Vertical Distribution of Microplastics in the Water Column and Surficial Sediment from the Milwaukee River Basin to Lake Michigan

Peter L. Lenaker,[*,†] Austin K. Baldwin,[‡] Steven R. Corsi,[†] Sherri A. Mason,[§,⊥] Paul C. Reneau,[†] and John W. Scott[∥]

[†]Upper Midwest Water Science Center, U.S. Geological Survey, 8505 Research Way, Middleton, Wisconsin 53562, United States

[‡]Idaho Water Science Center, U.S. Geological Survey, 230 Collins Road, Boise, Idaho 83702, United States

[§]Department of Chemistry and Biochemistry, State University of New York at Fredonia, 280 Central Avenue, Science Complex 340, Fredonia, New York 14063, United States

[∥]Illinois Sustainable Technology Center/Prairie Research Institute, University of Illinois, Urbana-Champaign, One Hazelwood Road, Champaign, Illinois 61820, United States

S *Supporting Information*

ABSTRACT: Microplastic contamination was studied along a freshwater continuum from inland streams to the Milwaukee River estuary to Lake Michigan and vertically from the water surface, water subsurface, and sediment. Microplastics were detected in all 96 water samples and 9 sediment samples collected. Results indicated a gradient of polymer presence with depth: low-density particles decreased from the water surface to the subsurface to sediment, and high-density particles had the opposite result. Polymer identification results indicated that water surface and subsurface samples were dominated by low-density polypropylene particles, and sediment samples were dominated by more dense poly-ethylene terephthalate particles. Of the five particle-type

categories (fragments, films, foams, pellets/beads, and fibers/lines), fibers/lines were the most common particle-type and were present in every water and sediment sample collected. Fibers represented 45% of all particles in water samples and were distributed vertically throughout the water column regardless of density. Sediment samples were dominated by black foams (66%, identified as styrene–butadiene rubber) and to a lesser extent fibers/lines (29%) with approximately 89% of all of the sediment particles coming from polymers with densities greater than 1.1 g cm^{-3}. Results demonstrated that polymer density influenced partitioning between the water surface and subsurface and the underlying surficial sediment and the common practice of sampling only the water surface can result in substantial bias, especially in estuarine, harbor, and lake locations where water surface concentrations tend to overestimate mean water column concentrations.
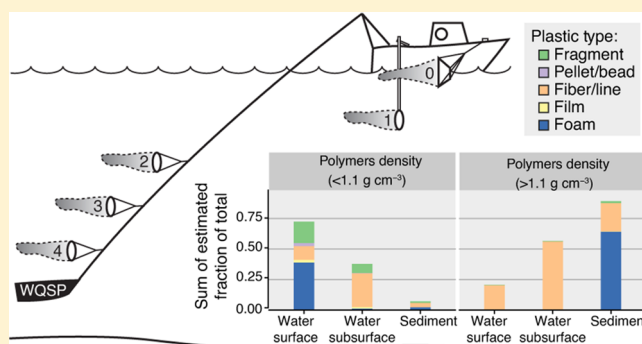
1. INTRODUCTION

The widespread occurrence of microplastics in aquatic environments has become increasingly evident in recent years. Microplastics (plastic particles less than 5 mm in diameter) come from a variety of sources including microbeads from personal care products, broken-down litter, tire wear particles, and fibers from synthetic textiles, among others.[1−6] Pathways to the aquatic environment are also diverse and include domestic, commercial, and industrial wastewater (e.g., plastic shavings and dust, synthetic fibers, and microbeads), stormwater runoff (e.g., litter and tire wear particles), wastewater treatment plant effluent and sludge (e.g., synthetic fibers), and atmospheric deposition (e.g., synthetic fibers).[5,7−10]

A primary concern surrounding microplastics is their potential to negatively affect aquatic organisms. Microplastics continue to break down into smaller and smaller particles over

time,[11] making them ingestible by all levels of the food web, from plankton to mussels, fish, and birds.[12−15] Harmful effects on individual organisms have been documented by a growing number of studies, but population-level effects remain unclear.[16,17]

To date, nearly all studies of microplastic occurrence in freshwater have focused on the water surface. Studies of microplastics in rivers, collected by skimming the water surface with a 330−333 μm mesh net, have reported mean concentrations of 0.35 particles per cubic meter (p m^{-3}) on the River Seine (Paris),[18] 1.9 p m^{-3} on Chicago's North Shore Channel (17.9 p m^{-3} downstream from a wastewater treatment

plant),[19] 2.0 p m^{-3} on the Upper Mississippi and St. Croix Rivers (Minnesota and Wisconsin),[20] and 4.2 p m^{-3} on 29 Great Lakes tributaries.[21] In these and other studies of microplastics in rivers,[22] fibers were the dominant type, often representing a majority of all microplastic particles. Microplastic types at the surface of receiving waters (lakes, nearshore marine), however, appear to be more variable, often dominated by fragments or other nonfibrous particles.[23−26] In the Great Lakes, fibers were reported to constitute 14% or less of all surface microplastics.[25,26] The decrease in the relative abundance of fibers at the water surface of the Great Lakes, compared to their tributaries, may be explained by fibers remaining in suspension in the tributaries but distributing through the water column and settling upon reaching the lakes.

Studies of microplastics in freshwater sediment are limited. In five tributaries draining into northern Lake Erie and seven draining into northern Lake Ontario, mean microplastic sediment concentrations with particle sizes greater than 0.063 mm were 117 p kg^{-1} dry weight (dw) and 610 p kg^{-1} dw, respectively, with fragments and fibers being most abundant.[27,28] Maximum concentrations with a particle size of 0.5 mm to greater than 1.0 mm in sediment from a small urban lake in the U.K. were up to 250−300 p kg^{-1} dw, with fibers and films dominating.[29] Nearshore sediments in Lake Ontario and Erie were reported to have mean concentrations of 980 and 90 p kg^{-1} dw, with fibers and fragments being the most abundant of all particles.[27,28]

The vertical distribution of different types of microplastics in the water column, and how that distribution might change with varying flow velocities, is virtually unknown and is critical for estimating microplastic loads. Relying on water surface concentrations alone may result in substantial under- or overestimation of actual microplastic quantities. Water surface samplers such as manta trawls underestimated total buoyant microplastic amounts by a factor of 1.04−30.0 in a study of buoyant microplastics in the marine environment.[30] Current knowledge on the vertical distribution of microplastics in freshwater environments is limited to a single study on the Marne River (Paris), which reported synthetic fibers to be similarly distributed at three depths.[31] Although insightful, that study focused on fibers only and was limited to a single sampling location.

The goals of this study were to determine the extent of microplastic contamination in Milwaukee waterways and to improve the understanding of the vertical distribution of different types of microplastics in the water column. Specific objectives were to (1) characterize microplastics in water and sediment, (2) determine whether concentrations and types of microplastics at the water surface differ from the water subsurface, (3) determine how a better understanding of the vertical distribution of microplastics in the water column influences overall concentration estimates, and (4) evaluate polymer densities to determine where certain polymers and particle types are distributed among the water surface, water subsurface, and sediment.

2. MATERIALS AND METHODS

2.1. Sample Collection. The study area was focused on the Kinnickinnic, Menomonee, and Milwaukee Rivers in the Milwaukee, Wisconsin, metropolitan area, which, collectively, constitute the Milwaukee River Basin. Each river was sampled at upstream and downstream locations (Figure 1 and Table S1). A third sampling location was added partway through the

study on the Kinnickinnic River (KKE) when the upstream location (KKJ) had to be abandoned because of low water levels. In addition to the rivers, samples were collected from the inner harbor (INH, the confluence of the three river systems), the outer harbor (OUH) within the Milwaukee break wall, and Lake Michigan (LAK, Figure 1, and Table S1).

Samples were collected at the water surface at all 10 locations and in the surficial sediment at 9 locations (sediment was not collected at KKE). At a subset of six locations, water subsurface samples were also collected at 1−4 different depths below the water surface. Water samples (water surface and subsurface) were collected from each location during four trips, from May to September 2016, for a total of 96 samples. Sediment samples were collected once, on June 2016 for a total of nine samples (Table S1). All samples were collected during stable, non-precipitation-driven hydrologic periods.

Samples were collected either by wading or from a boat, depending on the water depth (Table S1). Water surface samples were collected using methods and equipment consistent with a previous study of microplastics in Great Lakes tributaries.[21] Briefly, a neuston net (1.5 m long × 100 cm wide × 40 cm high; Sea-Gear Corp., Miami, FL) was used to skim the upper ∼20 cm of the water surface for a period of 15−30 min. The net mesh size was 333 μm, like many previously published studies.[4,19,21,24,25,34] Water subsurface samples were collected using a 333 μm mesh net with a 15.2 cm circular opening. Water subsurface samples were collected between 0.40 and 13.7 m below the water surface at the six locations (Table S2). Sampling duration for water subsurface samples ranged from 40 to 330 min (median 60 min). Volume measurements were determined by collecting velocity using a SonTek FlowTracker at wadeable sampling locations and a Teledyne RD Instruments Acoustic Doppler Current Profiler (TRDI, Rio Grande 600 kHz ADCP) at boat locations.[35] Details on the water sample collection and net processing are presented in the Supporting Information (Text S1).

At wadeble streams, sediment was collected from multiple depositional areas near the water sampling locations. Stainless-steel spoons were used to collect the upper 25−50 mm of sediment, which was composited into a stainless-steel pan, homogenized, and transferred to a 500 mL glass bottle. For sediment collection at the boat locations, a petite ponar sampler was used. Multiple ponar grab samples were collected along the same global positioning system tracks used during water sample collection. Sediments were composited in a stainless-steel pan, homogenized, and transferred to a 500 mL glass bottle.

2.2. Sample Processing & Analysis. Water samples were processed using a wet peroxide oxidation method with each sample filtered through a series of 8 in diameter stainless-steel sieves of 4.75, 1.00, and 0.355 mm, separating the solid material into three size fractions (0.355−0.999, 1.00−4.749, and ≥4.75 mm, respectively). The method chosen for the current study has been used in numerous studies[15,21,22,29,36−44] and is supported by the National Oceanic and Atmospheric Administration.[45] Sediment samples were processed using an improved NOAA laboratory method,[45] as modified by Zobkov and Esiukova.[46] Briefly, sediment processing consisted of a three-step method: extraction using a zinc chloride solution (ρ = 1.6 g mL^{-1}), wet peroxide oxidation of floating materials, and calcite digestion using 4.5% hydrochloric acid. After processing, samples were filtered and microscopically analyzed to enumerate and categorize inherent microplastic particles
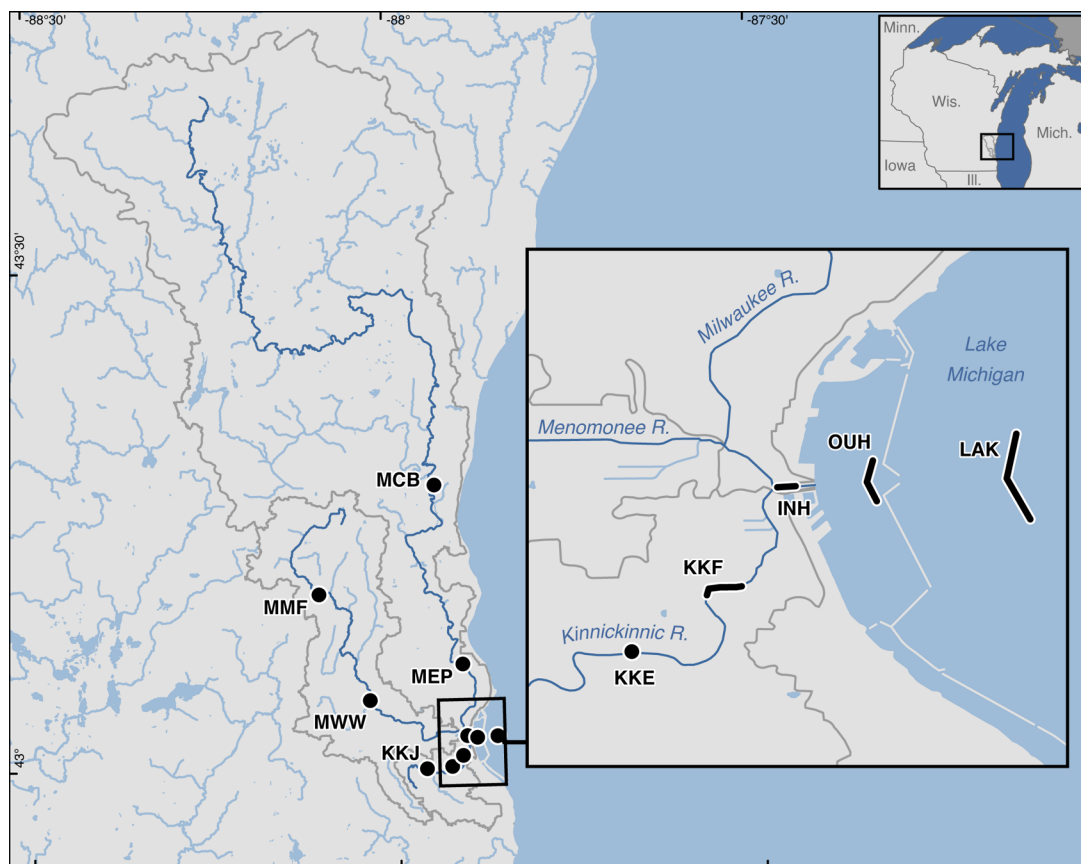
Figure 1. Site location map. Microplastic sampling locations, including wading points (black dots) and boat transects (black lines) are shown along with streams (blue lines) and watershed boundaries (darker gray lines) for the Milwaukee, Menomonee, and Kinnickinnic Rivers.[32,33] The harbor rock wall separating Lake Michigan from the Outer Harbor is also shown (light gray lines). [MCB, Milwaukee River near Cedarburg; MMF, Menomonee River at Menomonee Falls; MEP, Milwaukee River at Milwaukee; MWW, Menomonee River at Ridge Blvd.; KKJ, Kinnickinnic River at Jackson Park; KKE, Kinnickinnic River at S. 11th St.; KKF, Kinnickinnic River at S. 1st St.; INH, Milwaukee Inner Harbor; OUH, Milwaukee Outer Harbor; LAK, Lake Michigan].

according to morphology as fragments, pellets/beads, fibers/lines, films, or foams. Further details are provided in the Supporting Information (Text S2).

To confirm the polymeric nature of collected particles, a subset of water surface (4.4%, 553), water subsurface (7%, 218), and sediment (4%, 156) particles were selected for further analysis by Fourier transform infrared (FTIR) spectroscopy (Table S3). Several nonrigid, sponge-like black foam particles observed in sediment samples from four of the river locations could not be identified using FTIR spectroscopy. These black sponge-like foam particles from three of the four river locations and two reference automotive tires were analyzed using pyrolysis gas chromatography mass spectrometry (py-GCMS) for six known styrene−butadiene rubber (SBR) pyrolysis compounds, styrene, xylene, limonene, butadiene trimers, styrene−butadiene dimers, and styrene−butadiene−butadiene hybrid trimers. Additional details on FTIR and py-GCMS analyses are presented in the Supporting Information (Text S3).

Plastic particle concentrations in water were computed using the total number of particles divided by the volume of water filtered through the net, reported as particles per cubic meter ($p\ m^{-3}$). Plastic particle concentrations in sediment are reported as particles per kilogram (dry weight) sediment ($p\ kg^{-1}$, dw).

All sample results for this study are available online.[35]

2.3. Data Analysis. At locations where the water surface and subsurface were sampled, depth-weighted mean concentrations (DWCs) were computed using eq 1

$$DWC = \frac{\sum (\text{individual net concentration} \times \text{depth of water column represented})}{\text{total water column depth}}$$

(1)

A conceptual example of DWC computation is provided in Figure S4.

FTIR results were used to extrapolate the particle−polymer associations to the entire population of particles collected using eq 2

$$PPE = \left(\frac{NP}{PT}\right) \times TP$$

(2)

Where NP equals the number of particles identified as a specific polymer (e.g., polypropylene) per particle type (e.g., fiber/line), PT equals the number of individual particles analyzed via FTIR by particle type, TP equals the total number of particles collected by particle type for each of the compartments sampled (water surface, water subsurface, and sediment), and PPE equals the estimated number of particle morphologies by polymer type. Additional interpretation included a comparison of particles by density within each compartment.

Table 1. Summary of Microplastic Concentrations in Water Samples[a]

sampling location	number of depths sampled	mean fragment concentration p m⁻³	mean pellet/bead concentration p m⁻³	mean fiber/line concentration p m⁻³	mean film concentration p m⁻³	mean foam concentration p m⁻³	mean total concentration p m⁻³
MCB	1	0.16	0.00	1.64	0.08	0.04	1.93
MMF	1	0.18	0.00	2.37	0.01	0.04	2.61
MEP	2	0.27	0.03	1.01	0.04	0.05	1.58
MWW	2	0.27	0.01	2.40	0.01	0.13	2.71
KKJ	1	0.09	0.00	2.47	0.01	0.01	2.57
KKE	1	0.53	0.00	4.51	0.14	0.49	5.67
KKF	2	2.32	0.44	0.97	0.20	7.69	1.00
INH	5	0.94	0.12	0.95	0.15	0.99	1.27
OUH	5	0.10	0.01	0.57	0.01	0.08	0.55
LAK	5	0.07	0.00	0.43	0.01	0.03	0.42

[a]Each sampling location was sampled four times except KKJ and KKE, which were sampled two times each. Where multiple depths were sampled, concentrations are depth-weighted means. [p m⁻³, particles per cubic meter; MCB, Milwaukee River near Cedarburg; MMF, Menomonee River at Menomonee Falls; MEP, Milwaukee River at Milwaukee; MWW, Menomonee River at Ridge Blvd.; KKJ, Kinnickinnic River at Jackson Park; KKE, Kinnickinnic River at S. 11th St.; KKF, Kinnickinnic River at S. 1st St.; INH, Milwaukee Inner Harbor; OUH, Milwaukee Outer Harbor; LAK, Lake Michigan].
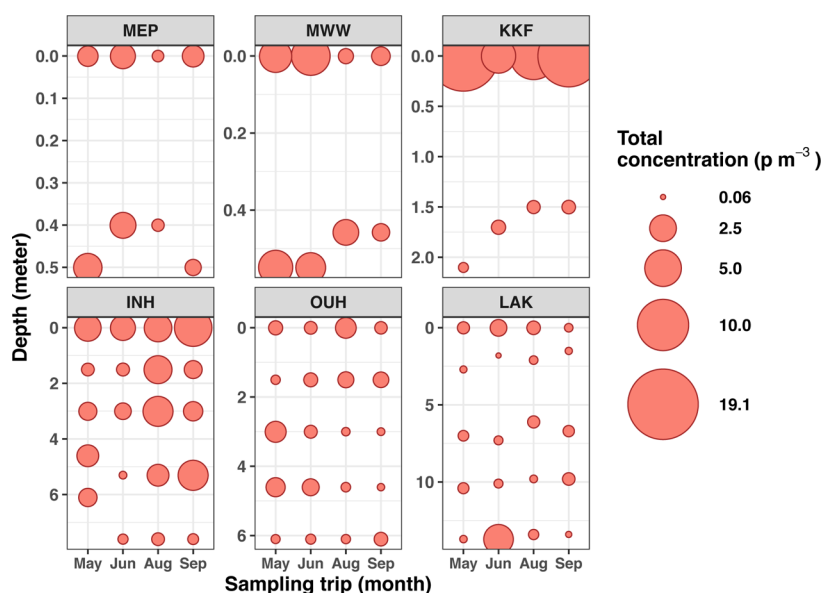

Figure 2. Total water sample concentrations by sampling trip (month) and depth for the six sampling locations where samples were collected at different water subsurface depths. [MEP, Milwaukee River at Milwaukee; MWW, Menomonee River at Ridge Blvd.; KKF, Kinnickinnic River at S. 1st St.; INH, Milwaukee Inner Harbor; OUH, Milwaukee Outer Harbor; LAK, Lake Michigan; Jun, June; Aug, August; Sep, September; p m⁻³ = particles per cubic meter].

Statistical significance was determined with a pairwise Wilcoxon rank-sum test with corrections for multiple comparisons ($p < 0.05$).[47]

Methods used to determine watershed boundaries, land cover, percent impervious cover, and population density are described in the Supporting Information (Text S4).

2.4. Quality Assurance and Quality Control. Laboratory-based quality assurance and quality control (QA/QC) included lab blanks and sample recounts (Text S5). To assess potential contamination from laboratory materials or air, two laboratory blanks were collected and analyzed alongside the environmental water samples, resulting in the presence of 3 and 6 fibers/lines. To assess consistency among different analysts, 25% of samples ($n = 24$) was recounted by a second analyst. The mean/median relative percent difference by particle type was 33/0% for pellets/beads, 46/7.5% for

fibers/lines, 56/0% for foams, 58/13.5% for fragments, and 60/0% for films (Text S5, Figure S5).

Field-based QA/QC included field blanks for water samples and field duplicates for sediment samples. Field blank samples ($n = 8$) were collected to assess the potential of the nets as sources of cross-contamination among samples. The field blank samples averaged 14 plastic particles (range 5−35, median 12), of which 86% was in the 0.355−0.999 mm size and 88% was fibers/lines (Text S5, Figure S6).

Two duplicate sediment samples were collected at the MMF and OUH sampling locations. Fibers/lines were 88 and 95% of total particles in the environmental and duplicate sample collected at OUH, and foam was 63 and 84% of total particles in the environmental and duplicate sample collected at MMF (Figures S7 and S8).
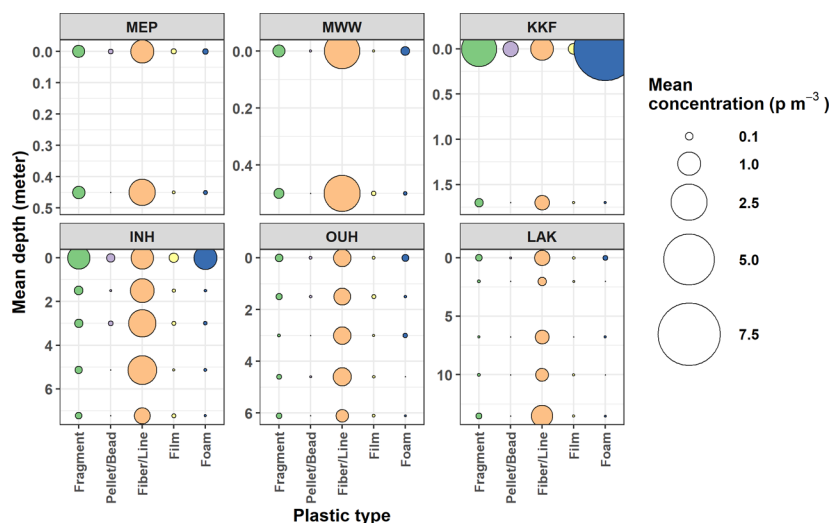
Figure 3. Mean water concentrations by microplastic particle type and mean depth for the six sampling locations where samples were collected at different water subsurface depths. [MEP = Milwaukee River at Milwaukee; MWW = Menomonee River at Ridge Blvd.; KKF = Kinnickinnic River at S. 1st St.; INH = Milwaukee Inner Harbor; OUH = Milwaukee Outer Harbor; LAK = Lake Michigan; p m^{-3} = particles per cubic meter].

3. RESULTS

3.1. Water. Plastic particles were found in all 96 water samples for a total of 15 545 particles (Table S3). Mean depth-weighted sample concentrations for the water column varied from 0.42 to 5.67 p m^{-3} (median 0.85 p m^{-3}, mean 1.8 p m^{-3}) (Table 1). Of all particles (water surface and subsurface), 51% was in the smallest size range analyzed (0.355−0.999 mm), 46% was in the 1.00−4.749 mm size range, and 3% was larger than 4.75 mm. Fibers/lines were the most frequently occurring particle type, present in every water sample collected and accounted for 45% of all particles in water samples, followed by foam (33%), fragments (17.4%), film (2.4%), and pellets/beads (2.2%; Table S3). A detailed description of the relative abundance of particles by size class for each sampling location and all water samples collected is provided in Figure S9.

Mean water surface sample concentrations (sum of all particle types) for the 10 sampling locations varied from 0.54 to 11.6 p m^{-3} (Figure S10), and individual water surface sample concentrations ($n = 36$) varied from 0.21 to 19.1 p m^{-3} (Figure 2). The most abundant particle type in water surface samples was foam (41%) followed by fibers/lines (34%), fragments (20%), films (3%), and pellets/beads (3%; Table S3). The mean concentrations of foams and fibers/lines in water surface samples were 1.03 and 1.54 p m^{-3}, respectively, significantly higher than the other three particle types ($p < 0.05$).

Mean water subsurface concentrations (sum of all particle types) at the six subsurface sampling locations varied from 0.14 to 2.7 p m^{-3}, and individual water subsurface sample concentrations ($n = 60$) varied from 0.06 to 4.3 p m^{-3} (Figure 2). Total concentrations from water surface samples were greater than water subsurface samples at KKF ($p < 0.05$) but did not differ significantly at the other five sampling locations where water subsurface samples were collected.

Microplastic particles observed in water subsurface samples were dominated by fibers/lines (89%). Other particles observed in water subsurface samples included fragments (8%), films (1.5%), foams (1.1%), and pellets/beads (0.4%; Table S3). The mean water subsurface concentration of fibers/lines (0.82 p m^{-3}) was approximately an order of magnitude

greater than other particle types ($p < 0.05$; Figure 3). Mean water surface concentrations of foams, fragments, and pellets/beads were significantly greater than water subsurface concentrations at KKF ($p < 0.05$; Figure 3) but did not differ significantly for fibers/lines and films at KKF or for any particle types at the other five water subsurface sampling locations.

3.2. Sediment. A total of 4218 plastic particles was observed in the nine sediment samples (Table S3). Total sample concentrations varied from 32.9 to 6229 p kg^{-1}, dw (Figure 4). The majority (62%) of particles was in the smallest size range (0.125−0.3549 mm), 24% was in the 0.355−0.999 mm size range, and 14% was larger than 1.00 mm. A detailed description of the relative abundance of particles by size class for each sampling location and all sediment samples collected is provided in Figure S11.

Microplastic particles observed in sediment samples were dominated by foam (66%), with approximately 97% of all of the foam being black in color and identified as SBR. Other particles observed in sediment samples included fibers/lines (29%), which were present in all nine sediment samples collected, fragments (3.8%), film (0.47%), and pellets/beads (0.12%; Table S3). Black SBR foams were the dominant particle type in samples from the four locations on the Milwaukee (MCB and MEP) and Menomonee (MMF and MWW) Rivers with concentrations from 240 to 5523 p kg^{-1}, dw (Figure 4). Concentrations of fibers/lines from all locations sampled ranged from 29.3 to 881 p kg^{-1}, dw (Figure 4).

3.3. Polymer Identification. FTIR analysis of 553 particles from water surface samples (4.4% of all water surface particles) resulted in identification of 12 different polymers. Analyzed particles (32%) were identified as polypropylene (PP), 26% as polystyrene (PS), and 17.2% as low-density polyethylene (LDPE). The other nine identified polymers each accounted for less than 5% of the total, and polymers could not be identified for 7.2% of the particles (Figure S12).

FTIR analysis of 218 particles from water subsurface samples (7.0% of all water subsurface particles) resulted in identification of 12 different polymers. Analyzed particles (29%) were identified as PP, 16% as LDPE, 14% as poly(ethylene terephthalate) (PET, "polyester"), and 11.5% as Nylon. The other eight identified polymers each accounted
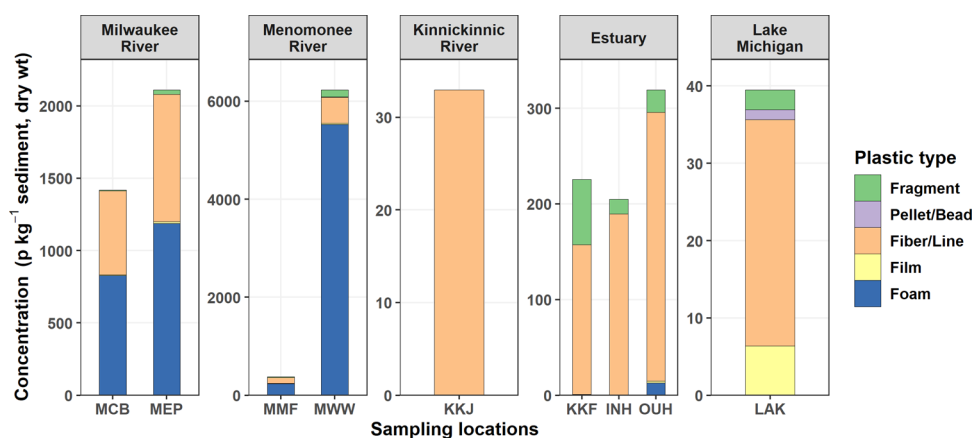
Figure 4. Sediment concentrations by microplastic particle type. Sampling locations are grouped by a river system, estuary and Lake Michigan with river sampling locations arranged from upstream to downstream locations, left to right for each river, the three estuary locations (KKF, INH, and OUH) and Lake Michigan (LAK). [MCB = Milwaukee River near Cedarburg; MEP = Milwaukee River at Milwaukee; MMF = Menomonee River at Menomonee Falls; MWW = Menomonee River at Ridge Blvd.; KKJ = Kinnickinnic River at Jackson Park; KKF = Kinnickinnic River at S. 1st St.; INH = Milwaukee Inner Harbor; OUH = Milwaukee Outer Harbor; LAK = Lake Michigan; p kg^{-1} sediment, dry wt = particles per kilogram of sediment, dry weight].

for less than 10% of the total, and polymers could not be identified for 5% of the particles (Figure S12).

FTIR analysis of 156 particles from sediment samples (4% of all sediment particles) resulted in identification of 14 different polymers. FTIR-analyzed particles (44%) were identified as PET, 8.3% as high-density polyethylene (HDPE), 7.7% as PP and as Nylon, 6% as Rayon, and 5% as polyacrylonitrile (PAN). The other eight identified polymers each accounted for less than 5% of the total. Polymers, including SBR, could not be identified for the remaining 11.5% of the FTIR-analyzed particles (Figure S12).

The nonrigid, sponge-like black foam particles (characterized as foam) could not be identified using FTIR analysis but were identified by py-GCMS as SBR. These black SBR foam particles accounted for 66% of all particles observed in sediment samples. All six of the target SBR pyrolysis compounds were detected in the nonrigid, sponge-like black SBR foam particles and two tire reference samples (Figures S13−S18). The black SBR particles were estimated to represent approximately 97% of foam particles in the sediment and between 56 and 88% of all microplastic particles in sediment samples from the four river locations (Figure 4). SBR co-polymer is the most common and abundant material used by the tire industry for manufacturing automotive tires.[48]

4. DISCUSSION

4.1. Water. Microplastics, especially microfibers, were ubiquitous across the three Milwaukee area streams, estuary, and nearshore Lake Michigan sampling locations in water surface and subsurface samples. The ubiquity of microfibers in freshwater and freshwater fauna has been observed in many previous studies.[13,21,49,50] Foam and fragment water surface concentrations at two of the three estuarine sampling locations, INH and KKF, were greater relative to the other sampling locations (Figure 3). Floating foams and fragments appear to be prevalent in the estuarine locations in the current study, and similar observations have been noted in previous estuarine and harbor environments.[51,52]

Plastic concentrations from water surface samples for this study (0.21−19.1 p m^{-3}, mean 3.2 p m^{-3}) were similar to concentrations in other freshwater studies. A study of 29 Great

Lake tributaries using the same sampling methodology and laboratory reported concentrations of 0.05−32 p m^{-3} (mean 4.2 p m^{-3}).[21] In nine creeks and rivers around Chicago, Illinois, upstream and downstream from a wastewater treatment plant, mean microplastic concentrations ranged 0.48−5.92 and 0.80−11.22 p m^{-3}, respectively.[53] Fiber concentrations in water surface samples (0.16−5.3 p m^{-3}, mean 1.5 p m^{-3}) were similar to fiber concentrations from 29 Great Lakes tributaries (0−22.8 p m^{-3}, mean 1.3 p m^{-3}).[21] Fiber concentrations were much higher in the highly urbanized Marne (5.7−398 fibers m^{-3}, mean 100.6 fibers m^{-3}) and Seine Rivers (22.1−48.5 fibers m^{-3} across four locations) in Paris, France, although that study used a smaller mesh size (80 μm).[31]

The vertical distribution of microplastics in the water column varied by location and particle type. Channel depth, stream velocities, particle type, and density were likely factors affecting how microplastic particles were distributed in the water column. Of the sampling locations deep enough to warrant water subsurface sampling, the site characteristics varied from relatively shallow and rapid flowing water in river locations (MEP and MWW) to deep and wide channels with slow-moving water at estuarine locations (KKF, INH, and OUH), to the deepest and most quiescent sampling location that was in Lake Michigan (LAK) (Table S1). At the two river locations, the composition of particle types did not change as a function of vertical location. Turbulent flow resulting from the shallow depth and rapid water velocity may have created a homogeneous mixture of microplastic particles throughout the water column. At two of the three estuarine locations (KKF and INH), other particle types were concentrated at the water surface, especially at KKF where water surface concentrations of foams, fragments, and pellets/beads were significantly greater than water subsurface concentrations (Figure 3). This vertical heterogeneity at KKF is likely related to a combination of factors inherent to the microplastic particles, such as type, morphology, and density in addition to a decrease in streamflow velocity and turbulence, allowing for the settling of particles with densities greater than water. Additionally, KKF has the highest population density and percent urban land use of all sampling locations, which leads to the potential

for a greater concentration of litter-related microplastics such as expanded polystyrene foam that tend to float at the water surface. High population density and percent urban land use have been positively correlated to higher litter-related microplastic concentrations in Great Lakes tributaries and estuarine rivers of the Chesapeake Bay.[21,34] Urban land use characteristics along with very low-flow, low-velocity, and, therefore, low-turbulent waters in the KKF estuary could have contributed to the low-level vertical mixing of microplastics in the water column. The vertical distribution of particles did not vary significantly at OUH and LAK locations.

With few exceptions,[31] previous studies of microplastics in freshwater have sampled only the water surface, potentially biasing overall estimates of microplastics in the water column. To evaluate this potential bias, relative percent differences were computed between the water surface and depth-weighted concentrations by particle type, particle size fraction, and the six locations where water surface and subsurface sampling was performed (Figure 5). Relative percent differences between the water surface and depth-weighted concentrations at river locations (MWW and MEP) were slightly negative, indicating that surface-only sampling would slightly underestimate water column concentrations. Conversely, relative percent differences

Figure 5. Relative percent difference between the water surface and depth-weighted concentration in water samples by (A) sampling location, (B) microplastic type, and (C) particle size fraction. [MEP = Milwaukee River at Milwaukee; MWW = Menomonee River at Ridge Blvd.; KKF = Kinnickinnic River at S. 1st St.; INH = Milwaukee Inner Harbor; OUH = Milwaukee Outer Harbor; LAK = Lake Michigan].

between the water surface and depth-weighted concentrations were 22–162% at estuarine (KKF, INH, and OUH) and lake (LAK) locations, indicating the overestimation of overall water column microplastic content by sampling only the water surface (Figure 5A). Surface-only sampling overestimated water column concentrations of some particle types more than others (Figure 5B). Water column fiber concentrations appear to be the least overestimated (12%) by surface-only sampling because fiber concentrations were not significantly different throughout the water column. However, water column concentrations of films, fragments, pellets/beads, and foams may be considerably overestimated by surface-only sampling (up to 116% for the samples in this study). Surface-only sampling overestimated water column concentrations in all fractions of particle sizes as well (Figure 5C). The smallest size fraction (0.355–0.999 mm, 49% of particles analyzed) was the least overestimated (12.5%) by surface-only sampling, while the medium particle size fraction (1.00–4.749 mm, 48% of particles analyzed) was overestimated by 95%. Surface-only sample results for the largest size fraction overestimated the total water column concentrations by 66% but only represented 3% of all particles analyzed, so additional data would be needed to gain confidence in these results. Overall, results indicate sampling throughout the water column provided a more complete understanding of microplastic presence in addition to the valuable information gained by many studies that focused only on water surface sampling.

A very limited number of studies have compared water surface and subsurface microplastic concentrations. In the only other freshwater study, fibers were found to be vertically mixed in the Marne River, Paris, but other microplastic types were not analyzed.[31] Although fiber concentrations were greater than those from the current study, fiber concentrations did not vary significantly within the water column or across the sampling locations. Studies from the North Atlantic have also reported fibers to be similarly distributed at the water surface and in the water subsurface (0–5 m depth).[30,54,55] However, at 5 m depth in the marine environment, concentrations of fragments, foams, films, and pellets/beads were found to approach zero,[30,55] whereas at the OUH and LAK locations, they were similarly distributed with depth (Figure 3), which is similar to a recent finding from the Monterey Bay, California, pelagic system where microplastics were found to be distributed from 5 to 1000 m depths.[56]

Collectively, the small number of studies that have examined the vertical distribution of microplastics have indicated that results can vary by location, and that accuracy of depth-weighted mean concentrations and associated loading estimates would be improved by sampling at multiple depths rather than only at the water surface.

Multiple-depth sampling in the current study highlighted the uneven distribution of polymer types through water column compartments and sediment (Figure 6A,B). There was a clear gradient of polymer presence with depth: the presence of low-density particles decreased from the water surface to the subsurface to the sediment, and the presence of high-density particles had the opposite result (Figure 6A). Individual polymers had more variable results with the lowest-density particles (e.g., PS), primarily present as expanded polystyrene, almost exclusively detected at the water surface, other low-density particles more prevalent in the water surface and subsurface than in sediment samples (PP, ethylene/propylene/diene terpolymer (E.P.D.TP), LDPE), and most higher-density
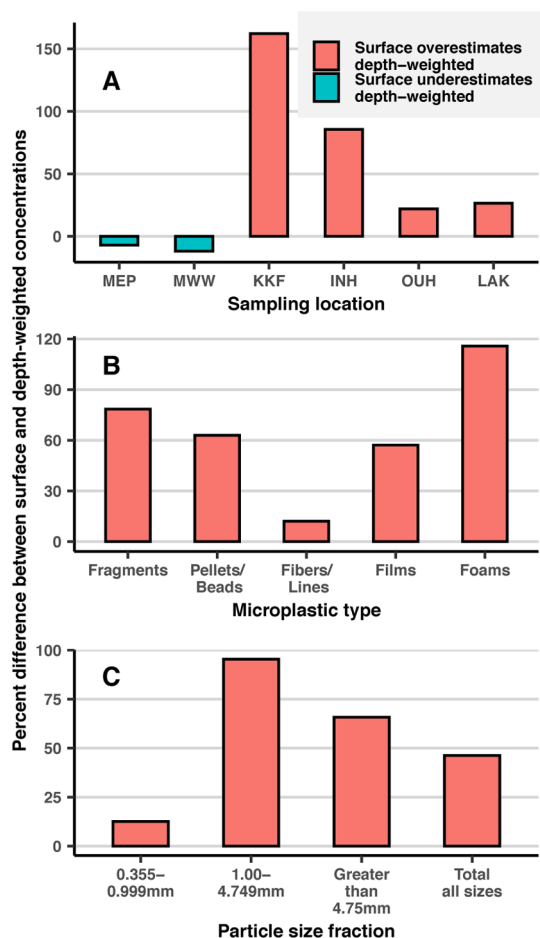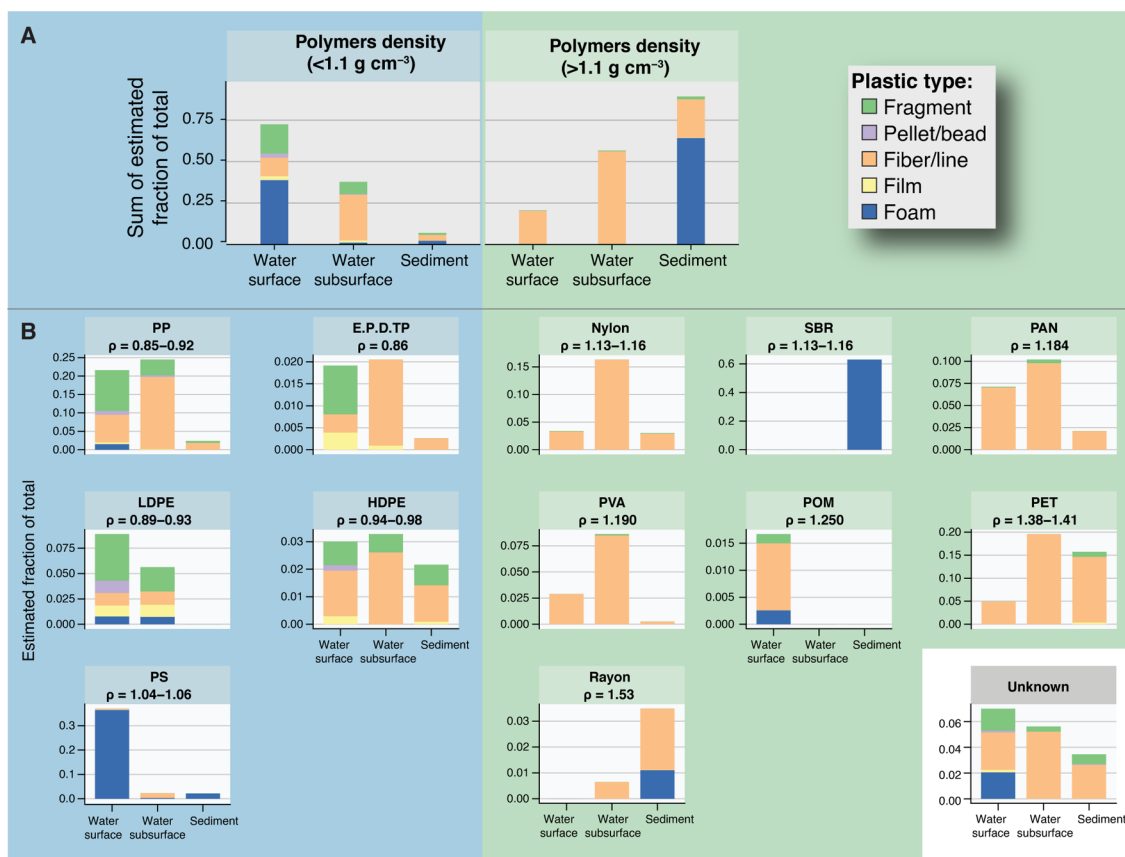
Figure 6. (A) Sum of the estimated fraction of total particles and polymers by density. (B) The estimated fraction of total particles and polymers by compartment sampled, arranged by increasing density (ρ)[58,62−64] from top left to right within each color group. Roughly 97% of the foam in the sediment was black foam identified as SBR. The density of tire wear particles was used for SBR. Only polymers that represented greater than 1% of particles collected are represented in individual polymer charts. [PP = polypropylene; E.P.D.TP = ethylene/propylene/diene terpolymer; LDPE = low-density polyethylene; HDPE = high-density polyethylene; PS = polystyrene; Nylon = nylon; SBR = styrene butadiene rubber; PAN = polyacrylonitrile; PVA = poly(vinyl acetate); POM = polyoxymethylene; PET = poly(ethylene terephthalate); Unknown = the polymer was not identified; ρ = density].

polymers more prevalent in the water subsurface or sediment samples than in water surface samples (PET, SBR, Nylon, poly(vinyl acetate) (PVA), and Rayon). Tire wear particles (ρ = 1.13−1.16 g cm^{-3})[57] containing SBR were exclusive to the sediment (Figure 6B).[27,51,58] Similar to the current study, research from Monterey Bay, California observed higher-density polymers, especially PET, to be the most common polymer identified from all water subsurface depths and pelagic species sampled.[56] Additionally, in a modeling study in freshwater systems, retention of microplastics with a size greater than 5 μm in the sediment increased as the polymer density increased.[59] This vertical sorting of polymers, a function of density and other factors such as mineralization, biofilm colonization, and functional fillers added during manufacturing,[60,61] further demonstrates how surface-only sampling may yield biased results.

4.2. Sediment. Sediment sampling revealed a ubiquitous presence of microplastics although concentrations and the presence of different particle types were highly variable across the nine sampling locations. Black foams were the dominant microplastic type in sediment samples from the Milwaukee and Menomonee Rivers and accounted for 66% of sediment microplastics overall. The majority of these black foam particles (~97%) were SBR and could provide a basis for when certain synthetic material is placed into a different or new morphological category other than the foam, as was done

for this study. Likely, sources of SBR include tire wear particles, other roadway products (e.g., roadway crack sealant, asphalt containing rubber), crumb rubber from artificial turf athletic fields, and rubber mulch used in landscaping and on playgrounds. In studies from two estuaries in South Carolina[51] and nearshore tributary and beach sediments of northern Lake Ontario,[27] a similar observation of black microplastic particles was made in sediment samples. A very high abundance of the black particles was noted in the South Carolina estuaries but not in northern Lake Ontario, and both studies categorized these black particles as fragments and suggested them to be tire wear particles.[27,51] Logic suggests that tire wear emission rates and, therefore, concentrations of tire wear particles in the sediment would positively relate to the degree of urbanization in the watershed. Estimates from the United States indicate that tire wear particle emissions from passenger cars and trucks are approximately 1 120 000 metric tons per year with about two-thirds of the emissions occurring in urban environments.[7] Transport of these particles to receiving water bodies would likely occur through multiple vectors such as atmospheric deposition and stormwater runoff. However, the lack of tire wear particles containing SBR in samples from the most urban locations (i.e., those on the Kinnickinnic River) indicates a more in-depth analysis of transport pathways and sources warrants consideration to better understand the presence of SBR containing particles.

Previous research from nearshore and tributary sediments around Lake Ontario and Lake Erie observed a large range in sediment microplastic concentrations similar to the current study.[27,28] In addition, compared with these studies, which reported a dominance of fragments and fibers, the current study found SBR black foams and fibers to be most dominant, although the placement of black SBR particles in the foam category could have alternatively been categorized as fragments.[27,51] Studies from two lakes in central Italy and an urban lake in the UK found concentrations and relative abundances of fibers similar to those in the current study.[65] There are several potential explanations for variability in particle-type abundance among different studies including differences in sources, variable transport pathways, differences in methods and objectives, and subjectivity of personnel in laboratory and field protocols.

4.3. Final Perspectives. Assigning sources to microplastic particles based on the shape and polymer type is challenging and would be speculative due to their size, fragmented nature, the diversity of sources, variability in particle description and categorization, and time-intensive process to identify 100% of particles from a water or sediment sample using FTIR or other analytical techniques. For example, a PP fragment could have started out as an auto part, food container, bottle cap, or straw. Similarly, a PP fiber could have come from rope, clothing, or carpet.[54,63] More information is needed to identify and confirm microplastic sources.

This study contributes to our understanding of microplastic transport and fate in freshwater environments by demonstrating how different particle types can vertically partition between the water surface, subsurface, and sediment, based on hydrologic environment and particle/polymer density. This vertical partitioning of particles is an important consideration when estimating microplastic concentrations and the use of these concentrations to compute loads: studies, which sample only the water surface, may under or overestimate concentrations and loads of some particle and polymer types.

Standardized methods for sampling the water surface, subsurface, and sediment, including standard approaches in laboratory identification techniques and data reporting, are greatly needed for the advancement of microplastic research and comparability among studies. This investigation provides a foundation for the development of a more comprehensive sampling approach that will reduce bias in the mean concentration of microplastics in a water column. The methods presented herein offer steps toward a standardized sampling approach that would enhance the ability to quantify microplastics in the aquatic environment. Adoption of these steps in addition to others can lead to a better understanding of transport pathways, sources, and environmental effects that can provide resource managers with the information necessary to develop effective remediation and control measures.

ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.est.9b03850.

> Sample locations, watershed basin land cover characteristics table, net depths table, water surface and subsurface sample collection, schematic illustration for sampling water column at depth, sediment processing methodology, conceptual example and formula for depth-weighted concentration calculation, field blank results, laboratory comparison of analyst count one and analyst count two, total number of microplastic particles collected, total number of particles analyzed using FTIR spectroscopy, total ion chromatogram results, duplicate environmental sample comparison results, mean relative abundance of microplastic particles by type for water and sediment samples, mean water surface microplastic concentration, percentage of different polymers identified from FTIR analysis on the water surface, subsurface and sediment particles, mean gas chromatogram for styrene butadiene rubber sediment particles, and high-resolution gas chromatography mass spectrometry spectra results (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: plenaker@usgs.gov. Phone: 608.821.3829.

ORCID ⓘ

Peter L. Lenaker: 0000-0002-9469-6285
Austin K. Baldwin: 0000-0002-6027-3823
Steven R. Corsi: 0000-0003-0583-5536

Present Address

⊥Penn State Behrend, 4701 College Dr. 27 Hammermill, Erie, Pennsylvania 16563, United States (S.A.M.)

Author Contributions

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

Notes

The authors declare no competing financial interest.

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