek at Roseville WWTP	38.734098	-121.3144446	-	-	9/30/2020	9/30/2020, 1/27/2021, 4/14/2021, 6/16/2021

[1]Water and bivalve samples originally recorded with Station Code 519SWPDCP.
[2] Water and sediment samples originally recorded with Station Code 519LSAC12.

519ST1309	Sacramento River at Veterans Bridge-03SWSBIO	38.67468	-121.62751	9/9/2020	-	-	-
519SUT108[3]	Sacramento River at Elkhorn Boat Launch Facility	38.67245	-121.625	-	10/15/2020	-	9/30/2020, 1/27/2021, 4/14/2021, 6/16/2021
541SJC501	San Joaquin River at Airport Way near Vernalis	37.67555556	-121.2641667	9/22/2020	-	-	9/30/2020, 4/14/2021, 6/16/2021
544LSAC13	San Joaquin R at Buckley Cove	37.971833	-121.373619	9/8/2020	10/16/2020	-	9/30/2020, 4/14/2021, 6/16/2021

[3] Water and bivalve samples originally recorded with Station Code 519SWPVTB.

Figure 1 Map of sampling locations. Labels show the CEDEN station code, station name, and type of samples collected.



Methods

Sample Collection

Water

DWR-MWQI water sampling was conducted by a modified version of the "Direct Dip Method" described in the DWR Standard Operating Procedure (SOP) document "Collection of Water Quality Samples for Laboratory Analysis." A clean empty bottle for each station was attached to a pole. The empty bottle was quickly submerged below the water surface, facing upstream, and allowed to fill, avoiding contact with the bottom sediment, or any debris or surface scum. The filled bottle was then removed from the water, and the contents poured into clean sample bottles which were then capped. The process was repeated until all the needed samples were collected. Samples were labeled and placed in an ice chest for transport back to the laboratory of the collection agency. Samples were then packed on ice and shipped, or delivered directly, with Chain of Custody forms (CoCs) to the respective analytical laboratories. SFEI-ASC water sampling was conducted by direct submersion of bottles by hand, in alignment with DWR protocols, and separately packed and shipped, or delivered directly, with CoCs to the respective analytical laboratories.

Handheld portable YSI instruments were taken to the field and used to measure the following ancillary water column parameters: temperature, pH, dissolved oxygen concentration and percent saturation, specific conductivity, and turbidity at each site and event.

Sediment

Sediment sampling conducted by SWRCB-SWAMP-SPoT and SFEI-ASC was performed by using shallow polycarbonate cores and scoops together to remove the top 5 cm of sediment from each site. A single core at each site could not provide sufficient material to perform all analyses, so several cores were collected at regular intervals along the reach of a site until sufficient material for all analyses was obtained. For PFOA and PFOS, core contents were scooped directly into sample jars. For PBDEs and TOC, core grabs were composited in a container before subsampling into separate jars for the respective analyses. Samples were kept chilled in an ice chest for return to each collection agency's laboratory, where they were packed chilled on ice and shipped to the analytical laboratory with CoCs. Upon receipt at the analytical laboratory, samples were kept frozen until extraction and analysis.

Handheld portable YSI instruments were used to measure the following ancillary water quality parameters in the field: temperature, pH, dissolved oxygen concentration and percent saturation, specific conductivity, and turbidity. These parameters were measured at each site and event, with the exception of American River at Discovery Park, where dissolved oxygen percent saturation and turbidity were not measured by SWRCB-SWAMP-SPoT (see deviation form 2020-06 in Appendix 4). The CEC QAPP requested ("if possible") measurement of porewater pH, which was not done for any of the sites. Porewater pH may be useful for understanding speciation and partitioning behavior for some CECs, but PBDEs have no acid-base forms, and PFOS and PFOA are

affected only at low pH (<3), which occurs rarely in natural sediment. Future sediment pore water pH measurement may be unnecessary for these specific CECs.

Fish

Fish sampling was conducted by Marine Pollution Studies Laboratory (MPSL-DFW), described briefly here, and in further detail in Appendix 1. Fish (channel catfish, largemouth bass, Sacramento sucker) were collected from stations by electrofishing. At each location, five or more fish, of one or two of the target species, were collected. Upon collection, each fish collected was tagged with a unique ID. Physical parameters measured for each individual fish included: weight, total length, fork length, and presence of any abnormalities. Large fish were partially dissected in the field at the dock; fish were placed on a cutting board covered with a clean plastic bag where the head, tail, and entrails were removed using a clean cleaver. Fish samples were stored on dry ice for the duration of transport to MPSL-DFW at Moss Landing Marine Labs (MLML) in Moss Landing, CA. At MPSL-DFW samples were stored in a -30 °C freezer until processed for authorized dissection, composited and shipped to SGS-AXYS for analysis (as described in the Sample Preparation and Analytical Methods section).

Bivalve

Collection of resident *Corbicula fluminea* was conducted by Applied Marine Sciences (AMS) at 5 locations, with a sixth planned site not sampled due to inaccessibility by boat. Samples were collected using a stainless steel clam dredge towed behind a research boat proceeding slowly upcurrent within the target sampling area. If clams were present in the dredge cage, they were dumped into a pre-cleaned cooler. Live clams were selected and rinsed to remove adhered sediments, then placed into a second pre-cleaned cooler for temporary storage. The dredging process was repeated until a sufficient number and volume of clams was collected to support all analyses, but for two sites the masses collected were not sufficient to do the analyses at the targeted detection limits; affected results include the following comment "MDL elevated due to limited sample mass collected" (Deviation Form 2020-11). Each collected clam had its length, width, and weight recorded, and was then sorted into an approximate size class. Clams were randomly assigned to groups for each sample, with approximately the same proportion of each size class as found overall within the site. Samples were shipped frozen with their CoCs to the analytical lab.

For the bivalve collections, handheld portable YSI instruments were taken to the field to record water quality parameters of temperature, pH, dissolved oxygen concentration and percent saturation, specific conductivity, and turbidity at each site.

Sample Preparation and Analytical Methods

Water

Vista analyzed samples for PFAS (PFOA and PFOS) in water using Vista SOP 49 Rev. 22, a lab modification of EPA Method 537 for determination of PFAS in Drinking Water by

Solid Phase Extraction and Liquid Chromatography/Tandem Mass Spectrometry (LC/MS/MS). Target analytes were loaded by passing the collected samples, spiked with internal standards, through a solid phase extraction cartridge, which was then eluted with solvent. The extract was concentrated to a reduced final volume, and the final extract analyzed on the LC/MS/MS system.

Vista subcontracted measurement of galaxolide in aqueous samples to Physis, which used a lab modification of EPA 625.1 (Base/Neutrals and Acids by GC/MS) for analysis. In the EPA method, a measured volume of sample is serially extracted with methylene chloride at pH 11 - 13 and again at a pH less than 2 using a separatory funnel or continuous liquid/liquid extractor. The extract is concentrated to a reduced volume, and analyzed by GC/MS. Qualitative identification of an analyte is made using the retention time and the relative abundance of two or more characteristic masses (m/z's), and quantified using an internal standard technique.

Weck analyzed water samples using their internal SOP ORG111.R4.0, for Determination of Endocrine Disrupting Compounds, Pharmaceuticals, and Personal Care Products. The method is a variant of EPA Method 1694. Solid phase extraction (SPE) was used for aqueous samples, with the extract quantified by liquid chromatography and electrospray ionization tandem mass spectrometry (LC- ESI/MS/MS) or atmospheric pressure chemical ionization tandem mass spectrometry (LC-APCI/MS/MS). Isotopic dilution was used as an attempt to account for effects from the analytical process and matrix interferences.

Weck also analyzed water samples for suspended sediment concentration (SSC) using a method derived from ASTM D3977. Suspended solids are separated from water samples, dried, and weighed.

Sediment

SGS AXYS received sediment samples for CECs, which were frozen after receipt for storage until analysis. After samples were removed from frozen storage, they were thawed, and samples were homogenized following SGS AXYS SOP SLA-013 Rev. 10 "Procedures for Homogenization of Solids and Tissues". Samples were homogenized within their containers to minimize contamination, then aliquots of appropriate size removed for analysis.

SGS AXYS analyzed sediment samples for PBDEs using AXYS method MLA-033 Rev. 06 "Analytical Method For The Determination Of Brominated Diphenyl Ethers (BDE) And Other Brominated Flame Retardants (BFR)", a lab modification of EPA Method 1614A. Samples were spiked with ^{13}C-labelled surrogate standards before analysis, then solvent extracted. The extracts were cleaned up by column chromatography, reduced to a final extract, and analyzed by high-resolution gas chromatography with high-resolution mass spectrometric detection (HRGC-HRMS).

SGS AXYS analyzed sediment samples for PFAS using AXYS method MLA-110 Rev. 02 "Analytical Procedure for the Analysis of Per- and Polyfluoroalkyl Substances (PFAS) in Aqueous Samples, Solids, Tissues, AFFF Products and Solvent Extracts by LC-MS/MS."

After spiking with isotopically labeled surrogate standards samples were solvent extracted and cleaned up by Solid Phase Extraction (SPE). The extracts were then analyzed by liquid chromatography/mass spectrometry (LC-MS/MS). Final sample concentrations were determined by isotope dilution/internal standard quantification.

Weck analyzed sediment samples for TOC using a modified version of EPA Method 9060. Organic carbon is measured using a carbonaceous analyzer. This instrument converts the organic carbon in a sample to carbon dioxide (CO_2) which is then measured by a detector.

Fish Tissue

MPSL generated fish tissue composites from the collected fish. Fish selected for analysis (of the collected species, only Sacramento sucker and channel catfish were chosen) were dissected skin-off, with only the fillet muscle tissue used to generate composite samples to send to the analytical laboratory. Fish tissue samples were shipped with their CoCs in coolers with ice packs to SGS AXYS.

Upon receipt of the chilled fish composites at the analytical laboratory SGS AXYS, samples were frozen and stored in the dark in clean amber glass jars with screw caps at -20°C prior to analysis. After composite samples were removed from frozen storage at SGS AXYS, they were thawed and processed using the same SOPs for homogenization (SOP SLA-013 Rev. 10) and analysis of PBDEs (MLA-033 Rev. 06) and PFAS (MLA-110 Rev. 02) as used for sediment samples.

Bivalve Tissue

SGS AXYS received whole bivalves shipped frozen. Bivalves were removed from their shells and homogenized following the SOP SLA-013 Rev. 10. The SOP specifies various alternatives for homogenization depending on the sample material and size; due to the small mass of bivalve tissue in the samples, samples were manually homogenized using lab scissors and forceps to minimize material loss. Following homogenization, samples were analyzed for PBDEs using MLA-033 Rev. 06.

Table 2 Sample collection, preparation, and analysis methods and agencies for water and sediment samples

Parameter Group	Collection Agencies	Lab Agency	Collection Method	Preparation/ Preservation	Digest Extract Method	Analytical Method
Sediment PBDE	SFEI, SWRCB-SWAMP-SPoT	SGS AXYS	Sed_Core	LabFrozen	AXYS MLA-033 Rev 06	AXYS MLA-033 Rev 06
Sediment PFAS	SFEI, SWRCB-SWAMP-SPoT	SGS AXYS	Sed_Core	LabFrozen	SGS AXYS MLA-110 Rev 02	SGS AXYS MLA-110 Rev 02
Sediment TOC	SFEI, SWRCB-SWAMP-SPoT	WKL	Sed_Core	None	None	EPA 9060M
Water Galaxolide	DWR-MWQI, SFEI	Physis	Water_Grab	None	EPA 625	EPA 625.1M
Water PFAS	DWR-MWQI, SFEI	VAL	Water_Grab	None	EPA 537M	EPA 537M
Water PPCPs	DWR-MWQI, SFEI	WKL	Water_Grab	FieldAcidified	EPA 3535	EPA 1694M
Water SSC	DWR-MWQI, SFEI	WKL	Water_Grab	None	None	ASTM D3977M

Table 3 Sample collection, preparation, and analysis methods and agencies for tissue samples

Parameter Group	Collection Agency	Compositing Agency	Lab Agency	Collection Method	Preparation/ Preservation	Digest Extract Method	Analytical Method
Bivalve PBDE	AMS-CA	SGS AXYS	SGS AXYS	Trawl	FieldFrozen, LabFrozen	AXYS MLA-033 Rev 06	AXYS MLA-033 Rev 06
Fish PBDE	MPSL-DFW	MPSL-DFW	SGS AXYS	Shock	Skin off, LabFrozen	AXYS MLA-033 Rev 06	AXYS MLA-033 Rev 06
Fish PFAS	MPSL-DFW	MPSL-DFW	SGS AXYS	Shock	Skin off, LabFrozen	SGS AXYS MLA-110 Rev 02	SGS AXYS MLA-110 Rev 02

Quality Assurance

Additional details of the quality assurance review of the data for this CEC study are provided in Appendix 3. In that review, individual QC samples that failed MQOs were flagged using CEDEN QACodes. This section provides a high level summary of that review.

Field and Analytical Completeness

In the first water sampling event, completeness issues were primarily insufficient counts of lab QC samples for PPCPs due to insufficient material collected. For the second water event, only 3 of 8 planned sites were sampled, as one team could not sample due to COVID-19 restrictions. For clam sampling one site was inaccessible and was not sampled. For sediment TOC analysis, although a matrix spike/matrix spike duplicate (MS/MSD) pair was reported as one measure of lab precision, no unspiked lab replicate was reported. Several fish tissue results for N-methyl perfluorooctane sulfonamide ethanol(N-MeFOSE) and N-ethyl perfluorooctane sulfonamide ethanol (N-EtFOSE) were flagged as not quantitative and not reported (rejected) by the lab due to poor surrogate recoveries (<8% recovery). The remaining desired field and lab QC samples were successfully collected and analyzed.

Precision and Accuracy for Field and Laboratory QC

Recoveries for water galaxolide MS/MSDs ranged 104% to 264%, many over the 50-150 target. Although LCS samples met recovery targets, there were numerous very high MS recoveries, which were flagged. No deviations were found for PFAS recovery or precision in water samples. In PPCP LCS samples, BPA was recovered up to 4x of its expected value, and an ibuprofen LCS had 163% recovery. BPA and iopromide also had a few MS/MSD recoveries outside of the target 50-50% range. Thus, although BPA may be among the most often detected PPCPs, its quantitation may be uncertain.

In sediment samples, PBDE recoveries in LCS and MS samples met the target 70-130% recovery range. RPDs for PBDE 209 also exceeded the MQO of <35% in replicate samples from 519DRYCRK (125%) and replicate analyses of sediment from 511SOL011 (175%). Of the PFAS, Perfluoro-3,6-dioxaheptanoate had one MS recovery of 182% and one LCS at 141%, exceeding the 70-130% target, which were flagged. No deviations from TOC recovery or precision targets were found.

Tissue PBDE recoveries in LCS and MS samples were all within the target 70-130% recovery range. Of the PFAS, Methyl-perfluorooctanesulfonamidoethanol, N- also had 326% recovery in one LCS and was flagged. Some MS recoveries were high for 5:3 Fluorotelomer Carboxylic Acid (up to 194%), and 7:3 Fluorotelomer Carboxylic Acid (152%), and low for Perfluorododecanesulfonate (27%), outside the 50-150% target range, and were flagged in those samples. MS/MSD precision RPDs were above the target 25% for PBDE 209 (39%) and Ethyl-perfluorooctanesulfonamidoethanol, N- (46%).

However, the recoveries and precision on the most abundant PBDE compounds and PFOS had no deviations.

Blank Contamination

Blank contamination was encountered for a number of CECs. For water samples, Galaxolide was detected in 3 of 4 blanks (maximum 145 ng/L), a similar magnitude as sites with lower concentration samples, but the highest field sample concentrations were much higher than in blanks. PFOA and PFOS were not detected in blank water samples. Of the PPCPs, Bisphenol A, had blank concentrations similar to those in many field samples, with concentrations up to 180 ng/L. One field blank had measured SSC of 21 mg/L and was flagged.

PBDEs 047, 099, 100, and 154 were found in the sediment blank and flagged in that sample, but field sample concentrations averaged more than 100x higher so were likely minimally impacted. None of the PFAS were detected in the sediment blank.

For the tissue blank, PBDEs 047, 099, 100, 154, and 209 were found. PFOS, undecanoate, and tridecanoate, were also detected and flagged in the blank. Blank contamination likely impacted the results in all species for PBDE 209, and Sacramento sucker for PBDE 099, as the blanks accounted for more than ⅓ of the concentrations in the field samples. The Perfluoroundecanoate blank was also over ⅓ the field sample result for one Sacramento sucker and one channel catfish sample, so those results may be noticeably impacted.

Corrective Actions

After the first water collection event in which insufficient material to generate lab QC samples, field and lab procedures were altered so sufficient material was available for subsequent events. Other deviations such as variable recovery and precision occurred sporadically and are generally difficult to reproduce consistently to diagnose causes, so no specific corrective actions were identified. Similarly the blank contamination found for chemicals such as BPA and PBDEs, are compounds commonly found in many products, so their sources are difficult to fully identify and eliminate in both lab and field environments.

Results

All analytical and field parameter results are available for download through the CEDEN database (https://ceden.waterboards.ca.gov/AdvancedQueryTool) using the sampling event and station identification information found in Table 1.

Water

Appendix 5 presents a tabulation of results for all of the parameters measured in water samples.

With quarterly water collections at eight sites (three of the sites sampled four times and five of the sites sampled three times), each target water analyte was analyzed in 27 field samples (not including QA samples).

There were no detections of Triclosan, Diclofenac, Estrone, or Estradiol, 17beta- in any of the water samples collected. Ibuprofen was detected at three of the eight sites, and in 5 of 27 samples overall, with concentrations ranging from 13 ng/L to 80 ng/L. Bisphenol A was detected at every site, and in 15 of 27 samples overall, with concentrations ranging from 12 ng/L to 330 ng/L. However, the lowest concentration samples were in a similar range as seen for lab blanks, so those concentrations are uncertain. Results for 7 additional secondary PPCP parameters were also reported for the water samples, as part of the suite of analytes included in the analytical method. Concentrations detected for these secondary PPCP parameters are listed along with the primary target analytes in Appendix 5. The reported detections were generally in a similar range as reported in the literature for other freshwater bodies: salicylic acid in some rivers were over 200 ng/L (https://pubs.acs.org/doi/10.1021/acs.chemrev.8b00299), similar to the maximum in this study of ~500 ng/L; a compilation of naproxen in various worldwide freshwater bodies (https://doi.org/10.1007/s00253-019-10343-x) generally reported concentrations around 1ug/L or lower; some reported ibuprofen data (https://doi.org/10.1016/j.heliyon.2020.e04087) were mostly <1ug/L, so results here often were a similar order of magnitude..

Galaxolide was detected at every site, and in every water sample collected, with concentrations ranging from 55.6 ng/L to 47100 ng/L. The four highest concentrations were all detected at Old Alamo Creek at Lewis Road, with the lowest concentration detected at that site being 33900 ng/L. Galaxolide lab and field blanks ranged up to 145 ng/L, so blank contamination may have impacted some of the lower concentration sites, but were negligible compared to the Old Alamo Creek results. A study in Toronto (DOI: 10.1039/C8EM00341F) with measurements from creeks had concentrations <1000 ng/L, and wastewater effluents >10000 ng/L, so the Old Alamo Creek results are consistent with wastewater influence.

PFOS (*reported as Perfluorooctanesulfonic acid*) was quantified (above the Reporting Limit) for water at three of eight sites, and in 11 of 27 water samples overall, and detected but not quantified (below the Reporting Limit) in one sample at one other site. Quantified concentrations of PFOS ranged from 2.35 ng/L to 11.7 ng/L. PFOA (*reported as Perfluorooctanoic acid*) was quantified (above the Reporting Limit) for water at two of eight sites, and in 8 of 27 water samples overall, and detected but not quantified (below the Reporting Limit) in four samples at two other sites. Quantified concentrations of PFOA ranged from 2.21 ng/L to 10.3 ng/L. San Francisco Bay concentrations reported by the Bay RMP (downloaded from cd3.sfei.org) were in a similar range: PFOS averaged 6 ng/L and PFOA 15 ng/L.

Suspended sediment concentration (SSC) was measured as an ancillary parameter, and was detected in 15 of 27 water samples, at 6 of 8 sites, in concentrations ranging from 5 mg/L dw to 64 mg/L.

The following ranges in field water quality parameters were measured in Delta surface water over the 4 sampling events: temperature = 6.81-25.72 °C; pH = 6.7-9.2; dissolved

oxygen = 3.79-22.18 mg/L; dissolved oxygen = 46.6-177 % saturation; specific conductivity = 0.11-1091 µS/cm; turbidity = 0-7.6 FNU and 2.7-49.6 NTU. Field habitat observations were also recorded at each sample site and event, and are available for download through the CEDEN database.

Sediment

Appendix 6 presents a tabulation of results for all of the parameters measured in sediment.

PBDE 047 was detected at all three sites sampled for sediment, in concentrations ranging from 0.0153 ng/g dw to 0.721 ng/g dw. PBDE 099 was detected at all three sites sampled for sediment, in concentrations ranging from 0.0165 ng/g dw to 0.561 ng/g dw. For both PBDE 047 and PBDE 099, the highest concentrations were detected at Old Alamo Creek at Lewis Road and the lowest at American River at Discovery Park.

Results for six additional secondary PBDE parameters were also reported for the sediment samples, as part of the suite of analytes included in the analytical method (PBDE 028/33, PBDE 100, PBDE 153, PBDE 154, PBDE 183, PBDE 209). Concentrations detected for these secondary PBDE parameters are listed along with the primary target analytes in Appendix 6. The reported PBDE concentrations are in a similar range as reported for San Francisco Bay (cd3.sfei.org), with individual PBDE congeners typically < 1ng/g dw in sediment.

PFOS (reported as Perfluorooctanesulfonate) was detected but not quantified (below the Reporting Limit) at one of the three sites sampled, and not detected at the other two sites. PFOA (reported as Perfluorooctanoate) was not detected in any of the sediment samples collected. The concentrations were lower than in San Francisco Bay, where the maximum detected PFOS concentration was <4 ng/g dw in sediment.

Results for 38 additional secondaryPFAS parameters were also reported for the sediment samples, as part of the suite of analytes included in the analytical method. Concentrations detected for these secondaryPBDE parameters are listed along with the primary target analytes in Appendix 6.

Total organic carbon (TOC) was measured as an ancillary parameter, with concentrations ranging from 474 mg/Kg dw to 4560 mg/Kg dw at the three sediment sites.

The following ranges in ancillary field water quality parameters were measured in Delta surface water during sediment sampling: temperature = 19.82-25.72°C; pH = 7.41-8.4; dissolved oxygen = 3.79-8.51 mg/L; dissolved oxygen = 46.6-75.8% saturation; specific conductivity = 0.112-65.9 µS/cm; turbidity = 4.5-6.4 NTU. Neither turbidity or dissolved oxygen (% saturation) were recorded at the site and event where SWRCB-SWAMP-SPoT collected sediment. Field habitat observations were also recorded at each sample site and event, and are available for download through the CEDEN database.

Fish

Appendix 7 presents a tabulation of results for all of the parameters measured in fish.

PBDE 047 was detected at all four sites sampled, in concentrations ranging from 1.62 ng/g dw to 55.5 ng/g dw. PBDE 099 was detected at three of four sites sampled, in concentrations ranging from 0.0125 ng/g dw to 2.87 ng/g dw. The reported concentrations are generally comparable to those in fish from San Francisco Bay (cd3.sfei.org) with a maximum PBDE 047 of 27 ng/g ww, and maximum PBDE 099 of 1.2 ng/g ww for Shiner Surfperch (in the period 2000-2019).

Results for six additional secondaryPBDE parameters were also reported for the fish samples, as part of the suite of analytes included in the analytical method (PBDE 028/33, PBDE 100, PBDE 153, PBDE 154, PBDE 183, PBDE 209). Concentrations detected for these secondaryPBDE parameters are listed along with the primary target analytes in Appendix 7.

PFOS (*reported as perfluorooctanesulfonate*) was quantified (above the Reporting Limit) for fish from three of four sites sampled, and detected but not quantified (below the Reporting Limit) for the fourth site. Quantified concentrations of PFOS ranged from 3.72 ng/g dw to 7.99 ng/g dw. PFOA (*reported as Perfluorooctanoate*) was not detected in any of the fish samples collected. PFOS concentrations in San Francisco Bay fish were higher, averaging up to 10 ng/g ww in some fish species; bioaccumulation will differ by species, but results appear to be a similar order of magnitude.

Results for 38 additional secondary PFAS parameters were also reported for the fish samples, as part of the suite of analytes included in the analytical method. Concentrations detected for these secondary PBDE parameters are listed along with the primary target analytes in Appendix 7.

Ancillary field water quality parameters were not measured in Delta surface water during fish sampling (see deviation form 2020-06 in Appendix 4). Field habitat observations were recorded at each sample site and event, and are available for download through the CEDEN database.

Bivalve

Appendix 8 presents a tabulation of results for all of the parameters measured in clams.

PBDE 047 was detected at all five sites sampled, in concentrations ranging from 7.51 ng/g dw to 131 ng/g dw. PBDE 099 was detected at all five sites sampled, in concentrations ranging from 1.65 ng/g dw to 70.9 ng/g dw. For both PBDE 047 and PBDE 099, the highest concentrations were detected at Sacramento River at Hood Monitoring Station Platform and the lowest at Sacramento River at Elkhorn Boat Launch Facility.

Results for six secondary PBDE parameters were also reported for the clam samples, as part of the suite of analytes included in the analytical method (PBDE 028/33, PBDE 100,

PBDE 153, PBDE 154, PBDE 183, PBDE 209). Concentrations detected for these secondary PBDE parameters are listed along with the primary target analytes in Appendix 8.

The following ranges in ancillary field water quality parameters were measured in Delta surface water during clam sampling: temperature = 17.5-21.5°C; pH = 6.96-8.06; dissolved oxygen = 7.04-9.58 mg/L; dissolved oxygen = 79.9-101.9% saturation; specific conductivity = 57.4-620 µS/cm; turbidity = 0.02-4.9 FNU. Field habitat observations were also recorded at each sample site and event, and are available for download through the CEDEN database.

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