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Seasonal and Distributional Changes in the Composition and Flux of Anthropogenic Microparticles in the Surface Waters of the Charles River, Massachusetts, United States

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Abstract: Plastic is a growing global environmental problem. While much of the focus of anthropogenic microparticles has focused on microplastics and their occurrence in marine systems, anthropogenic microparticles are found in freshwater systems. The Charles River is a highly impacted and historically important river within Massachusetts and runs for 80 miles within the state of MA through a variety of land uses. Microparticle concentrations were found to vary along the length of the river and ranged in concentrations from 1–19 pieces/L, with generally higher concentrations downstream. Microfibers were the dominant (72%) type of microparticles found, and the majority (avg 76%) of microparticles were synthetic. The highest estimated flux of microparticles occurred in May, with an estimated flux of 2 billion microparticles per day via the Charles River into the Boston Harbor. The average annual concentration of microparticles was correlated with land use, with higher concentrations occurring in regions with higher impervious coverage and in areas designated as industrial or high-density residential. Polyester, polypropylene, and polyamides were the dominant plastic polymers. However, seasonal changes in the relative importance of each polymer, along with changes in the abundance and flux rates, indicate that there would be seasonal variability in the type of microparticles exported. Changes in composition occurred between stations and between the head and mouth of the river, suggesting particle retention due to either deposition, degradation, or biological consumption.

Keywords: microplastic; microfiber; river; anthropogenic particle

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1. Introduction

Microplastics, plastics that are <5 mm, are a dominant source of pollution in all types of waterways [1]. While most research on microplastics is focused on their presence and impact in marine environments, they are present in freshwater bodies such as lakes, ponds, streams, rivers, and sediments [2–4]. Differences in the physical characteristics of water bodies, e.g., water density, stratification, etc., can affect the behaviors and impacts of microplastics in aquatic systems [5–7]. Additionally, turbulent currents in streams and rivers can advance the mechanical breakdown of larger plastics into many microparticles and affect their deposition. Vertical mixing, seasonal turnover of water, and quiescent versus turbulent flow vary between the types of rivers, ponds, and lakes. These differences in the physical vertical structure of the water column, along with the geomorphology of the river, can affect the retention, deposition, and transport of particles [8,9]. River flow can transport plastics from input sources upstream and export them to another body of water [8], providing an important avenue for particle transport.

Globally, the estimates of riverine input into the oceans range from 0.5 to 2.41 million tons of plastic [10,11]. It is estimated that over 20–30 tons of plastic debris are exported into the North Sea and 120 tons into the Mediterranean Sea by rivers [12]. While these studies report on both macro- and micro-plastics present, they reveal that rivers can be an

important avenue for plastic transport. Other studies suggest that much of the plastic debris within rivers is retained either by riparian vegetation, as well as in the river sediments or deposited near the mouth of a river [9,13]. Like oceans, rivers have been found to be dominated by microfibers [13–16], which include both natural, semisynthetic and synthetic fibers from textiles, ropes, cigarettes, tires, and sanitary products. Important sources of microplastics and microfibers to river systems include stormwater systems, wastewater treatment plants, combined sewer outfalls, and land use, along with the fragmentation of macro debris and inputs from aquatic industries and recreation (Figure 1). The abundance and distribution of microplastics in rivers can be related to land use, human population, and the natural and human built nature of the river [17–20]. Seasonal variations in the river discharge of plastics have been observed [21,22] and appear to be related to a combination of river vegetation, discharge rates, wind, precipitation, and land use. Currently, we do not understand all the variables that control and influence the concentration and flux of anthropogenic microparticles such as microplastics and microfibers in rivers [3,23].

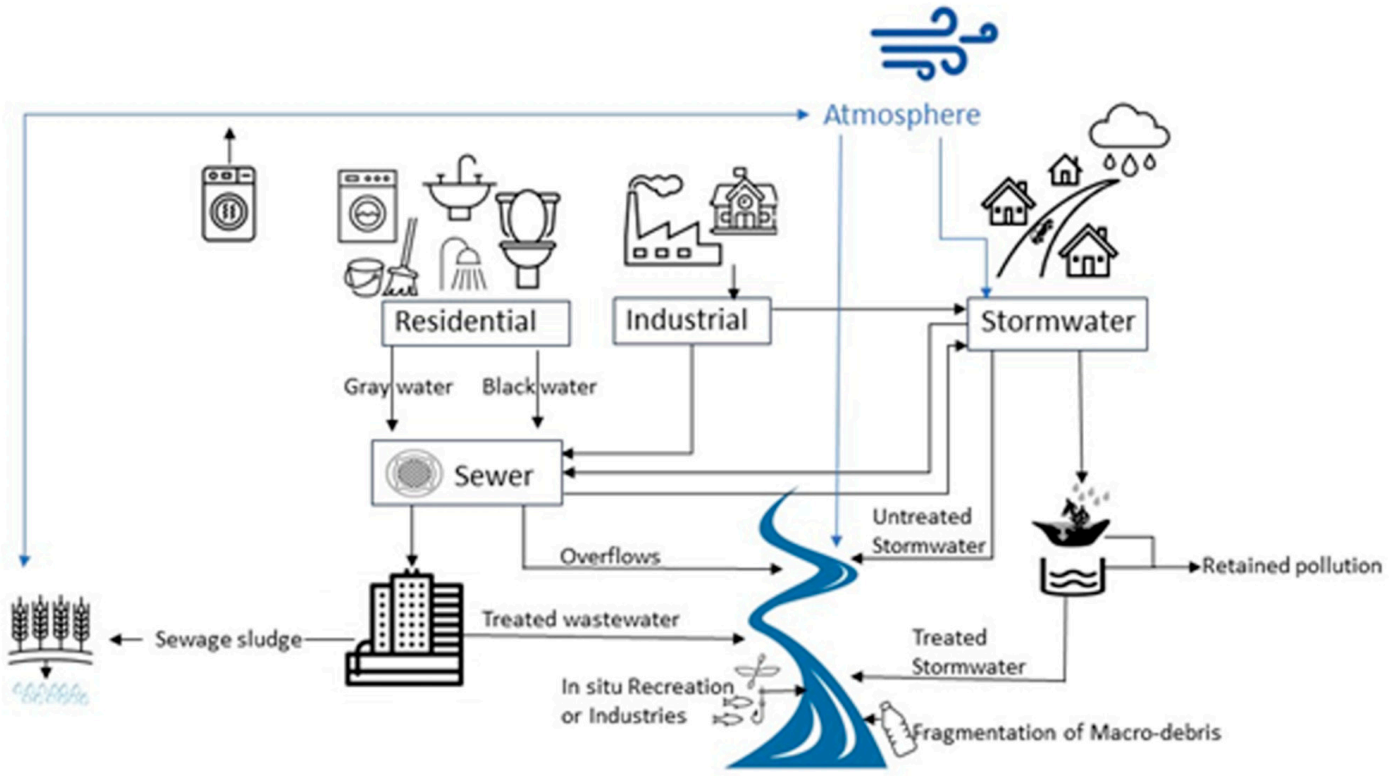

Figure 1. Sources of plastic debris (macro- and micro-sized) into New England Rivers. Blue lines represent environmental processes, while black lines represent man-made processes.

Rivers are vital waterways, as they drain nearly 75% of the earth's land surface; provide freshwater for irrigation, consumption, and transportation; are a source of energy; and provide critical habitats for many plants and animals. In 2011, over 50% of the world's population lived within 3 km of a freshwater body [24], and historically, rivers have played an important role in human settlement, as well as in development and cultures [25,26]. Rivers are an important aspect of the landscape in the northeastern portion of the United States, and within Massachusetts, there are hundreds of rivers and streams that discharge into the Atlantic Ocean. The Charles River is the fourth longest river in Massachusetts and the largest river flowing into the Boston Harbor. It flows 80 miles through 58 cities and towns and through a variety of landscapes before flowing directly between Boston and Cambridge, MA and emptying into Boston Harbor. The Charles River watershed covers 308 square miles, transitioning from a more rural and wetland-spotted environment in the upper watershed to a more developed and urban lower watershed. There are 19 dams

along the length of the Charles River that impact and regulate the flow of water. The river supports an ecosystem of freshwater fish, birds, and native plants. It is used heavily for recreation by its adjacent residents for swimming, fishing, rowing, and sailing in permitted areas. Due to its size and the variety of landscapes, e.g., marshes, small towns, and cities, examining the abundance of microplastics along the length of the Charles River allows us to examine how land use may affect microplastic abundance in what is ultimately a major urban river. The objectives of this study were the following:

1. Determine the concentration and composition of anthropogenic microparticles (microplastics and microfibers) in the Charles River;
2. Determine if the concentration or composition of the anthropogenic microparticles varied along the length of the river and between different sampling times, as well as if the variations were correlated to adjacent land use and impervious cover;
3. Estimate the export flux of anthropogenic microparticles into the Boston Harbor via the Charles River.

2. Materials and Methods

2.1. Charles River Sampling

Surface water samples for anthropogenic microparticles were collected from 21 sites using the water grab method [27] using a triple-rinsed metal bucket with neon green polypropylene rope. The rope was held out from the bridge to avoid any friction and to reduce input of fibers from the rope. The sample was poured into a triple-rinsed, 10 L carboy for storage until processing. Water depth and temperature measurements were taken at every sampling site for analysis (Appendix A). Sampling sites started at 3.1 miles downstream of the Charles River's headwaters in Milford, MA, USA, and subsequent sites were less than 6 miles apart along the 80 miles of the Charles River at a total of 21 sampling sites (Figure 2). All but two sites were accessible by bridges that permitted sampling over the middle of the river; Site 20 was sampled at the edged due to the extreme height of the adjacent bridge; and Site 5 was sampled by wading into Populatic Pond to a depth of 1 m. Surface samples were taken from the middle of each bridge site on the upstream side except for Sites 2, 13, and 16—where access was blocked to sample over the upstream side of the bridge. Sites were sampled in a single day, from approximately 7:30 a.m. to 5:30 p.m., on 28 January 2019, 1 May 2019, 5 August 2019, and 25 October 2019. Collection began furthest downstream at the New Charles River Dam (Site 21) near downtown Boston, MA USA and ended at the Central Street (Site 1) in Milford, MA, USA. Immediately after collecting all samples, they were returned to the University of Massachusetts Boston and stored in a temperature-controlled room at 12 °C until processed, which occurred within 5 days.

2.2. Processing

Samples were processed by subsampling each 10 L carboy into three well-mixed, 3 L samples that were filtered through a 20 µm nitex mesh, digested using 3% H_2O_2 [28] to remove excess organic material and any biofilms, rinsed with 10 µm filtered DI water, and backwashed into a combusted glass beaker to a volume of 10 mL. This 10 mL volume of concentrated debris from the 3 L sample was pipetted onto a clean glass microscope slide placed on a warming plate situated in a laminar flow hood. The dried slides were stored in sealed cardboard slide trays to prevent contamination by atmospheric deposition before µFTIR analysis.

2.3. Blanks

Blanks were created by rinsing filtration equipment with 100 mL of DI water, which was the volume used during pre-rinsing and processing of a sample onto a 20 µm mesh filter. The contents of the filter were rinsed into a beaker to 10 mL and pipetted onto a clean glass slide and counted microscopically. Blank values were subtracted from each sample slide created in one processing period. Also, while counting sample slides under a microscope, a clean glass slide was set on the stage of the apparatus to the side of the slide

being counted. This clean slide was counted after the sample slide to find if any plastic particles had accumulated by atmospheric deposition, and this number was subtracted from the sample slide. Additionally, any neon green fibers were not recorded, as they may have come from the rope used during sampling. Two sites along the river were sampled at the edge or by wading into a pond. To ensure that Site 20 (sampled at the edge) could be included in the analysis, a cross-section sample analysis was conducted just upstream of this location. Surface water samples were collected across the width of the Charles River at Site 19 to test for microplastic variability across the width of the river. Results showed that variation in microplastic concentrations across the width of the river was not significant, allowing for the data from Site 20 to be included in the analysis.

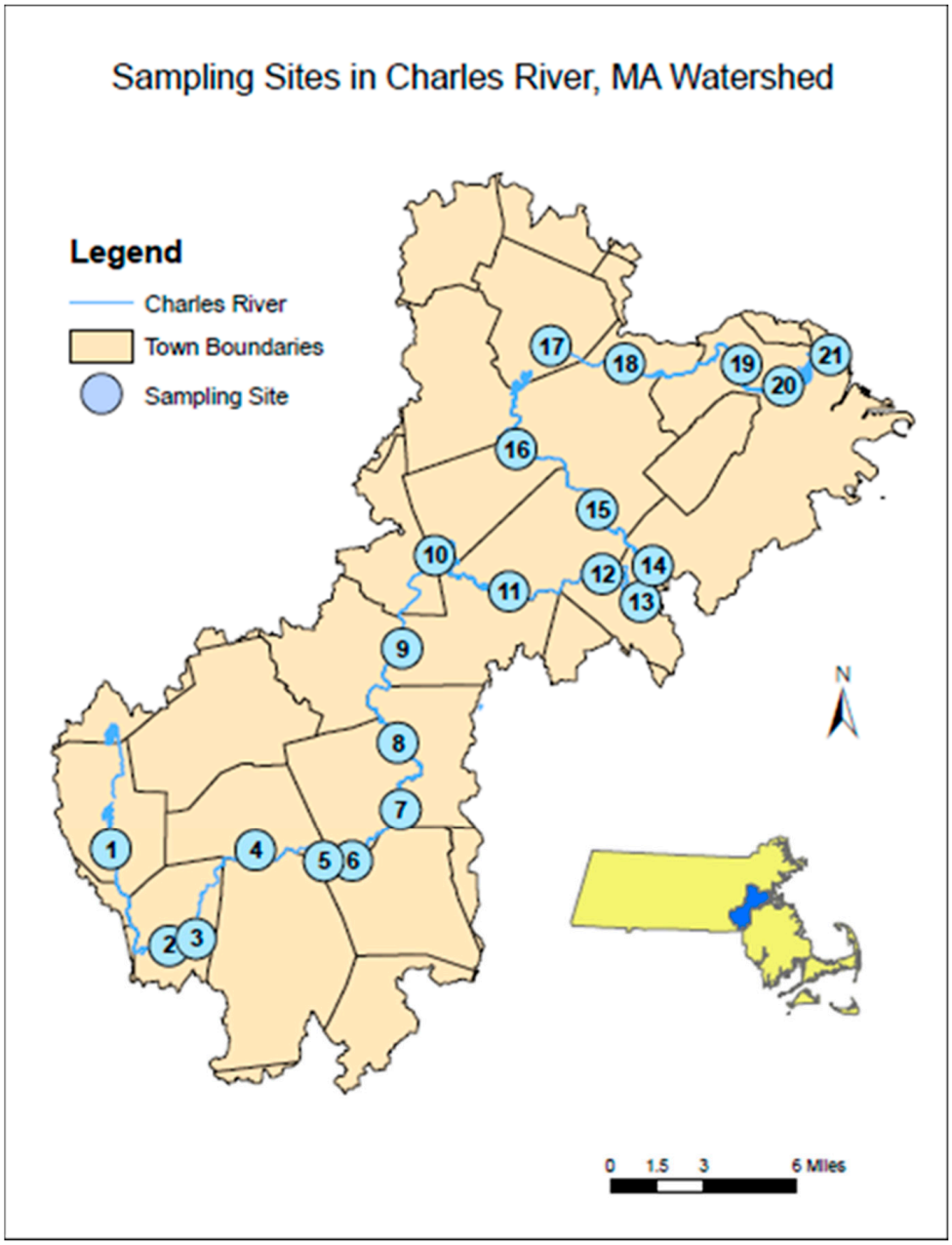

Figure 2. Charles River watershed map showing sampling sites, 1–21, in upstream (site 1) to downstream order (site 21). Insert of the state of Massachusetts, which shows the location of the Charles River watershed in blue.

2.4. Verification

Initial verification of microplastics occurred using the hot needle test [29] when examining the samples under a microscope. The microscope was fitted with an adjustable polarized lens to aid in identifying plastics by their reflective properties under polarized light [30]. An Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR) microscope (Smiths IlluminatIR, Danbury, CT, USA coupled to an Olympus microscope) was used to determine composition of the microparticles. The ATR-FTIR was set to 4 cm^{-1} resolution, Objective 36×-ATR, full spectral range 650–4000. FTIR spectra were obtained in transmission mode, and CO2 interference was removed for clarity. The spectra were read by an integrated software (Spectral ID version 3.03) and then were matched to commercial libraries, Sigma Aldrich and Thermo-Fisher Scientific, Waltham, MA, USA and/or processed using Open Specy [31]. Spectral matches with a confidence greater than 70 percent were considered as positively identified. A total of 1331 particles were positively identified with an average of 333 for each sampling period.

2.5. Impervious Cover and Land Use

Sampling sites were categorized in low, medium, or high human impact by two separate measures using MassGIS Data: impervious cover (IC) and adjacent land use (LU). ESRI ArcMap 10.7.1 was used to map the Charles River, its watershed, and the 21 sampling sites along the river. A 100 m buffer zone [32] from the edge of the river and associated water bodies was generated, which was then overlaid with data for IC and adjacent LU. This information (e.g., IC and LU) in the buffer zone between each site and the next upstream site was then designated into three categories of low, medium, and high human impact (Table 1). The IC data reflect the developed areas with impervious surface cover, with lower IC % suggesting low development and lower human impact versus higher IC % suggesting high development and higher human impact.

Table 1. Land use and impervious cover low/medium/high human impact site categories. Data Source: MassGIS Land Use Land Cover 2016.

	Low	**Medium**	**High**
Land Use	Open Land	Residential Multi-Family	Mixed Use, Primarily residential
Land Use	Tax Exempt	Residential Single-Family Unknown Right-of-Way	Mixed Use, Other Commercial Industrial
Impervious Cover	0% to 33%	34% to 66%	67% to 100%

For adjacent land use within the buffer zone, the MassGIS LULC 2016 data were categorized in terms of Commercial; Industrial; Mixed Use, Other; Mixed Use, Primarily Residential; Open Land; Residential—Multi-Family; Residential—Single Family; Right-of-Way; Tax Exempt; and Unknown (Table 1). High human impact land use categories included Commercial; Industrial; Mixed Use, Other; and Mixed Use, Primarily Residential. Medium human impact land use categories included Residential Multi-Family; Residential Single Family; and Unknown. Low human impact land use categories included Open Land, Tax Exempt, and Right-of-Way. The percentage of land area used by each of these categories within the 100 m buffer zone designated to each site was calculated to determine which level of human impact held the highest percentage, as well as which level of low, medium, or high human impact could be attributed to its respective site. Figure 3 shows the distribution of sites based on low, medium, and high impact for both IC and LU.

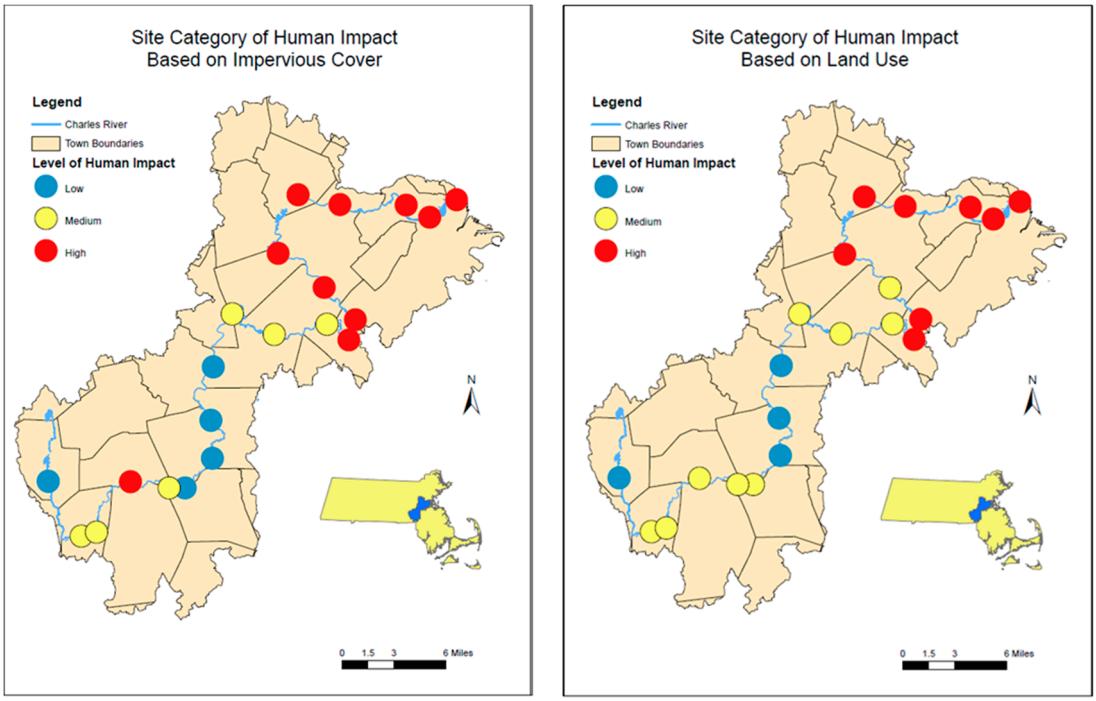

Figure 3. Distribution of stations categorized as Low, Medium, and High Impact for the sampling sites along the Charles River base on (**Left Panel**) Impervious cover and (**Right Panel**) Land use.

2.6. Data Analysis

An analysis of variance test (ANOVA) was applied to both temporal and spatial variability to determine if there was a significant variability between sampling times and between sampling sites. Levine's Test was performed to test the assumptions of normality for the low, medium, and high IC and LU categories, as there was an unequal number of sites for each category. Impervious coverage was then analyzed using an ANOVA in MATLAB, while the non-parametric Kruskal–Wallace Test was used for land use versus microplastic/fiber concentrations.

2.7. Estimation of Export Flux

An estimation of the flux of microplastics at each site along the river and export of microplastic particles to the Boston Harbor from the outlet of the Charles River at the New Charles River Dam was calculated using the method described by [14]. Flow data were collected from four USGS gages at Medway, Dover, Wellesley, and Waltham. Average flow rate data from USGS stream gages for each sampling day was converted from F_m (m^3s^{-1}) to F_L (Ls^{-1}). A proportional flow rate of depth for the top 18 cm of the water's surface was calculated with the top proportion (D_p) equaling the top depth (D_i), which is 18 cm divided by total depth (D_t).

$$D_p = D_i/D_t \quad (1)$$

The proportional depth was multiplied by the flow rate (F_L) to determine proportional flow (F_{Lp}). Then, the number of microfibers per liter found at a sampling site of interest (M_p) was multiplied by this proportional flow to approximate the number of microplastic particles traveling through that site during the time of collection (N_m).

$$N_m = F_L \times M_p \quad (2)$$

The range of potential discharge of microplastics in the Charles River into Boston Harbor was calculated from site data with the lowest concentration of microplastics, median concentration of microplastic found, and 3rd quartile concentration out of all sites.

3. Results

3.1. Anthropogenic Microparticle (MP) Abundance and Composition

Anthropogenic microparticles (MPs), including natural, semisynthetic, and synthetic polymers, were found at every site sampled in the surface water of the Charles River from near the headwaters to the mouth of the river in Boston—a distance of 77 miles—during each sample date. The combined microparticles and microfibers ranged from 1–19 MP/L with an average of 9 ± 4 MP/L (Table 2). Seventy six percent of the anthropogenic particles were synthetic, 23% were cellulose-based, and 1% were wool fibers. Polyester (PET), polypropylene (PP) and polyamides (PA) were the dominant polymers, comprising about 80% of the microplastics (Figure 4). Differences in the relative percent of microplastic particles to microfibers occurred (Table 3) such that August had a much lower ratio of microfibers to microparticles, and January, May, and October had similar ratios. Fibers comprised 0–100% of the microparticles, with an average of 72%, and the dominant colors were clear, red, yellow, brown, black, and blue.

Table 2. Average number of particles per liter (MP/L) ± standard deviation (n = 3) at each site along the Charles River in the surface water. Site 1 is near the head of the Charles, and Site 21 is near the mouth in Boston.

Site #	January	May	August	October	Average
1	15 ± 1	7 ± 2	8 ± 1	8 ± 2	**9 ± 4**
2	13 ± 2	14 ± 5	5 ± 3	7 ± 1	**10 ± 5**
3	9 ± 1	11 ± 4	12 ± 0	13 ± 1	**11 ± 2**
4	10 ± 3	12 ± 4	10 ± 2	12 ± 3	**11 ± 3**
5	ND	14 ± 6	4 ± 1	14 ± 3	**11 ± 6**
6	4 ± 1	18 ± 0	10 ± 3	6 ± 2	**9 ± 6**
7	2 ± 1	2 ± 1	6 ± 3	9 ± 1	**5 ± 3**
8	1 ± 2	2 ± 1	12 ± 2	2 ± 1	**4 ± 5**
9	1 ± 0	5 ± 2	8 ± 4	5 ± 3	**5 ± 3**
10	2 ± 2	7 ± 3	5 ± 2	19 ± 3	**8 ± 7**
11	3 ± 3	8 ± 7	7 ± 2	18 ± 4	**9 ± 7**
12	6 ± 2	15 ± 4	6 ± 3	3 ± 1	**7 ± 5**
13	5 ± 1	8 ± 1	2 ± 2	10 ± 1	**6 ± 3**
14	5 ± 1	14 ± 3	5 ± 1	3 ± 1	**7 ± 5**
15	7 ± 1	10 ± 3	3 ± 2	13 ± 1	**8 ± 4**
16	3 ± 1	10 ± 4	3 ± 2	9 ± 2	**6 ± 4**
17	5 ±2	16 ± 6	10 ± 3	17 ± 2	**12 ± 6**
18	2 ± 0	7 ± 5	9 ± 1	19 ± 12	**9 ± 9**
19	1 ± 1	13 ± 2	11 ± 4	20 ± 5	**11 ± 8**
20	18 ± 2	7 ± 1	15 ± 2	2 ± 2	**11 ± 7**
21	19 ± 2	10 ± 1	16 ± 2	15 ± 5	**15 ± 4**
Average	**7 ± 6**	**10 ± 5**	**8 ± 4**	**11 ± 7**	**9 ± 4**

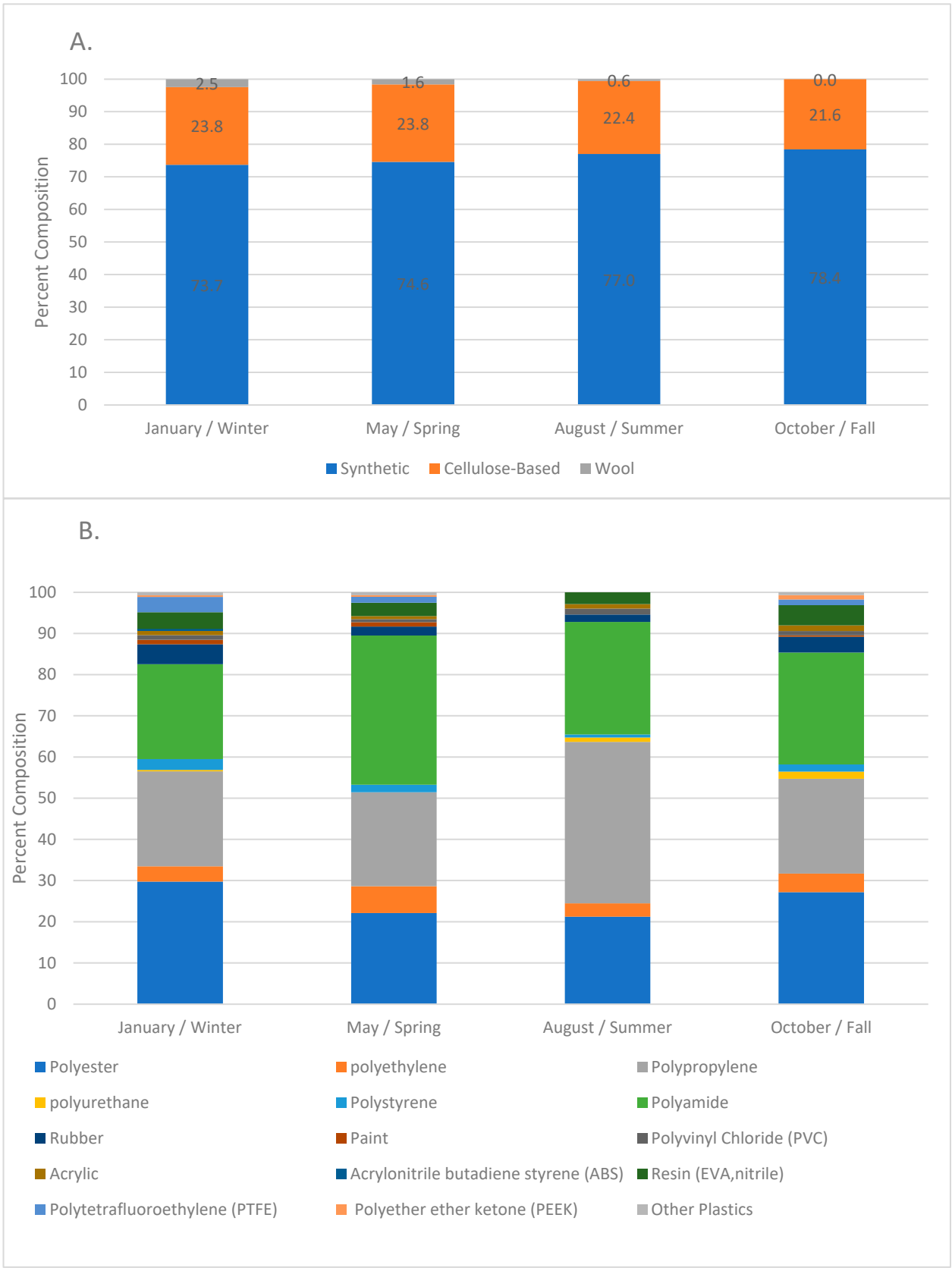

Figure 4. (**A**). Percent composition of the anthropogenic particles during each sampling time; data from all the sites were combined (n = 343 January, n = 330 May, n = 323 August, n = 335 October). (**B**). Percent composition of the synthetic particles during each sampling time; data from all the sites were combined (n = 254 January, n = 246 May, n = 248 August, n = 265 May).

Table 3. Percent Fibers/Percent Particles (films, fragments, foams, beads) at each station along the Charles River. Average values were calculated for all stations within a sampling period. Site 1 is near the head of the Charles River, and Site 21 is near the mouth in Boston.

Site	January	May	August	October
1	98/2	86/14	27/73	20/80
2	87/13	90/10	53/47	9/91
3	95/5	92/8	86/14	95/5
4	85/15	92/8	54/46	98/2
5	ND	53/47	53/47	70/30
6	66/34	93/3	46/54	18/82
7	77/23	0/100	68/32	92/8
8	100/0	30/70	36/64	91/9
9	0/100	78/22	52/48	99/1
10	85/15	90/10	33/67	90/10
11	81/19	90/10	82/18	80/20
12	79/21	95/5	53/47	78/22
13	80/20	90/10	53/47	85/15
14	81/19	92/8	6238	78/22
15	72/28	90/10	38/62	88/12
16	32/68	91/9	57/43	97/3
17	95/5	98/2	53/47	95/5
18	55/45	87/13	60/40	96/4
19	75/25	97/3	56/44	90/10
20	90/10	92/8	8/92	73/27
21	92/8	85/15	50/50	80/20
Average	**76/24**	**82/18**	**51/49**	**77/23**

Significant differences in the concentration of anthropogenic microparticles (ANOVA; $p < 0.001$) along the river within a single sampling time (Figure 5) were detected. Significant differences were also found at single sites between the four sampling times (ANOVA, $p < 0.0001$). Variation in the relative distribution of synthetic polymers occurred at sites along the Charles River (Figure 6) both within a single month and between months. The highest diversity of polymers occurred in the January and October sampling periods. Seasonal variation in polymer composition was also present with higher relative contributions from PP in the August, along with lower contribution from PET in the August (Figure 4B). The PP that was found near the head and middle of the Charles River was dominated by a mesh-type material (Figure 7), especially in the summer, where this material was not seen below Station 17; the PP in the lower basin of the Charles River constituted either fibers or fragment chunks. The vast majority of PET amounts collected were fibers, while PA amounts collected were primarily films and fibers. Overall, there was the greatest diversity of plastic polymer types in the winter samples.

3.2. Relationship to Impervious Coverage and Land-Use

The variation in anthropogenic microparticle concentrations along the Charles River was compared to the impervious coverage (IC) and to the land use (LU). The sites were grouped into low, medium, and high IC or LU. The low IC and LU sites comprised only 19–24% of the sites along the Charles River. In general, IC and LU sites were grouped in a similar manner, though there were a few differences (Figure 3). On an annual scale, sites

categorized as low human impact for both IC and LU had significantly fewer (IC $p = 0.0018$; LU $p = 0.0003$) microplastics and/or microfibers present compared to the medium and high use sites, and there was no significant difference between medium and high IC and/or LU sites. However, when we look at individual sampling times, only May and October had significant relationships between IC and LU and microparticle concentrations (LU $p << 0.001$, $p = 0.0176$; IC $p = 0.0135$, $p = 0.0074$, respectively). Comparing the relative contribution of polymers versus IC and/or LU showed that annually, PP had a significant (ANOVA; $p < 0.05$) negative relationship with IC and LU, while PET had a positive trend with IC and LU. The greatest diversity of plastic types generally occurred at high or medium IC or LU sites, though two low IC/LU sites also had higher diversity.

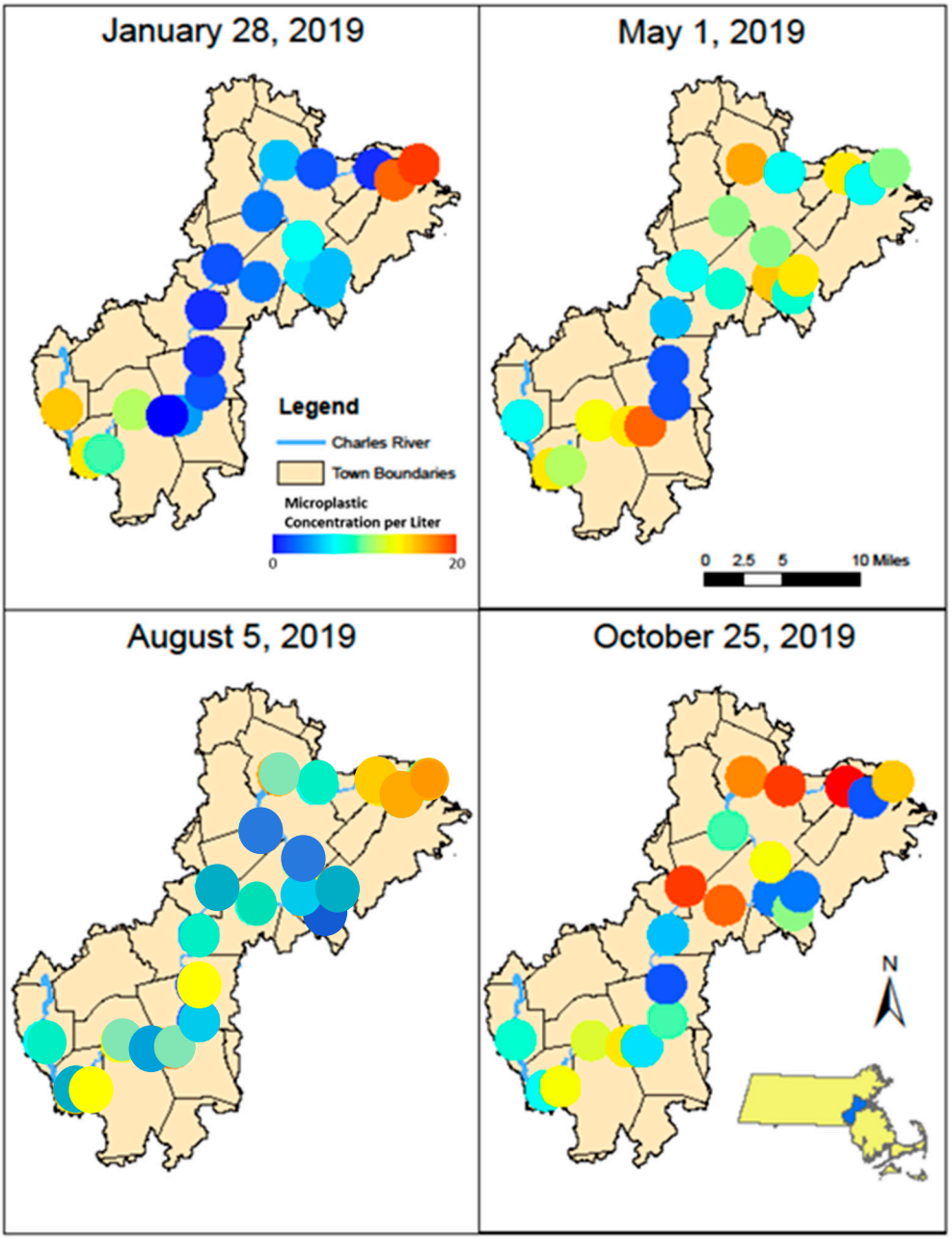

Figure 5. Maps showing microparticle concentration (MP/L) at each station along the Charles River during January, May, August, and October 2019.

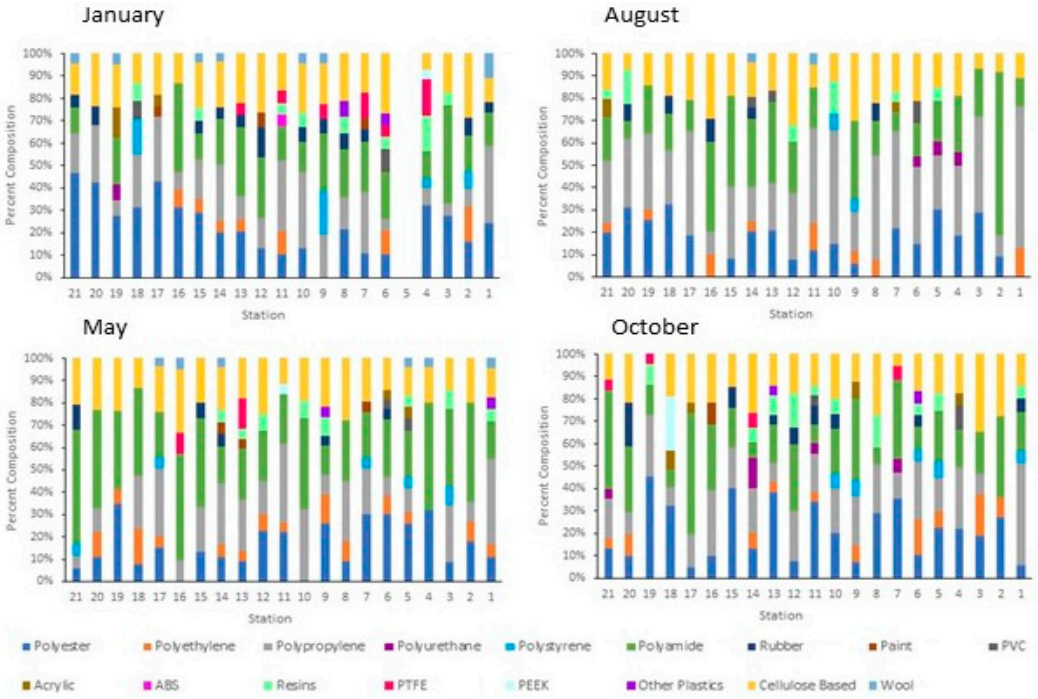

Figure 6. Percent composition of the microparticles at each station along the Charles River at each sampling date. Station 1 is at near the head of the river in Milton, MA, and Station 21 is at the mouth in Boston, MA. Each station is about 3.5 miles apart. Samples were not collected at Station 5 during the winter.

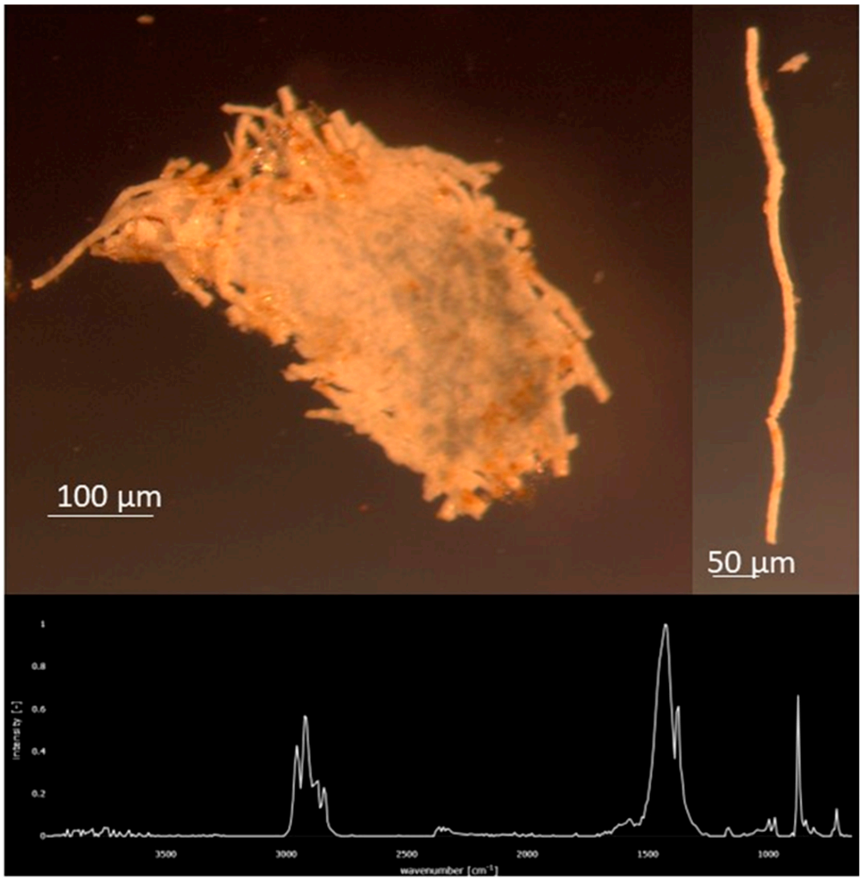

Figure 7. Common miscellaneous fragment of Polypropylene (PP) that fragments into thinner "thread-like" pieces was found primarily in August at stations 1–15. FTIR Spectrum of the PP piece.

3.3. Estimated Export Flux of Anthropogenic Microparticles into Boston Harbor

To determine the annual discharge of microparticles along the river, three different plastic concentrations (Cp) were used: the lowest positive concentration of any sample (1 MP L^{-1}); the medium number of fibers (8 MP L^{-1}); and the 3rd quartile concentration (13 MP L^{-1}). Using the average flow data obtained from four USGS gages along the Charles River, annual average flux rates ranging from 459 to 11,092 microparticles per second were calculated (Table 4A). This indicates that between 40 and 960 million microparticles could have been flowing down the Charles River per day from its headwaters to the Boston Harbor, with a median average of 500 million microparticles per day, which could lead to an export of 182 trillion microparticles/year into the Boston Harbor. On an annual scale, the microparticle flux increased downriver (Table 4A).

Table 4. Estimated ranges of export flux of microplastics per second (MP/s) using USGS gage streamflow data at four gage sites and the measured lowest, medium, and 3rd Quartile MP/L concentration for (A) Annually, (B) January, (C) May, (D) August, (E) October.

***A*. Annual**					**Lowest (MP/L = 1)**	**Medium (MP/L = 8)**	**3rd Quartile (MP/L = 13)**
Gage Site	***Flow (L/s)***	***Total Depth (cm) (Dt)***	***Depth Proportion (Dp)***	***Flow w/Dp (L/s)***	***Low (MP/s)***	***Med (MP/s)***	***3rd Q (MP/s)***
Medway	3837	151	0.12	459	459	3672	5966
Dover	11,479	317	0.06	652	652	5217	8477
Wellesley	10,272	225	0.08	823	823	6580	10,693
Waltham	11,709	247	0.07	853	853	6826	11,092
***B*. January**					**Lowest (MP/L = 1)**	**Medium (MP/L = 5)**	**3rd Quartile (MP/L = 9)**
Medway	11,236	239	0.08	847	847	4235	7623
Dover	34,971	330	0.05	1906	1906	9532	17,157
Wellesley	27,086	272	0.07	1794	1794	8969	16,145
Waltham	29,845	284	0.06	1888	1888	9442	16,995
***C*. May**					**Lowest (MP/L = 2)**	**Medium (MP/L = 10)**	**3rd Quartile (MP/L = 14)**
Medway	8394	152	0.12	991	1983	9914	13,880
Dover	34,508	351	0.05	1772	3544	17,721	24,809
Wellesley	24,452	251	0.07	1750	3501	17,503	24,504
Waltham	27,753	216	0.08	2314	4628	23,138	32,394
***D*. August**					**Lowest (MP/L = 2)**	**Medium (MP/L = 8)**	**3rd Quartile (MP/L = 10)**
Medway	869	86	0.21	181	362	1449	1812
Dover	3494	267	0.07	236	472	1886	2358
Wellesley	3294	191	0.09	311	623	2490	3113
Waltham	3763	244	0.07	278	556	2222	2778
***E*. October**					**Lowest (MP/L = 2)**	**Medium (MP/L = 10)**	**3rd Quartile (MP/L = 15)**
Medway	1346	124	0.14	195	389	1946	2919
Dover	4261	320	0.06	240	479	2396	3595
Wellesley	5217	185	0.10	506	1013	5065	7597
Waltham	4818	244	0.07	356	711	3556	5335

Looking at individual sampling times, Table 4D shows that the lowest estimated flux of microparticles per second was 362 MP/s at the Medway gage station in August. In Table 4C, the highest estimated flux was 32,394 MP/s at the Waltham gage station in May. Based on the four sampling times, the Medway gage station, furthest upstream on the Charles River, consistently had the lowest estimated flux for each sampling time. The gage site with the highest estimated flux per sampling time varied between the other three downstream gages, indicating the potential removal of microplastics through sedimentation, fragmentation, or biological consumption before actual export into the Boston Harbor. Only May had

the highest estimated flux at the lowest downstream station (Waltham) at 32,394 MP/s, suggesting continual addition of microparticles and transport along the river. Using the most downstream station (Waltham) at each sampling time showed a 6-fold variation in daily export potential (Table 4). Using the maximum export potential with the downstream station (Waltham) along with the percent composition of microparticles from the last four stations that occurred at and after the Waltham gage (Figure 6), indicates not only potential seasonal variation in the amount exported but also seasonal variation in the composition exported (Figure 8). January had the greatest variety of microparticle polymers and export was dominated by PET (35%), while May had the highest export potential and was dominated by PA (40%), August had the lowest export and was dominated by PP (29%), while October was relatively evenly distributed between PET (26%), PA (25%), and PP (17%).

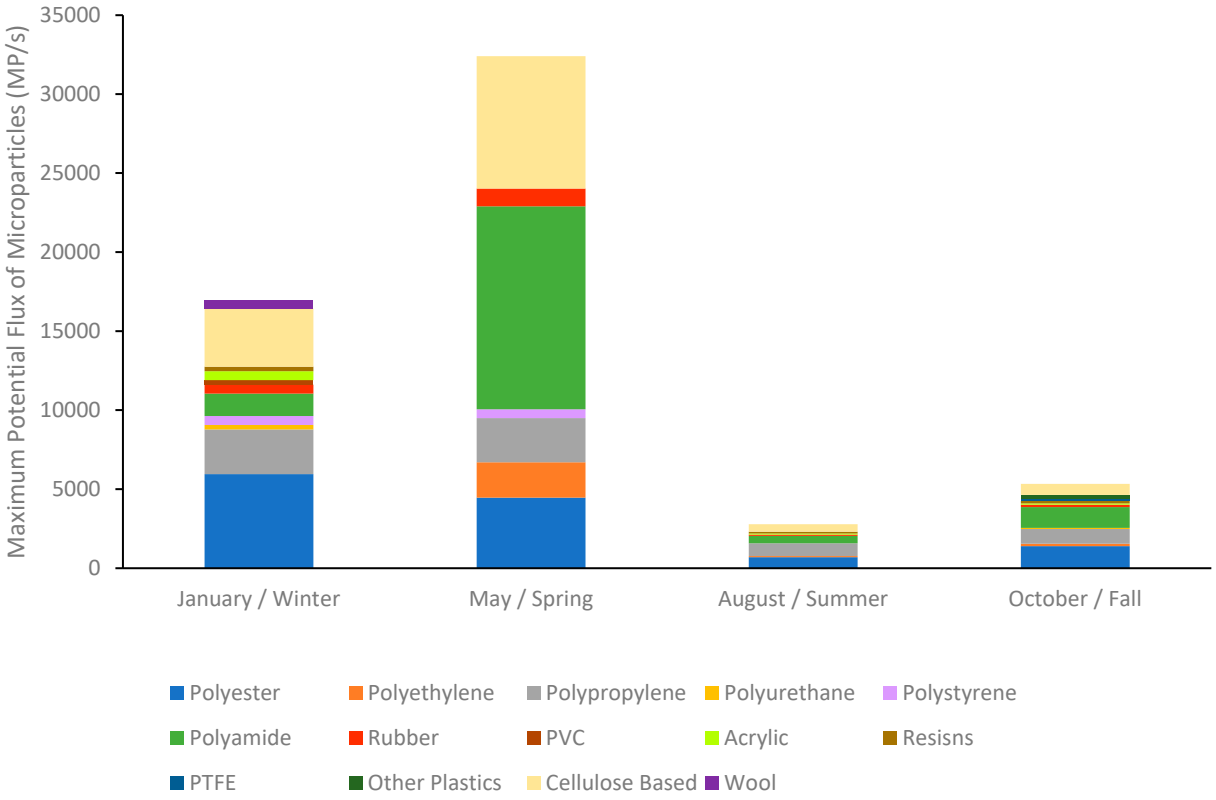

Figure 8. Estimated maximum export flux and composition of microparticles from the Charles River to Boston Harbor. This is estimated using the maximum concentration of microparticles in the river during this sampling time point, along with the percent composition of the microparticles determined from the most downstream stations located after the final stream gage. Cellulose-based particles include dyed cotton fibers and cellulose acetate.

4. Discussion

Anthropogenic microparticles were found at all 21 sampling sites along the Charles River during sampling in January, May, August, and October. Microparticle concentrations ranged from 1–19 MP/L, with an average concentration of 9 ± 4 MP/L (Table 2). Similar concentrations have been reported in other rivers in the United States [14,28]. Globally, concentrations of microplastic particles and/or fibers found in rivers range from 0.03 MP/L to 2867 MP/L [33,34]. Variation in collection methods and reporting methodology from the number of particles per volume or area or the weight of particles per volume or area can make comparisons between studies difficult and limit our understanding of global concentrations and variations within river systems [23].

The potential explanation for such a wide range of microparticle and fiber concentrations found across studies in freshwater environments may be due in part to the methodology [27,28,35,36], the geomorphology of the river [9,37], the surrounding land use, and the human density along the river [38], along with plastic waste management in the area [39]. Significantly higher concentrations of microparticles, particularly fibers, have been found using the water grab method compared to nets [27,35]. Additionally, the size of the net mesh can affect the amount of microplastics measured [36]. Yet, the significantly lower sample volume in water grab samples reduces the chance of detecting less abundant microparticles. The type of river, e.g., meandering or braided, along with changes in its geomorphology and its path, can affect the concentration and flux potential of microplastics [39]. Where rivers slow and form marshes macro- and microplastic debris is where they are more likely to settle and be buried in the sediments [9,40]. Macroplastic debris that are retained either in riparian vegetation or in the sediments have the potential to be a source of microplastics for years, as the macrodebris slowly fragment into smaller pieces through physical and biological processes [9]. Man-made modifications to rivers such as dams can also change the flow of rivers, artificially creating retention areas [41] and regions with exaggerated turbulence that can fragment larger debris. The Charles River has 19 remaining dams along its 80-mile path, along with culverts, bridges, and other man-made structures, which can impact the input, transport, and sedimentation of micro- and macrodebris. We still do not have a good understanding of how different structures within and along the shoreline of rivers, along with a river's natural flow and morphology, affect microplastic sedimentation and transport.

Temporal and spatial changes in the concentration and composition of microparticles occurred along the Charles River (Figures 5 and 6) in a similar manner to other river studies [14,42,43]. The vast majority of the anthropogenic particles, 72%, were microfibers. This is slightly lower than study on the Magdalena River in Neiva, Colombia where 84% of microparticles were fibers [44], yet they constitutedmore than the 58% of microparticles reported in the Snake and Lower Columbia River [35]. In a study examining 29 tributaries to the Great Lakes, fibers comprised 71% of microparticles [16]. Changes in the relative percentage of microfibers to microplastics were observed along the river and between sampling times (Table 3). Changes in microparticle concentrations were observed between sampling time periods (Figure 5), and generally higher concentrations were observed in May and October. Changes in the relative percentage of the dominant polymers were also observed between the seasons (Figure 4).

The microparticle concentration in the Charles River was significantly related to land use and impervious cover like what has been found in other studies of urbanized rivers [20,42,45]. Sites with low (<33%) impervious coverage (IC) or land use (LU) categorized as undeveloped land (e.g., forests, wetlands, etc.) had significantly lower microplastic concentrations than sites with high or medium impervious coverage or developed land (e.g., high-density residential, industrial, etc.). There was no detectable difference between sites with medium or high impervious coverage nor development suggesting that for a river flowing through primarily developed lands, where only large tracts of undeveloped forest/wetlands led to lower concentrations. The sites with low IC/LU levels were located more midstream (Figure 3), with higher concentrations of microparticles found both upstream and downstream suggesting riverine that processes such as deposition or biological consumption played a partial role in this relationship. The geomorphology of wetlands has slower flowing water, so microparticles have the potential to settle to the sediments and are regions that support more fish and bird life. Supporting this is the relative increase in polyethylene (PE), PP, and polystyrene (PS), which are all polymers with a density lighter than freshwater and the decrease in polyester (PET) and polyamide (PA), which are polymers with a density greater than freshwater (Figure 9). So, interactions between land use/impervious coverage (e.g., sources of the microparticles) and a river's geomorphology may control the microplastic concentrations and compositions. A study found high concentrations of microplastics in the Snake River adjacent to land being used for

large-scale agricultural farms in the Northwest United States [35], indicating that land use is an important influence on microplastic and fiber concentrations. Polymer composition alone does not reflect the whole story in the Charles River: if it did, one would expect the relative contribution of the lighter polymers to increase downstream, but this does not occur (Figure 9), and the loss of a distinctive PP particle (Figure 7) from the lower Charles River indicates that even these particles can either fragment, sink, or be consumed.

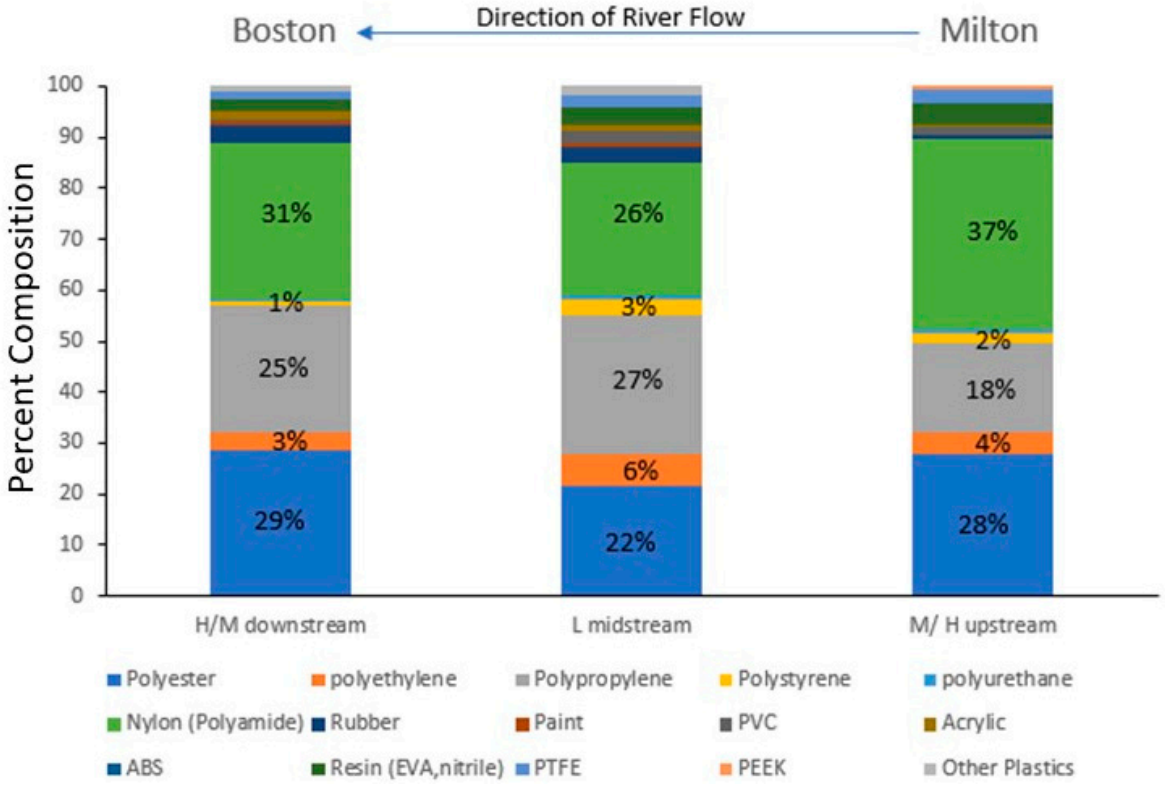

Figure 9. Annual changes in the percent composition of the synthetic microparticles as they move from High/Medium land use in the upper river through the Low land use in the middle river to High/Medium land use in the lower Charles River adjacent to the city of Boston, MA. The percent composition of the dominant polymers—polyester, polyethylene, polypropylene, polystyrene, and polyamides—is shown on the figure.

Studies have found that the primary sources of microplastics to the environment are textiles, landfills, wastewater treatment plants, abrasion from tires, road markings, paint, fragmentation of macroplastics, and dust [46–48]. Urban stormwater systems have been found to be a large source of microplastics [49–51], with estimates of up to 9.6 billion microplastics discharged into receiving waters from a single outfall in a rain event [50]. The changes in concentration and composition along the Charles River during each sample time suggest that localized sources of microparticles, along with river morphology and in situ processes, affect microparticle flux in the river, and to understand the impact of microplastic pollution now and into the future, we need to examine these processes, especially in impacted rivers. Water management of rivers, through diversions of water for agricultural irrigation, can change the distribution and sedimentation of microplastics [52].

Globally, it is estimated that 1.15 to 2.41 million tons of plastic waste enter the ocean yearly from rivers [11]. This includes both macroplastic and microplastic debris. Studies of European and Asian rivers have found averaged hourly flux rates of macroplastic to be from 3 to 10,000 pieces/hour [53], while our study was focused solely on microparticle flux. Microplastic concentrations (mp/L) are expected to be higher than macroplastic cocentrations, so a higher flux in terms of the number of particles would be expected from microplastic debris. Recent research has also shown that North American rivers tend to be

dominated by microplastics compared to macroplastic debris [10]. The estimated export flux of microplastic particles from the Charles River into the Boston Harbor ranged from 40 to 960 microparticles per day, with an average of 500 microparticles per day. This is within the same range as that estimated for the export of microfibers from the Hudson River [14], but it is lower than that estimated for microplastics in-stream in the metropolitan area of Chicago, Illinois, USA [54] and for the Trent River in the United Kingdom [43]. This may be due in part to the size of the rivers and difference of methods used in estimating the flux. Maximum flux potential from the Charles River into Boston Harbor occurred during January and May which agree with the seasonal inputs of plastics from rivers to the ocean in New England [11]. The changes in the relative contribution of the main polymers (PET, PP and PA) suggest that more PET would be exported in January, more PA in May, and more PP in August. High concentrations of PET and PA in Boston Harbor support these results [55]. More research is needed to understand the flux of microplastics from the Charles River, as the estimated flux potential was not always highest at the gage and site furthest downstream (Table 4). This suggests behaviors of microplastic within the river, such as aggregation, sedimentation and/or consumption, can influence its flux potential. These processes may be influenced by dams along the river. This was seen in that the occurrence of PP mesh-type particles (Figure 7) were very abundant in the upper Charles River but were never seen in the lower Charles River (sites 21–18). While this study looked at the concentration and composition of anthropogenic microparticles along the Charles River in the surface water, we did not examine the impacts of man-made structures such as dams, bridges and/or culverts. This study shows that more work is needed to really understand the processes governing the transport of microplastics along an impacted river and the potential environmental impact of the microplastics throughout the river. It is estimated that by 2030 up to 90% of the world's rivers will be impacted by at least one dam [56], with this continued growth and development of dams it is important to really understand their effect on microplastic transport, flux and sedimentation and their potential to create future environmental pollution hotspots.

5. Conclusions

Changes in microparticle composition have implications not only for the Charles River ecosystem but also for Boston Harbor. Results from this study show that fibers are the primary microparticle exported to Boston Harbor. However, microplastic particles (fragments, films, and foams) would be more likely exported to Boston Harbor during high flow seasons in January and May (Table 4B,C). Polyester and polyamides will be the dominant type of plastic exported during the high flow seasons. The impacts of microplastic particles and microfibers on the Charles River is not currently known, but their prevalence throughout the river suggests the impacts should be examined. With climate change, New England is experiencing more high intensity precipitation events [57,58] which could affect the input, distribution, and flux of plastic debris and microplastics from regional rivers and streams which will be important for management and mitigation efforts.

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Appendix A

Record of GPS coordinates, site depth, and surface water temperature per sampling site.

	28 January 2019		**1 May 2019**		**5 August 2019**		**25 October 2019**	
Site # GPS Coordinates	Depth (cm)	Temp (°C)	Depth (cm)	Temp (°C)	Depth (cm)	Temp (°C)	Depth (cm)	Temp (°C)
1 (−71.512, 42.139)	64	5.3	48	13.3	25	27.3	30	14
2 (−71.476, 42.094)	140	5.4	107	14	64	26.7	36	12.8
3 (−71.459, 42.097)	112	5.8	102	14.6	79	25.3	86	13.2
4 (−71.422, 42.139)	239	2.1	152	13.4	86	24.6	124	11.9
5 (−71.379, 42.133)	ND	ND	89	14.7	109	29.1	84	13.6
6 (−71.362, 42.134)	119	5.2	102	13.3	470	25.8	30	12.5
7 (−71.332, 42.158)	267	4.2	264	13.3	155	25	163	11.7
8 (−71.333, 42.189)	356	3.4	358	14.1	239	26.7	231	11.7
9 (−71.33, 42.233)	290	3.5	310	13.8	173	28.2	163	12.7
10 (−71.31, 42.276)	305	3.4	312	13.9	107	26.3	163	12
11 (−71.263, 42.259)	330	3.7	351	13.8	267	26.7	320	12.2
12 (−71.205, 42.267)	244	3.3	193	13.8	107	25.4	140	11.9
13 (−71.181, 42.254)	229	3.3	226	13.9	147	26.2	137	11.9
14 (−71.173, 42.271)	323	3.2	272	13.8	257	25.9	216	11.5

	28 January 2019		1 May 2019		5 August 2019		25 October 2019	
15 (−71.208, 42.297)	272	2.9	251	13.3	191	26.7	185	11.8
16 (−71.259, 42.325)	168	2.8	272	13.4	226	25.6	46	12.4
17 (−71.237, 42.373)	284	2.6	216	13.6	244	26.7	244	12.6
18 (−71.19, 42.365)	142	2.5	160	13.5	74	25.2	66	12.1
19 (−71.117, 42.364)	384	2.5	480	13.5	508	26.1	508	12.6
20 (−71.091, 42.354)	137	2.5	178	14	224	25.5	198	12.6
21 (−71.061, 42.369)	800	2.2	742	13.9	762	25.7	777	12.6

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