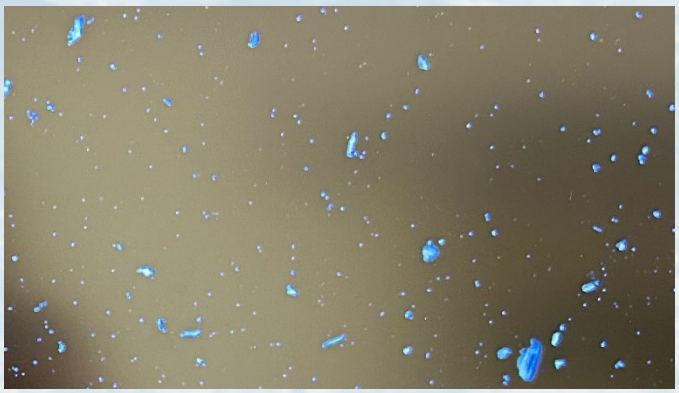
Multimedia investigations of microplastic concentrations in the Los Angeles and San Gabriel Rivers



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SOUTHERN CALIFORNIA COASTAL WATER RESEARCH PROJECT

Technical Report 1389

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Southern California Coastal Water Research Project, Costa Mesa CA

December 2024

Technical Report 1389

Acknowledgements

We thank Danhui Xin, Dario Diehl, Marina Salmon, Ashton Espino, Joshua Quinn, Kevin Mosqueda, Cody Fees, and Syd Kotar for assistance in field collection and laboratory work. We thank Andy Gray and his research group at the University of California, Riverside for loan their box trawl and other water sampling equipment, and for valuable advice. We also thank Ellen Roosen of Woods Hole Oceanographic Institution for organizing and sending the sediment cores used for quality assurance/quality control in this study. We also thank Neil Jayswal and Louis Tisinger of Agilent Technologies, Inc. for the generous loan of the LDIR instrument and for their training to enable us to use it in this study. We appreciate Fen Zheng and Kaikuo Zhang for sampling help.

Prepared for:

As a Deliverable for the California Surface Water Ambient Monitoring Program

"Multimedia investigations of microplastic concentrations in the Los Angeles and San Gabriel Rivers"

(Agreement No. 19-078-270, Task 2)

This report should be cited as:

Wong, C.S., W. Lao, S. Dial, D. Nguyen, and L.M. Thornton Hampton. 2024. Multimedia investigations of microplastic concentrations in the Los Angeles and San Gabriel Rivers. Technical Report 1389. Southern California Coastal Water Research Project. Costa Mesa, CA.

Keywords:

Microplastics; rivers; surface water; sediment; fish

EXECUTIVE SUMMARY

This report describes microplastics concentrations in water, bed sediment, and fish in the heavily urbanized Los Angeles and San Gabriel Rivers of Southern California. Two sites in each river were sampled between 2021 and 2023: a midstream site that was within the influence of treated wastewater effluent discharge nearby, and a downstream site at which waterborne contaminants in the watershed may pass through in transport to the ocean. Concentrations of microplastics in surface water averaged 8.9 particles/m^3 (range 0.05 to 16 particles/m^3) in the Los Angeles River, and averaged 74 particles/m^3 (range 0.1 to 330 particles/m^3) in the San Gabriel River. Concentrations in surficial sediments averaged 19 particles g/dry weight (range 0.3 to 100 particles/g) in the Los Angeles River, and 6.7 particles/g dry weight (range 1.5 to 14 particles/g) in the San Gabriel River. Two fish species were most commonly found and collected in the two rivers: mosquitofish (*Gambusia affinis*) and tilapia (*Oreochromis niloticus*), for which average concentrations were 70 particles per individual (range 0.7 to 140 particles per individual). The majority (average 83%) of the microplastic particles in fish were in the 53-125 µm size fraction. Most microplastic particles in surface water and sediments were also in smaller size fractions (average of 65% in the smallest 355-500 µm fraction in surface water, and 84% in the smallest 125-355 µm fraction in sediments). There were few, if any, trends in concentrations in any of the matrices spatially, temporally, or among species. Both fibers and fragments were observed in all matrices throughout the study site. The most common synthetic polymers observed were polyethylene, rubber, polystyrene, polyamide, and polyurethane with considerable variability, as with the other microplastic characteristics noted above, from sample to sample. These were all present in surface waters; however, the polymer composition of particles in sediments was dominated by polystyrene (average of 40%) and that in fish was dominated by polyethylene (average of 45%). There were distinct differences in microplastic polymer composition in the rivers compared to that typically found in wastewater effluent. This observation, as well as the presence of putative rubber particles possibly arising from tire wear and polyurethane possibly from building insulation and automotive upholstery and construction materials, are consistent with both urbanized rivers receiving road runoff as well as inputs from treated wastewater effluent discharge. The levels of microplastics are consistent with literature reports of these contaminants in water and surficial sediment in other urbanized and anthropogenically impacts streams worldwide. However, the levels in fish appear to be higher than literature reports in similar aquatic systems, and should be confirmed in further work. Because of logistical constraints that stem from the significant time and expense of microplastics sampling and analysis, a robust statistical study design to ascertain trends in levels and compositions and to account thoroughly for estimates of variability is beyond the scope of this study. Analysis of microplastics in this study, using laser direct infrared spectroscopy (LDIR) with selected confirmation by Fourier-transform infrared spectroscopy (FTIR), found that the

former technique has considerable logistical advantages in time and effort at identifying and quantifying microplastics, which can be improved with greater spectral library development. These results are useful in evaluating the impact of microplastics contamination in the Southern California aquatic environment, and for future monitoring analytical development for this class of contaminants.

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1. INTRODUCTION

There is increasing environmental interest in microplastics. This class of contaminants is ubiquitous in the aquatic environment, whether impacted or remote (González-Pleiter et al. 2020; Suaria et al. 2020). Microplastics continually enter waterways through use and disposal of plastic materials, which may weather chemically and mechanically into smaller particles (Cooper and Corcoran 2010). Plastic production has increased by an order of magnitude (Geyer et al. 2017) since plastics were first noted in waters in the 1970s (Carpenter et al. 1972), and is expected to increase by at least three-fold over the next 20 years (Lau et al. 2020). Accordingly, levels of microplastics in the aquatic environment are likely to increase over time (Borelle et al. 2020). Many plastics are persistent and degrade very slowly under environmentally relevant conditions (Chamas et al. 2020). Microplastic particles may be bioavailable to aquatic organisms through breathing or through diet, either through direct feeding or via bioaccumulation (Gouin 2020). Once microplastics are in the food web, they have the potential to cause a variety of acute and chronic biological effects. These include false satiation from the inability of many organisms to distinguish microplastic particles from food such as algae or organic particulate detritus (de Ruijter et al. 2020), endocrine disruption (Amereh et al. 2020), inflammation and tissue damage (Pirsaheb et al. 2020), changes in gene expression (Zhang et al. 2020a), altered development (Gardon et al. 2020), decreased reproductive success (Sussarellu et al. 2016), and reduced growth (Zimmerman et al. 2020). The extent to which these effects occur in environmentally relevant conditions is currently an open question (Mehinto et al. 2022) given limited quality data (Thornton Hampton et al. 2022a). Given these issues, understanding the occurrence, fate, and effects of microplastics in the aquatic environment is important to evaluate the risks they may pose to human and ecosystem health.

To address these issues, the State of California passed several pieces of legislation to help tackle the issue of microplastics in its aquatic ecosystems. In particular, SB 1263 (State of California 2018) requires the development of a strategy to manage microplastics contamination in the state's coastal waters. This strategy would include understanding the occurrence of microplastics in rivers that drain into the state's coastal waters, not only in the waters of such rivers, but also in their bed sediment, and in the organisms (e.g., fish) that are present.

Microplastic occurrence in freshwater systems has been documented all over the world (Horton et al. 2017), with studies reported on the occurrence of microplastics in river water (Moore et al. 2011, Dris et al. 2015, Baldwin et al. 2016, Wiggin et al. 2019, Baldwin et al. 2021, Xiong et al. 2019, Scherer et al. 2020, Yan et al. 2021), sediment (Crew et al. 2020, Baldwin et al. 2021, He et al. 2020, Scherer et al. 2020, Yan et al. 2021), and biota such as fish (Campbell et al. 2017, McNeish et al. 2018, Baldwin et al. 2021). However, limited baseline data has been collected in Southern California rivers (Moore et al. 2011, Wiggin et al. 2019). Surface water, and not sediment or biota, have been published thus far. This represents an important gap in knowledge given that microplastics ultimately accumulate in sediments (Kaiser et al. 2017, Van Melkebeke et al. 2020), and microplastic ingestion by biota may cause adverse health effects (Thornton Hampton et al. 2022b).

This study addresses data gaps in the occurrence of environmental microplastics in Southern California, by evaluating microplastics in surface water, sediment, and fish tissue from the Los Angeles River and the San Gabriel River. These rivers are heavily urbanized and receive a variety of contaminants, including microplastics, from a variety of sources, including treated wastewater effluent discharge, stormwater, and street runoff. In addition, we also discuss the efficacy of various spectroscopic techniques, such as Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, and laser direct infrared spectroscopy (LDIR) in the measurement of environmental microplastics, through select analyses of samples from these rivers. The

information in this report will help to ascertain the levels and compositions of microplastics in the aquatic environment of this urbanized area, as part of the prioritization for managing microplastic contamination as required by SB 1263, and in identification and quantification of microplastics in environmental media. A robust statistical study design to characterize levels and compositions of microplastics is beyond the scope of this study, given the logistical and resource constraints arising from the significant time and expense associated with microplastics sampling and analysis. For the same reason, a thorough accounting of estimates of variability is also beyond scope. Therefore, the results of this study should be considered an initial screening estimate that can be further refined through future study.

2. EXPERIMENTAL

2.1 Materials

Polycarbonate track etch (PCTE) membrane filters of 20, 10, and 1 µm pore size and 47 mm diameter were purchased from Sterlitech (Auburn, WA). Sulfuric acid (98%), methanol, and sodium bromide were purchased from Thermo-Fisher Scientific (China, CA). Potassium hydroxide pellets were purchased from Sigma-Aldrich (St. Louis, MO). Microplastics-analysis-grade (MAG) water and MAG methanol were prepared by filtering deionized water or methanol, respectively, through a 1µm PCTE membrane filter to remove particulates larger than that size. Solutions of sulfuric acid and KOH were prepared into appropriate concentrations with MAG water. Full-height stainless steel sieves (20.3 cm diameter, 6.67 cm height, 5.08 cm depth) were purchased from Hogentogler & Co. (Columbia, MD). Wide-mouth mason canning jars (950 mL) were used as sampling containers, and were purchased from Uline (Pleasant Prairie, WI). Conical polypropylene centrifuge tubes (50 mL) were purchased from VWR (Radnor, PA). PetriSlides and disposable glass Pasteur pipets were purchased from Sigma-Aldrich. Surrogate polyethylene microplastic microspheres, consisting of blue (600-710 µm), green (300-355 µm), and red (75-90 µm) of 0.98-1.0 g/mL density, were purchased from Cospheric (Santa Barbara, CA). All solvents were optima grade or better.

2.2 Sampling

Samples in this report were collected at four sites, with two along each river (Figure 1, Table 1) at mid-stream (e.g., representing some wastewater effluent and runoff flows) and downstream (e.g., representing drainage from treated wastewater effluent discharge and runoff from the watershed). Specific sites were selected on the basis of a variety of factors, including use in previous studies on chemical contaminants (Maruya et al. 2022), presence of sediments and fish populations, and accessibility. The Los Angeles River mid-stream site was approximately 500 meters downstream of the Glendale wastewater treatment plant outfall, in a part of the river with continuous flow from effluent and a natural bed. The Los Angeles River downstream site was near the end of the channelized part of the river, but sufficiently upstream so that tidal influences had limited effect. The San Gabriel River mid-stream site was just downstream of the confluence with San Jose Creek, and also downstream of the San Jose Creek wastewater treatment plant that discharges into its eponymous waterway. This site also receives continuous, effluent-dominated flow. The San Gabriel River downstream site is at the downstream terminus of the channelized portion of the river, at the confluence with Coyote Creek and at the start of the natural bed estuary that extends to the mouth of the river in Long Beach Harbor. Further sampling (e.g., upstream to evaluate levels prior to wastewater inputs) could not be done due to logistical constraints.

There were four sampling events: two during the nominal wet season (defined in this report as 5/4/21-5/27/21 and 4/7/23-4/14/23), and two during the nominal dry season (defined in this report as 5/12/22-5/19/22 and 9/29/23). Fish were collected on separate sample dates for logistical reasons, and only collected once per season, as further attempts to find fish during other times were unsuccessful. Wet-season fish were collected 6/18/21-7/9/21 and dry-season fish were collected 5/20/22-7/22/22. It should be noted that there was little precipitation during the nominal 2021 and 2022 wet seasons, and indeed over most of those entire calendar years. In addition, it should also be noted that sampling events differed among media at the various sites for logistical reasons. For example, it was not possible to collect all sites on the same day, or to follow the same plug of water, particularly in dry seasons when both rivers ran dry, aside from those parts engineered to receive treated effluent discharges, between the mid-stream and downstream sites.

Water samples were collected using a 48 cm square box trawl with 330 µm mesh size (45.72 cm mesh width) attached to a collection cod end. Briefly, the box trawl was deployed mid-stream and allowed to collect for 15 min, while the stream flow rate, which varied from 0.08 to 3.15 m/s, was measured using a flow meter (Marsh-McBirney Model 2000 Flo-Mate, Frederick, MD) to determine total volume sampled (Table 2). The net contents were rinsed into a glass 1 L container with MAG water, and kept at 4°C until return to the laboratory. Water was not collected during the fourth sampling event as the box trawl was unavailable.

Surficial sediment samples were collected from the top 15-30 cm of sediment using a metal trowel. A total of ca. 200-1000 g wet weight of sediment was collected for a singular location at each site. Sediment was kept at 4 °C until return to the laboratory.

Fish samples were collected using fishing poles and a seine. Specimens were individually wrapped with clean aluminum foil, if large enough. Smaller specimens and species (i.e., mosquitofish) were composited and kept under ice until return to the laboratory. A list of fish collected and analyzed in this study is noted in Table 3; only tilapia and mosquitofish were commonly found at the sites. However, no singular fish species was found at all four sites across sampling events.

2.3 Extraction

Water and sediment samples were kept in the dark at 4 °C until analysis, while tissue samples were frozen at -20 °C. Samples were processed using an acid/alkaline digestion method developed in-house (Lao et al. 2024). This method is highly efficient at removing both organic and inorganic particulate interferences from water, sediment, and tissue, and are described briefly below for each matrix.

Surrogate particles (10 of each Cospheric type) were added to each water sample to monitor extraction recovery. If the particle load was too high, the samples were homogenized and 15 mL subsamples were taken for processing. In cases where duplicate samples were processed, 15 mL subsamples were taken from the same concentrated sample for each duplicate. The water samples were poured through a sieve stack and size fractioned (4700, 500, and 355 µm). Solids larger than 4700 µm were discarded. The sample was then filtered through a 20 µm PCTE filter to remove the liquid phase, and then rinsed first with MAG water, then with methanol to hasten drying. Filters were rinsed again with MAG methanol prior to transfer to a 50 mL conical centrifuge tube and air-dried overnight. Once dry, ca. 5 mL of 80% H_2SO_4 was added to the centrifuge tube to digest organic matter. The tube was shaken by hand or vortex mixer for 5 mins to mix the digesting acid thoroughly with the particulates. An aliquot of 30-35 mL MAG water was then added to dilute the acid prior to transfer of all materials in the tube, including the filter, to a sieve of an appropriate size fraction. The filtrate was discarded, and solids on the

sieve were transferred into a clean centrifuge tube containing 20% KOH solution. The tube was then capped and incubated at 48 °C for 24 h to digest the sample further. The KOH solution was again transferred to a sieve of an appropriate size fraction to remove any broken-down particulates, and solids left on the sieve were transferred to a clean centrifuge tube with MAG water. The centrifuge tube contents were then filtered, and the filter rinsed with MAG water and MAG methanol. Particulates were then transferred into a petri dish for storage and subsequent particle counting by visual microscopy.

Table 1. Sampling sites of this study. Events 1 and 3 are during the wet season, and Events 2 and 4 during the dry seasons, as defined in this report.

Site name	Coordinates (Latitude, Longitude)	Water sampling dates	Sediment sampling dates	Fish sampling dates
Los Angeles River midstream (LAR Mid)	34.129728, -118.273352	Event 1: 5/04/21 Event 2: 5/13/22 Event 3: 4/07/23	Event 1: 5/04/21 Event 2: 5/13/22 Event 3: 4/07/23 Event 4: 9/29/23	Event 1: 7/1/21 Event 2: 7/22/22
Los Angeles River downstream (LAR Down)	33.804286, -118.205527	Event 1: 5/27/21 Event 2: 5/12/22 Event 3: 4/11/23	Event 1: 5/27/21 Event 2: 5/12/22 Event 3: 4/11/23 Event 4: 9/29/23	Event 1: 6/24/21 Event 2: 5/27/22
San Gabriel River midstream (SGR Mid)	34.037914, -118.024794	Event 1: 5/25/21 Event 2: 5/19/22 Event 3: 4/14/23	Event 1: 5/25/21 Event 2: 5/19/22 Event 3: 4/14/23 Event 4: 9/29/23	Event 1: 6/18/21 Event 2: 5/27/22
San Gabriel River downstream (SGR Down)	33.791013, -118.091955	Event 1: 5/25/21 Event 2: 5/12/22 Event 3: 4/11/23	Event 1: 5/25/21 Event 2: 5/12/22 Event 3: 4/11/23 Event 4: 9/29/23	Event 1: 7/09/21 Event 2: 5/20/22

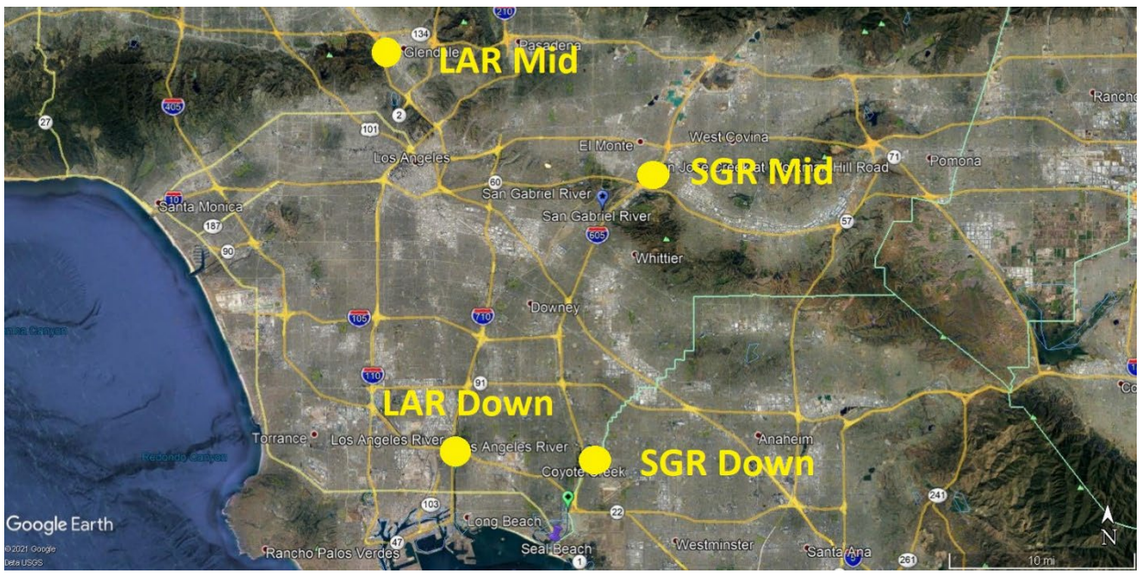

Figure 1. Map of the Los Angeles River (LAR) and San Gabriel River (SGR) mid-stream (Mid) and downstream (Down) sampling sites in

Table 2. Amount of water (m^3) sampled by box trawl in this study.

Site name	Sampling Event	Sample Date	Stream width (m)	Stream depth (cm)	Average velocity (m/s)	Stream flow (m^3/s)	Volume sampled (m^3)
LAR Mid	Event 1	5/4/21	29	6	0.46	0.80	11.4
LAR Down	Event 1	5/27/21	49	26	0.59	7.52	63.1
SGR Mid	Event 1	5/25/21	26	6	0.08	0.12	0.198
SGR Down	Event 1	5/25/21	5.5	38	0.18	0.38	28.1
LAR Mid	Event 2	5/13/22	42	12	0.69	3.48	34.1
LAR Down	Event 2	5/12/22	7.7	26	0.68	1.36	72.7
SGR Mid	Event 2	5/19/22	26	30	0.03	0.23	0.37
SGR Down	Event 2	5/12/22	7.1	46	0.22	0.79	40.6
LAR Mid	Event 3	4/7/23	54.5	16	0.70	6.02	45.4
LAR Down	Event 3	4/11/23	8.2	38	1.28	3.99	200.
SGR Mid	Event 3	4/14/23	23	16	0.24	0.88	15.8
SGR Down	Event 3	4/11/23	7.5	46	3.15	14.9	596

Table 3. Mosquitofish (*Gambusia affinis*) and tilapia (*Oreochromis niloticus*) sampled and in this study from the Los Angeles River (LAR) and San Gabriel River (SGR) midstream (Mid) and downstream (Down) sites. *=Duplicate samples taken.

Site name	Sampling event	Species	Number of fish analyzed	Average standard length (cm)	Total digested mass (g)
LAR Mid	1	Mosquitofish	15	2.36	0.34
LAR Mid	2	Tilapia	21	1.69	0.13
LAR Down	1	Mosquitofish	7	2.36	0.65
LAR Down	2	Mosquitofish	11.5	2.88	1.15
SGR Mid	1	Tilapia	15	2.34	0.5
SGR Mid*	2	Tilapia	4, 3	3.21	0.95, 2.33
SGR Mid	2	Mosquitofish	7	2.32	0.77
SGR Down*	1	Tilapia	4, 4	3.15	1.55, 1.52
SGR Down	2	Mosquitofish	4.5	3.85	2.04
SGR Down	2	Tilapia	10	2.82	1.92

An aliquot of sediment (ca. 5 g wet weight) was subsampled from each sediment sample, spiked with Cospheric surrogate particles, then subject to a density separation using a 1.4 g/mL sodium bromide solution with centrifugation for 5 min (Langknecht et al. 2023) to remove inorganic particulates. The liquid phase from the density separation was sieved and size fractioned (500, 355, 125 µm), after which particulates were further digested with sulfuric acid as described above for aqueous samples (Lao et al. 2024). The remaining solids were sieved, then transferred to a centrifuge tube using 20% KOH solution to digest for 48 h. The digested sample was then size-fractioned and filtered again as above. The filtered particulates were transferred to a petri dish for storage and microscopy. A separate aliquot of wet sediment was weighed, dried at 110 °C, and reweighed to determine percent moisture.

Fish extracted were typically of similar size. Tilapia tended to be smaller individuals which are more likely to be younger, although accurate aging of these fish is beyond the scope of this report. Such individuals are likely to have accumulated less microplastics over their lifetimes, and may thus represent a lower bound of accumulation. Fish were partially defrosted, rinsed with MAG water, and fillets were collected from composites due to the smaller specimens and species. Approximately 0.5 to 1 g wet weight was digested using 20% KOH solution for 48 h. The digested sample was then size-fractioned and filtered as above, and the collected particulates were further digested with sulfuric acid as described above for aqueous samples (Lao et al. 2024). However, for fish, an additional size fraction (53-125 µm) was retained. Fish were composited together and homogenized prior to extraction.

2.4 Quantification

2.4.1 Microscopy

Particles were counted on fully processed filters following guidelines from previous interlaboratory intercomparison work (Kotar et al. 2022), using a LAXO microscope (Washington) with a Z203P digital camera. Each particle on the filter was recorded with its associated morphology and color. A polar coordinate grid was placed underneath the petri slide to assist in navigation of the filter and to prevent duplicate particle counting. All particles were counted.

2.4.2 Spectroscopy

Particulates needed to be transferred off filters to another suitable support medium for spectroscopy, given spectra interferences from the filter for some samples. A metal spatula was used to scrape particulates from filters to 1.2 mL glass autosampler vials. MAG methanol was used to rinse the filter and spatula into the vial, and a gentle stream of nitrogen was then used to evaporate the liquid completely. Once dry, a small volume of MAG methanol (<0.2 mL) was added to the vial, the particulate resuspended by vortex mixing, and the suspension was plated dropwise onto Kevley low-emission microscope slides (Agilent, Santa Clara, CA). Care was taken to minimize the size of the droplets. Slides were placed into a clean aluminum container loosely covered with clean aluminum foil to minimize airborne contamination and allowed to dry in a fume hood and covered to minimize airborne particulate contamination prior to spectroscopic analysis. Inspection of the filter by visual microscopy confirmed that all particulates were transferred and quantification of particles on selected slides corresponded to visual microscopy counts.

Identification of particle material composition was done using laser direct infrared imaging, using an Agilent 8700 LDIR (Agilent, Santa Clara, CA). Transfer spots were scanned automatically, with conditions manually set by the user to identify only particles within the size fraction parameters as defined by the sample (e.g., 125-355 µm). The size parameters set for each size fraction are 500 µm: 450-1000 µm; 355 µm: 300-500 µm; 125 µm: 100-355 µm; 53 µm: 40-125 µm; and 20 µm: 20-125 µm. Slides with few particles were analyzed manually; these were typically in 355 and 500 µm size fractions. Infrared spectra were recorded for all particles identified by the instrument, and hit quality indexes (HQI) were determined for particles by searching available spectral instrument and threshold for positive identification of particle material type was HQI $\geq$ 60% (California State Water Resources Control Board 2022).

Select samples were also analyzed using FTIR to cross-check with the LDIR analysis. These were selected randomly. Analysis was done with a Nicolet iN10 MX Infrared Imaging Microscopy (Thermo Scientific, Madison, WI). All spots on slides with particles were scanned manually. FTIR spectra were recorded for particles found and counted. The HQI for each particle was determined by searching available spectral libraries. The same criterium of $\geq$ 60% was used for positive material confirmation for FTIR.

2.4.3 Calculations

Concentrations of microplastic particles in water (# particles/m^3), biological tissues (average # particles per individual organism), and sediment (# particles/gram dry weight) were determined by scaling the number of particles identified by spectroscopy in the subsample extracted, to the size (volume, individual, or weight as appropriate) of the original collected sample. The total number of particles in a sample was the sum of the particle count of its individual size fractions. Particle morphologies were determined by the width and length of each particle. Particles with a length-to-width or width-to-length ratio between 0.5 and 0.0001 were labeled as fibers (Kooi

& Koelmans 2019) and all other particles were labeled as fragments. Particle colors cannot be determined by LDIR analysis.

Minimum detectable amounts (MDAs) for determining detection limits were calculated (California State Water Resources Control Board 2022, 2022a; Lao and Wong 2023), and expressed as minimum detectable amounts (MDA_A):

$$MDA_A = N_b + 3 + 3.29 \times SD_b \times \sqrt{1 + \frac{1}{n}}$$

where N_b and SD_b are the mean and standard deviation of the particle counts of relevant blanks, respectively, and n the total number of blanks. Analogous MDA_A values were calculated, as recommended by Lao and Wong (2023), for each size fraction, for fibers and non-fibers (i.e., all other morphologies other than fibers), and for plastic particles in blanks analyzed by spectroscopy. Batch-specific minimum detectable amounts (MDA_B) quantify the extent of particulate contamination for individual batches of samples (Lao and Wong 2023), which may vary depending on conditions at the time of laboratory work:

$$MDA_B = N_b + 3 + 4.65\sqrt{N_b}$$

Unless otherwise specified, all error estimates in this report are standard deviations. The Student's t-test and ANOVA were used for comparisons between and among groups, as appropriate, unless otherwise stated. Statistical significance was set at $\alpha = 0.05$.

2.5 Quality Assurance/Quality Control

2.5.1 Quality assurance/quality control for sampling

A suite of quality control measures quantified and mitigated particulate contamination, from airborne particulates or from materials and equipment used, irrespective of whether these particles were plastic or otherwise. These included pre-cleaning of sampling supplies, travel and field blanks, and sampling procedures to minimize plastic and particulate contamination.

All sampling equipment was pre-washed with detergent and tap water and a natural sponge, rinsed with MAG water, and wrapped in clean aluminum foil to remove particulates and prevent deposition of airborne particulates between cleaning and use. Non-volumetric glassware was also ashed at 500 °C for 4 h to destroy all organic matter, including microplastics, then wrapped with foil. Equipment was left wrapped until just prior to use and was then rinsed as appropriate with MAG water.

Travel blanks, to monitor for particulate contamination during shipment and storage between SCCWRP and the field site and back, consisted of 1 L MAG water in a collection container. The travel blank accompanied all other field sampling materials and was left sealed throughout.

Field blanks were deployed at each site during field sampling. Water sample field blanks were comprised of 1 L mason jars containing approximately 800 mL MAG water. For sediment samples, field blanks consisted of 8 oz glass containers filled with approximately 5 g of ashed sodium bromide (calcium chloride in sediment samples taken in 2022). The containers were opened and subjected to atmospheric exposure during the time of collection for their subsequent matrices. Field blank containers were otherwise treated, extracted, and counted as with any other sample.

During sampling, all personnel wore waders and purple nitrile gloves to minimize sample contamination by particulates, and particularly by plastic particulates. All plastic materials used in sampling (laboratory-grade squirt bottles for rinsing and cleaning with MAG water) were made of materials known not to shed synthetic polymer particles and would in any event be accounted for in field blanks (California State Water Resources Control Board 2022, 2022a; Thornton Hampton et al. 2023).

2.5.2 Quality assurance/quality control for laboratory work

All sampling processing and analysis followed recommended procedures to minimize particulate contamination (California State Water Resources Control Board 2022, 2022a; Munno et al. 2023) in a laboratory with HEPA air filtration and positive pressure. Personnel wore clean 100% white cotton laboratory coats. Every working day, benches and floors were cleaned either with a HEPA vacuum cleaner, or with tap water and natural-fiber wipes (e.g., paper towels). Soap and water, and a natural sponge, were used to clean glassware and sieves. This equipment was rinsed with MAG water before use. To monitor background airborne particulate contamination in the laboratory, air blanks were placed at various locations in the laboratory (e.g., processing benches, microscope stations, spectroscopy instrumentation) and periodically quantified.

Method procedural blanks (MPBs) were processed with each batch of samples. Water and tissue sample MPBs consisted of MAG water of similar volume as the samples in that batch. Sediment sample MPBs consisted of 5 g ashed sodium bromide. Field blanks (FBs) were extracted in the same manner as samples. Blank particles were quantified via visual microscopy. Larger size fractions generally showed low contamination by visual microscopy. Therefore, we subjected the smallest size fraction of that blank to spectroscopy to ascertain how many synthetic polymer particulate interferences were present. Spectroscopy was conducted on blanks that were not size fractioned. Additionally, matrix spikes (MS) were created and processed to test method efficacy and recovery among each matrix. Water MS consisted of approximately 800 mL of MAG water. Fish tissue MS were comprised of ca. 5 g of store-bought salmon filets, which were known to be free of microplastic particles (Thornton Hampton et al . 2023). Sediment MS were created using 5 g of radio-dated, pre-industrial sediment core slides from Woods Hole Oceanographic Institution previously used to create interlaboratory intercomparison samples (Langknecht et al. 2023, Thornton Hampton et al. 2023). Each MS was spiked with Cospheric particles processed as with samples. MS particles and Cospheric microsphere surrogate particles were quantified via visual microscopy.

3. RESULTS

3.1 QA/QC

No detectable particles were found in the MAG water and methanol, sulfuric acid and KOH solutions, or organic solvents. For all six laboratory locations, air blank counts averaged to 21.5±21.8 particles per day, during the course of this study, or 3.6±3.7 particles per location per day. These blank values are comparable to those observed in a previous multi-laboratory intercomparison study, in which our laboratory participated, that evaluated various laboratory extraction and analytical methods for microplastics in environmental matrices (Kotar et al. 2022, Thornton Hampton et al. 2023). The laboratory air blanks are a result of the physical infrastructure (e.g., HEPA filtration), and the various procedures discussed above to minimize

and mitigate particulate contamination. Thus, it is unlikely that atmospheric contamination in the laboratory is significant in this study.

Microplastic particle counts in both method procedure blanks (MPB) and field blanks (FB) were generally also low (Table 4), and in the range of 3-9 particles with the exception of 16 particles found in the MPB of fish in sampling event 1, which was an outlier for unknown reasons (Grubbs test, G= 2.97922, p-value = 0.019). These levels of microplastic particles in blanks were seven-fold lower than the average particle count in the corresponding samples. As a result, the minimum detectable amounts were similar in magnitude, and were 21 overall (15 without the outlier), with batch specific MDA_B values of 8 to 34, with no significant differences between FB and MPB MDA_B values after removing the outlier. Accordingly, trip blanks were not analyzed in this study.

Recoveries of Cospheric polyethylene microspheres (Tables 5-8) averaged 79±49% overall across all samples and blanks. Somewhat better recovery (average 87±59%) was observed for the larger blue 600-710 µm surrogate recovery microspheres corresponding to the 355-500 µm and >500 µm size fractions, than the green 300-355 µm microspheres (average 73±21%) corresponding to the 125-355 µm size fraction. The smallest surrogate particles added, the red 63-75 µm microspheres, were associated with size fractions <125 µm (average 51±27%). The decrease in recovery with smaller surrogate particle size is expected, given the greater ease of finding and identifying larger particles. Recoveries of surrogate particles in method procedural blanks and field blanks were generally similar to those in samples and in matrix spikes (Tables 5-8). Recoveries of surrogate microspheres of similar size were also similar across the different matrices (Table 8), indicating that varying particulate levels and complexity in samples of different matrices did not affect the behavior of surrogate particles, and by extension microplastic particles present in the samples, during sample extraction and analysis. Of course, spherical polyethylene particles cannot represent all microplastic particles. For example, fibers may be caught by sieves or go through them. In addition, a handful of polymers, such as nylon, may partially degrade in reagents in typical extraction media for microplastics, including those used in this study (Lao et al. 2024), and accordingly might cause a small underestimation. Given these issues, it is not feasible to perform an exhaustive evaluation of surrogate particles representing all morphologies, size fractions, and polymer types. Nonetheless, the recoveries observed suggest there were only limited losses of synthetic polymer particulates from laboratory procedures, with the likely exception of losses in the 53-125 µm size fraction observed in fish, for which the resultant data and its interpretation should be treated with caution. No recovery correction was done in this study.

Table 4. Microplastic particle counts in blanks of this study, and overall and batch-specific minimum detectable amounts (MDA_A and MDA_B, respectively). LAR = Los Angeles River, SGR = San Gabriel River, All = blanks used in all samples, Mid = midstream site. Sed = sediment. *=outlier as per Grubb's test.

Site (or MDA_A)	Sampling event	Matrix	Blank type	Size fraction	Number of microplastic particles in blank or MDA_A	Fraction of microplastic particles in blank (%)	MDA_B
LAR Mid	1	Sed.	FB	>125	7	77.8	20
LAR Mid	2	Sed.	FB	>125	1	33.3	8
LAR Mid	3	Sed.	FB	>125	5	83.3	16
LAR Mid	4	Sed.	FB	>125	3	60.0	12
SGR Mid	1	Water	FB	355	3	100	12
LAR Mid	2	Water	FB	355	2	50.0	10
LAR Mid	3	Water	FB	355	1	30.0	8
All	1	Tissue	MPB	125	16*	28.1	34
All	2	Tissue	MPB	125	4	44.4	14
All	1	Sed.	MPB	125	9	50.0	23
All	2	Sed.	MPB	125	1	33.3	8
All	3	Sed.	MPB	125	7	58.3	20
All	4	Sed.	MPB	125	4	80.0	14
All	1	Water	MPB	355	2	66.7	10
All	2	Water	MPB	355	2	100	10

Site (or MDA_A)	Sampling event	Matrix	Blank type	Size fraction	Number of microplastic particles in blank or MDA_A	Fraction of microplastic particles in blank (%)	MDA_B
All	3	Water	MPB	355	4	80.0	14
MDA_A					21 (*15 w/o outliner)		

Table 5. Surrogate particle recovery in Method Procedural Blanks (MPBs) in water, sediment (sed), and fish. SD = standard deviation, RSD = relative standard deviation. Blue surrogate polyethylene microsphere particles are 600-710 µm diameter, green ones are 300-355 µm diameter, red ones are 63-75 µm diameter.

MPB	Sampling Event	Size fraction (µm)	Surrogate	Sample size (n)	Average recovery (%)	SD	RSD	max	min
water	1-3	355+500	Blue	14	84.3	10.9	12.9	100	70
sed.	1-4	355+500	Blue	4	97.5	5	5.1	100	90
sed.	1-4	125	Green	4	90	29	35	100	80
fish	1-2	355	Blue	3	100	0	0	100	100
fish	1-2	125	Green	3	86.7	0.2	0.2	100	70
fish	1-2	53	Red	3	58.3	0.2	0.3	70	40

Table 6. Surrogate particle recovery in Field Blanks (FBs). SD = standard deviation, RSD = relative standard deviation. Blue surrogate polyethylene microsphere particles are 600-710 µm diameter, green ones are 300-355 µm diameter, red ones are 63-75 µm diameter.

FB	Sampling Event	Size fraction (µm)	Surrogate	Sample size (n)	Average recovery (%)	SD	RSD	max	min
water	1-3	355+500	Blue	8	83.8	20.7	24.7	100	50
sediment	1-4	>125	Blue	4	97.5	5	5.1	100	90
sediment	1-4	>125	Green	4	82.5	28.7	34.8	100	40

Table 7. Surrogate particle recovery in matrix spikes (sed = sediment). SD = standard deviation, RSD = relative standard deviation. Blue surrogate polyethylene microsphere particles are 600-710 µm diameter, green ones are 300-355 µm diameter, red ones are 63-75 µm in diameter.

Matrix Type	Duplicate	Size fraction (µm)	Surrogate	Sample size (n)	Average recovery (%)	SD	RSD	max	min
water	1-2	355+500	Blue	2	80	0	0	80	80
fish	1-3	355	Blue	6	81.7	14.7	18	100	60
fish	1-3	125	Green	6	75	15.2	20.2	100	60
fish	1-3	<125	Red	6	25	13.8	55.1	40	10
sed.	1-3	355+500	Blue	3	87.7	11.5	13.3	100	80
sed.	1-3	355+500	Green	3	47.7	40.4	86.6	70	0

Table 8. Surrogate particle recovery in samples by matrix (sed = sediment). SD = standard deviation, RSD = relative standard deviation. Blue surrogate polyethylene microsphere particles are 600-710 µm diameter, green ones are 300-355 µm diameter, red ones are 63-75 µm diameter.

Sample	Sampling Event	Size fraction (µm)	Surrogate	Sample size (n)	Average recovery (%)	SD	RSD	max	min
water	1-3	355+500	Blue	24	70.8	29.4	41.5	100	0
fish	1-2	355	Blue	10	95	9.7	10.2	100	70
fish	1-2	125	Green	10	80	22.1	26.7	100	30
fish	1-2	<125	Red	10	65	23.7	36.4	100	30
sed.	1-4	355+500	Blue	15	85	5.8	6.8	100	70
sed.	1-4	125	Green	15	62.7	13.3	21.3	80	50

3.2 Spectroscopy

Of the 5052 total particles identified by LDIR in all samples of this study, 18.6% of the particulates found were positively identified not to be a synthetic polymer. The most common of these were chitin, making up 74% of non-plastic particles, followed by silica (8.4%) and cellulose (7.7%). These are likely to be natural particles and are probably residuals of biological material and inorganic particles such as sand that were not removed during extraction procedures. Of the particles identified by LDIR (i.e., with HQI $\geq$ 60%) as synthetic polymer, 34.6% were polyvinyl alcohol, the most common polymer identified by the instrument.

The additional analyses done on samples by both LDIR and FTIR found that particle counts from both techniques were comparable, i.e., within $\pm$25% and within the mean relative percent differences of 37% observed for recounts of wastewater samples analyzed by FTIR in another study (Wong et al. 2024). However, LDIR identified on average 53% more polymer particles than FTIR, the vast majority of which were identified by LDIR as polyvinyl alcohol (PVA). Few, if any, PVA particles were identified by FTIR, in contrast to the analyses by LDIR on the same slides of the same samples. Similar results were also observed for samples from wastewater of a separate study (Wong et al. 2024). The reasons for this discrepancy are not clear. In addition, known artifacts such as (inorganic) residue occasionally left from the evaporating methanol used to resuspend and transfer particulates to low-emission slides for LDIR analysis were also identified as PVA. These were easily spotted and excluded from the dataset, and visual inspection confirmed that no other particulates were present in these regions. The FTIR could not identify this residue, with all matches having poor HQI well below our acceptance criteria. These observations indicate that PVA was being overidentified by LDIR. Given the time and expense of manual spectroscopic analysis (e.g., up to tens of hours per size fraction of a sample, Thornton Hampton et al. 2023), it was impractical to analyze all samples of this study by both spectroscopic techniques to confirm the extent of this issue. Accordingly, particles identified as PVA by LDIR are considered unconfirmed, and thus not included as microplastics in the rest of this report. More details about other synthetic polymer types are described and discussed below (e.g., Section 3.4.2).

3.3 Concentrations

Concentrations of microplastics in water (Table 9, Figures 2-3) averaged 8.9 particles/m^3 and ranged from 0.5 to 16 particles/m^3 in the Los Angeles River, and averaged 74.4 particles/m^3 with a range of 0.1 to 330 particles/m^3 in the San Gabriel River. Replicate measurements at the Los Angeles River downstream site during sampling event 2 were within $\pm$20%, indicating good agreement amongst replicates (Table 9). Concentrations in the mid-stream site were

comparable in both rivers to those in the downstream site, except for the San Gabriel River mid-stream site during the first sampling event which had the highest concentrations observed in water in this study, an order of magnitude greater than the corresponding first water sampling event in the Los Angeles River. Concentrations in the Los Angeles River were generally least in the third sampling event, whereas concentrations in the San Gabriel River were greatest during the first sampling event. The reasons for the observed variability are not clear. There were no significant differences in concentrations between the two rivers, nor any significant spatial or temporal trends, bearing in mind that samples were not necessarily taken at the same time during each sampling event (Table 1).

Sediment concentrations of microplastics (Table 10, Figures 4-5) averaged 19.1 particles/g dry weight and ranged from 0.3 to 100 particles/g dry weight in the Los Angeles River, and averaged 6.7 particles/g dry weight with a range of 1.5 to 14 particles/g dry weight in the San Gabriel River. There were no significant differences in concentrations in sediments between the two rivers, or across any of the sites. Concentrations also did not significantly increase or decrease across sampling events at a given site. Concentrations in the Los Angeles mid-stream sediment during sampling event 1, and in the San Gabriel sediment during sampling event 4 appeared to be greater than those of earlier events at this river. The most likely explanation for the variability observed in concentrations at each site, across sampling events, is heterogeneity of microplastic levels at specific areas sampled at each site. No data was available for the San Gabriel River mid-stream site during sampling event 1.

As noted, only two species of fish were commonly found at the sampling sites: tilapia and mosquitofish (Table 3). Mosquitofish were found in the Los Angeles River at both sites during both fish sampling events, except at the mid-stream site during fish sampling event 2, and at both downstream sites during fish sampling event 1. Tilapia was found at the Los Angeles River mid-stream site during fish sampling event 1 only, and at both San Gabriel sites during both fish sampling events. Neither of these species were found at all sites over all sampling events.

Concentrations of microplastics in fish were generally considerably greater than in the other media. Average levels in mosquitofish were 46 particles/individual with a range of 6 to 48 particles/individual (Table 11) and were greatest at the San Gabriel River mid-stream site. In tilapia (Table 11), average concentrations of microplastics were 88 particles/individual with a range of 0.7 to 140 particles/individual, with the greatest concentrations at the San Gabriel River downstream site. The majority of microplastic particles (average of 83%) were in the smallest size fraction for fish (<125 μm). There were no significant differences in fish concentrations between the two rivers, between sampling events, or between the two species.

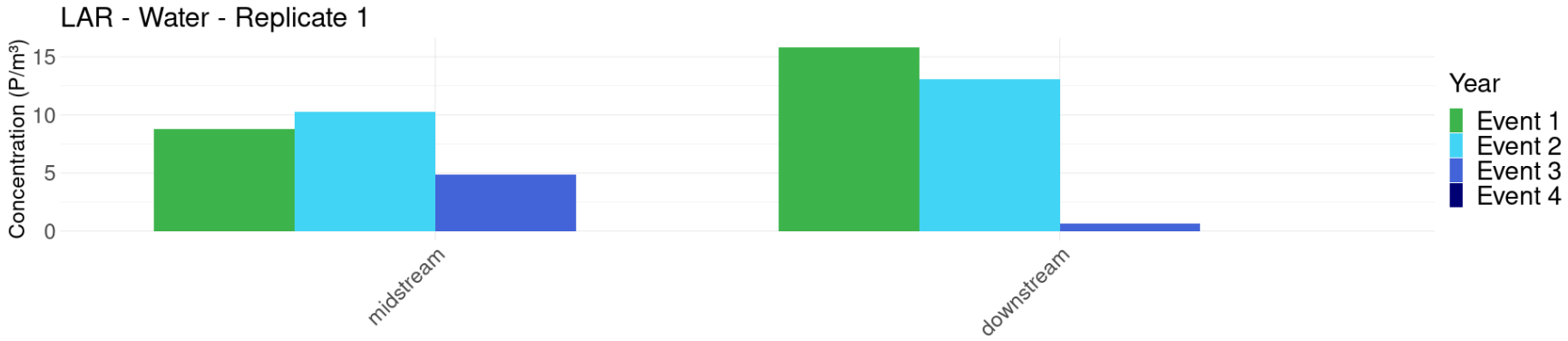

Figure 2. Concentrations of microplastics (>355 µm) in water of the Los Angeles River (LAR). Only one of the replicates taken the LAR downstream site during sampling event 2 is shown. There is no data for Event 4.

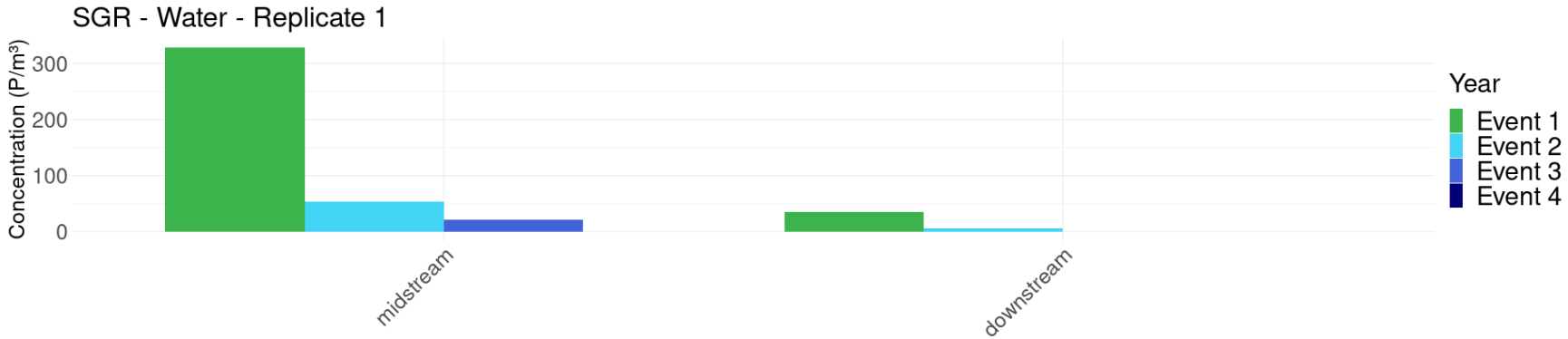

Figure 3. Concentrations of microplastics (>355 µm) in water of the San Gabriel River (SGR). There is no data for Event 4.

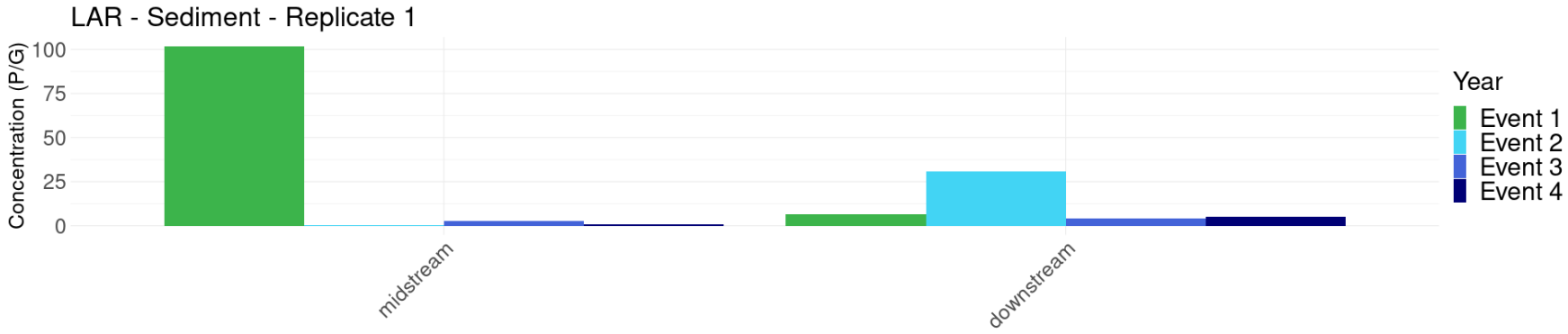

Figure 4. Concentrations of microplastics (>125 µm) in sediment of the Los Angeles River (LAR).

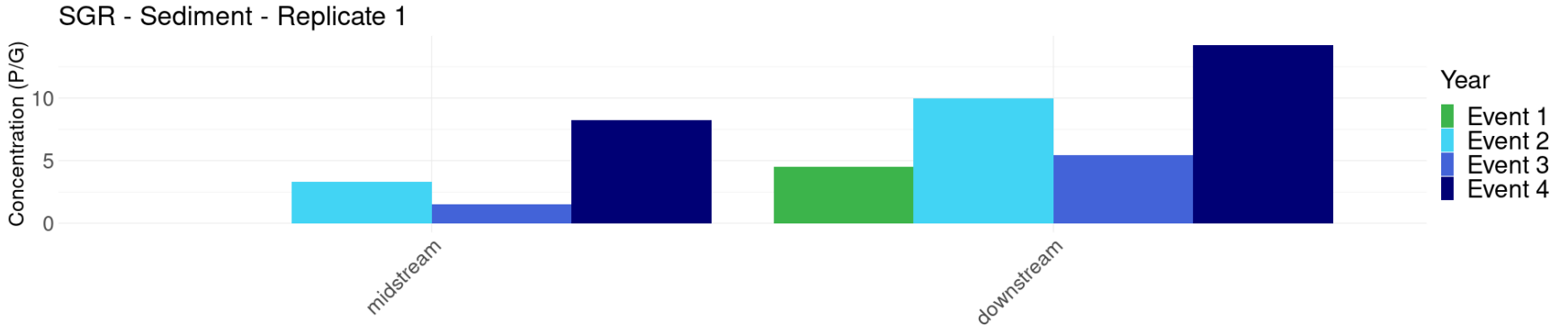

Figure 5. Concentrations of microplastics (>125 µm) in sediment of the San Gabriel River (SGR).

Table 9. Concentrations (particles/m^3), size fraction distributions (in percent), and morphology distributions (in percent) of microplastics (>355 µm) in surface water of the Los Angeles River (LAR) and San Gabriel River (SGR) at the mid-stream (Mid) and downstream (Down) sites.

Site	Media	Sampling Event	Replicate	Concentration	% >500 µm	% 355-500 µm	% fiber	% fragment
LAR Mid	Water	1	-	8.8	0	100	100	0
LAR Mid	Water	2	-	13	43	57	34	66
LAR Mid	Water	3	-	4.6	10	90	20	80
LAR Down	Water	1	-	16	20	80	70	30
LAR Down	Water	2	1	11	60	40	20	80
LAR Down	Water	2	2	10	85	15	46	54
LAR Down	Water	2	3	7.6	25	75	50	50
LAR Down	Water	3	-	0.5	50	50	0	100
SGR Mid	Water	1	-	330	15	85	85	15
SGR Mid	Water	2	-	54	85	15	23	77
SGR Mid	Water	3	-	21	0	100	40	60
SGR Down	Water	1	-	35.5	67	33	11	89
SGR Down	Water	2	-	5.6	25	75	12	88
SGR Down	Water	3	-	0.1	0	100	0	100

Table 10. Concentrations (particles/g dry weight), size fraction distributions (in percent), and morphology distributions (in percent) of microplastics (>125 µm) in surficial sediments (Sed.) of the Los Angeles River (LAR) and San Gabriel River (SGR) at the mid-stream (Mid) and downstream (Down) sites.

Site	Media	Sampling Event	Concentration	% >500 µm	% 355-500 µm	% 125-355 µm	% fiber	% fragment
LAR Mid	Sed.	1	100	4	0	96	43	57
LAR Mid	Sed.	2	0.3	0	100	0	0	100
LAR Mid	Sed.	3	2.6	0	0	100	80	20
LAR Mid	Sed.	4	1	0	0	100	67	33
LAR Down	Sed.	1	6.5	25	4	71	54	46
LAR Down	Sed.	2	31	0	53	47	27	73
LAR Down	Sed.	3	4.4	12	0	88	35	65
LAR Down	Sed.	4	5.2	0	6	94	25	75
SGR Mid	Sed.	1	-	-	-	-	-	-
SGR Mid	Sed.	2	3.3	0	0	100	38	62
SGR Mid	Sed.	3	1.5	0	0	100	17	83
SGR Mid	Sed.	4	8.2	0	0	100	41	59
SGR Down	Sed.	1	4.5	17	0	83	11	89
SGR Down	Sed.	2	10	0	8	92	31	69
SGR Down	Sed.	3	5.5	0	6	94	33	67

Site	Media	Sampling Event	Concentration	% >500 µm	% 355-500 µm	% 125-355 µm	% fiber	% fragment
LAR Mid	Sed.	1	100	4	0	96	43	57
LAR Mid	Sed.	2	0.3	0	100	0	0	100
LAR Mid	Sed.	3	2.6	0	0	100	80	20
SGR Down	Sed.	4	14	0	5	95	33	67

Table 11. Concentrations (average particles/individual), size fraction distributions (in percent), and morphology distributions (in percent, frag. = fragment) of microplastics in fish of the Los Angeles River (LAR) and San Gabriel River (SGR) at the mid-stream (Mid) and downstream (Down) sites.

Site	Species	Sampling Event	Replicate	Conc (>125 µm)	Conc (<125 µm)	% >125 µm	% <125 µm	% fiber	% frag.
LAR Mid	Mosquitofish	1	-	37	36	2	98	31	69
LAR Mid	Tilapia	2	-	10	8.3	2	98	45	55
LAR Down	Mosquitofish	1	-	8.4	5.7	32	68	27	73
LAR Down	Mosquitofish	2	-	9.8	7.9	19	81	35	65
SGR Mid	Mosquitofish	2	-	9.7	8.7	10	90	28	72
SGR Mid	Tilapia	1	-	3.3	0.7	78	22	54	46
SGR Mid	Tilapia	2	1	10	9.5	6	94	21	79
SGR Mid	Tilapia	2	2	68	57	16	84	36	64
SGR Down	Mosquitofish	2	-	56	48	14	86	29	71
SGR Down	Tilapia	1	1	32	29	11	89	36	64
SGR Down	Tilapia	1	2	140	140	4	96	17	83
SGR Down	Tilapia	2	-	50	50	5	95	37	63

3.4 Particle characteristics

There was considerable variability in the composition of microplastic particles in the various media of the two rivers. This was evident for size distributions, morphologies, color, and polymer type, as described below.

3.4.1 Size fraction

As noted, size fractions are matrix dependent. There are distinct trends in sizes of microplastic particles in the three different matrices, but other trends are not in evidence.

For water, there were two size fractions: >500 µm, and 355-500 µm with the latter corresponding to the box mesh size of 350 µm. Water samples tended to have microplastic particles in the 355-500 µm size fraction than in the larger fraction, with some having none larger than 500 µm, but there was considerable variability (Table 9). There were no significant differences in size distributions between the two rivers, across all sites, and across all events. Nor were trends evident for location, or sampling event. The size fractions of two of the replicate samples, taken at the Los Angeles River downstream site for event 2, resembled each other, but one had a considerably greater proportion of smaller particulates (Table 9) than the other two, possibly due to sample-to-sample variability.

Microplastics in sediment were more likely to be smaller (Table 10), with many sites only having such particulates in the 125-355 µm size range. The first sampling event did have significantly more of the largest >500 µm microplastic particles present than the other events. However, there were also no other significant trends between rivers, across sites, and across sampling evident for any size fraction.

Fish tissue was also dominated by smaller microplastic particles, with the majority <125 µm in size (Table 11). For that particle size fraction, no other apparent trends by site, sampling event, or species were evident.

3.4.2 Morphology

There were sizeable levels of both fibers and fragments in all media sampled of both rivers, as well as considerable variability (Tables 9-11).

In water (Table 9), fibers were dominant during sampling event 1 in the Los Angeles River, with no fragments observed at the mid-stream site, and with 70% observed at the downstream site. However, fragments were the majority of microplastics during the other sampling events in this river and made up all of the observed synthetic polymer particles at the downstream site of sampling event 3. In the San Gabriel River, fibers were dominant at the mid-stream site during

sampling event 1 (85%), but otherwise fragments were the major morphology observed (60-100%). The proportion of fibers in waters were greater, and the proportion of fragments was less, in sampling event 1 than in other sampling events, but no other significant differences were observed in morphology of aqueous microplastic particles between rivers or across sites.

In sediment (Table 10), fragments were generally more common than fibers, except in the Los Angeles River mid-stream site in sediments of sampling event 3 (33%). However, fibers were also evident in the sediments. Except for tilapia in the San Gabriel River mid-steam site during sampling event 1, fragments were otherwise generally the most common morphology in both species of fish in both rivers (55-83%, Figure 11), but the relative distribution in fish was more even than it was in water and in sediment. No significant differences were observed in morphology distributions between rivers, across sites, across events, and between fish species for either matrix.

3.4.3 Polymer type

As with the other microplastic characteristics discussed above, there was considerable sample-to-sample variability in synthetic polymer compositions in this study. Seven types were most common throughout all samples: polyamide, polyethylene, polyethylene terephthalate, polypropylene, polystyrene, polyurethane, and rubber (both natural and synthetic). Less commonly found polymers were grouped together as “other polymers” (Tables 12-13, Figures 6-7), which were in decreasing order of abundance: polycarbonate, polytetrafluoroethylene, and polyvinyl chloride. The polymers in the “other polymers” category are minor ones in this study, as they made up only 6.4% of the total number of microplastic particles that were positively identified.

Water had more diverse distributions of synthetic polymer types (Table 12) than sediments or fish. On average, polyamide and polyurethane were the two most common single polymers found in waters (average of 27% and 25%, respectively), followed by polyethylene, polystyrene, polyethylene terephthalate, and rubber (18, 16%, 16%, and 13%, respectively). There were sizeable fractions of other polymers as defined above. There were no significant differences in water proportions of polyamide, polyurethane, polyethylene, and rubber; there was insufficient data for other comparisons.

Polystyrene (Figures 6-7) was the most common type of synthetic polymer in microplastics found in sediments (average 41%), distantly followed by polyamide (average 22%), and then by other polymers, polyurethane, and rubber (16%, 14%, and 13%, respectively). For the major individual polymer types, there were no significant differences in polymer types between rivers, nor were there differences for polystyrene across sites or across events. There were insufficient numbers of samples for the other polymers for comparisons to be made.

For fish (Table 13), polyethylene was the most common polymer observed (average 43%), followed by rubber, the other polymers, and polystyrene (average 13%, 12%, and 10%, respectively) and the other major individual polymers (all averages <10%). Fish from the Los Angeles River had greater proportions of polystyrene than those from the San Gabriel River. Also, fish from the second sampling event had greater proportions of polyethylene than those from the first event. There were no other significant differences observed in the relative distributions of polyethylene, polystyrene, or rubber between rivers, between species, and between sampling events.

Table 12. Distributions of synthetic polymers, in percent, in microplastics in water samples. PA = polyamide, PE = polyethylene, PET = polyethylene terephthalate, PP = polypropylene, PS = polystyrene, PU = polyurethane.

Site	Sampling Event	Replicate	PA	PE	PET	PP	PS	PU	rubber	other polymer
LAR Mid	1	-	-	-	-	-	-	-	-	100
LAR Mid	2	-	29	14	14	14	-	14	14	-
LAR Mid	3	-	55	15	-	-	-	15	-	15
LAR Down	1	-	20	30	-	10	10	-	-	30
LAR Down	2	1	25	-	15	5	-	15	30	10
LAR Down	2	2	15	8	8	-	-	54	8	8
LAR Down	2	3	8	-	17	-	-	17	8	50
LAR Down	3	-	-	50	50	-	-	-	-	-
SGR Mid	1	-	8	-	-	8	8	38	8	31
SGR Mid	2	-	54	-	-	8	8	15	8	8
SGR Mid	3	-	20	30	-	-	30	-	-	20
SGR Down	1	-	-	-	-	-	-	444	-	56
SGR Down	2	-	31	6	-	25	6	6	12	13
SGR Down	3	-	33	-	-	-	33	33	-	-

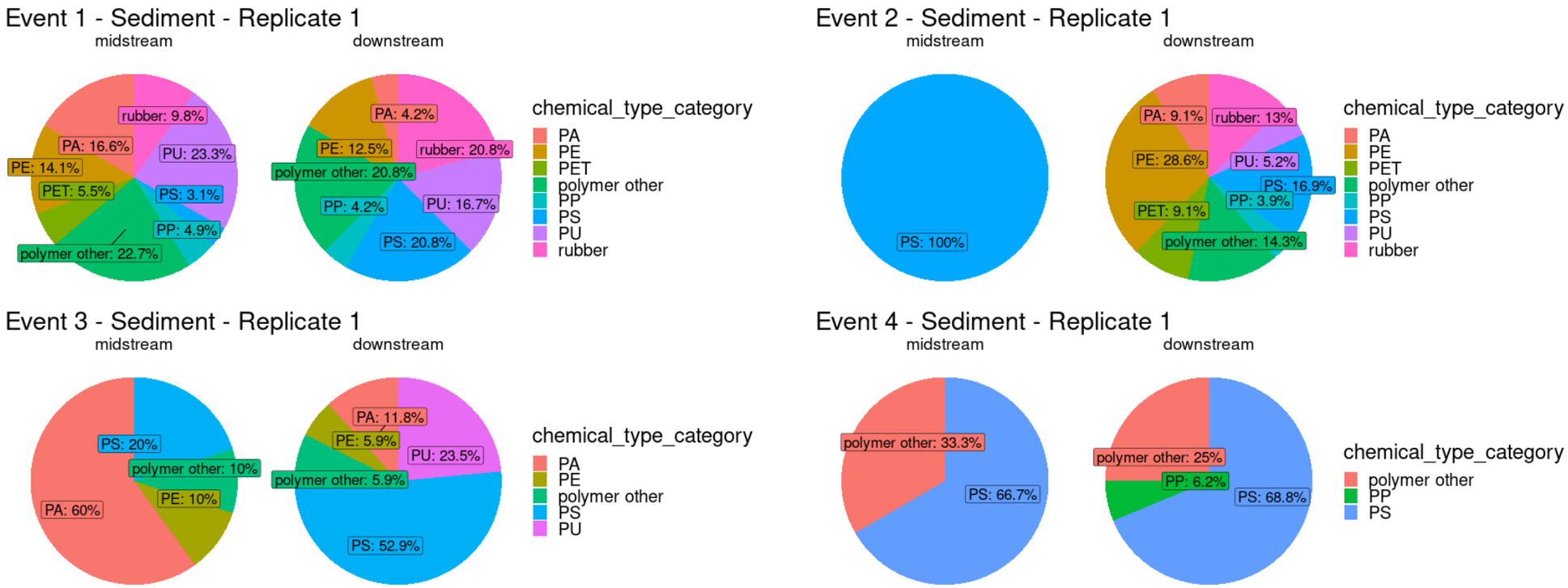

Figure 6. Distributions of synthetic polymers, in percent, in microplastics in Los Angeles River sediment samples. PA = polyamide, PE = polyethylene, PET = polyethylene terephthalate, PP = polypropylene, PS = polystyrene, PU = polyurethane.

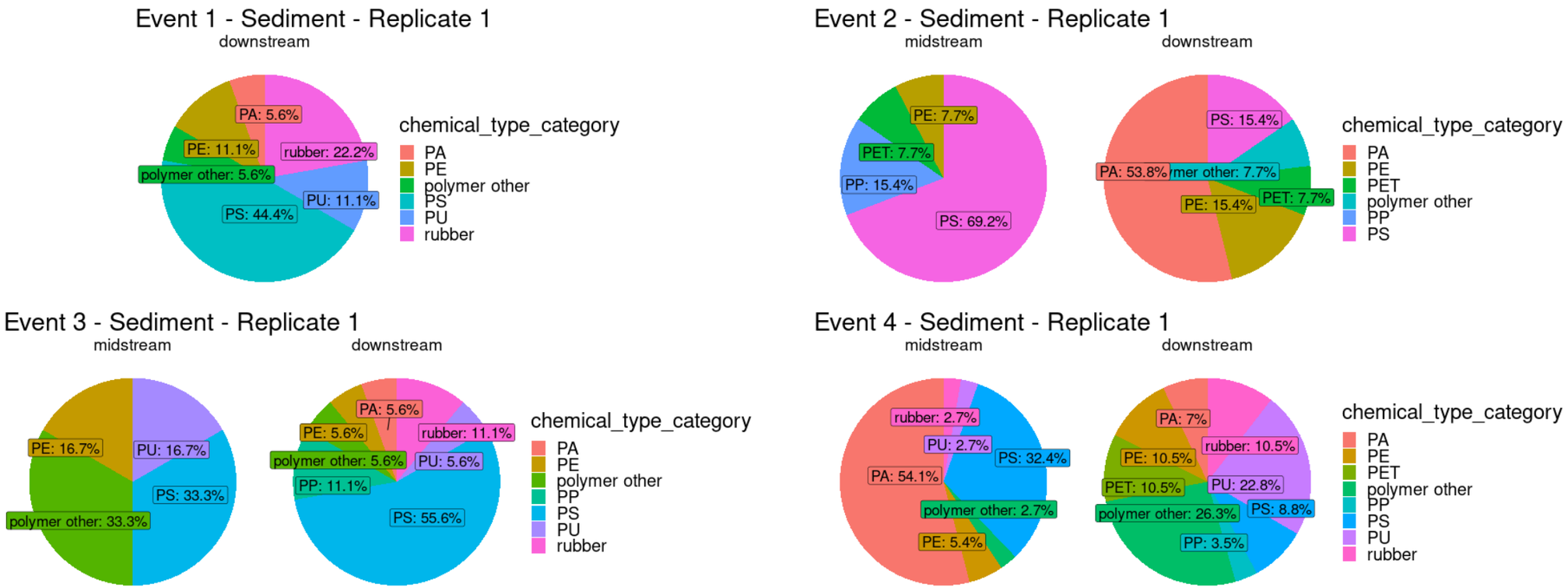

Figure 7. Distributions of synthetic polymers, in percent, in microplastics in San Gabriel sediment samples. PA = polyamide, PE = polyethylene, PET = polyethylene terephthalate, PP = polypropylene, PS = polystyrene, PU = polyurethane.

Table 13. Distributions of synthetic polymers, in percent, in microplastics in fish samples. PA = polyamide, PE = polyethylene, PET = polyethylene terephthalate, PP = polypropylene, PS = polystyrene, PU = polyurethane.

Site	Species	Sampling Event	Replicate	PA	PE	PET	PP	PS	PU	rubber	other polymer
LAR Mid	Mosquitofish	1	-	4.7	64	0.4	1.6	7	5	12	5.4
LAR Mid	Tilapia	2	-	10	23	2	1	27	10	25	4.3
LAR Down	Mosquitofish	1	-	17	8		7	36	3	14	15
LAR Down	Mosquitofish	2	-	14	14	4	4	15	23	24	2
SGR Mid	Mosquitofish	2	-	4	38	2		3	10	28	15
SGR Mid	Tilapia	1	-	4	6	12	2	6	24	16	30
SGR Mid	Tilapia	2	1	1	83		1	1	6	5	3
SGR Mid	Tilapia	2	2	1	87		1	4	1	4	2
SGR Down	Mosquitofish	2	-		86	0.8		6	0.8	2.4	4
SGR Down	Tilapia	1	1	31	23	2	5	7	16	11	5
SGR Down	Tilapia	1	2	15	12	1	3	4	2	8	54
SGR Down	Tilapia	2	-	2.1	75	1	0.2	5.7	2.1	13	1.3

4. DISCUSSION

4.1 Method performance

4.1.1 Extraction method

The extraction method used in this study (Section 2.3) has not, to our knowledge, been previously used for processing ambient environmental waters, sediments, and biota for microplastics. The acid/alkaline digestion method (Lao et al. 2024) was developed for processing wastewaters. Short exposures (ca. 5 min) to concentrated sulfuric acid destroys much of a sample's natural organic material while leaving most synthetic polymer particulates untouched, while the KOH alkaline (basic) digestion eliminates natural organic material not already destroyed by sulfuric acid. Density separations can be performed as needed to remove inorganic particulates. The resulting cleaned-up sample has minimal interferences from non-plastic particulates, which is necessary to identify and quantify microplastics.

Our results show that this method was suitable for other environmental matrices besides wastewater. Lao et al. (2024) observed that the method was more effective at removing natural wastewater particulates, both organic and inorganic, than other published methods for microplastics processing of wastewaters (e.g., nitric acid, enzymatic digestion). Oxidation methods in use for environmental matrices to eliminate organic particulates include, for example, the use of wet peroxide (Thornton Hampton et al. 2023). While these can be effective, our results verify that the acid/alkaline digestion method is suitable not just for wastewater, but for surface waters, sediments, and aquatic biotic tissues. While residual natural particles were found and identified, these are inevitable as no extraction procedure will completely remove every single interference, and the residuals observed are readily quantified and are not so abundant as to interfere with analysis of the target microplastic particulates.

3.3.3 Spectroscopic analysis

This study used LDIR, which has been commercially available only for a few years, for automated counting and material identification of particles. This is uncommon in ambient environmental microplastics research. Other IR technologies (e.g., FTIR) or Raman spectroscopy are far more frequently used to identify particles. Both FTIR and Raman spectroscopy were equally effective at correctly identifying both plastic particles from non-plastic particles in waters, sediments, and fish tissues spiked with known amounts of particulates, and analyzed blind by multiple laboratories in an intercomparison exercise (De Frond et al. 2022, 2023; Thornton Hampton et al. 2023). They were also equally effective at correctly identifying specific

types of synthetic polymers in these samples (De Frond et al. 2022, 2023; Thornton Hampton et al. 2023). Accordingly, no evaluation of FTIR compared to LDIR was done in this study.

With regards to technical performance, the LDIR was suitable at counting particles, as automated counts of microplastic particles were comparable with those done during manual particle material confirmation by FTIR. However, the LDIR identified many particles as PVA, including known artifacts, whereas FTIR found little to no PVA in those same samples. PVA has not been reported as a major synthetic polymer component in wastewater (Liu et al. 2021, Wong et al. 2024) and in environmental matrices of interest in this study (Li et al. 2020). While the specific reasons for over-identification of PVA by LDIR are not clear, it is known that the spectral library for LDIR is limited (https://www.agilent.com/en/product/molecular-spectroscopy/ldir-chemical-imaging-spectroscopy/best-technologies-for-microplastics-analysis), particularly when compared to FTIR spectral libraries. The libraries for the two techniques are mutually incompatible, in part because the LDIR scans a more limited portion of the IR spectrum (1800-975 cm^{-1}) due to its use of a Quantum Cascade Laser. The focus of LDIR on the fingerprint region of the IR spectrum makes differentiating more difficult samples, including environmentally weathered microplastic particles, more challenging. These observations suggest that expanding and updating LDIR spectral libraries may provide considerable improvements in technical performance.

Another limitation of LDIR is its inability to sort particles by color in its use of IR images to identify and count particles prior to selecting them for IR spectroscopic analysis. Color appears to have little effect on toxicity (Thorton Hampton et al. 2022b), and is therefore unlikely of interest in most applications. That said, we note some of the particles identified in this study were rubber. Visually, a number of particles on some slides were black in color, consistent with the presence of rubber particulates. Given that the LDIR does measure relative opacity of particles, it may be possible to use this metric, along with LDIR spectral libraries of rubbers, to characterize tire wear particles (i.e., rubber) that are of increasing interest and are otherwise difficult to identify by other means (Sutton et al. 2019, Kovochich et al. 2021, Rosso et al. 2023).

The principal advantages of using LDIR were the use of automated counting and particle identification via spectroscopy, as per the instrument's design. This resulted in considerable logistical advantages of using LDIR compared to FTIR or Raman, which can be highly labor-intensive taking tens of hours per sample (De Frond et al. 2022, 2023; Thornton Hampton et al. 2023). In our study, size fractions >125 µm were counted and analyzed generally within 10-60 min without user intervention (i.e., a full sample with size fractions 125-355 µm, 355-500 µm, and >500 µm could be analyzed in 1-3 hours). This compares favorably with manual counting of particles by visual microscopy, for which that same sample with three size fractions took 6-8 hours (i.e., most to all of a working day). Size fractions <125 µm with more particles,

microplastics or otherwise, generally took longer by LDIR to analyze (e.g., several hours each), and were typically left to run overnight. Of course, the same size fraction analyzed manually by FTIR would take correspondingly longer for an analyst to measure actively. Typical times per particle, as whole analysis time by total number of particles, averaged 2.2 min for using LDIR in this study, compared to 7.9 min per particle with data from interlaboratory intercomparison work using FTIR (Thornton Hampton et al. 2023).

In summary, the use of LDIR is promising in providing straightforward counts and identification of environmental microplastics with limited user intervention to save time and labor and can be improved with further work such as expansion of its spectral libraries.

4.2 Comparison of results with literature

Microplastic occurrence in freshwater systems has been documented all over the world. Studies have reported on the occurrence of microplastics in river water, sediment, and biota. How do the concentrations observed in this study compare to such data elsewhere?

It is important to recognize that comparisons amongst studies for microplastics are problematic, and that there are many caveats. Individual studies use different techniques and protocols for sampling, extraction and processing, and identification and quantification. In many cases, method performance (e.g., accuracy and precision of particle counts and material identification, extent, and impact of blank contamination) is unknown and unknowable, as QA/QC procedures are either not present or are poorly described (Brander et al. 2020). Moreover, no multi-laboratory intercomparison or intercalibration studies exist, so differences in performance are not evident. Study scope is another issue, as different and possibly mutually incompatible size ranges, size fractions, morphologies, and polymer types may have been defined and measured. In addition, the time and expense of microplastics laboratory sample processing and analysis limits the number of samples of the study, which in turn precludes a robust statistical analysis to understand trends in concentrations and compositions of microplastics. Given all these issues, comparisons across studies are likely most meaningful to address the question of whether microplastic levels are, in a broad sense, similar to each other or not.

Of the matrices of interest in this study, water is the most studied, with reported concentrations ranging from less than one particle to hundreds of thousands per cubic meter (Table 14). These values are in line with the values we observe in this study (Figure 2), taking all the caveats noted above into account. With regards to regional comparisons with available data, water concentrations in our study are generally lower than that observed previously, likely due to differences in scope and in analytical techniques. The first study conducted in the Los Angeles and San Gabriel Rivers estimated concentrations of plastic particles between 1-4.75

mm to range from 0-12,932 particles/m^3, depending on the sampling method used and concurrence with rainfall events (Moore et al. 2011). These particulates are much bigger than those of the current study. Later, sites along these same rivers in closer proximity to coast and the Port of Los Angeles were surveyed, and average microplastic concentrations for particles ranging 3-1000 µm in size were estimated to be 4,161-641,292 particles/m^3, depending on various laboratory practices, e.g., if a nile red stain was used to attempt to distinguish plastic from natural particles (Wiggin et al. 2019). In addition, smaller sample volumes such as that taken from grab samples, as noted in some of the reported literature studies (Table 15) may have higher concentrations than those taken from the larger volumes sampled by trawls (including in this study), as smaller volumes may not necessarily account for heterogeneity in matrices with relatively low concentrations (Coffin et al. 2022).

The majority of microplastic particles are most often found in sediments as they will eventually sink after biofouling (Kaiser et al. 2017, Van Melkebeke et al. 2020), if they are not already denser than water. As with water, concentrations of microplastics found in sediment are also highly variable spanning at least three orders of magnitude, oftentimes along the same river (Table 15). These values are also in line with our observations in this study (Figure 3). Variability amongst reported microplastic concentrations in sediments may be in part due to the use of different sampling techniques. For instance, a recent direct comparison of sediment sampling devices revealed that some microplastics, particularly small particles, may be lost when using a shovel or spade to collect sediments rather than a grab sampler or corer (Adomat et al. 2022). Differences in sampling depth may also contribute to variability as microplastic concentrations are known to decrease with increasing sampling depth (Yu et al. 2023). While these challenges are somewhat unique to microplastics sampling, inherent differences amongst habitats (e.g., sediment deposition rates, grain size, organic matter content) are also likely to influence measured microplastic contamination rates, as they would any other contaminant. These issues notwithstanding, the levels of microplastics in our urbanized and anthropogenically impacted fluvial sediments are similar to observations elsewhere.

A plethora of studies have also documented the presence of microplastics in freshwater biota, with fish being the most highly studied taxa. Most studies focus on the presence of microplastics in the gastrointestinal tract. However, smaller particles, typically those less than ~100 µm, may translocate into other tissues such as the liver or the muscle (i.e., fillet), which has been previously documented in wild-caught freshwater fish previously (Table 16). Indeed, we did observe greater relative abundances of smaller microplastic particles in fish,

The microplastic concentrations in fish tissue were greater than in previously reported studies (Table 16). How the fish had accumulated such levels is uncertain, given that both water and sediment levels observed in this study are in line with literature reports in heavily impacted

rivers as previously noted. In addition, the fish in this study were small and fairly young and may not have accumulated as much contaminant as older fish in other studies may have done. However, fish levels of microplastics come with their own sets of caveats. First, it should be noted that fish were frozen whole, thawed, and then dissected in the laboratory to collect fillets. Performing dissections in a clean laboratory environment, as done in this study, should reduce the likelihood of contamination in comparison to the field. However, filleting was challenging due to the relatively small size of the fish (Table 3). As such, tissues were exposed longer than expected, and this may have led to elevated background contamination rates despite extensive quality assurance protocols (see Section 2.5). Though particle counts on air blanks did not indicate abnormal levels of contamination during dissections, the possibility cannot be eliminated given the somewhat elevated levels of particles in the fish tissue relative to previous findings (Table 16). In summary, it is unclear why the fish in this study have greater concentrations of microplastics than in other studies, and the levels reported here should be confirmed by further work.

The potential impacts of microplastics on aquatic organisms are not fully understood. However, plastic particles that translocate from the gastrointestinal tract to other tissues such as muscle may cause inflammation and the over production of reactive oxygen species, both of which may lead to tissue damage (Thornton Hampton et al. 2022b). Regardless, an assessment of fish health was outside the scope of this study.

Table 14. Selected microplastic concentrations in water collected from major rivers. NR = not reported.

Reference	Location	Sampling Method	Volume Sampled (m^3)	Minimum Particle Size Analyzed (µm)	Concentration Range (particles/m^3)
Baldwin et al. 2021	Delaware River, USA	Net	17.9-113	100	2.42-18.3
Baldwin et al. 2016	Great Lakes Tributaries, USA	Net	6-768	333	0.05-32
Scherer et al. 2020	Elbe River, Germany	Net	3.2-32.7	150	0.88-13.24
Xiong et al. 2019	Yangtze River, China	Net	NR	333	0.9 (mean)
Yan et al. 2021	Qinhuai River, China	Pump/ Sieve	0.02	54	1,467-20,567
Dris et al. 2015	Seine River, France	Net	182-200	330	0.28-0.45
Moore et al. 2011	Los Angeles River, USA	Net	NR	333	0-9
Moore et al. 2011	San Gabriel River, USA	Net	NR	333	<1
Moore et al. 2011	Coyote Creek, USA	Net	NR	333	<1
Wiggin et al. 2019	Los Angeles River, USA	Grab	0.02	3	8,394-808,749
Wiggin et al. 2019	San Gabriel River, USA	Grab	0.02	3	2,822-97,209

Table 15. Selected microplastic concentrations in sediment collected from major rivers. NR = not reported.

Reference	Location	Sampling Depth (cm)	Sediment Mass (g)	Minimum Particle Size Analyzed (µm)	Concentration Range (#/g dry weight)
Baldwin et al. 2021	Delaware River, USA	~3	112-492	355	0.045-1.838
Scherer et al. 2020	Elbe River, Germany	NR	85.2-1,375	20	0.009-15.962
Yan et al. 2021	Qinhuai River, China	~5	200	54	0.1,115-6.380
He et al. 2020	Brisbane River, Australia	0-3	100	NR	0.010-0.520
Crew et al. 2020	St. Lawrence River, Canada	Not Reported	300	10	0.065-7.562

Table 16. Selected microplastic concentrations in fish muscle tissue (i.e., fillet) collected from major freshwater systems. ND = not detected.

Reference	Location	Species	Minimum Particle Size Analyzed (µm)	Concentration Range	Concentration Units
McIlwraith et al. 2021	Lake Simcoe, Canada	Smallmouth Bass	63	0-6	particles/fillet
McIlwraith et al. 2021	Lake Simcoe, Canada	Largemouth Bass	63	0-35	particles/fillet
McIlwraith et al. 2021	Lake Simcoe, Canada	Yellow Perch	63	0-7	particles/fillet
McIlwraith et al. 2021	Lake Simcoe, Canada	Northern Pike	63	1-22	particles/fillet
McIlwraith et al. 2021	Lake Simcoe, Canada	Brown Bullhead	63	0-9	particles/fillet
McIlwraith et al. 2021	Lake Simcoe, Canada	Lake Whitefish	63	1-6	particles/fillet
McIlwraith et al. 2021	Lake Simcoe, Canada	White Sucker	63	0-14	particles/fillet
Collard et al. 2018	Marne and Seine Rivers, France	European Chub	5	ND	particles/gram
Su et al. 2019	Hangzhou Bay and Yangtze Estuary, China	Asian Seabass	20	ND	particles

4.3 Potential sources and fate

The microplastic particles observed in this study may come from several major processes. The first is wastewater effluent. Both rivers receive treated discharges of treated wastewater effluent from various treatment facilities, e.g., Glendale near the Los Angeles River mid-stream site, and Los Coyotes near the San Gabriel River mid-stream site. Wastewater effluent inputs in both rivers are continuous and occur year-round. A second major input process is runoff from roads and drains that enter the rivers. This input process would also include stormwater, which can be significant during the wet season (roughly mid-autumn to mid-spring, or October to April/May). This input process would be episodic. The extent of runoff as a contributor to microplastics in these rivers may be potentially insignificant during dry weather. Conversely, it may potentially be overwhelming during the wet season, as stormwater has been observed to have levels of microplastics dwarfing those in wastewater effluent, as observed in the San Francisco Bay area (Sutton et al. 2019). Finally, atmospheric deposition of microplastics (Zhang et al. 2020b) may also contribute to microplastic levels in the rivers by an unknown and unknowable amount, either by direct wet or dry deposition into the waters themselves (which would be low given the small surface area of the rivers compared to their watersheds), or such deposition into the watershed followed by transport via runoff to the rivers (which would likely to be indistinguishable from contributions to runoff from non-atmospheric sources).

The extent to which these three input processes contribute to microplastic levels in the Los Angeles and San Gabriel Rivers is unknown. That said, the levels of microplastics in the surface waters of both rivers are in line with what may be present in wastewater effluent discharge. The wastewater treatment plants near the mid-stream sites provide tertiary treatment. Wong et al. (2024) found 2 to 100 microplastic particles/m^3 in tertiary effluent from California coastal treatment facilities. While the specific facilities in that study were anonymized, these levels are in line with previous observations in tertiary effluent both in Los Angeles County at 0.00088 particles/L (Carr et al. 2016), in San Francisco Bay at 63 particles/m^3 (Sutton et al. 2019) and around the world with an average of 400 particles/m^3 (Liu et al. 2021). Concentrations of microplastics in river water in this study are along these lines (Figure 2). That said, it is important to recognize that the box trawl used for sampling surface water in this study is not designed to collect particles smaller than its mesh size (i.e., 330 nm). Moreover, literature studies of microplastics in the aquatic environment vary considerably in the size ranges of particles reported (e.g., >125 µm for Sutton et al. 2019 and Wong et al. 2024, 20 µm for Carr et al. 2016, and various sizes for the review article of Liu et al. 2021), for which smaller particles tend to be more numerous (Kooi et al. 2021).

There is likely also a runoff contribution to the microplastics in both rivers, given the composition of microplastic particles observed for two reasons. First is the presence of rubber

particles. Second is the material composition of microplastics in the rivers, compared to those of other sources.

The presence of rubber particles in our samples suggests that at least some of the microplastic contamination is due in part to runoff from roads and other impervious surfaces. While rubber particles are difficult to identify in microplastics analysis (Sutton et al. 2019), such particles are less commonly reported in wastewater effluents. Sutton et al. (2019) observed that stormwaters in the San Francisco Bay area had considerably different compositions of microparticles than wastewaters, with black particles with a rubbery texture much more common in the former than in the latter. This observation is consistent with observations in wastewater effluents in selected coastal wastewater treatment plants throughout the state (Wong et al. 2024) in which common microplastic polymer types included polyethylene, polyvinyl chloride, and polystyrene, with few particles identified as rubber.

The polymer composition of microplastics present appears to differ from wastewaters. The most common synthetic polymers in the particles observed in this study, in decreasing order, were polyethylene, rubber, polystyrene, polyamide, and polyurethane. Despite variability in polymer types from one treatment plant to another, the most common in California coastal wastewater treatment plants (Wong et al. 2024) were, in descending order, polystyrene, polyethylene, polyvinyl chloride, polypropylene, poly(methyl methacrylate), and polyethylene terephthalate. Both of the most common polymers were also among the most common six polymers found in wastewaters worldwide (Liu et al. 2021), and is consistent with what has been observed in San Francisco Bay (Sutton et al. 2019). Polyamide and polyurethane, which were common in both rivers, were less commonly observed, suggesting that their presence in the rivers may not be solely from wastewater effluent inputs. Polyurethane is commonly used in building materials e.g., insulation, and as automotive molding, upholstery, and padding. These uses are consistent with their presence in both rivers.

The lack of correlation of microplastic levels or characteristics (e.g., size fraction, morphology, particle composition) with sampling event suggests that there were no seasonal trends affecting these contaminants, at least in these rivers. This is in contrast to some previous studies where microplastic concentrations and compositions have been found to fluctuate according to weather patterns and seasons (Wang et al. 2021, Xia et al. 2021). Both rivers are dominated by wastewater effluent, in the reaches for which such discharge was designed to enter. This is year-round, and any temporal changes in inputs or removal efficiencies for different types of microplastics are likely to be reflected in the receiving waters, at least to some level. No such differences were found in California coastal wastewaters and effluents (Wong et al. 2024). Stormwater runoff would send microplastics to both rivers, and changes in the contents of this runoff would likewise influence riverine levels. This was not observed, in

part because of the drought that resulted in little precipitation over most of the study period. Further work would be needed to determine what climatic factors may influence microplastic levels in this region.

The greater levels of microplastics in the bed sediments of both rivers are consistent with the behavior of microplastic particles, many of which are denser than water on their own or become that way once biofilms grow on them (Kaiser et al. 2017, Van Melkebeke et al. 2020). As a result, these particles settle out of the water column. They may also be resuspended, which is likely in both rivers given their shallow depths and their use in flood control—indeed, the reason both are partially channelized was to mitigate bank overflow and shifts in the flow of the rivers, and the flooding damage that such events would case. Events such as these may contribute to the heterogeneity of sediment levels observed in this study (Figure 3).

5. Conclusions

In this report, samples of water, sediment, and fish were collected in the urbanized and anthropogenically impacted Los Angeles River and San Gabriel River of Southern California to determine microplastics levels in these environmental media. The samples were successfully processed by a method previously developed for wastewater. Concentrations of microplastics in both rivers were generally similar within each media studied, and there was considerable variability in these levels as well as in the characteristics (e.g., size distribution, morphology, particle composition) of the particles found from sample to sample. Levels of microplastics in water and sediment were in line with observations in those media at similar sites in other regions; however, fish concentrations in this study were greater than that reported in studies that were analogous to this one, for reasons unknown. Further research is needed to confirm or refute these concentrations, as well as to improve LDIR spectral libraries to take further advantage of the time and labor savings of this analysis technique compared to more established spectroscopic means, such as FTIR.

REFERENCES

Adomat, Y., M. Kahl, F. Musche, and T. Grischek. 2022. Evaluation of microplastics sediment sampling techniques—efficiency of common methods and new approaches. Microplastics and Nanoplastics 2:27.

Amereh, F., M. Babaei, A. Eslami, S. Fazelipour, and M. Rafiee. 2020. The emerging risk of exposure to nano (micro) plastics on endocrine disturbance and reproductive toxicity: from a hypothetical scenario to a global public health challenge. Environmental Pollution 261:114158.

Baldwin, A.K., S.R. Corsi, and S.A. Mason. 2016. Plastic Debris in 29 Great Lakes Tributaries: Relations to Watershed Attributes and Hydrology. Environmental Science & Technology 50:10377–10385.

Baldwin, A.K., A.R. Spanjer, B. Hayhurst, and D. Hamilton. 2021. Microplastics in the Delaware River, northeastern United States (Report No. 2020–3071), Fact Sheet. Reston, VA.

Borelle, S.B., J. Ringma, K.L. Law, C.C. Monnahan, L. Lebreton, A. McGivern, E. Murphy, J. Jambeck, G.H. Leonard, M.A. Hilleary, M. Eriksen, H.P. Possingham, H. De Frond, L.R. Gerber, B. Polidoro, A. Tahir, M. Bernard, N. Mallos, M. Barnes, and C.M. Rochman. 2020. Predicted growth in plastic waste exceeds efforts to mitigate plastic pollution. Science 369:1515-1518.

California State Water Resources Control Board. 2022. Standard Operating Procedures for Extraction and Measurement by Infrared Spectroscopy of Microplastic Particles in Drinking Water, version SWB-MP1-rev1 (May 20, 2022). https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/microplastics/swb-mp1-rev1.pdf.

California State Water Resources Control Board. 2022a. Standard Operating Procedures for Extraction and Measurement by Raman Spectroscopy of Microplastic Particles in Drinking Water, version SWB-MP2-rev1 (May 20, 2022). https://www.waterboards.ca.gov/drinking_water/certlic/drinkingwater/documents/microplastics/swb-mp2-rev1.pdf.

Campbell, S.H., P.R. Williamson, and B.D. Hall. 2017. Microplastics in the gastrointestinal tracts of fish and the water from an urban prairie creek. FACETS 2:395–409.

Carpenter, E.J., S.J. Anderson, G.R. Harvey, H.P. Miklas, and B.B. Peck. 1972. Polystyrene spherules in coastal waters. Science 178:749-50.

Carr, S.A., J. Liu, and A.G. Tesoro. 2016. Transport and fate of microplastic particles in wastewater treatment plants. Water Research 91:174-182.

Chamas, A.l., H. Moon, J. Zheng, Y. Qiu, T. Tabassum, J.H. Jang, M. Abu-Omar, S.L. Scott, and S. Suh. 2020. Degradation rates of plastics in the environment. ACS Sustainable Chemical Engineering 8:2494-3511.

Coffin, S., S.B. Weisberg, C. Rochman, M. Kooi, and A.A. Koelmans. 2022. Risk characterization of microplastics in San Francisco Bay, California. Microplastics and Nanoplastics 2:19.

Collard, F., J. Gasperi, B. Gilbert, G. Eppe, S. Azimi, V. Rocher, and B. Tassin. 2018. Anthropogenic particles in the stomach contents and liver of the freshwater fish *Squalius cephalus*. Science of The Total Environment 643:1257–1264.

Cooper, D.A., and P.L. Corcoran. 2010. Effects of mechanical and chemical processes on the degradation of plastic beach debris on the island of Kauai, Hawaii. Marine Pollution Bulletin 60:650-654.

Crew, A., I. Gregory-Eaves, and A. Ricciardi. 2020. Distribution, abundance, and diversity of microplastics in the upper St. Lawrence River. Environmental Pollution 260:113994.

De Frond, H., L. Thornton Hampton, S. Kotar, K. Gesulga, C. Match, W. Lao, S.B. Weisberg, C.S. Wong, and C.M. Rochman. 2022. Monitoring microplastics in drinking water: An interlaboratory study to inform effective methods for quantifying and characterizing microplastics. Chemosphere 298:134282.

De Frond, H., W. Cowger, V. Renick, S. Brander, S. Primpke, S. Sukumaran, D. Elkhatib, S. Barnett, M. Navas-Moreno, K. Rickabaugh, F. Vollnhals, B. O'Donnell, A. Lusher, E. Lee, W. Lao, G. Amarpuri, G. Sarau, and S. Christiansen. 2023. What determines accuracy of chemical identification when using microspectroscopy for the analysis of microplastics? Chemosphere 313:137300.

De Ruijter, V.N., P.E. Redondo Hasselerharm, T. Gouin, and A.A. Koelmans. 2020. Quality criteria for microplastic effect studies in the context of risk assessment: a critical review. Environmental Science & Technology 54:11692-11705.

Dris, R., J. Gasperi, V. Rocher, M. Saad, N. Renault, and B. Tassin. 2015. Microplastic contamination in an urban area: a case study in Greater Paris. Environmental Chemistry. 12: 592–599.

Gardon, T., H. Arnaud, I. Paul-Pont, A.-L. Cassone, M.S. Koua, C. Soyez, R. Jezequel, J. Receveur, and G. Le Moullac. 2020. Toxic effects of leachates from plastic pearl-farming gear on embryo-larval development in the pearl oyster Pinctada margaritifera. Water Research 179:115890.

Geyer, R., J.R. Jambeck, and K.L. Law. 2017. Production, use, and fate of all plastics ever made. Science Advances 3:e1700782.

González-Pleiter, M., C. Edo, D. Velázquez, M.C. Casero-Chamorro, F. Leganés, A. Quesada, F. Fernández-Piñas, and R. Rosal. 2020. First detection of microplastics in the freshwater of an Antarctic Specially Protected Area. Marine Pollution Bulletin 161:111811.

Gouin, T. 2020. Toward an improved understanding of the ingestion and trophic transfer of microplastic particles: critical review and implications for future research. Environmental Toxicology and Chemistry 39:1119–1137.

He, B., A. Goonetilleke, G.A. Ayoko, and L. Rintoul. 2020. Abundance, distribution patterns, and identification of microplastics in Brisbane River sediments, Australia. Science of The Total Environment 700:134467.

Horton, A.A., A. Walton, D.J. Spurgeon, E. Lahive, and C. Svendsen. 2017. Microplastics in freshwater and terrestrial environments: Evaluating the current understanding to identify the knowledge gaps and future research priorities. Science of the Total Environment 586:127–141.

Kaiser, D., N. Kowalski, and J.J. Waniek. 2017. Effects of biofouling on the sinking behavior of microplastics. Environmental Research Letters. 12:124003.

Kooi, M., & Koelmans, A. A. 2019. Simplifying microplastic via continuous probability distributions for size, shape, and density. Environmental Science and Technology Letters, 6:551–557.

Kooi, M., S. Primpke, S.M. Mintenig, C. Lorenz, G. Gerdts, and A.A. Koelmans. 2021. Characterizing the multidimensionality of microplastics across environmental compartments. Water Research 202:117429.

Kotar, S., R. McNeish, C. Murphy-Hagen, V. Renick, C.-F.T. Lee, C. Steele, A. Lusher, C. Moore, E. Minor, J. Schroeder, P. Helm, K. Rickabaugh, H. De Frond, K. Gesulga, W. Lao, K. Munno, L. Thornton Hampton, S.B. Weisberg, C.S. Wong, G. Amarpuri, R.C. Andrews, S.M. Barnett, S. Christansen, W. Cowger, K. Crampond, F. Du, A.B. Gray, J. Hankett, K. Ho, J. Jaeger, C. Lilley, L. Mai, O. Mina, B. O'Donnell, S. Primpke, S. Singh, J. Skovly, T. Slifko, S. Sukumaran, B. van Bavel, J. Van Brocklin, F. Vollnhals, C. Wu, and C.M. Rochman. 2022. Quantitative assessment of visual microscopy as a tool for microplastic research: Recommendations for improving methods and reporting. Chemosphere 308:136449.

Kovochich, M., J.A. Parker, S.C. Oh, J.P. Lee, S. Wagner, T. Reemtsma, and K.M. Unice. 2021. Characterization of Individual Tire and Road Wear Particles in Environmental Road Dust, Tunnel Dust, and Sediment. Environ. Sci. Technol. Letters 8:1057–1064.

Langknecht, T., W. Lao, C.S. Wong, D. El Khatib, S. Kotar, S. Robinson, R.M. Burgess, and K.T. Ho. 2023. Comparison of two procedures for microplastics analysis in sediments based on an interlaboratory exercise. Chemosphere 313:137479.

Lao, W., S. Dial, S. Salmon, and C. S. Wong. 2024. Development and validation of an acid/alkaline digestion method for efficient microplastic extraction from wastewater treatment plant effluents: Sulfuric acid concentration and contact time do matter. Science of the Total Environment 917:170528.

Lao, W., and C.S. Wong. 2023. How to establish detection limits for environmental microplastics analysis. Chemosphere 327:138456.

Li, C., R. Busquets, and L.C. Campos. 2020. Assessment of microplastics in freshwater systems: A review. Science of The Total Environment 707:135578.

Liu, W., J. Zhang, H. Liu, X. Guo, X. Zhang, X. Yao, Z. Cao, and T. Zhang. 2021. A review of the removal of microplastics in global wastewater treatment plants: Characteristics and mechanisms. Environment International 146:106277.

Maruya, K.A., W. Lao, D.R. Vandervort, R. Fadness, M. Lyons, and A.C. Mehinto. 2022. Bioanalytical and chemical-specific screening of contaminants of concern in three California (USA) watersheds. Heliyon 8:e09534.

McIlwraith, H.K., J. Kim, P. Helm, S.P. Bhavsar, J.S. Metzger, and C.M. Rochman. 2021. Evidence of Microplastic Translocation in Wild-Caught Fish and Implications for Microplastic Accumulation Dynamics in Food Webs. Environmental Science & Technology 55:12372–12382.

Mehinto, A.C., S. Coffin, A.A. Keolmans, S.M. Brander, M. Wagner, L.M. Thornton Hampton, A.G. Burton Jr., E. Miller, T. Gouin, S.B. Weisberg, and C.M. Rochman. 2022. Risk-based management framework for microplastics in aquatic ecosystems. Microplastics and Nanoplastics 2:17.

Moore, C.J., G.L. Lattin, and A.F. Zellers. 2011. Quantity and type of plastic debris flowing from two urban rivers to coastal waters and beaches of Southern California. Journal of Integrated Coastal Zone Management 11:65–73.

Munno, K., P.A. Helm, D.A. Jackson, C. Rochman, and A. Sims. 2018. Impacts of temperature and selected chemical digestion methods on microplastic particles: Impacts of temperature and digestion method on microplastics. Environmental Toxicology and Chemistry 37:91–98.

Munno, K., A.L. Lusher, E. Minor, A. Gray, K. Ho, J. Hankett, C.-F.T. Lee, S. Primpke, R. McNeish, C.S. Wong, and C. Rochman. 2023. Patterns of microplastics in blank samples: a study to inform best practices for microplastic analysis. Chemosphere 333:138883.

Pirsaheb, M., H. Hossini, and P. Makhdoumi. 2020. Review of microplastic occurrence and toxicological effects in marine environment: experimental evidence of inflammation. Process Safety and Environmental Protection 142:1-14.

Rosso, B., E. Gregoris, L. Litti, F. Zorzi, M. Fiorini, B. Bravo, C. Barbante, A. Gambaro, and F. Corami. 2023. Identification and quantification of tire wear particles by employing different cross-validation techniques: FTIR-ATR Micro-FTIR, Pyr-GC/MS, and SEM. Environmental Pollution 326: 121511.

Scherer, C., A. Weber, F. Stock, S. Vurusic, H. Egerci, C. Kochleus, N. Arendt, C. Foeldi, G. Dierkes, M. Wagner, N. Brennholt, and G. Reifferscheid. 2020. Comparative assessment of microplastics in water and sediment of a large European river. Science of The Total Environment 738:139866.

State of California. 2018. Senate Bill 1263 Ocean Protection Council: Statewide Microplastics Strategy. https://leginfo.legislature.ca.gov/faces/billTextClient.xhtml?bill_id=201720180SB1263.

Su, L., H. Deng, B. Li, Q. Chen, V. Pettigrove, C. Wu, and H. Shi. 2019. The occurrence of microplastic in specific organs in commercially caught fishes from coast and estuary area of east China. Journal of Hazardous Materials 365:716–724.

Suaria, G., V. Perold, J.R. Lee, F. Lebouard, S. Aliani, and P.G. Ryan. 2020. Floating macro- and microplastics around the Southern Ocean: results from the Antarctic circumnavigation expedition. Environment International 136:105494.

Sussarellu, R., M. Suquet, Y. Thomas, C. Lambert, C. Fabioux, M.E.J. Pernet, N. Le Goic, V. Quillien, C. Mingant, Y. Epelboin, C. Corporeau, J. Guyomarch, J. Robbens, I. Paul-Pont, P. Soudant, and A. Huvet. 2016. Oyster reproduction is affected by exposure to polystyrene microplastics. PNAS 113:2430-2435.

Sutton, R., A. Franz, A. Gilbreath, D. Lin, L. Miller, M. Sedlak, A. Wong, C. Box, R. Holleman, K. Munno, X. Zhu, and C. Rochman. 2019. Understanding microplastic levels, pathways, and transport in the San Francisco Bay region. San Francisco Estuary Institute, SFEI-ASC Publication No. 950.

Thornton Hampton, L.M., H. Bouwmeester, S.M. Brander, S. Coffin, M. Cole, L. Hermabessiere, A.C. Mehinto, E. Miller, C.M. Rochman, S.B. Weisberg. 2022a. Research recommendations to better understand the potential health impacts of microplastics to humans and aquatic ecosystems. Microplastics and Nanoplastics 2:18.

Thornton Hampton, L.M., S.M. Brander, S. Coffin, M. Cole, L. Hermabessiere, A.A. Koelmans, and C.M. Rochman. 2022b. Characterizing microplastic hazards: which concentration metrics and particle characteristics are most informative for understanding toxicity in aquatic organisms? Microplastics and Nanoplastics 2:20.

Thornton Hampton, L.M., H. De Frond, K. Gesulga, S. Kotar, W. Lao, C. Matuch, S.B. Weisberg, C.S. Wong CS, S. Brander, S. Christiansen, C.R. Cook, F. Du, S. Ghosal, A.B. Gray, J. Hankett, P.A. Helm, K.T. Ho, T. Kefela, G. Lattin, A. Lusher, L. Mai, R.E. McNeish, O. Mina, E.C. Minor, S. Primpke, K. Rickabaugh, V.C. Renick, S. Singh, B. van Bavel, F. Vollnhals, and C. M. Rochman. 2023. The influence of complex matrices on method performance in extracting and monitoring for microplastics. Chemosphere 334:138875.

Van Melkebeke, M., C. Janssen, and S. De Meester. 2020. Characteristics and Sinking Behavior of Typical Microplastics Including the Potential Effect of Biofouling: Implications for Remediation. Environmental Science and Technology. 54:8668–8680.

Wang, G., J. Lu, W. Li, J. Ning, L. Zhou, Y. Tong, Z. Liu, H. Zhou, and N. Xiayihazi. 2021. Seasonal variation and risk assessment of microplastics in surface water of the Manas River Basin, China. Ecotoxicology and Environmental Safety 208:111477.

Wiggin, K.J., and E.B. Holland. 2019. Validation and application of cost and time effective methods for the detection of 3–500 µm sized microplastics in the urban marine and estuarine environments surrounding Long Beach, California. Marine Pollution Bulletin 143, 152–162.

Wong, C.S., W. Lao, S. Dial, D. Nguyen, R. Butler, and D. Lin. 2024. Project report, Characterizing the removal of microplastics by California wastewater treatment plants: Implications for management Strategies. Report to California Ocean Protection Council.

Xia, F., Q. Yao, J. Zhang, and D. Wang. 2021. Effects of seasonal variation and resuspension on microplastics in river sediments. Environmental Pollution 286:117403.

Xiong, X., C. Wu, J.J. Elser, Z. Mei, and Y. Hao. 2019. Occurrence and fate of microplastic debris in middle and lower reaches of the Yangtze River – From inland to the sea. Science of The Total Environment 659:66–73.

Yan, Z., Y. Chen, X. Bao, X. Zhang, X. Ling, G. Lu, J. Liu, and Y. Nie. 2021. Microplastic pollution in an urbanized river affected by water diversion: Combining with active biomonitoring. Journal of Hazardous Materials 417:126058.

Yu, L., R. Li, M. Chai, and B. Li. 2023. Vertical distribution, accumulation, and characteristics of microplastics in mangrove sediment in China. Science of The Total Environment 856:159256.

Zhang, W., Z. Liu, S. Tang, D. Li, Q. Jiang, and T. Zhang. 2020a. Transcriptional response provides insights into the effect of chronic polystyrene nanoplastic exposure on Daphnia pulex. Chemosphere 238:124563.

Zhang, Y., Kang, S., Allen, S., Allen, D., Gao, T., Sillanpää, M., 2020b. Atmospheric microplastics: A review on current status and perspectives. Earth-Science Reviews:203, 103118.

Zimmerman, L., S. Göttlich, J. Oehlmann, M. Wagner, and C. Völker. 2020. What are the drivers of microplastic toxicity? Comparing the toxicity of plastic chemicals and particles to Daphnia magna. Environmental Pollution 267:115392.

APPENDIX A. DATA AVAILABILITY

Raw data from this study is available at https://microplastics.sccwrp.org.