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Plastic Debris in 29 Great Lakes Tributaries: Relations to Watershed Attributes and Hydrology

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Supporting Information

ABSTRACT: Plastic debris is a growing contaminant of concern in freshwater environments, yet sources, transport, and fate remain unclear. This study characterized the quantity and morphology of floating micro- and macroplastics in 29 Great Lakes tributaries in six states under different land covers, wastewater effluent contributions, population densities, and hydrologic conditions. Tributaries were sampled three or four times each using a 333 μm mesh neuston net. Plastic particles were sorted by size, counted, and categorized as fibers/lines, pellets/beads, foams, films, and fragments. Plastics were found in all 107 samples, with a maximum concentration of 32 particles/m^3 and a median of 1.9 particles/m^3. Ninety-eight percent of sampled plastic particles were less than 4.75 mm in diameter and therefore considered microplastics. Fragments, films, foams, and pellets/beads were positively correlated with urban-related watershed attributes and were found at greater concentrations during runoff-event conditions. Fibers, the most frequently detected particle type, were not associated with urban-related watershed attributes, wastewater effluent contribution, or hydrologic condition. Results from this study add to the body of information currently available on microplastics in different environmental compartments, including unique contributions to quantify their occurrence and variability in rivers with a wide variety of different land-use characteristics while highlighting differences between surface samples from rivers compared with lakes.

INTRODUCTION

There has been growing concern in recent years surrounding plastics, and especially microplastics, in aquatic environments. Defined as plastic particles less than 5 mm in diameter, microplastics enter aquatic environments in a number of ways. One source is photodegradation and/or mechanical breakdown of larger items, such as Styrofoam, plastic bags, bottles, wrappers, cigarette butts, and tires.[1−3] Spillage of preproduction pellets and powders, beadblasting media, and atmospheric deposition are other potential sources.[4−6] Wastewater treatment plant (WWTP) effluent has also been cited as a source: abrasive microbeads in toilet cleaners, face and hand scrubs, and toothpastes—often made from positively buoyant polyethylene—may pass through WWTPs and into receiving waters.[1,7] Other more dense particles, such as polyester fibers, are largely captured in WWTP sludge,[8,9] which may subsequently be applied over land[10,11] and remobilized to receiving waters via runoff.

Marine organisms, including mammals, birds, fish, turtles, and invertebrates, have been shown to ingest microplastics.[12−15] Physical hazards of ingestion can include obstruction of the digestive system,[13] clogging of feeding appendages,[16] oxidative stress,[17] impaired reproduction,[18] and death.[19,20] In addition, ingestion of microplastics can result in uptake and bioaccumulation of harmful chemicals.[14,19,21] Additives in plastics such as phthalates, brominated flame retardants, nonylphenol, and antimicrobials have been associated with cancer and endocrine disruption.[1,19] The high sorption capacity of plastics enables the accumulation of persistent organic pollutants such as polychlorinated biphenyls, polycyclic aromatic hydrocarbons, and organochlorine pesticides, with concentrations 10^5−10^6 times higher than in the surrounding water column.[4,21] Trace metals[14,22] and pathogens[23] have also been shown to accumulate on microplastics.

Recent studies on microplastics in lakes and rivers have reported microplastic concentrations to be as high, or higher, than in oceanic gyres.[24−29] The first study of microplastics in the surface waters of the Great Lakes[30] reported a median surface concentration of 5350 microplastic particles/km^2, with a maximum of greater than 466 000 particles/km^2. Fragments were the most common microplastic particle type in the Great Lakes samples, making up 52% of particles in each sample on average.[30] Pellets/beads made up an average of 16% of particles

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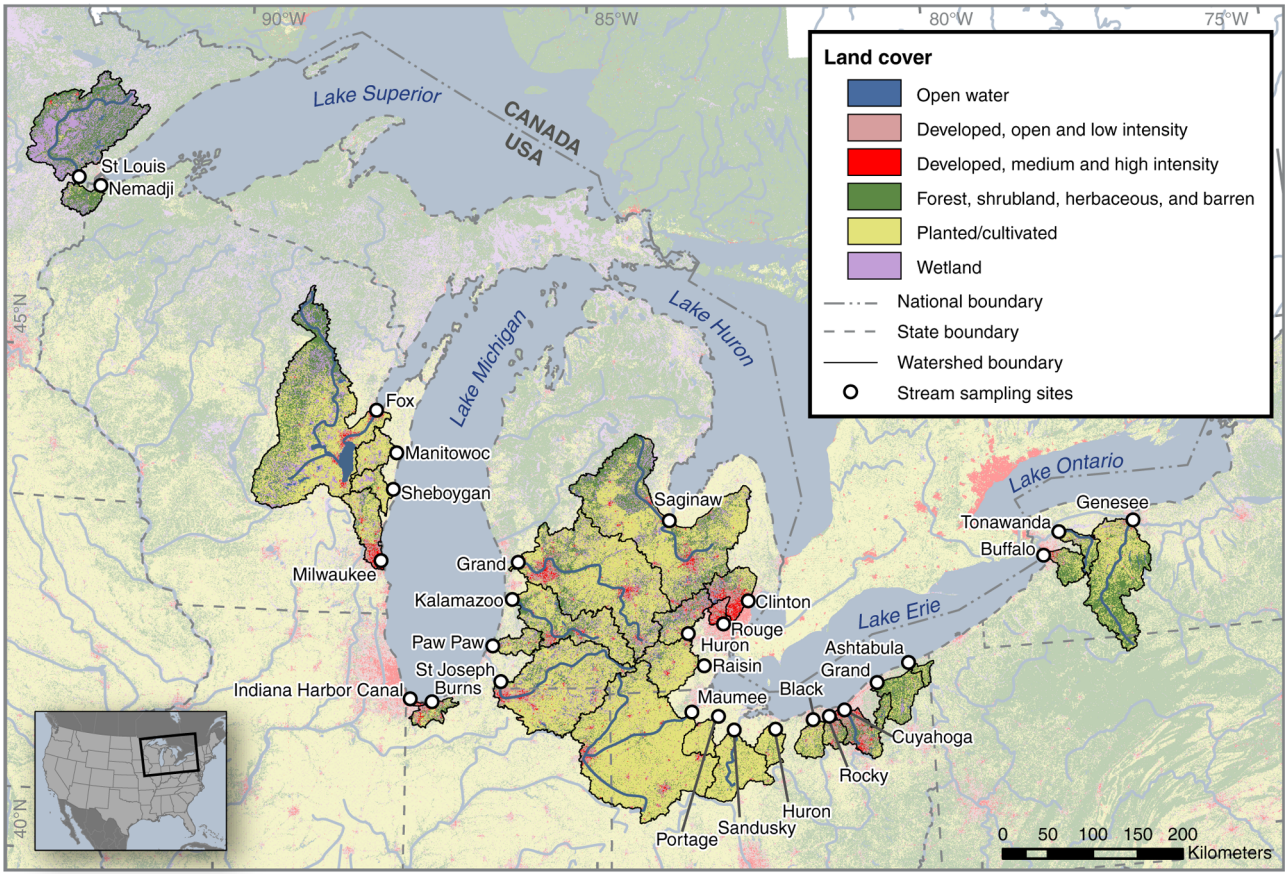

Figure 1. Sampling locations, watershed boundaries, and watershed land uses.

in each sample, although 97% of all pellets/beads were in only two samples.[30] The least-occurring particle type in the Great Lakes study was fibers/lines, which made up only 2% of the sampled particles on average.[30]

The objectives of this study were (1) to determine the occurrence and concentrations of micro- and macroplastics in Great Lakes tributaries, (2) to determine the relations between plastics and watershed attributes such as land cover, population density, and wastewater effluent contribution, and (3) to explore the role of hydrology in the occurrence of plastics.

The number and diversity of sampling locations, the regional scale, and the incorporation of varying hydrologic conditions provide a multifaceted study that begins to explore the many factors that may influence the prevalence of plastic debris in rivers. The results will provide a baseline for future studies and will advance our currently limited understanding of the sources, transport, and fate of plastics in fluvial systems.

MATERIALS AND METHODS

Sample Collection. Samples were collected from April 2014 to April 2015 at 29 Great Lakes tributaries in six states (Figure 1 and SI Table 1). The watershed drainage areas of the tributaries varied from 101 to 16 400 km^2, with mean annual discharges from 5 to 185 m^3/s (2014). Together, these 29 tributaries account for approximately 22% of the total tributary contribution to the Great Lakes (on the basis of a total runoff inflow of 5930 m^3/s[31]). The watersheds spanned a broad range of land covers and degrees of urban influence, with 2.9−92% urban land cover (SI Table 1). Likewise, WWTP influence varied considerably, from watersheds with no wastewater effluent discharges to those with up to 122 discharges with various WWTP treatment levels. Wastewater effluent as a percentage of streamflow ranged from 0 to 89%.

Each tributary was sampled three or four times, capturing low-flow and runoff-event conditions. Runoff-event conditions were defined as increased streamflow resulting from rainfall or snowmelt. Runoff-event samples were triggered by observation of rainfall and snowmelt patterns in each watershed and verified by examination of the hydrographs (streamflow data from ref 32). All samples were collected during daylight hours. Samples from each tributary were collected at least 1 week apart, and typically more than a month apart, to minimize serial correlation. The sampling methods and equipment were consistent with those previously used in the Great Lakes,[30] with some modifications for the river setting. Samples were collected using a 1.5 m long neuston net with an opening 100 cm wide by 40 cm high (Sea-Gear Corp., Miami, FL, USA). The net mesh size was 333 μm, a commonly used size in microplastic studies.[2,23,24,27,30] The net skimmed the surface and upper 20−35 cm; a portion of the net opening was kept above water. The amount of net submerged was monitored and recorded, and an effort was made to maintain a consistent submersion depth throughout the sample duration. Sampling duration ranged from 5 to 82 min (median 15 min) and was dependent on the velocity of water entering the net and how quickly the net began to clog with organic material, especially algae. Velocity was measured using a Sea-Gear Corp. flow meter, SonTek FlowTracker, or other method.[33] The total volume of water filtered through the net was computed from

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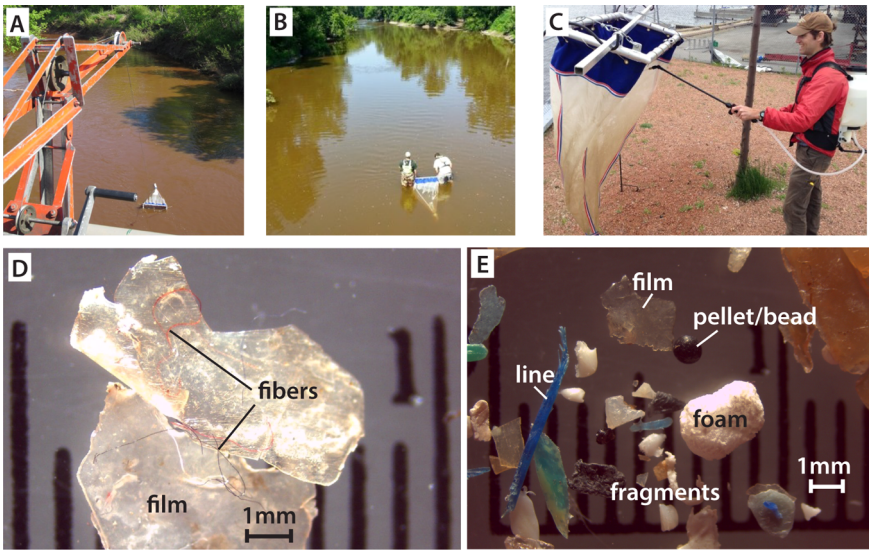

Figure 2. (A, B) Sample collection (A) using a bridge crane and (B) by wading. (C) Washing of particles from the net into the cod end using a backpack sprayer. (D, E) Microscopic images of assorted microplastic particles.

the width and height of the submerged portion of the net, the sampling duration, and the average velocity.

Samples were collected by boat, from a bridge (Figure 2A), or by wading (Figure 2B), depending on the river depth, velocity, and access at each location. For boat-collected samples, the net was towed alongside the boat and held out beyond the bow wake using a fixed metal pole. For bridge-collected samples, the net was suspended using a crane. For wading-collected samples, the net was held between and upstream of two people standing in the river, allowing the river current to flow through the net. Care was taken not to stand upstream of the net to minimize potential contamination from waders or disrupted sediment. Bridge and wading samples were collected from a fixed location at the center of the channel.

Following sample collection, the net was hung and sprayed from the outside using a pressurized backpack sprayer (Figure 2C) with 8−15 L of tap water or streamwater filtered through a 333 μm mesh. Spraying the outside of the net washed the sampled material—plastics, organic debris, fine sediment, and other items—down into the detachable mesh cod end at the bottom of the net. The sample was then transferred to a glass jar using a stainless steel spoon and squirt bottle with tap water and preserved with isopropyl alcohol.

Three samples were omitted from the results because a flow meter malfunction precluded computation of the sampled water volume. An additional three samples were broken in transit or spilled during processing. One hundred and seven samples were successfully collected and analyzed.

Sample Analysis. Because the study of microplastics in the environment is a relatively new field, studies have employed a number of analytical methods for isolation and identification of microplastic particles in environmental samples. In this study, samples were analyzed using a method developed and supported by the National Oceanic and Atmospheric Administration[34] that has been used in numerous published studies in the past few years (see, e.g., refs 14 and 35−43). Briefly, each sample was filtered through a series of 8 in. diameter Tyler sieves of 4.75, 1.00, and 0.355 mm stainless steel mesh, separating the solid material into three size classifications (0.355−0.999 mm, 1.00−4.749 mm, and ≥4.75 mm). The solids in each size class were subjected to a wet peroxide oxidation (WPO), which digests labile organic material but not plastics, using 30% hydrogen peroxide in the presence of an iron(II) catalyst.[34] After processing, samples were filtered using a 125 μm mesh sieve. With a 40× dissection microscope, all of the microplastic particles were removed, enumerated, and categorized according to morphology as fragments (broken-down pieces of larger debris such as plastic bottles), pellets/beads (preproduction pellets, microbeads from personal care products and bead blasting, and other spheroids), lines/fibers (particles of fishing line and nets and fibers from synthetic textiles), films (plastic bags and wrappers), or foams (foam cups, take-out containers, packaging) (Figure 2D,E). These categories were morphology-based rather than source-based because, with only limited information about each particle, attributing a source would be somewhat subjective. For example, while most microbeads from personal care products are <100 μm, they occur in sizes up to >2000 μm,[44] overlapping with sizes of preproduction pellets and spheroids from other sources. Therefore, to avoid making incorrect assumptions, all spheroids were grouped together in the pellets/beads category. Likewise, the lines/fibers category contains two end members (straight, thick lines and curly, thinner fibers) but also more ambiguous particles that fall between those two end members and cannot confidently be attributed to a specific source. The method of visual identification and categorization of plastics employed here has been used in numerous recent studies (see, e.g., refs 14, 30, 35−43, and 45), though it has been shown to underestimate some particle types and overestimate others compared with spectroscopic methods such as Fourier transform infrared (FTIR) and Raman spectroscopy,[46] which, by identifying the polymer composition, provide an additional level of verification.

Throughout the sample analysis process, precautions were taken to minimize potential contamination from within the laboratory: airborne particles were removed from laboratory air using an air filtration system, samples were processed in a fume hood and remained covered, and cotton laboratory coats and clothing were worn by all individuals.

Data Analysis. Plastic particle concentrations are reported in particles per cubic meter (p/m^3). Spearman correlation analysis was used to assess possible relations between plastic

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concentrations and different watershed attributes. Concentration differences between nonurban low-flow, nonurban runoff-event, urban low-flow, and urban runoff-event samples were evaluated using the Kruskal–Wallis multiple comparisons test, with urban samples defined as those from watersheds with greater than 15% urban land cover. Spearman and Kruskal–Wallis tests were performed in R,[47,48] with statistical significance reported at $p = 0.05$.

Methods used to determine watershed boundaries, land cover, percent impervious cover (defined as ground with low permeability, such as roads, parking lots, and buildings), population density, and wastewater effluent contribution are described in the Supporting Information.

Quality Assurance and Quality Control. Five field blank samples were collected to assess the potential of the nets as sources of cross-contamination from one sample to another. Cleaned nets were hung, and the outsides of the nets were thoroughly sprayed with tap water from either a water hose or pressurized backpack sprayer, as was done with environmental samples (as described above in Sample Collection). Microplastic particles remaining in the net from previous environmental samples were washed down and captured in the detachable mesh cod end. The particles were then transferred to a glass jar, preserved, and analyzed using the same laboratory method as environmental samples. A mean of 17 plastic particles on average (range 2–30, median 22) were recovered from the five blank samples. On average, 78% of the plastic particles in the blank samples were in the 0.355–0.999 mm size range, and 73% were fibers/lines. For comparison, the 107 environmental samples averaged 368 plastic particles (range 4–4464, median 170). The potential for cross-contamination from sample to sample was therefore relatively low, given the numbers of plastic particles in most environmental samples (SI Figure 1).

Eleven laboratory blanks were collected and analyzed alongside the environmental samples to assess potential contamination from laboratory containers or air. Laboratory blanks consisted of deionized water stored in open sample containers for periods of 1–14 days. None were found to have any plastic particles, indicating a low potential of contamination from within the laboratory.

In 19% of the samples ($n = 20$), the particles were counted and categorized twice, by two different analysts, to verify consistency. The total counts of plastics were very consistent between analysts (<5% variation), though the exact categorization within the smallest size class did show variations of up to 10% due to subjectivity of the classifications.

RESULTS

Plastic particles were found in all 107 samples analyzed (complete sample results were published previously[33]). Sample concentrations ranged from 0.05 to 32 p/m^3 (median 1.9 p/m^3, mean 4.2 p/m^3; SI Table 2). Ninety-eight percent of the sampled plastic particles were in the microplastic size range; of those, 72% were in the smallest size range sampled (0.355–0.99 mm), and 26% were in the 1.0–4.75 mm size range. Only 2% of sampled plastic particles were larger than 4.75 mm. The most frequently occurring plastic particle type was fibers/lines, making up on average 71% of each sample. The majority of plastic particles categorized as fibers/lines were fibers rather than lines. Fragments were the second most abundant plastic particle type, making up on average 17% of each sample, followed by foams, films, and pellets/beads (8%, 3%, and 2%, respectively).

The concentrations of fragments, foams, pellets/beads, and films were significantly positively correlated with the percentage of the watershed in urban land use (Figure 3), watershed population density, and (films excepted) percent impervious cover (Table 1). Hydrology also affected the concentrations of these particle types: in urban and nonurban watersheds, the concentrations of fragments, foams, films, and pellets/beads were higher during runoff events than during low-flow

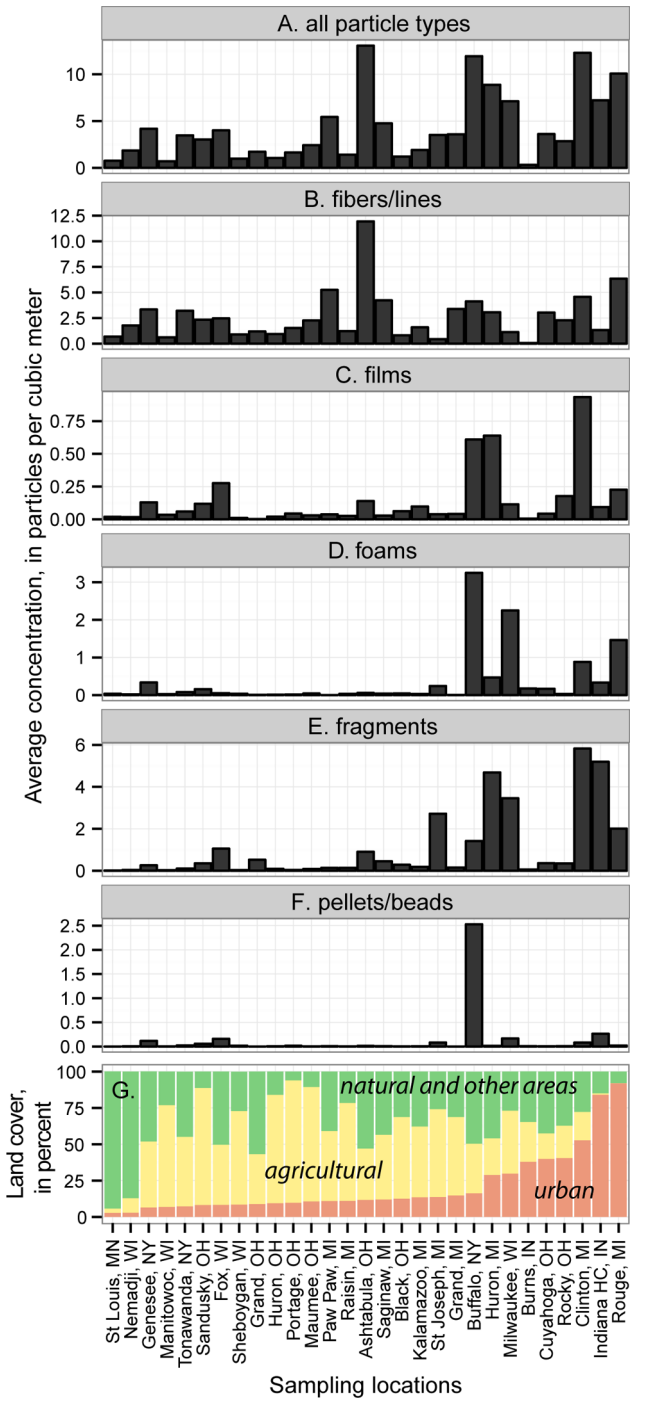

Figure 3. (A–F) Average concentrations of plastic particles and (G) watershed land cover at sampled Great Lakes tributaries (2014–15).

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Table 1. Spearman Correlation Coefficients between Plastic Concentrations and Watershed Attributes

watershed characteristic	all plastic types	fragments	foams	pellets/beads	films	fibers/lines
urban (%)	0.32[a]	0.40[a]	0.33[a]	0.27[a]	0.19[a]	0.11
agriculture: pasture, hay (%)	−0.11	−0.04	−0.03	−0.03	0.03	−0.06
agriculture: crops (%)	−0.22[a]	−0.21[a]	−0.33[a]	−0.15	−0.09	−0.14
agriculture: total (%)	−0.24[a]	−0.25[a]	−0.32[a]	−0.16	−0.08	−0.14
forest (%)	0.04	−0.08	−0.17	−0.16	−0.09	0.17
water, wetland (%)	−0.11	−0.05	−0.07	−0.03	−0.05	−0.12
impervious (%)	0.30[a]	0.42[a]	0.37[a]	0.30[a]	0.19	0.08
population density	0.37[a]	0.45[a]	0.38[a]	0.29[a]	0.21[a]	0.16
WWTP[b] effluent contribution (%)	−0.07	−0.07	0.02	0.08	−0.05	−0.17

[a]Significant at $p < 0.05$. [b]WWTP = wastewater treatment plant.

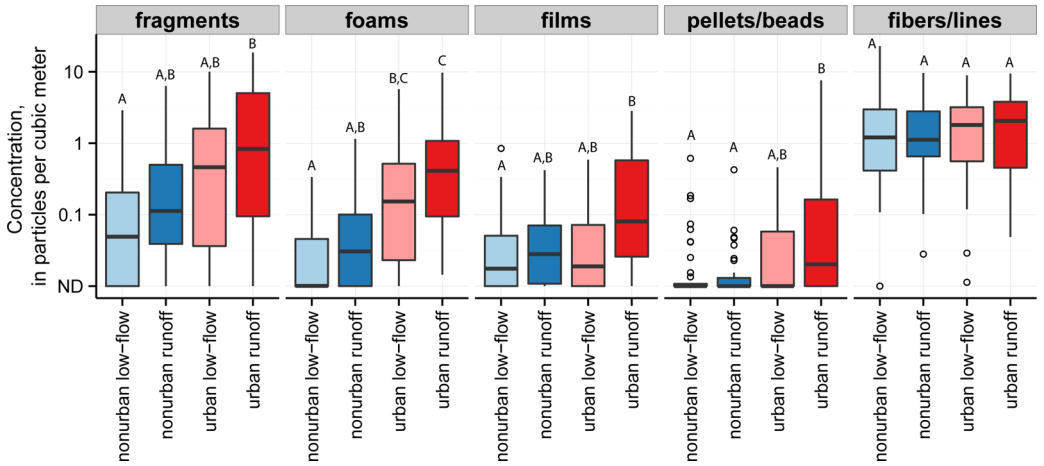

Figure 4. Plastic concentrations in nonurban low-flow (n = 40), nonurban runoff (n = 35), urban low-flow (n = 17), and urban runoff (n = 15) samples. Urban watersheds are those with greater than 15% urban land cover. Boxplot labels A, B, and C indicate which groups of samples are statistically similar (those sharing a common letter) and statistically different (those not sharing a common letter) using the Kruskal−Wallis multiple comparisons test ($p < 0.05$). Legend: boxes, 25th to 75th percentiles; dark lines, medians; whiskers, 1.5 × the interquartile range (IQR); circles, values outside 1.5 × the IQR; ND, not detected.

conditions, though this relationship was not significant (Figure 4).

Fibers/lines were ubiquitous across all land-use types (Figure 3). The concentrations of fibers/lines were not correlated with any of the tested watershed attributes (Table 1), nor were they affected by hydrology (Figure 4). None of the plastic types were significantly correlated with the contribution of wastewater effluent to streamflow (Table 1 and SI Figure 2).

DISCUSSION

Relations with Watershed Attributes and Hydrology. Litter-related plastics (fragments, foams, and films) were found at higher concentrations in samples from more urban watersheds and during runoff-event conditions. Plastic litter is not only more prevalent in urban watersheds than in areas with other land covers, but it is also more mobile because impervious surfaces and storm sewers facilitate conveyance of plastics to receiving water bodies during runoff-event conditions. Previous research has also reported a correlation between microplastic concentrations (predominantly fragments and films) and urban-related attributes (population density and urban/suburban development).[24]

Pellets/beads were not significantly related to the wastewater effluent contribution to streamflow but were associated with other urban-related watershed attributes (i.e., urban land cover, imperviousness, and population density). Because many personal care product-related beads are smaller than the 333 μm mesh size used,[7,44] it is likely that the majority of the sampled particles in this category were from industrial sources (e.g., preproduction pellets and bead blasting), which may explain the poor relation between pellets/beads and wastewater effluent contribution. A finer mesh size capable of capturing personal care product-related beads may have yielded better relations with wastewater effluent contribution. However, a study of eight WWTPs in Southern California found that tertiary wastewater effluent was not a significant source of pellets/beads, or any other type of microplastic, to receiving waters.[9]

Like pellets/beads, the concentrations of fibers/lines were not related to wastewater effluent contribution. The role of wastewater effluent as a source of fibers remains unclear; some studies[23,49] have shown wastewater effluent to be a source of fibers, while others[8,9] have shown that most if not all fibers settle out and are captured in sludge.

Previous studies have shown that some microplastic fibers in environmental samples can come from atmospheric contamination in the laboratory,[23,50,51] with contributions of up to 10 fibers per sample.[50] A number of precautions were taken in this study to prevent laboratory contamination, and laboratory control samples did not show contamination. Atmospheric deposition may be one important source of fibers in streams, with fibers accumulating on the landscape and washing off during runoff-event conditions. A study of atmospheric deposition of fibers in Paris reported deposition rates of up

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to >100 synthetic fibers m^{-2} day^{-1}, with rates in an urban area approximately double those of a suburban area.[6] Rainfall seemed to be an important factor as well, with higher deposition rates during rainfall periods compared with dry-weather periods. However, the current study found similar fiber concentrations in urban and nonurban areas and in low-flow and runoff-event samples.

Land application of WWTP sludge may be a significant source of fibers in agricultural areas, as fibers are known to accumulate in sludge[8,9] and have been shown to be good indicators of sludge application on fields.[10,52] However, if this were the case, higher concentrations would be expected during runoff-event conditions, which were not observed. The lack of correlation between fiber concentrations and hydrologic conditions and between fiber concentrations and watershed attributes highlights the need for further work to better understand the sources of fibers in streams.

Comparisons to Other Studies. *Size Distributions.* Plastic concentrations were inversely related to particle size in the current study: 72% of the plastic particles were in the smallest size fraction sampled (0.35−0.99 mm). This inverse relationship between concentration and size has also been observed in other studies in fluvial, lacustrine, and marine environments.[30,53−55] This has potentially led to an under-representation of the true microplastic concentrations due to an artifact of the mesh size chosen for sampling. One study found up to 100 000 times more microplastic particles using an 80 μm mesh compared with a 450 μm mesh,[54] indicating that the 333 μm mesh used in the current study captured only a small fraction of the actual microplastic particles present. High concentrations of particles smaller than 100 μm may have important implications for aquatic organisms, as those particles can be taken up into cells and can translocate from the gut into the circulatory system.[56,57] Smaller particles also have larger surface to volume ratios, increasing their potential as vectors for sorbed contaminants.

Concentrations. The plastic concentrations measured in Great Lakes tributaries (0.05−32 p/m^3, mean 4.2 p/m^3) are comparable to or greater than those reported in other river studies, although there are few other river studies with which to compare. In Chicago's highly urbanized North Shore Channel, the mean concentrations were 1.9 and 17.9 p/m^3 upstream and downstream of a WWTP, respectively.[23] Concentrations in the Seine River upstream and downstream of Paris were 0.28−0.47 p/m^3.[8] A mean concentration of 0.32 p/m^3 was reported for the Danube, but that study used a larger mesh size (500 μm) and did not include fibers.[25] A study of floating plastics in four Chilean rivers reported concentrations similar to those in the current study using a 1000 μm mesh size.[58]

Particle Types. The observed dominance of fibers (71% of the particles on average) and, to a lesser extent, fragments (17% on average) in tributary samples is in agreement with results from other fluvial studies, such as Chicago's North Shore Channel[23] and the Seine River in Paris,[8] but contrasts with that reported for the Rhine, where fibers made up only 2.5% of the sampled particles.[28] The Rhine was instead dominated by fragments and, in downstream reaches, spherules of 300−1000 μm diameter, thought to originate from plastic manufacturers or other industry in the area.

Comparison of plastic particle types in tributary samples with those from the surface of the Great Lakes and other lacustrine environments reveals striking differences. Unlike in tributary samples, fibers/lines were rare in Great Lakes samples, making up only 2% of the plastic particles on average[30] (Figure 5). In a large, remote lake in Mongolia, fibers/lines made up 20% of the particles on average,[27] which is higher than in the Great Lakes but still considerably lower than in Great Lakes tributaries. Pellets/beads, which made up a large portion of the plastic particles in some of the Great Lakes samples (especially those from Lake Erie), were rare in tributary samples.

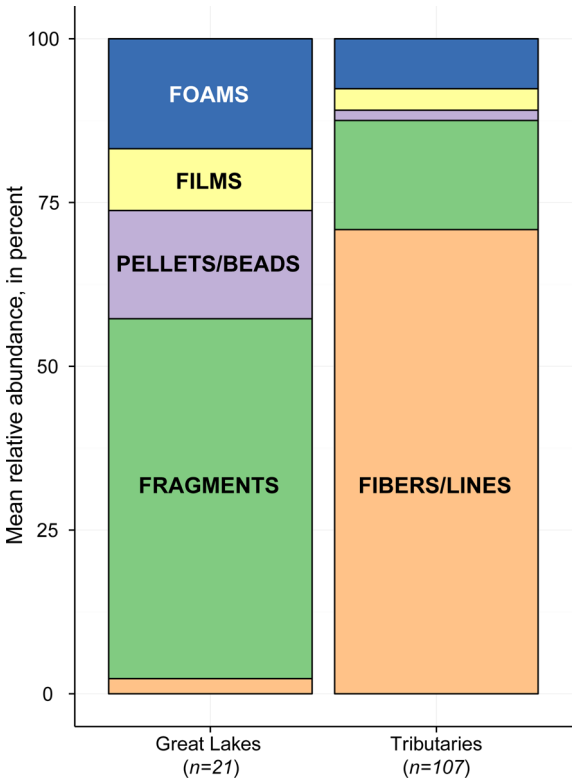

Figure 5. Mean relative abundances of different plastic particle types in the Great Lakes compared with tributaries. Great Lakes data are from Eriksen et al.[30]

The discrepancy in plastic particle types between the Great Lakes and their tributaries (Figure 5) is likely due, in part, to analytical methods but also to the physical properties of different plastics and the hydraulics of the different water bodies. Although the tributary and Great Lakes samples were collected using the same methods and equipment and analyzed by the same laboratory, the laboratory modified their analytical method in 2013, after analyzing the Great Lakes samples and prior to analyzing the tributary samples. Specifically, the laboratory switched from isolating plastic particles using salt water flotation to using WPO. The WPO method is thought to be more effective at capturing dense particles. Samples from Lake Michigan analyzed using the WPO method contained 14% fibers on average,[45] compared with <2% fibers using the salt water floatation method. Therefore, the average relative abundance of fibers in the samples from the Great Lakes published in 2013[30] was likely artificially low. Even so, the average relative abundance of fibers in tributary samples (71%) was considerably higher.

Hydraulics within the river systems compared with the Great Lakes and the physical properties of the plastics may explain this difference in abundance of fibers. Negatively buoyant fibers made of polymers such as polyester, rayon, nylon, and cellulose acetate may remain in suspension in the turbulent flow of a

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river (allowing them to be captured by surface sampling) but likely settle out upon reaching the more quiescent lakes. In contrast, many foams, films, and pellets/beads are made of positively buoyant polymers such as polystyrene, polyethylene, and polypropylene, which likely remain afloat in the lakes for some time, until biofouling or adsorption of minerals increases their density and causes them to sink.[59] It would be expected, then, that surface samples from the Great Lakes would have lower abundances of fibers relative to samples from the tributaries. The fibers enter the lakes but likely settle and accumulate in the lakebed sediments rather than at the surface. A recent study of nearshore sediments in Lake Ontario supports this hypothesis, reporting an average of 980 microplastics/kg dry weight (predominantly fibers and fragments).[59] This accumulation of microplastics in lakebed sediments may have important effects on benthic organisms as well as organisms at higher trophic levels that are reliant on benthic organisms.

Results from this study add greatly to the current body of information on this topic given the very few previous studies that have focused on microplastics in the riverine environment. This is notable given that tributaries are presumably a substantial source of the overall microplastics burden in large water bodies such as the Great Lakes or marine environments. The difference in results from the tributaries compared with the Great Lakes provides insight into the fate and transport of different microplastics types. These differences could be influential when considering the potential effect that microplastics of different morphology may have on aquatic organisms. In addition, this study provides unique information on the prevalence of different types of microplastics in relation to land cover within watersheds. Collectively, this study has helped to improve our understanding of the sources, transport, and fate of microplastics in freshwater environments. While the implications of microplastics on ecological and human health are poorly understood, the increase in plastic production, stability of plastics in the environment, and long residence time in the Great Lakes ensure that these contaminants will continue to be of concern as they accumulate in the Great Lakes well into the future.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.6b02917. All of the sample results have been published separately online.[33]

Site characteristics, GIS methods, field blank sample results, site-specific result summaries, and relations between plastic concentrations and wastewater contribution (PDF)

SI Table 1 (XLSX)

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Notes

The authors declare no competing financial interest.

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