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Urban Stormwater Runoff: A Major Pathway for Anthropogenic Particles, Black Rubbery Fragments, and Other Types of Microplastics to Urban Receiving Waters

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ABSTRACT: Stormwater runoff has been suggested to be a significant pathway of microplastics to aquatic habitats; yet, few studies have quantified microplastics in stormwater. Here, we quantify and characterize urban stormwater runoff from 12 watersheds surrounding San Francisco Bay for anthropogenic debris, including microplastics. Depth-integrated samples were collected during wet weather events. All stormwater runoff contained anthropogenic microparticles, including microplastics, with concentrations ranging from 1.1 to 24.6 particles/L. These concentrations are much higher than those in wastewater treatment plant effluent, suggesting urban stormwater runoff is a major source of anthropogenic debris, including microplastics, to aquatic habitats. Fibers and black rubbery fragments (potentially tire and road wear particles) were the most frequently occurring morphologies, comprising ∼85% of all particles across all samples. This suggests that mitigation strategies for stormwater should be prioritized. As a case study, we sampled stormwater from the inlet and outlet of a rain garden during three storm events to measure how effectively rain gardens capture microplastics and prevent it from contaminating aquatic ecosystems. We found that the rain garden successfully removed 96% of anthropogenic debris on average and 100% of black rubbery fragments, suggesting rain gardens should be further explored as a mitigation strategy for microplastic pollution.
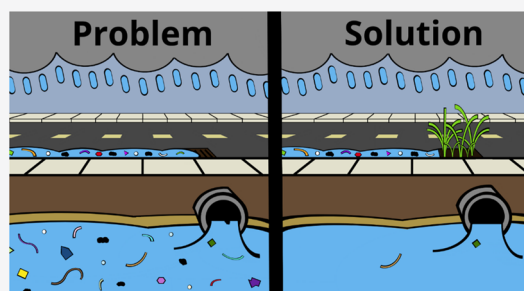
KEYWORDS: Stormwater, microplastics, tire and road wear particles, rubbery fragments, bioretention cells, rain gardens

1. INTRODUCTION

Plastics have become ubiquitous in society. Since their invention in the early 1900s, over 8300 million metric tons of virgin plastic materials have been produced, most of which have become waste.[1] Unfortunately, as a consequence of current waste management practices, the majority of this waste has ended up in landfills or entered the natural environment as plastic debris.[1] In addition to mismanaged waste, plastic debris enters the environment via atmospheric deposition,[2] treated wastewater effluent,[3] agricultural runoff,[4] industrial wastewater,[5] and stormwater runoff.[6]

Plastic debris is defined according to size with particles less than five millimeters (mm) in length referred to as microplastics.[7] Microplastics consist of a diverse group of plastic types, shapes, and sizes[8] with diverse and complex additive suites.[9]

Both the physical and chemical properties of microplastics influence their toxicity and, in turn, their effects on organisms.[9−11] Because microplastics can result in adverse outcomes for wildlife,[12,13] calls to remove them from the environment or to prevent contamination in the first place are common.

Once released into the environment, microplastics are difficult to remove.[14] Thus, the prevention of their release is critical. In addition to controlling upstream sources, there are various pathways that can be studied to inform solutions. For example, microplastics can enter the aquatic environment via atmospheric deposition,[2] effluent from wastewater treatment plants,[15] and illegal dumping.[16] In addition, mismanaged waste (or litter) and particles shed from plastic items (e.g., tires) in outdoor urban areas can be mobilized from the landscape by precipitation and transported via stormwater runoff to adjacent water bodies. This pathway will be the focus of this paper.

Urban stormwater runoff is a complex mixture of precipitation, suspended sediment, natural and anthropogenic debris, and chemical pollutants that are washed off the urban landscape during rain events.[17,18] This mixture can include

total suspended solids, heavy metals, organic pollutants (e.g., pesticides, industrial chemicals, and polycyclic aromatic hydrocarbons (PAHs)), and nutrients.[19,20] More recently, microplastics have also been found in stormwater.[4,6,21] For example, Jönsson[22] found 5.4−10 microplastic particles per liter (L) of stormwater in three urban catchments, suggesting that stormwater may be a more significant pathway for microplastics than treated wastewater. There is a need for more studies to quantify the relative importance of stormwater as a transport pathway of microplastics to aquatic ecosystems, in addition to more studies considering relevant mitigation strategies.

Preventative trash capture measures such as high-flow capacity devices, trash wheels, and catch basin inserts are used to remove macrodebris from stormwater.[23−25] While not always specific to plastics, these strategies help remove large pieces of plastic pollution. Techniques that target macroplastics (plastics >5 mm) will also help mitigate microplastic pollution by reducing debris that will weather and fragment into smaller plastic pieces over time in the environment. Still, there is an urgent need for treatment systems that can remove microplastics as well.

A potential strategy for the mitigation of microplastics is rain gardens. Also referred to as bioretention cells, these landscapes are placed in a depression and are composed of native vegetation, engineered soil, organic matter, and oftentimes mulch.[26] Although numerous studies have documented the ability of rain gardens to remove metals, chemical pollutants, and nutrients from stormwater,[27−29] few have evaluated their efficacy in removing microplastics.[30,31]

The objective of this study is to understand stormwater as a pathway for microplastics and other anthropogenic particles to reach aquatic ecosystems. Samples were collected from watersheds with a range of land uses and sizes, and depth-integrated sampling was used to more fully characterize the debris. As a case study, we also sampled the inlet and outlet of a rain garden to evaluate its efficacy as an effective tool for the mitigation of microplastics in urban stormwater. Results from this paper can inform policy regarding pathways of microplastics to aquatic ecosystems and relevant mitigation strategies for stormwater management. This paper also helps fill a gap in the existing literature, as few studies have measured microplastics in urban stormwater runoff.

2. METHODS

Stormwater runoff was collected from 12 sites in the San Francisco Bay Area in California, USA (Figure 1), to quantify and characterize microplastics and other anthropogenic particles in stormwater. As a case study, we also sampled the inlet and outlet of a rain garden during three separate storm events to test the effectiveness of rain gardens in reducing microplastics in stormwater runoff discharged to an aquatic ecosystem. The results of the rain garden were briefly described in Gilbreath et al.[30] and are described in more detail here. The following outlines the sampling methodology for both stormwater and rain garden samples.

2.1. Quantification and Characterization of Microplastics and Other Anthropogenic Particles in Stormwater. *2.1.1. Site Information.* Twelve different streams in the San Francisco Bay Area that drain into San Francisco Bay were sampled during storm events (Figure 1). Watersheds varied in land use and size (see Table S1). Maps of each watershed's drainage lines are available in Figures S1−S7.
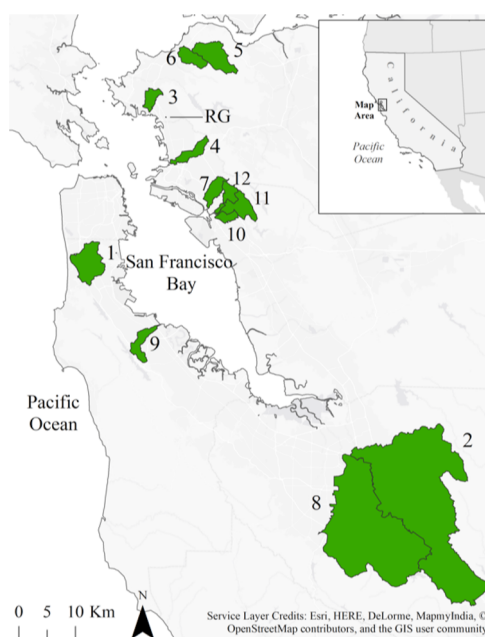

Figure 1. Site locations. Stormwater sites are indicated by their site number (1−12), and the rain garden case study site is indicated by the letters "RG". For greater detail regarding each watershed, see Figures S1−S7. Copyright OpenStreetMap contributors.

2.1.2. Stormwater Sampling. Each site was sampled once during six storm events from December 2016 to November 2018 (Table S2). Storms were chosen on the basis of strength; we sampled during those that were predicted to be sufficiently strong to mobilize contaminants (more than 1.3 cm (cm) of rainfall within 6 h or 1.9 cm within 12 h). Antecedent dry days, total storm rainfall, the maximum 2 h storm intensity, and percent imperviousness of the watershed for each sample are provided in Table S2. During each storm at each sampling site, a composite depth-integrated sample composed of 3−8 aliquots was collected across the hydrograph. A depth-integrated sample was taken from the center of the tributary with sample tubing secured to a metal pole. Once in the water column, the tubing was moved up and down (from just below the surface to just above the stream bed) during sampling. The field crew timed the collection of the first aliquot to occur at the beginning of the rise of the hydrograph. With one exception (site eight), an ISCO sampler was used to pump, on average, a total of 100 L of water (Table S3) from the stream through a foil lid and over two stacked stainless-steel sieves, sized 125 and 355 μm. At site eight, the bridge from which collection occurred was too high above the tributary to successfully deploy the pump, so a stainless-steel bucket and winch system were used. The bucket of water was poured over the stacked sieves. A clean stacked sieve set was used at each site; in between aliquots, the stacked sieves were covered in foil and placed in a cooler to reduce background contamination. After sample collection, the sieves were placed in coolers with foil over them and brought back to the laboratory at the San Francisco Estuary Institute where they were processed.

One field blank and one field duplicate were collected and subjected to similar collection, processing, and analyses. A field blank was collected by placing a set of sieves near the field sample for the duration of the sampling period. When the tubing was placed through the foil lid of the field sample, the foil lid of the field blank was entirely removed to reflect the

maximum amount of air exposure. A field duplicate was collected at site ten by setting up a second set of sieves adjacent to the primary sample sieve set. For each 17 L aliquot that was collected across the hydrograph, the primary sample was collected first and then covered with foil, and then, the duplicate sample was collected and then covered with foil. Upon completion of each aliquot, both sets of sieves were returned to the dedicated cooler to await the next aliquot. The field blank and duplicate samples were handled and processed in the same manner as the field samples.

Once in the laboratory, distilled water was used to gently rinse the contents of the sampling sieves into clean glass jars. Samples were shipped to the University of Toronto for laboratory analysis. Upon arrival, approximately 10% by volume of isopropyl alcohol was added to each sample to prevent algal growth prior to analyses.

2.1.3. Sample Processing and Analysis. We used a density separation method modified from Stolte et al.[32] to separate microplastic and other anthropogenic debris from the sediment in the stormwater samples (see Table S4 for extraction recovery). Samples were first rinsed through stacked stainless-steel sieves with 106 and 500 μm mesh to remove water. Those with little particulate matter were only rinsed through a 106 μm mesh sieve. When rinsed through both sieves, the content on the 500 μm sieve was transferred to a glass jar with reverse osmosis (RO) water and stored for microplastic quantification.

The content on the 106 μm sieve was transferred to a glass separatory funnel using a filtered 1.4 g/mL calcium chloride ($CaCl_2$) solution. We then added approximately 250 mL more of the $CaCl_2$ solution to the funnel, shook it to mix the contents, and allowed denser particles to settle for roughly 1.5−2.5 h. Once settled, we released the denser material over a 106 μm sieve and transferred it with RO water to a clean glass jar for storage. We then released the remaining floating material over a clean 106 μm sieve and transferred it with RO water to a glass jar for microplastic quantification.

Each jar with particles to be quantified and characterized was sieved through four stainless-steel stacked sieves to separate samples into four size fractions using a 125 μm, 355 μm, 500 μm, and 1 mm mesh. Content within each size fraction (125−355 μm, 355−500 μm, 500 μm to 1 mm, and >1 mm) was rinsed into four separate clean glass jars with RO water. Each size fraction was visually sorted using stereomicroscopes (Leica M80 Routine Stereomicroscope, 7.5−60× zoom; https://omaxmicroscope.com/, model # G42PT-L3WLED, 10−80× zoom). We extracted and counted microparticles that appeared anthropogenic and classified them according to color and morphology (i.e., sphere, fiber, fiber bundle, film, foam, firm fragment, rubbery fragment). To characterize and count microparticles, we removed the first ten particles of each color/morphology combination (e.g., blue fiber, clear sphere) from each size fraction and tallied all remaining particles for each color/morphology. All particles that we extracted were placed on double-sided tape and were photographed and measured using ImageJ software. The polymeric composition of a subsample of these extracted particles was identified using either Raman spectroscopy (Horiba Scientific Xplora Plus) with LabSpec6 software or Fourier transform infrared (FTIR) spectroscopy with an FPA-based Alpha II FTIR setup with OPUS/3D technology (Bruker Corporation). A small subsample of rubbery fragments was also identified using pyrolysis gas chromatography−mass spectrometry (GC-MS; see the Supporting Information for the full methodology). This

was necessary because rubbery fragments were difficult to identify with Raman or FTIR due to photodegradation, poor spectral matching, or size constraints.

The choice of Raman versus FTIR was based on particle size. Particles large enough to manipulate by hand, approximately >500 μm (or 1 mm long for fibers), were identified with FTIR (N = 45); all others were identified with Raman. For subsampling, we used the following rules. If the number of particles of a particular morphology within each sample (x) was ≤10, all particles were analyzed; if 10 < x ≤ 100, 10 particles were randomly selected and analyzed; if 100 < x ≤ 200, 10% of the particles were randomly selected and analyzed; if x > 200, 20 particles were randomly selected and analyzed. This resulted in the spectroscopic analysis of 858 particles. This is 6.8% of all 12 651 particles tallied from all samples (including both field samples and QA/QC samples) or 17.6% of the 4878 particles that were picked and mounted on tape.

Due to band overlay of dyes within a particle or fluorescence when using Raman spectroscopy, we were unable to determine the material type of all particles analyzed. This led to the creation of two categories: "unknown" and "anthropogenic (unknown base)". "Unknown" was used when we could not obtain a spectrum, if no match could be identified from the Raman spectroscopy database, or if the spectrum had an inconclusive database match. This category was common for black rubbery fragments. "Anthropogenic (unknown base)" was used when the spectrum matched with a synthetic dye, but we could not identify the material type. This category was common for dyed microfibers and is useful because it confirms a particle is anthropogenic. Particles classified as "unknown" or "anthropogenic (unknown base)" may or may not be plastic.

2.1.4. QA/QC. All glassware used for collection and analysis was washed with soap and water followed by three rinses with RO water. All water used for sample preparation and analysis was RO water. Good laboratory practice to avoid procedural contamination included sealing all glassware from air as much as possible, filtering the density separation solution prior to use, working in a clean cabinet as much as possible, and wearing cotton lab coats during laboratory analysis.

One field blank (45 particles) was collected to account for procedural contamination while sampling. Laboratory blanks (n = 4, range = 5−53 particles) and a bottle blank (7 particles) were also analyzed using the methods described above. The sums of the averages of the laboratory blanks (including the bottle blank) and the field blank were subtracted from each sample by color/morphology (e.g., blue fiber) to account for contamination.

A field duplicate was collected at one site (site ten) to measure sample variability. The primary and duplicate samples at this site had 24.6 and 33.4 particles/L, respectively, a relative standard deviation (RSD) of 21%. Only the primary sample is used in subsequent analyses.

2.2. Measuring the Effectiveness of Rain Gardens in Mitigating Microplastics and Other Anthropogenic Particles. *2.2.1. Site Information.* Influent and effluent were collected from an urban rain garden located in a small watershed (4080 m^2) in El Cerrito, California, USA (see Gilbreath et al.[30]). The watershed is composed of surface streets (67%), medium density residential land use (20%), and commercial offices (13%).[33] The rain garden is located along a major transit corridor that receives heavy foot and automobile traffic.[33]

The rain garden is rectangular in shape (3.7 m × 1.7 m), and the surface ponding depth is 0.28 m. From bottom to top, the garden is composed of the following components: native soil, drain rock, and rain garden soil media. The drain rock (1.3 cm diameter) is located approximately 0.7 m below the surface. Within this is an underdrain, which was necessary because of the native soil's infiltration rate of 0−1.3 mm/h. This native soil is classed as hydrologic soil group D with high clay content. The rain garden media is composed of engineered soil and native vegetation. This engineered soil has a minimum infiltration rate of 12.7 cm/h and is a mixture of sandy loam (70%), clay (10%), and composited organic matter (20%). The vegetation is drought-tolerant. Aside from losses due to some interception and evapotranspiration, the majority of incoming stormwater is filtered through the soil media and discharged to a storm drain. For further information about this rain garden and its efficiency for mitigating other contaminants, see Gilbreath et al.[30]

2.2.2. Stormwater Sampling. We sampled stormwater from the inlet and outlet of the rain garden during three storm events. This resulted in two different sets of samples: influent ($n = 3$) and effluent ($n = 3$). For each storm, a composite sample was collected by pumping 20−40 L aliquots of stormwater through two stacked stainless-steel sieves, sized 125 and 355 μm. Sample handling was as described for previous samples. Once in the laboratory, deionized water was used to transfer the content on the sieve to a clean glass jar. We then shipped the samples, along with two field blanks collected as previously described, to the University of Toronto for laboratory analysis. Upon arrival, approximately 10% by volume isopropyl alcohol was added to each sample to prevent algal growth.

2.2.3. Sample Processing and Analysis. Samples of the effluent that passed through the rain garden were transparent with little particulate matter. These samples were simply vacuum filtered onto 20 μm polycarbonate (PC) filters (47 mm in diameter; Whatman Millipore) to be later examined via microscopy. In contrast, the samples collected from the influent had high concentrations of sediment and plant matter. For these, we used the density separation method described above with slight deviations. These included: sieving samples through a 106 μm mesh if they were sieved to 125 μm prior to arrival or through both 106 and 500 μm meshes if they were sieved to 355 μm prior to arrival; allowing denser particles to settle for longer, often overnight; releasing the bottom, denser material over a 45 μm sieve instead of a 106 μm sieve; vacuum filtering the remaining floating material onto a 20 μm PC filter (47 mm in diameter; Whatman Millipore) instead of releasing over a 106 μm sieve.

We used the same quantification method described above with slight deviations. These included: not separating the samples into four size fractions, extracting and performing chemical identification on a larger subsample of particles, and using only Raman spectroscopy to identify particle composition (Horiba Scientific Xplora Plus, LabSpec6 software). Our goal was to take a Raman spectrum for all particles. Still, there were some particles where we could not get a good spectrum or a good match. In addition, sometimes there were multiple particles that were exactly the same. For these, we analyzed several of these particles with Raman but not all. In total, 337 particles were analyzed out of 648 (i.e., 52%).

2.2.4. QA/QC. QA/QC was the same as above with slight deviations. These include: collecting two field blanks instead of

one; not collecting field duplicates; analyzing two lab blanks instead of four; not including an empty jar (i.e., bottle blank) as a third type of blank. For sample preparation and analysis, we used water filtered through a 10 μm filter when we did not have access to RO water. The lab blanks and field blanks followed the effluent processing described above.

2.3. Statistics. To measure the relationship between concentrations of anthropogenic debris and land use, we performed independent simple linear regressions for each land use category between the concentrations of anthropogenic debris at each site (dependent variable) and each land use as a percentage (independent variable) described in Table S1 (agricultural, open, residential, commercial, industrial, and transportation). We also performed a simple linear regression between the concentrations at each site and "urban land use", here defined as the sum of residential, commercial, industrial, and transportation areas (Table S1). Lastly, we assessed the relationship between concentrations of anthropogenic debris and the hydrologic parameters in Table S2 (total storm rainfall, maximum 2 h storm intensity, antecedent dry days, and percent imperviousness) by performing independent simple linear regressions for each hydrologic parameter (independent variable) and the concentrations of anthropogenic debris at each site (dependent variable). Microsoft Excel was used for all analyses.

3. RESULTS AND DISCUSSION

3.1. Quantification and Characterization of Microplastics in Stormwater. Microplastics and other anthropogenic particles were observed in all samples. Particles visually identified as anthropogenic were characterized by morphology, color, size, and type. The concentrations of particles in each sample ranged from 1.1 to 24.6 particles/L of stormwater (Table S3; Figure 2).
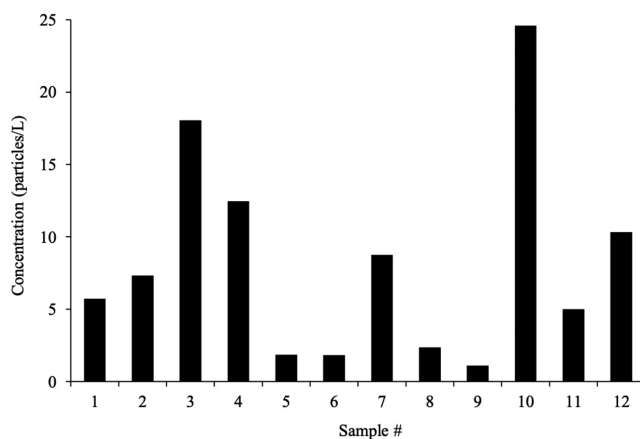

Figure 2. Concentrations of particles in stormwater samples. Particles included here are all those that were extracted and tallied, i.e., not just those that were chemically identified to material type.

With respect to particle morphology (Figure 3), fibers and rubbery fragments were most common at the 12 sites. Some samples were composed of as many as 97% fibers and others, 64% black rubbery fragments. Because of the aforementioned spectroscopic difficulties with rubbery fragments, the latter were classified mostly based on appearance and compressibility. Combined, fibers and rubbery fragments represented ~85% of all particles across all samples. Firm fragments, the
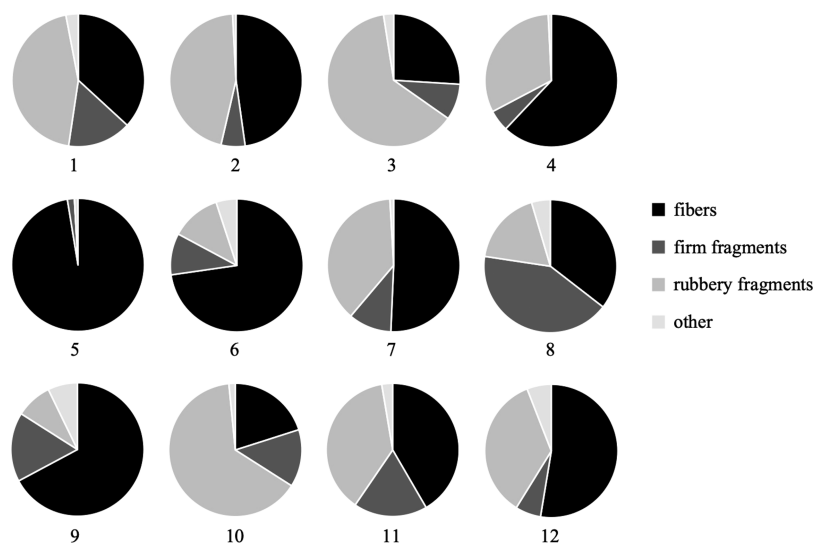
Figure 3. Morphologies of anthropogenic debris in stormwater samples. Numbers refer to the stormwater sample number. Particles included here are all those that were extracted and tallied, i.e., not just those that were chemically identified to material type.
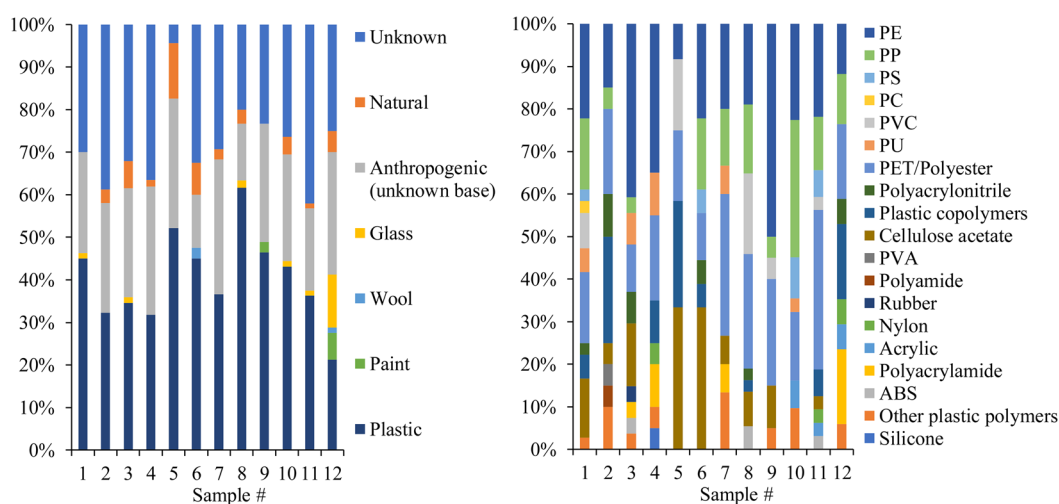

Figure 4. Types of anthropogenic debris (left) and plastic (right) found in stormwater samples (sites 1−12) determined by FTIR or Raman. "Unknown" was used when we could not obtain a spectrum, if no match could be identified from the Raman spectroscopy database, or if the spectrum had an inconclusive database match. "Anthropogenic (unknown base)" was used when the spectrum matched with a synthetic dye but we could not identify the material type. "Other plastic polymers" refers to polymers that were not common in our samples and includes: polytetrafluoroethylene, polyvinyl butyral, polyisobutylene-*co*-isoprene, poly(methyl methacrylate), fluoroelastomer, polyaryletherketone, polybutyl acrylate, and polybutylene terephthalate. For detailed information about each particle, see the Supporting Information.

next most common particle morphology, represented ~12% of all particles. The other categories we found were spheres, foam, film, and fiber bundles, which together comprised only ~2% of all particles. The large amount of rubbery fragments is consistent with current thinking that tire wear particles are a large source of microplastics into the environment.[34]

With respect to size (Figure S8), most particles in the samples were in the 125−355 μm range. There were more than 2.5 times as many particles in this size range than the second most common size range, >1 mm. The fewest particles were found in the 355−500 μm range.

With respect to particle composition (Figure 4), microplastics were common, comprising ~39% of all particles tested via spectroscopy. "Unknown" (i.e., unidentifiable) particles comprised ~30%, and "anthropogenic (unknown base)" particles comprised ~24%. The particle breakdown was as follows: natural particles, ~3%; glass, ~2%; paint, ~1%; wool,

~1%. Of the particles that were plastic, polyethylene (~25%), polyethylene terephthalate/polyester (~21%), polypropylene (~13%), cellulose acetate (~9%), and plastic copolymers (~7%) were most common. All other plastic types comprised ~5% or less of the plastic particles. Regarding the subsample of rubbery fragments (9 particles) that were tested with pyrolysis GC-MS, six were identified as styrene−butadiene rubber with natural rubber as a minor component and one particle appeared to have a petroleum origin. Two particles could not be identified, one of which had nitrogen-containing compounds and the other of which did not have any detectable marker peaks.

Concentrations also varied as a function of land use. Industrial land use was positively and significantly correlated with concentration ($p < 0.001$, $R^2 = 0.72$). All other relationships were not statistically significant ($p > 0.05$), but three were suggestive: urban land use and concentration were
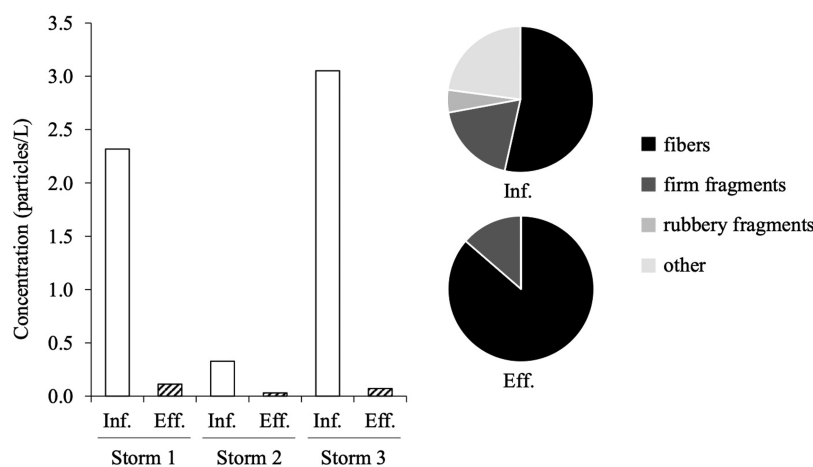
Figure 5. Concentrations and morphologies of anthropogenic debris in rain garden samples. Inf. refers to influent; Eff. refers to effluent. For the pie charts, storms were combined. Particles included here are all those that were extracted and tallied, i.e., not just those that were chemically identified to material type.

positively correlated ($p = 0.06$, $R^2 = 0.32$), transportation and concentration were positively correlated ($p = 0.05$, $R^2 = 0.33$), and open space and concentration were negatively correlated ($p = 0.05$, $R^2 = 0.33$). Full regression results are available in Table S5.

Percent imperviousness was positively and significantly correlated with concentration ($p < 0.01$, $R^2 = 0.65$). All other relationships between concentrations and hydrologic parameters (total storm rainfall, maximum 2 h storm intensity, and antecedent dry days) were nonsignificant ($p > 0.05$); however, there was a positive trend between maximum 2 h storm intensity and concentration ($p = 0.10$, $R^2 = 0.24$). Full regression results are available in Table S6.

3.2. Rain Gardens Reduce Microplastic Concentrations. As previously noted in Gilbreath et al.,[30] rain gardens can significantly reduce the concentration of chemical contaminants and anthropogenic debris in urban stormwater runoff. Here, the influent contained 1.9 ± 1.4 particles/L on average ($\pm$standard deviation), while the effluent contained 0.07 ± 0.04 particles/L ($\pm$standard deviation). The rain garden reduced the concentration of particles by 95%, 91%, and 98% for Storms 1, 2, and 3 respectively.

With respect to particle size (Table S7), rain gardens tend to more effectively remove larger particles. The highest reduction was for particles 3.5–5.0 mm, while the lowest was for particles less than 0.5 mm.

With respect to particle morphology (Figure 5), the effluent was much less diverse than the influent. The effluent contained just fibers (86%) and firm fragments (14%), whereas the influent contained fibers (53%), firm fragments (19%), rubbery fragments (5%), and "other" (23%), which is composed of spheres, fiber bundles, a film, and a cigarette filter. In one influent sample, there was an unusually high number of glass spheres (1.1 particles/L). These are believed to originate from roads, used as a reflector in paint.

With respect to particle composition (Figure S9), the effluent is again less diverse than the influent. The effluent only contained anthropogenic (unknown base) particles (~84%) and plastic (~10%), whereas the influent contained anthropogenic (unknown base) (~56%), glass (~20%), plastic (~16%), paint (~2%), and wool (~1%). In both influent and effluent, approximately 6% of particles was natural.

In the effluent, the plastic particles consisted of polyethylene terephthalate/polyester (40%), polyethylene (20%), acrylic (20%), and polyacrylamide (20%). In comparison, the plastic particles in the influent consisted of mainly polyethylene terephthalate/polyester (~30%), rubber (~29%), polyethylene (~12%), acrylic (~8%), and polyurethane (~7%). All other plastic types were ~5% or less of the plastic particles.

3.3. Significance and Implications. Our results indicate that urban stormwater runoff can be a significant source of anthropogenic debris, including microplastics, to aquatic ecosystems. The concentrations reported here, 0.3–24.6 particles/L (Tables S3 and S8), are similar to those reported in comparable studies, although sometimes much higher and sometimes much lower. For example, Baldwin et al.[35] reported much lower concentrations of 0.00005–0.032 microplastic particles/L in surface waters of several tributaries. Location likely played a role, as different watersheds have different land use characteristics, which can have a significant effect on the number of microplastics present.[35] The larger mesh sizes of 333 μm may have also contributed to this difference, as fewer particles may have been captured.[35] This is supported by the fact that the 125–355 μm size fraction in our study had the greatest number of particles (Table S7; Figure S8). Further, we sampled the entire water column, whereas Baldwin et al.[35] report concentrations from surface water only. A study that found higher concentrations than those observed here is Piñon-Colin et al.,[6] which reported 12–2054 microplastic particles/L in stormwater runoff in Tijuana, Mexico. The authors suggest various reasons for the high values, such as laundry effluent and industrial wastewater sometimes being discharged to the streets. Study location may also play a role.[35] Jönsson[22] reported more similar concentrations to ours: 5.4–10 microplastic particles/L. Eight of our samples are below this range; four are above, and three are within. Grbić et al.[4] reported similar concentrations to ours too: 2.3–29.4 microparticles/L. Four of our samples are below this range, and 11 are within.

The concentrations of anthropogenic particles observed in the stormwater in this study tend to be higher than other pathways, such as wastewater treatment plant (WWTP) effluent. For example, Mason et al.[3] reports an average of 0.05 ± 0.024 microparticles/L of effluent, Murphy et al.[36] reports 0.25 ± 0.04 microplastics/L of final effluent, and

Ziajahromi et al.[15] reports an average of 0.21−1.5 microplastics/L of final effluent. Our concentrations also tend to be much higher than those in WWTP effluent discharged to our study region, San Francisco Bay.[3,37] Because wastewater effluent undergoes significant treatment consisting of settling and removal of both dense and buoyant particles, this is not particularly surprising.

One of the most frequent morphologies of anthropogenic debris in our samples was rubbery fragments, some of which we confirmed to be tire and road wear particles. Automobile tires generate tire wear particles,[34] which can be mobilized via runoff and increase in receiving water bodies during storm events.[38] Here, we detected rubbery fragments in every sample (except rain garden-filtered effluent) with concentrations as high as 15.9 particles/L (Table S9). On the basis of our findings, we suggest rubbery fragments as a new category of microplastics.

A recent study reported 0 to 65 ± 7.36 tire particles per 5 mL of material such as river sediment and soil.[39] A number of previous studies also reported tire marker concentrations in units of mass per liter and/or mass per gram (e.g., Kumata et al.;[40] Zeng et al.[41]), making it difficult to compare results. We also cannot reliably compare our concentrations to the acute toxicity tests conducted in ecotoxicological studies because the dose concentrations are reported in mass per liter (e.g., Wik and Dave[42]). Further research is needed to understand how concentrations in the environment relate to concentrations that may cause toxicity. Tire dust is widely recognized as an environmental hazard, containing chemicals that can leach into aquatic environments and cause lethal effects on organisms (e.g., Peter et al.[43]). For example, the quinone transformation product of 6PPD (N-(1,3-dimethylbutyl)-N'-phenyl-p-phenyl-enediamine), a chemical commonly used in tire rubber, was recently identified as the toxicant that induces urban runoff mortality syndrome in adult coho salmon.[44] Smaller rubber particles in particular are suspected to be more harmful,[45] which is concerning given the quantity of rubbery fragments in our samples increases with decreasing size.

Overall, we show the significance of stormwater as a pathway for microplastics and other anthropogenic particles to aquatic ecosystems. Data from this study may inform policy and decision makers as they work to implement effective mitigation strategies not only in the San Francisco Bay Area but potentially in other locations too.[46] Various policies are currently in place to mitigate plastic pollution, such as bottle taxes and plastic bag bans. Unique strategies such as Mr. Trash Wheel in Baltimore, Maryland, are also being used successfully to prevent larger plastics in the watershed from entering the Atlantic Ocean.[25] These measures reduce macroplastic pollution and, therefore, microplastic pollution too; however, they alone are insufficient in combating the problem. Strategies specific to microplastics should be considered (e.g., McIlwraith et al.[47]). Regarding urban stormwater runoff, our work indicates imperviousness is positively correlated with microplastic concentrations and that rain gardens can be an effective strategy.

4. CONCLUSIONS

Stormwater is a major pathway of anthropogenic debris, including microplastics, to aquatic ecosystems. By quantifying and characterizing anthropogenic debris in depth-integrated samples from 12 different sites, we have illustrated the diversity and amount of anthropogenic particles in urban stormwater runoff. Rubbery fragments and fibers were particularly common, making up the majority of particles across all samples. The highest concentrations were found in our smallest size fraction, 125−355 μm, and plastics were the most common type of particle found. These findings are concerning given the negative impacts plastic can have on aquatic life. For this reason, our study also underscores the need for microplastic-specific mitigation strategies. Tactics dedicated to macroplastic pollution are expected to help ameliorate the problem but are ultimately insufficient to prevent both macro- and microplastics from entering aquatic ecosystems. Our study indicates that best management practices for managing legacy contaminants in stormwater, specifically rain gardens, may provide a valuable co-benefit as a mitigation strategy specific to reducing microplastics in stormwater runoff and deserve to be further explored.

■ ASSOCIATED CONTENT

ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsestwater.1c00017.

> Maps of each watershed; size distribution of particles found in stormwater samples; types of anthropogenic debris and plastic in rain garden samples; methods and results of the pyrolysis GC-MS analyses; land use raw data; sampling date, antecedent dry days, total storm rainfall, maximum 2 h storm intensity, and percent imperviousness for stormwater samples; sample counts, volumes, and concentrations; extraction spike-and-recovery results; full regression results; particle reductions for rain garden samples; rubbery fragment counts, volumes, and concentrations for stormwater samples (PDF)

> Raw data (morphology, color, type, size) for all samples (XLSX)

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Notes

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