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DOI:
10.1016/j.scitotenv.2023.162940

Document Version
Publisher's PDF, also known as Version of record

Citation for published version (Harvard):
Kurki-Fox, JJ, Doll, BA, Monteleone, B, West, K, Putnam, G, Kelleher, L, Krause, S & Schneidewind, U 2023, 'Microplastic distribution and characteristics across a large river basin: Insights from the Neuse River in North Carolina, USA', *Science of the Total Environment*, vol. 878, 162940.
https://doi.org/10.1016/j.scitotenv.2023.162940

Science of the Total Environment 878 (2023) 162940

Contents lists available at ScienceDirect

Science of the Total Environment

journal homepage: www.elsevier.com/locate/scitotenv

Microplastic distribution and characteristics across a large river basin: Insights from the Neuse River in North Carolina, USA

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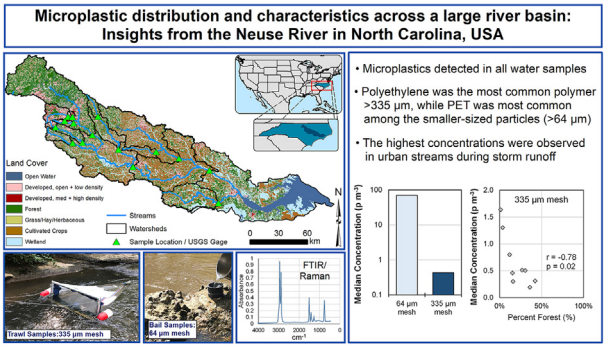
HIGHLIGHTS

- Stream water and sediment were analyzed for microplastics (MP) at 15 locations across a large river basin.
- MPs were detected in all water samples.
- Highest MP concentrations occurred in urban streams during storm runoff.
- MP concentrations identified with a 64 μm mesh were on average ~170 times larger than with a 335 μm trawl net.
- Polyethylene was the most common polymer found in trawl net samples, while PET was most common among the smaller-sized MP.

GRAPHICAL ABSTRACT



ARTICLE INFO

Editor: Yolanda Picó

Keywords:
Microplastics
Streamflow
Urban development
Sediment
Watershed
Sampling method

ABSTRACT

While microplastics (MP) have been found in aquatic ecosystems around the world, the understanding of drivers and controls of their occurrence and distribution have yet to be determined. In particular, their fate and transport in river catchments and networks are still poorly understood. We identified MP concentrations in water and streambed sediment at fifteen locations across the Neuse River Basin in North Carolina, USA. Water samples were collected with two different mesh sizes, a trawl net (>335 μm) and a 64 μm sieve used to filter bailing water samples. MPs >335 μm were found in all the water samples with concentrations ranging from 0.02 to 221 particles per m^3 (p m^{-3}) with a median of 0.44 p m^{-3}. The highest concentrations were observed in urban streams and there was a significant correlation between streamflow and MP concentration in the most urbanized locations. Fourier Transform Infrared (FTIR) analysis indicated that for MPs >335 μm the three most common polymer types were polyethylene, polypropylene, and polystyrene. There were substantially more MP particles observed when samples were analyzed using a smaller mesh size (>64 μm), with concentrations ranging from 20 to 130 p m^{-3} and the most common polymer type being polyethylene terephthalate as identified by Raman spectroscopy. The ratio of MP concentrations (64 μm to 335 μm) ranged from 35 to 375, indicating the 335 μm mesh substantially underestimates MPs relative to the 64 μm mesh. MPs were detected in 14/15 sediment samples. Sediment and water column concentrations were not correlated. We estimate MP (>64 μm) loading from the Neuse River watershed to be 230 billion particles per year. The findings of this study help to better understand how MPs are spatially distributed and transported through a river basin and how MP concentrations are impacted by land cover, hydrology, and sampling method.

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http://dx.doi.org/10.1016/j.scitotenv.2023.162940
Received 19 January 2023; Received in revised form 7 March 2023; Accepted 14 March 2023
Available online 20 March 2023

1. Introduction

The proliferation of inexpensive plastics since the end of World War II has resulted in significant environmental concerns about plastic pollution, particularly in regard to microplastics (MPs) in aquatic ecosystems (Krause et al., 2021; Kukkola et al., 2021). MPs are defined as plastic particles < 5 mm in size (Arthur et al., 2009), and come in a variety of shapes such as fibers, fragments, pellets, spheres, flakes, foams and films (Rios Mendoza and Balcer, 2019). They originate from a wide variety of point and non-point sources including wastewater, industrial processes, tire wear, and the degradation of discarded plastics (e.g., plastic bags, bottles, food containers). Over time, the problem of plastic pollution has become more acute as plastics in the aquatic environment break down into smaller pieces, but depending on the polymer type, complete degradation occurs only over very long-time scales. MPs are now ubiquitous in the aquatic environment and their presence has been documented in various rivers environments (Baldwin et al., 2016; Dendievel et al., 2023; Frei et al., 2019; Simon-Sánchez et al., 2019), lakes (Eriksen et al., 2013), estuaries (Nel et al., 2020; Yonkos et al., 2014), the open ocean (Cózar et al., 2014), groundwater (Viaroli et al., 2022; Re, 2019; see Moeck et al., 2022 for a recent review) and even the deep ocean (Choy et al., 2019). MPs are distributed across the globe, from the equator to both poles (Simon-Sánchez et al., 2019), with concentrations rising with increasing amounts of plastic pollution (Borrelle et al., 2020).

There are many unknowns regarding the severity or long-term environmental and human health impacts of MPs, but research has demonstrated that MPs pose an increasing threat to marine (Thompson, 2015) and freshwater biota (Kukkola et al., 2021). MPs have been found in sea turtles, fish, whales, sea birds, and other much smaller marine organisms (de Sá et al., 2018; de Stephanis et al., 2013; Mascarenhas et al., 2004). Because of the surface chemical properties of plastics and their high surface area to volume ratio, toxic substances such as persistent organic pollutants (Rochman et al., 2013) and heavy metals (Munier and Bendell, 2018) readily bind to MPs (Rochman, 2015). Leaching of plastic additives is also a concern (Koelmans et al., 2014). Because MPs are so widespread there is also the risk of bioaccumulation of toxins in the food chain (Benson et al., 2022; Teuten et al., 2009).

Previous research indicates a wide range of MP concentrations in river waters from <0.5 p m^{-3} in France (Dris et al., 2015) to over 1000 p m^{-3} in Chinese rivers (Lin et al., 2018). Differing sample collection procedures, analysis, and reporting methods make comparisons problematic. Studies using a ~330 μm mesh size in rivers have generally reported average concentrations of 0.3 p m^{-3} (Dris et al., 2015) to 4.2 p m^{-3} (Baldwin et al., 2016), with higher values reported in urban areas (e.g., Lenaker et al., 2019). Recent research also indicated higher MP concentrations in more populated watersheds and potential correlation with stream discharge in natural rivers (Baldwin et al., 2016; Moore et al., 2011).

Like other pollutants that originate in the terrestrial environment, plastics and MPs enter waterways and make their way through the river network before depositing into coastal waters (Jambeck et al., 2015; Margenat et al., 2021; Waldschläger et al., 2020). However, recent studies have shown that rivers are not just conduits for MPs on their way to the ocean, but depending on flow regimes and river morphology, riverbeds and banks can act as MP sinks over various timescales (Drummond et al., 2022, 2020). Previous studies have reported widely variable MP concentrations along rivers (e.g., Kapp and Yeatman, 2018; Mani et al., 2015), with concentrations potentially impacted by land use, population density (e.g., Huang et al., 2020), the location of point source inputs, and built infrastructure such as dams and reservoirs (Huang et al., 2020; Gao et al., 2023). MPs in rivers encompass a diverse mix of shapes and polymer types (e.g., Huang et al., 2020; Kapp and Yeatman, 2018; Lechner et al., 2014; Sankoda and Yamada, 2021). There are still many unknowns and a detailed understanding of how MPs are distributed within and transported through river catchments is imperative to evaluate the threat MPs pose to local freshwater environments and ecosystem services (Krause et al., 2021). Yet, there have been few (e.g., Baraza et al., 2022; Huang et al., 2020; Sankoda and Yamada, 2021; Yuan et al., 2022) watershed-scale studies of MPs distribution and sources and hence the mechanisms driving MP distributions and residence times across river basins and their transport towards the ocean remain largely unknown.

The primary objectives of this study were to: (1) characterize and quantify MP pollution throughout a large river basin, using the example of the Neuse River in North Carolina, USA, (2) identify possible relationships between land cover, hydrology and location in the watershed to MP concentrations, (3) characterize the composition of plastic types, (4) evaluate the impacts of different MP sampling techniques on concentrations established for MP in the water column, and (5) provide a first estimate of MP loading towards coastal waters. The findings of this study will help us better understand how MP are spatially distributed and transported through a major North Carolina watershed covering both piedmont and coastal plains regions and how MP concentrations are impacted by land cover, hydrology and sampling method.

2. Methods

2.1. Study location

The Neuse River Basin drains a catchment area of 14,600 km^2 into the Pamlico Sound in North Carolina, USA. The upper part of the basin is in the Piedmont physiographic region and is highly urbanized, containing the rapidly developing Raleigh-Durham metropolitan area that is home to a majority of the Basin's ~2 million inhabitants. The lower part of the basin covers the Coastal Plain physiographic region and is more rural, dominated by forest and agricultural land. Fifteen U.S. Geological Survey stream gaging stations, representing a range of sub-catchment sizes and land cover composition, were selected for MP sampling (Fig. 1). Watershed areas contributing to each of the gaging stations ranged in size from small tributaries in the upper watershed draining 3.0 km^2 to the mainstem of the Neuse River near the coast draining 10,100 km^2. Land cover varied from mostly forested and agricultural to highly urbanized (Fig. 1, Table S1).

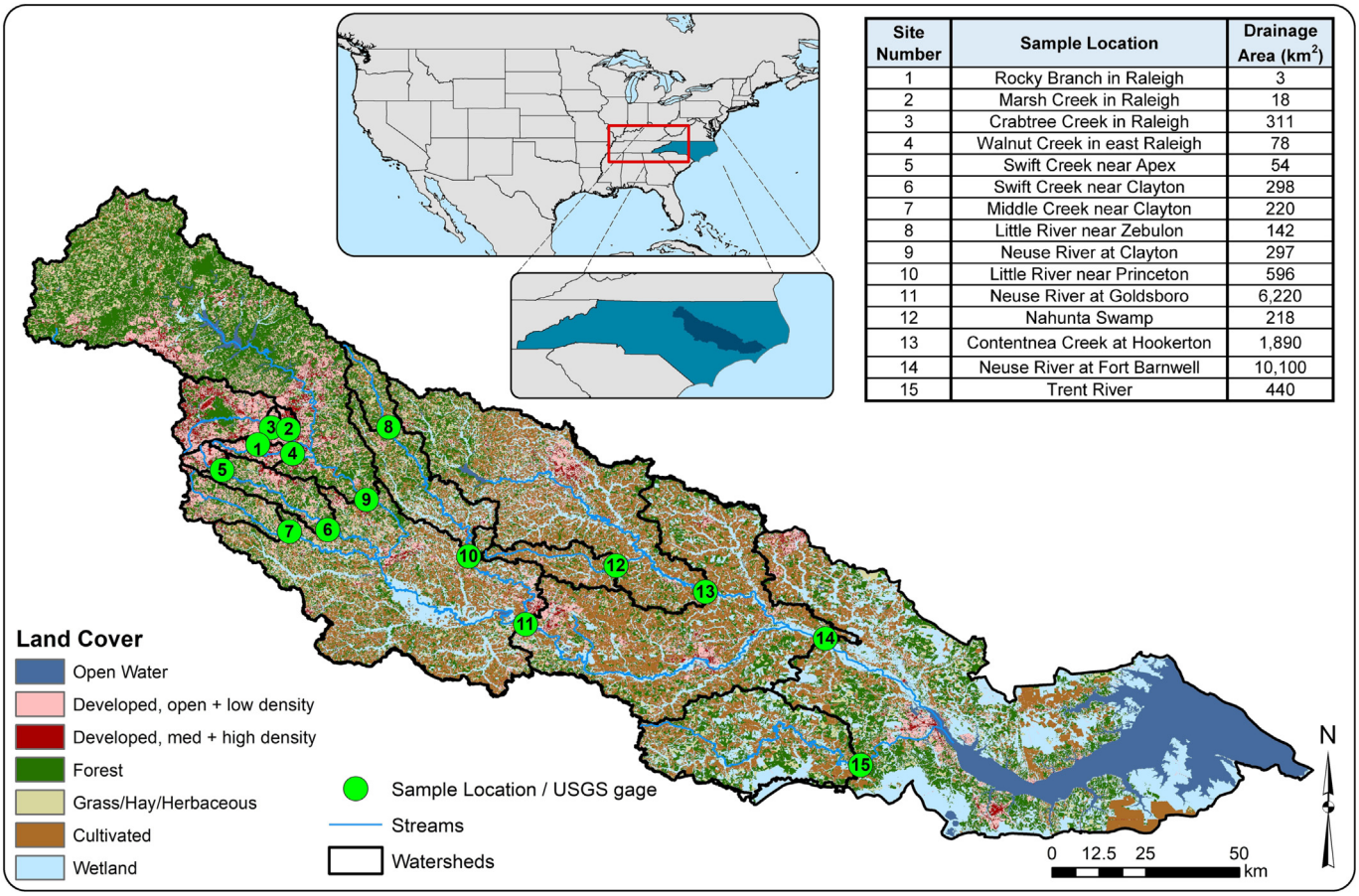
Potential MP sources in the Neuse River Basin are likely similar to other watersheds. Sources include plastic debris that has degraded into smaller pieces from litter and mismanaged waste in urban areas (e.g., bags and packaging films, foam or plastic containers, bottles), plastics from agriculture in the middle and lower basin (e.g., packaging, mulching film, biosolids), building materials from the rapidly developing upper basin (e.g., films, resins), and plastic manufacturing. There is also a maximum of 770,000 m^3 per day of permitted wastewater discharges (about 8 % of the mainstem river's mean daily flow), which presents another potential source of MPs (e.g., Conley et al., 2019). However, actual discharges are typically only a fraction of the permitted maximum.

2.2. Sample collection

2.2.1. Trawl samples (335 μm)

MP samples were collected bimonthly from July 2020 to July 2021 (6 times) at 15 locations (Fig. 1). An effort was made to sample across a range of streamflow conditions at each location (Table S2). Samples were collected closely following the methods described by Baldwin et al. (2016) using a 335 μm mesh, 1.5 m long neuston net with a 100 cm wide by 40 cm height frame opening (Sea Gear Corp., Miami, FL, USA). Buoys were attached to the sides of the frame so that the net captured the upper 20–25 cm of the streamflow (Fig. S1). Sample collection time ranged from 3 to 15 min depending on the streamflow and clogging of the net due to organic material accumulation. The average velocity of the streamflow entering the net was measured using a mechanical velocity meter (Sea Gear Corp.) attached at the net opening using stainless steel cables (Fig. S1). The total volume of water filtered through the net was calculated as the depth of water captured by the net, multiplied by the frame width, stream velocity and duration of sample collection. Total volumes ranged from 9 to 134 m^3.

The samples were collected as close to the thalweg as possible. Samples were collected from bridges, boat docks, boat, and by wading, dependent



Site Number	Sample Location	Drainage Area (km^2)
1	Rocky Branch in Raleigh	3
2	Marsh Creek in Raleigh	18
3	Crabtree Creek in Raleigh	311
4	Walnut Creek in east Raleigh	78
5	Swift Creek near Apex	54
6	Swift Creek near Clayton	298
7	Middle Creek near Clayton	220
8	Little River near Zebulon	142
9	Neuse River at Clayton	297
10	Little River near Princeton	596
11	Neuse River at Goldsboro	6,220
12	Nahunta Swamp	218
13	Contentnea Creek at Hookerton	1,890
14	Neuse River at Fort Barnwell	10,100
15	Trent River	440

Fig. 1. Land cover and sample locations in the Neuse River Basin study area.

on the size of the river, access points, discharge and stage at the time of sampling (Fig. S1, Table S2). In addition, two deeper water-column samples were collected using a smaller version of the neuston net (30 cm diameter).

After sample collection the net was suspended from a wood frame and washed from the outside using tap water, either pumped from a tank using a 414 kPa washdown pump in the field or from a rubber hose connected to a municipal potable water supply. A volume of 35 to 50 L of water was used to wash captured materials down the net into a 335 μm mesh cod end after each sampling. The cod end was then emptied into a 200 μm stainless-steel sieve where large fragments of organic debris (i.e., leaves, stalks, sticks, acorns, etc.) and occasional small fish were rinsed and discarded. The contents of the stainless-steel sieve were then washed into glass sample jars and refrigerated until delivery to the lab for analysis.

2.2.2. Bailing samples (64 μm)

A single bailing sample was collected at each study site in either winter or spring of 2021 to evaluate MP concentrations at a size range of 64–335 μm. Bailing was used as sampling with a trawl net with such small mesh sizes is usually not feasible. The sample was collected by filtering 100 L of water through a 64 μm sieve at each site. While positioned downstream of the sample collection point, a 5 L stainless steel bucket was used to repeatedly bail the water from the top 15 cm of the water column. Sampling took about 10 min. The filtered sample was then washed into a glass jar using deionized water (DI). The sample equipment and glass jars were rinsed with DI before each sample was collected. The samples were transported to the lab at NC State University (NCSU) and the glass jar covers were removed and replaced with aluminum foil. Perforations were made in the foil covers and the jars were placed in the oven at 60 °C until all the water was evaporated. After drying, the lids were replaced and sealed with Parafilm and tape. The samples were then shipped to the University of Birmingham, UK for further analysis.

2.2.3. Sediment samples

Sediment samples were collected once at each sampling location together with the bailing samples. Approximately 100 g of sediment were collected at the edge of the stream just below the water line. The samples were collected from the top 5 cm of the stream bed using a stainless-steel tube and stainless-steel spade. Standing downstream of the sample location, three samples were collected about 1 m apart moving upstream. The three samples were homogenized in a glass jar and transported to the lab at NCSU where they were dried in the same manner as described for the bailing samples. All sampling equipment and jars were rinsed with DI water prior to sample collection.

2.3. Sample processing and analysis

2.3.1. Trawl samples

2.3.1.1. Sample processing. Chemical digestion to remove organic material was performed on each sample by catalyst wet peroxide oxidation for approximately 1 h by adding 20 mL iron (II) sulfate ($FeSO_4$, Sigma Aldrich) and 20 mL 29–32 % hydrogen peroxide (H_2O_2, Thermo Fisher Scientific) and heating to 60 °C. H_2O_2 was added in 10 mL increments if the reaction ended prematurely. After digestion, the sample was rinsed with DI water through a 100 μm nylon filter. Potential MP particles and fibers were visually identified with a magnifier lamp, removed using stainless steel forceps and placed in an acrylic container with a drop of methanol.

The remains of the sample were subjected to density separation. First, 15 g of salt (NaCl, EMD Millipore Corporation) per 50 mL of solution were added to the sample jars and dissolved. The sample was left to settle

for at least 1 h for separation to occur. The putative MP particles were individually removed, and the surface liquid and buoyant particles were decanted and sieved. The sieved materials were visually inspected again, and all putative MPs were removed and placed into the acrylic container. The remainder of the sample, containing the settled materials, was inspected in the same manner.

Methanol was added to the acrylic containers holding the putative MP particles, the containers were placed into a 1210 Branson sonicator, and the contents were cleaned for 5 min. Next, the particles were examined using a Wolfe SMZ-161 stereomicroscope and putative MP particles were extracted, placed into clean, acrylic containers, and dried at 55 °C. Once fully dry, the particles were placed into a glass desiccator prior to polymer identification analysis. The particles were also categorized as fibers or fragments during the latter half of the project. See Fig. S2 for an example of putative MP particles extracted during sample processing procedures.

2.3.1.2. μFTIR-ATR analysis. All the putative MP particles were individually placed on aluminum EZ-Spot Micro Mounts. Analysis was conducted with a μFTIR (Thermo Fisher Scientific Nicolet iN10 MX) and an Attenuated Total Reflectance attachment (Thermo Fisher Scientific Nicolet iZ10) in reflectance mode. The spectral range was from 675 to 4000 cm^{-1} taking 16 scans in high resolution and the possible identities were compared to multiple polymer and biological libraries within the Omnic Picta™ software (Thermo Fisher Scientific) to determine the best fit. A threshold of 70 % was used for positive polymer identification. For three samples in which >2000 putative MP particles were identified, a random selection of 10 % of the particles was subjected to μFTIR analysis.

2.3.2. Sediment and bailing samples

2.3.2.1. Sample processing. MPs were extracted from the sediment samples by density separation using Sediment-Microplastic Isolation (SMI) units and $ZnCl_2$ (density = 1.45 g cm^{-3}) as described in Coppock et al. (2017) and Nel et al. (2019). Approximately 35 g of sediment and about 750 mL of $ZnCl_2$ were added to the SMI units and left to settle for 24 h. The supernatant was subsequently decanted over a 64 μm sieve and the SMI unit was disassembled and rinsed as described in Nel et al. (2019) to avoid MP loss to the walls of the unit. Sieve contents were then flushed into glass beakers (250 mL) and organic matter was digested over a 24-hour period using Fenton reagent (i.e., 30 % H_2O_2 mixed with Fe^{2+} (aq) (0.05 M)). During digestion, samples were covered loosely with aluminum foil to prevent airborne contamination. Digested samples were filtered over a 64 μm sieve and backwashed with DI into 250 mL glass beakers before staining with Nile Red (5 μg mL^{-1}). The staining process lasted for 1 h during which beakers were repeatedly and gently shaken. Stained samples were filtered onto GF/D filters (Whatman, 47 mm diameter, 2.7 μm pore size) using a glass vacuum filtration system (Merck) and a vacuum pump (GAST). The pump funnel was rinsed with DI to avoid particle loss to its glass surface. A UV light and yellow goggles were used to inspect glass beakers and the filtration system for potential MPs that were then placed on the respective GF/D filters. Filters were stored in polypropylene Petri dishes and oven-dried for 24 h at 50 °C. Bailing samples were digested, stained and filtered in a similar fashion, but an initial density separation was unnecessary.

2.3.2.2. Fluorescence microscopy. A fluorescence microscope (Olympus MVX-ZB10, 1 × 0.25 N objective (MVPLAPO 1×, Olympus, U-M49002XL green fluorescent protein filter cube (excitation filter: 470/40 nm, dichroic mirror: 495 nm high pass, emission filter: 525/50 nm), 100 W mercury light source)), was used to identify putative MP on the stained GF/D filters by applying 12 % light intensity on a 32× magnification with 50 ms exposure time at a set threshold of 100 fluorescence a.u. (arbitrary units). Fluorescence intensity was measured with a DP74 color camera using CellSens (Olympus). Parameters recorded for each MP included Ferret diameter, area, color and morphology (shape). Before use, the microscope had been calibrated and the fluorescence thresholds had been validated by experiments described in Kukkola et al. (2023). Putative MP were also observed under bright field (63× magnification). A morphology-specific identification key was used to aid in MP identification as outlined in Kukkola et al. (2023).

2.3.2.3. Raman spectroscopy. While fluorescence microscopy was performed on each sample location individually, Raman spectroscopy was conducted on composite samples for determining polymer types and confirming MP identification. For these, about 20 % of the putative MP from the sediment samples and 40 % of the water samples were randomly chosen and placed on Whatman Anodiscs (0.2 μm pore size, 25 mm diameter). A Renishaw Qontor Raman Microscope (Renishaw PLC, UK, 10× objective, 5 s exposure, three accumulations, 50 % power with pinhole in (approximately 30 mW at sample)) was used for the analysis. It was equipped with a 785 nm laser and spectra were acquired for the region from 607 to 1712 cm^{-1} using WiRE 5.5 (Renishaw PLC). Spectra were preprocessed and analyzed in Spectragryph v1.2.16.1 (Menges, 2020) as discussed in more detail in Kelleher et al. (2023). Polymer identification was made using the Identify function to an in-house library to match the sample spectra with confirmed polymer spectra. Results with a matching index of ≥70 % were considered as positive polymer identification.

2.4. Quality assurance and control

All materials used to secure the trawl net and other equipment were made of aluminum or stainless steel. Care was taken to stand downstream of the sample location at all times. The trawl net was inspected for damage prior to each sample collection. In the lab, all processing of the trawl collected samples was performed under a laminar flow fume hood to prevent particle contamination from the air and non-synthetic clothing and cotton lab coats were worn when processing the samples. The sample containers were covered when not accessing the samples and metal and glass tools and containers were used for all analyses (except for the acrylic containers).

All solutions used in the University of Birmingham laboratory were prefiltered over pre-furnaced Whatman GF/D filters. Laboratory equipment was washed with detergent and rinsed with DI between uses. Samples were processed under a laminar flow fume hood. Researchers wore nitrile gloves, 100 % cotton lab coats and non-synthetic clothing during sample processing and analysis. All analysis rooms contained HEPA air filtration units (WINIX Air Purifier Zero S) to minimize sample contamination by airborne particles. Lab blanks (n = 2) run during sample extraction and digestion showed no MP contamination.

Because the bailing and sediment samples targeted a much smaller size fraction than the trawl sampling, five air blank samples were collected during fieldwork to test for atmospheric deposition. These samples were processed in the same way as the collected sediment samples and underwent fluorescence microscopy. Three of these blanks were found to contain no plastic particles, however two blanks collected in the highly urbanized Raleigh area (near Crabtree Creek and Marsh Creek, respectively) indicated the presence of potential atmospheric deposition (one fragment, one fragment and two fibers, respectively) or potential contamination of the jars, the latter indicating a possible overestimate of 0 to ~20 % for those sampling sites.

2.5. Data analysis

MP concentrations were calculated for each water (particles per cubic meter, p m^{-3}) and sediment (particles per kilogram of soil dry weight, p kg^{-1}) sample. Water sample MP concentrations were compared to stream discharge at the time of sampling using the non-parametric Spearman Correlation test. The polymer types were compared between samples for the trawl data and cumulatively for the bailing and sediment data. Trawl sampling (335 μm mesh) results were compared to samples obtained from bailing (64 μm) using a Spearman Correlation test and by calculating the ratio of the MP concentrations obtained using the two mesh sizes (64 μm/335 μm). The trawl sampling plastic particles were divided into ten groups (e.g., polyethylene, polypropylene, etc.) based on the presence of polymers that represented at least 2 % of the overall plastic particles found. Polymers

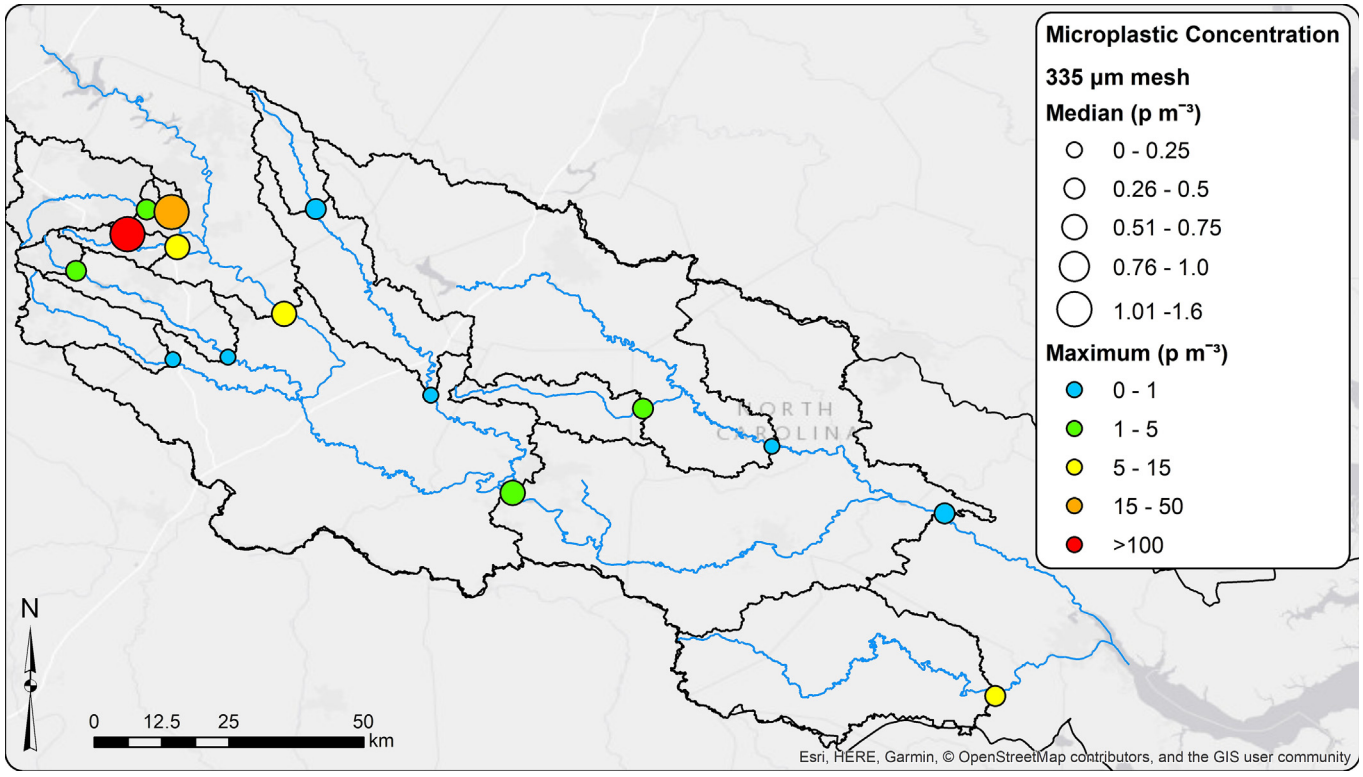


Fig. 2. Water sample results (335 µm) across the Neuse River Basin.

that made up <2 % of the total particles were assigned to a miscellaneous plastics group. The composition of polymer types was calculated for each site and principal component analysis (PCA) was completed using a matrix of the polymer types from each sample to evaluate if the samples were grouped by common factors including sample location, sample date (season), and streamflow (the samples were sorted by streamflow magnitude and grouped by the resulting rank). To examine the impacts of watershed land cover and development, the percent development and percent forest cover from the 2019 National Land Cover Database (MRLC, 2022) and population density from the 2020 U.S. Census (U.S. Census Bureau, 2022) were compared to the median MP concentration for each of the nine tributary catchments. The Spearman Correlation test was used to test for significant relationships.

2.5.1. Loading estimate

A first estimate of the total annual MP loading from the Neuse River basin to the Pamlico Sound was calculated. Following an approach proposed by Eo et al. (2019), the stream channel was divided into a surface

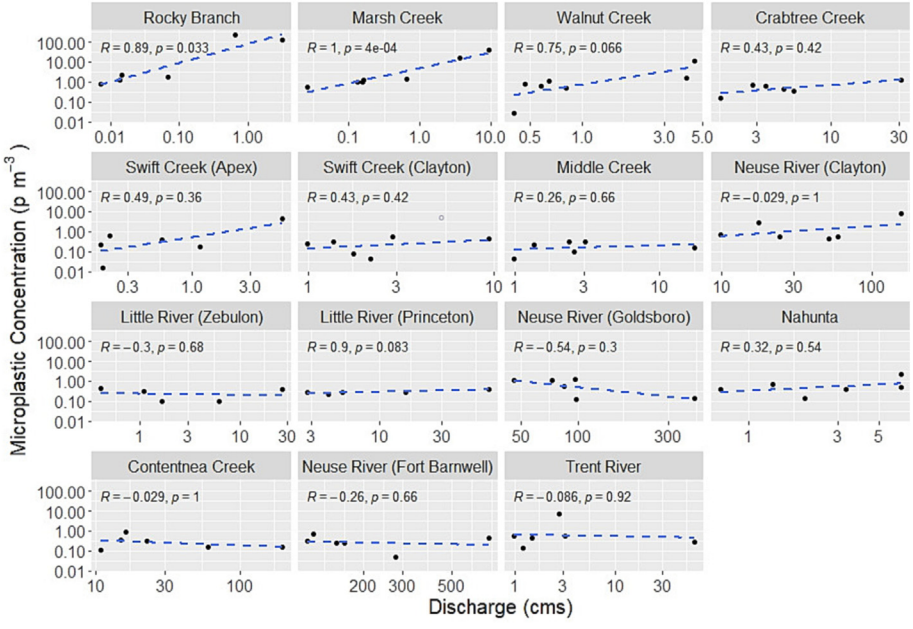


Fig. 3. Trawl (335 µm mesh net) collected MP concentration versus stream discharge. The Spearman correlation coefficient and associated *P*-value are shown for each location.

(top 0.2 m) and subsurface component. Because only two subsurface samples were collected, we assumed the subsurface MP concentration was 1/3 of the surface concentration based on the data reported by Eo et al. (2019). The mean MP concentration (p m^{-3}) for each site was then multiplied by the total flow volume for 2020 and 2021 and averaged to arrive at a total annual load in particles per year. This analysis was completed for both the trawl collected samples (335 μm mesh) and the bailing samples (64 μm mesh). The MP concentration and flow at Fort Barnwell, the most downstream stream gage on the Neuse River, were used for this estimate.

3. Results

3.1. Trawl sample results (335 μm)

MPs were detected in all the water samples. Concentrations for the 90 samples collected by trawling using the 335 μm mesh ranged from 0.02 p m^{-3} to 221 p m^{-3} with a median of 0.44 p m^{-3}; however, only five of the samples had concentrations >10 p m^{-3} (Fig. 2, Table S2). The highest concentrations were generally observed in vicinity of the most urbanized areas of the upper watershed (i.e., in and around Raleigh). There was one sample collected in the Trent River during a dry period with very low streamflow (stagnant conditions), where an MP concentration of 11 p m^{-3} was recorded. The other samples collected at this location had much lower concentration but were collected at higher streamflow, potentially indicating the buildup of MPs during dry periods with less dilution of local sources.

3.1.1. Impact of streamflow

The relationship between stream discharge and MP concentration was not consistent across all sites (Fig. 3). For the smaller, urban streams in the upper basin (Rocky Branch, Marsh, Walnut, Crabtree and Swift (Apex) Creeks), there appears to be a trend of increasing MP concentration with increased discharge; however, this correlation was only significant ($\alpha = 0.05$) for Rocky Branch and Marsh Creek (the most developed catchments). There was no clear relationship with flow for the other smaller catchments or along the mainstem river segments.

3.1.2. Watershed attributes

There was a strong correlation ($r > |0.6|$) between median MP (>335 μm) concentration and percent development, population density, and forest cover for the tributary catchments (Fig. 4); however, this relationship was only statistically significant ($\alpha = 0.05$) for forest cover.

3.2. Bailing samples (64 μm) and sediment samples

Bailing sample (64 μm mesh) concentrations ranged from 20 to 130 p m^{-3}, with high site-to-site variability (Figs. 5, S3, Table S3). However, all the samples collected along the mainstem of the Neuse River (3 locations) were in the range of 100 to 120 p m^{-3}, potentially indicating that MPs in this size fraction may already have an ambient concentration in the main river (Fig. S3). The correlation between bail sample (64 μm) concentration and land cover was lower than that for the median trawl samples (335 μm), and was not statistically significant (Fig. S4). The concentrations measured for the bailing samples were one to two orders of magnitude higher than the samples collected using the 335 μm mesh; the ratio of concentrations of 64 μm samples to 335 μm samples ranges from 35 to 375 ($r = 0.30$).

Streambed sediment concentrations (>64 μm) ranged from 0 to 808 p kg^{-1} of dry sediment, with a median of 147 p kg^{-1}; one location (Marsh Creek) had no MPs detected (Fig. 5). The water column and streambed sample concentrations were not correlated ($r = -0.09$).

3.3. Polymer types

3.3.1. Trawl samples (335 μm)

3.3.1.1. Polymer identification. Of the 7557 particles analyzed using FTIR, 6337 (84 %) were confirmed to be synthetic plastics, resins and paints (e.g., urea formaldehyde, polyurethane), plastic additives, or bioplastics (e.g., Rayon, Cellophane, Cellulose Acetate). Polyethylene (PE) was the most common polymer type (~30 % of particles) and was found in 98 % of the samples. Polypropylene (PP) was the next most plentiful polymer (18 %) and was present in 70 % of the samples. The third most abundant polymer was Polystyrene (PS, 15 %) and was found in 77 % of the samples. The remainder were made up of Polyvinyl polymers, bioplastics, rubber and other assorted miscellaneous polymers (acrylonitrile butadiene styrene, ethylene-vinyl acetate, polyamides, rubber (~1 % of particles)) (Table 1).

Individual plastics contain a complex mixture of additives used to modify their physical and chemical properties, including plasticizers, pigments, fillers, and stabilizers (Rochman et al., 2019). Similar to Kapp and Yeatman (2018), we assumed that the particles identified as these additives and chemicals by FTIR were plastics based on visual inspection and the presence of these additives. We also found various thermosetting plastic resins including alkyd resins, epoxy resins, and phenoxy resins. The most common thermosetting resin identified was urea formaldehyde (~6 %), which is the adhesive often used to manufacture chipboard, particleboard and plywood (Hiziroglu, 2018). These particles were often identified as urea formaldehyde in combination with chipboard or melamine. Paints and other sealants were also present, including polyurethane and latex paints.

Polyethylene terephthalate (PET) was present in about 6.5 % of the samples. About 5.5 % of the particles were identified as copolymers of other common plastic polymers, including poly(ethylene: vinyl chloride), poly(ethylene: propylene), polyethylene/ethyl acrylate. These common polymers are often combined to create new compounds with desirable properties inherited from their constituents.

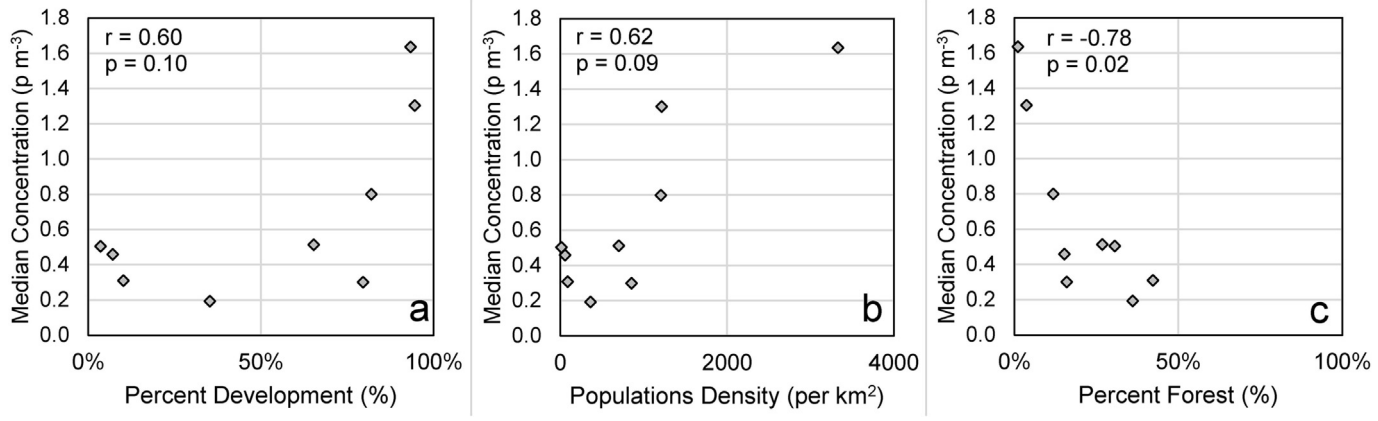


Fig. 4. Relationship between median MP (>335 μm) concentration and catchment developed land (a), population density (b), and forest cover (c) for the tributary catchments. The Spearman correlation coefficient and associated *p*-value are included for each plot.

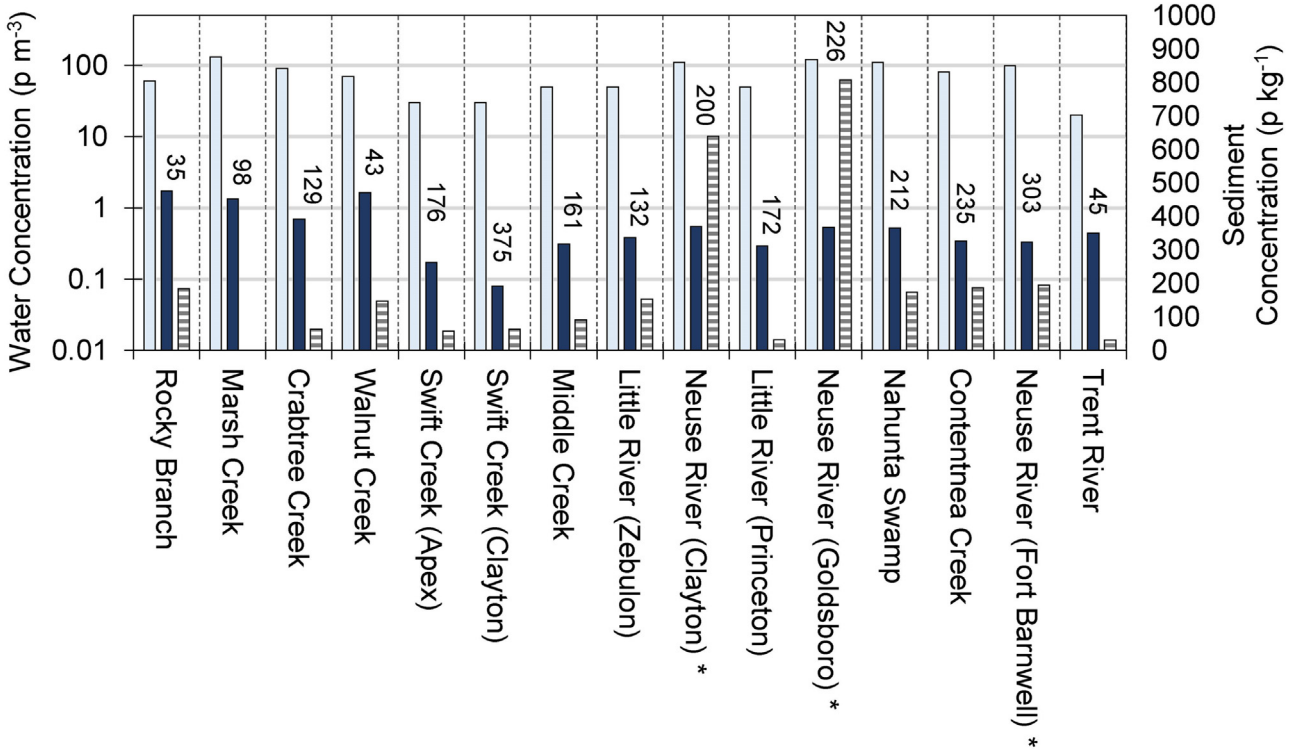


Fig. 5. Results of samples collected using bailing (64 μm mesh), trawling (335 μm) and sediment samples. The number above the bars is the ratio of the concentration of particles collected by bailing (64 μm) to the concentration of particles collected using the trawl net (335 μm). Asterisk (*) indicates location along the mainstem of the Neuse River.

For some of the particles, their chemical identity based on FTIR analysis did not match their physical appearance under the microscope. This was likely the result of the spectral signature of the MPs changing as the particles age in the environment. (Castelvetro et al., 2021; Sandt et al., 2021). For example, some particles were identified as (i.e., the closest match to) food additives (e.g., Sorbitan monopalmitate, Sorbitan monostearate). Because the FTIR signature of these particles was very similar to the signature of degraded PE reported by Castelvetro et al. (2021) and the particles resembled a plastic film under the microscope, we concluded the particles were either degraded polyethylene or plastic film coated with a food additive. Other particles identified as cork using FTIR also appeared to be films when examined under the microscope. Therefore, we assumed these particles were polyethylene based on the similar spectral signature and visual inspection.

Most of the plastic particles >335 μm were fragments, films and foams; only 20 % were fibers. Even fewer (2.7 %) of the particles in the water column collected using the 64 μm mesh were fibers.

3.3.1.2. Polymer distribution. Overall, there was substantial variability in both the types of plastics collected at each location as well as the composition of plastics between different sampling times (Figs. 6, S6). Principal component analysis (PCA) indicated that streamflow, season, and location were not strong contributors to the variability in types and composition of plastics in a sample (i.e., we did not observe grouping by these factors) (Fig. 7), although streamflow appeared to relate to the greatest variability in plastic composition. Rather the composition was highly variable among locations and changed between sampling times.

3.3.2. Bailing and sediment samples

Of the 201 particles counted as MPs during fluorescent microscopy, 110 were extracted from water samples and 91 from sediment samples. Of the MP obtained from the water samples, 3 of 110 (2.7 %) were identified as fibers with the remainder being fragments. All MP obtained from the sediment samples were identified as fragments. The most dominant color (see also Figs. S7, S8) in the water sample MP was clear (66.4 %) followed by grey (10.9 %), white and blue (6.4 %) while the most dominant colors in the sediment MP were clear (79.1 %) followed by grey (9.9 %) and blue (6.6 %).

MP extracted from the bail water samples ranged from 65 to 3587 μm with 90.9 % falling below 335 μm. Size ranges per sampling location are

Table 1
Proportion and presence of polymer types in trawl (335 μm mesh) water samples.

Polymer type	Overall proportion (%)	Fraction of samples w/ polymer present (%)
Polyethylene (HDPE, LDPE, LLDPE)	30.3	98
Polypropylenes	18.0	70
Polystyrenes	15.0	77
Resins and plastic additives (e.g., polyurethane, paints, plastic additives, pigments)	7.4	73
Polyethylene terephthalate (PET)	6.4	42
Urea formaldehyde resin (used as adhesive in particle board, chipboard and plywood)	6.3	69
Misc. plastics (ABS, PA, PC, PMMA, acrylics, rubber)	5.9	61
Various copolymers (e.g., poly(ethylene: vinyl chloride), poly(ethylene: propylene))	5.6	62
Polyvinyl polymers (e.g., PVA, PVC)	3.1	32
Bioplastics (e.g., cellophane, rayon, cellulose acetate)	2.0	37

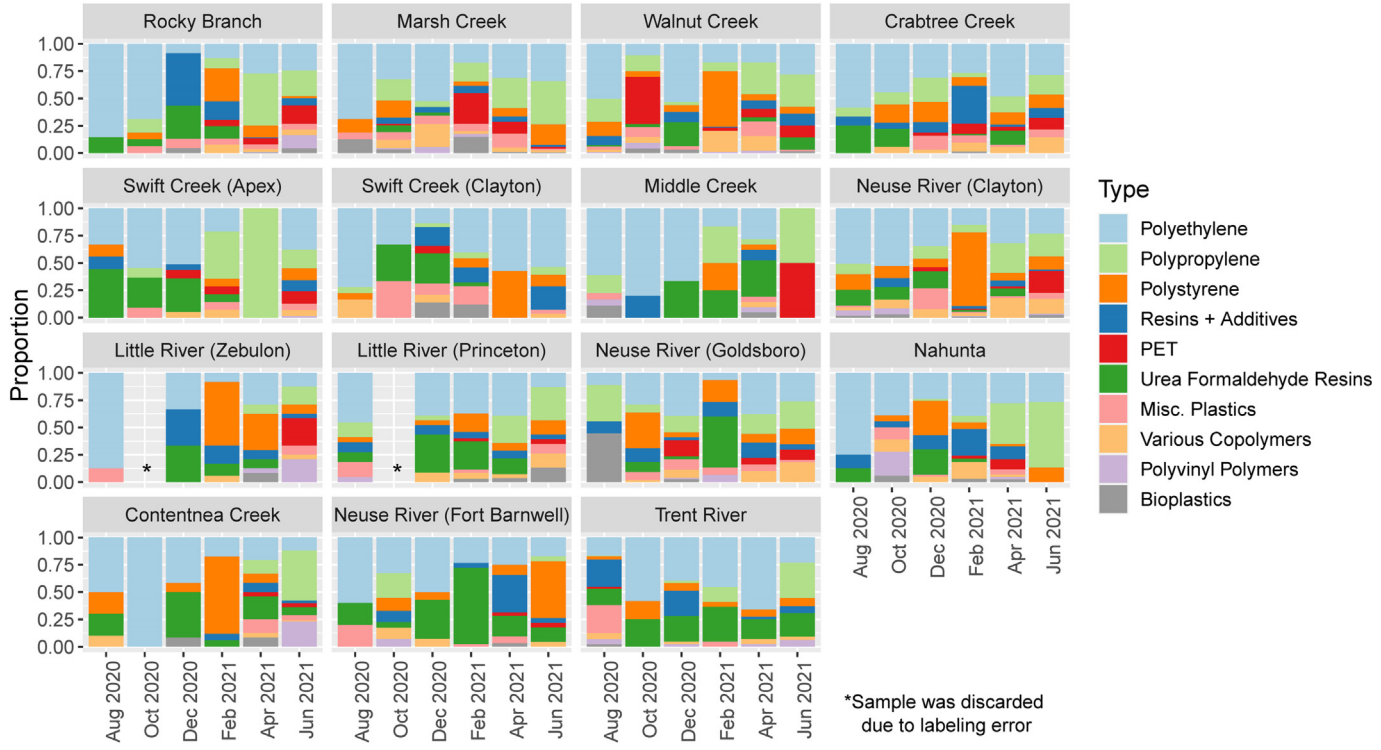


Fig. 6. Relative distribution of polymer types by sample location and date for particles >335 μm.

shown in Table S5. This is similar to our estimate using a normalized trawl sample volume, which indicated over 97 % of MPs are in the size range of 64–335 um (Table S4). MP extracted from the sediment samples ranged from 65 to 1457 μm with 95.6 % of the MP <335 μm. The average particle length per location (Table S6) for sediment MP is for most sampling locations smaller than that of the bail water MP.

Following fluorescent microscopy, polymer identification with Raman spectroscopy was applied to a subset of MP that were picked off the GF/D filters, including about 44 % (48 particles) of the MP extracted from the bail water samples and 15 % (14 particles) of the MP extracted from the sediment samples. Since a limited number of particles underwent Raman spectroscopy, only the polymer type distribution of the composite water and sediment data is reported. For the water samples, 96 % of the analyzed particles were positively identified as synthetic polymers while 86 % of the particles from the sediment samples were polymers. The most common polymer types identified in the sediment samples were PVC and PET (about 21 %, see Table S7) followed by PE, PS and ABS (about 15 %). In the water samples the most common polymer type identified was PET (42 %, see Table S7) followed by PP (23 %).

3.4. Microplastic loading

Using the mean concentration and mean daily river discharge at the most downstream gage we estimated that about 670 million MP particles >335 μm enter the Pamlico Sound from the Neuse River Basin each year. When considering smaller size fractions too (particles >64 μm), we estimated the load to be substantially higher at about 230 billion particles per year, or about 110,000 particles per capita per year.

4. Discussion

4.1. Trawl samples – watershed attributes and streamflow

The concentrations reported here were generally comparable to or lower than previous studies using analogous methods in areas with similar waste management infrastructure (e.g., waste management and water treatment systems). Dris et al. (2015) reported a range of 0.28 to 0.47 p m^{-3} in the Seine River in Paris using a 330 μm mesh. Similarly, Lechner et al. (2014) reported a mean concentration in the Danube River in Germany of 0.32 p m^{-3}, with a maximum of 142 p m^{-3}; however, they used a larger mesh size (500 μm). In the United States, Baldwin reported slightly higher average levels with a median of 1.9 and mean of 4.2 p m^{-3} in tributaries to the Great Lakes using a 333 μm mesh. In rivers of heavily urbanized Milwaukee WI, Lenaker et al. (2019) reported a range of 0.5 to 11.6 p m^{-3} also using a 333 μm mesh.

While our initial results seem to suggest a stronger discharge control of MP concentrations for urban catchments in the upper basin, it will be important to determine how transferable these findings are by comparing with future observations in other catchments. We therefore advocate for more deterministic field studies that establish MP concentrations in river networks alongside hydrological controls as larger sample sizes and wider ranges of analyzed conditions will improve our understanding of the relationship between flow and MP transport.

The relationship between discharge and MP concentration for urban streams indicates that there is potential for substantial MP transport occurring during storm events. The five samples with the highest MP concentrations were collected at or near the peak of the hydrograph following intense rainfall events in three urban creeks (Rocky Branch, Marsh Creek, and Walnut Creeks). These sample concentrations were an order of magnitude or higher than the samples collected at baseflow. Baldwin et al. (2016) also reported the highest concentrations of MPs in samples collected from urban sites during high streamflow, and Gündoğdu et al. (2018) found increased concentrations in estuaries following flooding events. There are a few factors that likely contribute to this increased MP transport during stormflow. First, there is likely a connection of MP sources including a flush of MPs that have built up on impervious surfaces that are transported into streams (Werbowski et al., 2021). Second, recent research has indicated that MPs in stream sediments can be mobilized during high flow events (Drummond et al., 2022, 2020; Hurley et al., 2018).

The MP correlation with increased watershed development intuitively makes sense given that more plastic products are consumed, and hence more waste is generated and handled in more populated areas. In addition,

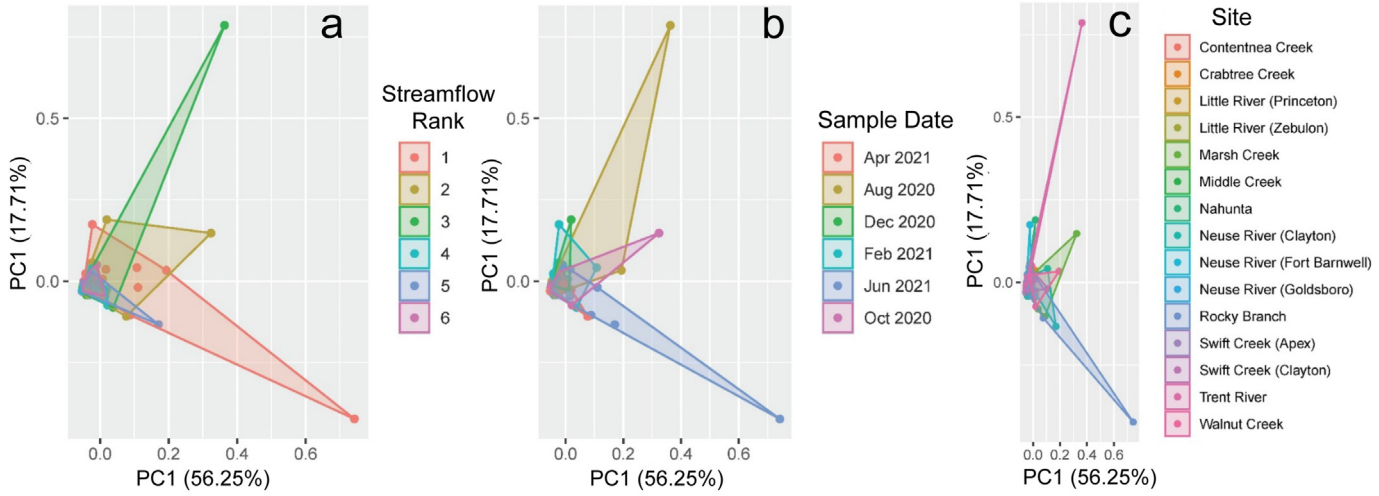


Fig. 7. Principal component analysis of polymer composition grouped by a) streamflow, b) sample date, and c) site.

developed areas also have other MP sources such as wastewater treatment plants and industrial sources. Global-scale estimates of MP export to the oceans have identified densely populated and urbanized areas with poor waste management as potential hotspots of riverine MP (Lebreton et al., 2019, 2017), yet case studies have previously reported differing findings regarding land cover, development, and MP concentration (see Talbot and Chang (2022) for a review). While some of these studies have reported a correlation between concentration and population density (Baldwin et al., 2016; Yonkos et al., 2014), others found no relationship with population density (Dikareva and Simon, 2019). In addition, other possible explanations for a decoupling of development/population density and MP concentrations include the presence of other dominant sources (e.g., agriculture) that super-impose the urban MP signature, waste management practices that potentially divert waste fluxes to the stream network at different locations (e.g., sewer network, landfills outside of urban areas), or the dominance of individual point sources, such as WWTP downstream of larger urban areas. This study covers only a few locations (9 sub-catchments) and a relatively small number of samples (6 per site). Given the differing results from past studies, more research is clearly warranted.

4.2. Bailing samples

The results reported here are in the range of previously reported studies using comparable mesh sizes. Dikareva and Simon (2019) reported 17 to 303 p m^{-3} (>64 μm) in urban streams in New Zealand and Dahms et al. (2020) reported on average 705 p m^{-3} (>53 μm) in the urban Braamfontein Spruit, South Africa.

The inverse relationship between mesh size and number of plastic particles has been reported previously (Baldwin et al., 2016; Dikareva and Simon, 2019; Eriksen et al., 2013; Mani et al., 2015) and would seem to validate previous researchers' inclinations that the use of a 335 μm mesh substantially underestimates MP concentrations relative to a finer mesh (Baldwin et al., 2016; Dikareva and Simon, 2019). However, the level of underestimation is uncertain and probably study-site specific. While we reported ratios from 35 to 375, recent research has reported even wider ranging assessments of the level of underestimation resulting from using larger mesh sizes. For example, Lindeque et al. (2020) reported that using a 100 μm net resulted in 2.5 times higher concentrations compared to a 335 μm mesh. Another study reported 100,000 times more particles collected with an 80 μm net compared to a 450 μm net (OSPAR, 2009). Both these studies were conducted in marine environments. Dris et al. (2015) also reported much higher concentrations using an 80 μm mesh (3 to 103 p m^{-3}) compared to a 330 μm mesh (0.28 to 0.47 p m^{-3}). Results from Kapp and Yeatman (2018) indicate a ratio of 335 between the mean concentration of particles in grab samples and the concentration of MPs collected using a 100 μm net in the Snake and Columbia Rivers in the western U.S. Regardless, the results from this study (mean of ~170 times more particles with the 64 μm net compared to the 335 μm net) indicate a substantial increase of smaller sized MPs. In fact, these results indicate that over 97 % of the MP particles >64 μm are in the size range of 64–335 μm (Table S4). Most of the samples (12 of 15) used for comparison between the mesh sizes (335 μm versus 64 μm) were collected near base flow conditions (Fig. S5) so it is unclear if this relationship would differ during storm events.

4.3. Sediment samples

The sediment concentrations fell in the range of or below the concentrations observed in previous studies (Baldwin et al., 2017; Lenaker et al., 2019). For example, Kelleher et al. (2023) found 57 to 400 p kg^{-1} for the Okavango Delta, Botswana. The highest sediment concentrations were not found in the urban areas but rather along the mainstem of the Neuse River. However, not all locations along the mainstem had high concentrations and given the MP-sediment-streamflow dynamics reported by Hurley et al. (2018) (mobilization and translocation of sediment MPs during flooding) there is likely substantial temporal variability in in-stream sediment concentrations.

Surprisingly, MPs were not detected at Marsh Creek, a highly urbanized stream with the highest water column MP concentration observed. One possible explanation for the absence of MPs at this location is the mobilization/removal of MP particles from streambed sediment following high flows/flooding. Hurley et al. (2018) reported that MP concentrations were substantially lower following flooding, and in some locations, MPs were completely undetectable after flood events. The sediment sample at Marsh Creek was collected the day after an intense rainfall-runoff event.

The average particle length for sediment MPs was shorter than for the bail water MPs, indicating that smaller MP are trapped in streambed sediment more frequently than larger MP. Additionally, sediment MP often remain trapped in streambeds for extended amounts of time (Drummond et al., 2022), potentially leaving them subjected to longer periods of degradation as well as different types of degradation mechanisms (subjected to more biochemical degradation) than MP extracted from the river water column (more subject to UV degradation and mechanical degradation).

4.4. Polymer types, shapes and color

We found very few of the MP particles were fibers. This is very different from some previous studies of MPs in streams in the United States as many studies using a ~ 335 μm net have reported that fibers are the dominant shape (Baldwin et al., 2017; Kapp and Yeatman, 2018). For example,

Baldwin et al. (2016) reported that 71 % of the particles they found in Great Lakes tributaries were fibers. However, riverine studies from other areas have also reported a much lower percentage (e.g., 2.5 %) of fibers (Mani et al., 2015).

Dozens of synthetic compounds were identified through FTIR analysis, confirming that MPs make up a diverse and complex mixture of different chemical compounds, not just the most common polymers (Rochman et al., 2019). The composition of polymer types from sample-to-sample and between sites varied widely. This lack of consistency in the composition of MPs at a given location indicate high spatial and temporal variability and the likelihood of diverse sources contributing to the observed MP concentrations. However, the most common polymers extracted from the trawl net samples are ubiquitous in the products society consumes. The most common polymer type recovered, PE, is also the most produced plastic in the world (Jeremic, 2014), widely used for plastic bags, films, packaging, and bottles. The next most common, PP, is often used for food containers and other packaging and PP fibers are used for carpeting, outdoor gear, and rope. The third most common polymer, PS, is widely used for packaging, insulation, and foam food and drink containers. We also recovered PET, which is used in single use plastics and is the most common synthetic fabric (i.e., polyester). While PE was the most common polymer type recovered from the trawl net samples, surprisingly, PE only amounted to about 4 % of the particles captured from bailing. This apparent discrepancy could be due to differing sources for small versus larger MP and/or the potential misidentification of environmentally aged particles.

Concurrent to this study of microplastics, bimonthly cleanups of plastic litter were completed at the streams in the Raleigh Area (Crabtree Creek, Walnut Creek, Marsh Creek and Rocky Branch) (Doll et al., 2023). Of all the plastic pieces collected, ~25 % was made up of foam (polystyrene), ~43 % was made up of plastic bags, wrappers, and films (PE, PP), and ~13 % was comprised of bottles, cups, and lids (PET, PP, PE) (Doll et al., 2023). This data indicates the presence of sources that, over time, are likely contributors to the stream microplastic loading.

Some of the rarer MP particles included several thermoplastics used for nonstick coatings (polytetrafluoroethylene and Xylan), and Bakelite particles, the first plastic ever made from synthetic components, were identified in one sample collected from Crabtree Creek in Raleigh. The presence of Bakelite, which was patented in 1909, and mostly phased out after World War II, highlights the longevity of MP in the environment. Interestingly, this site was undergoing sewer line construction work upstream that involved excavation of the streambed, which may have resulted in re-suspended legacy deposits of material including plastic particles.

Clear or "see through" were the most abundant particle color collected in the bailing samples. Some of the clear particles also exhibited different color tones across the particle. Despite subjectivity in particle color characterization, this parameter might be important in future studies as some aquatic fauna may preferentially uptake certain colors that more closely resemble the color of their food sources (McNeish et al., 2018; Roch et al., 2020; Yuan et al., 2019).

Bailing samples (i.e., filtering 100 L of water in the field over a 64 μm sieve) showed no specific bias towards larger/smaller MPs at any of the sample locations. Therefore, the bailing method would be expected to collect a reasonable number of smaller MPs while larger MPs, which are less common, are more easily captured when filtering large water volumes (average of 79 m^3) over extended amounts of time using a trawl net.

4.5. Study limitations

Sample collection for this study (July 2020–July 2021) was initiated when businesses and schools were closed due to the COVID-19 pandemic. This could have affected sample results, but the magnitude is uncertain. The closures and the increased prevalence of working from home led to a decline in vehicle traffic (Yasin et al., 2021), which could have resulted in a reduction in automobile derived microplastics (e.g., tire wear). In addition, with less mobility of the population there was likely a decline in the generation of plastic litter; however, research also showed an increase in discarded personal protective equipment due to COVID-19 (Roberts et al., 2021). Given the varying time required for discarded plastics to degrade to the size of microplastics, the impacts these changes could have had on the results reported here remain uncertain; however, an increase in MP concentration was not detected later in the study as COVID-19 restrictions and closures were phased out.

Our estimate of MP loading to the Pamlico Sound is a very coarse approximation of MP loading with a high degree of uncertainty. More intensive sampling focused on characterizing spatial and depth variability of MP dynamics in rivers (as identified by Lenaker et al. (2019) and Dris et al. (2018)) as well as temporal trends is recommended to reduce uncertainty and refine this estimate. While over 200 billion particles per year is a large number, it may be conservative as other studies of more populated basins of similar size (in South Korea) have reported loading estimates up to 10 trillion MP particles (>50 μm) per year (Eo et al., 2019).

5. Conclusions

We analyzed MPs at 15 locations across a large watershed to examine spatial, land cover, and streamflow related impacts on MP concentrations. MPs were found in all water samples, but the MP concentrations and composition of polymer types were widely variable from sample to sample, and also differed depending on whether the water column was sampled by bailing (64 μm) or using a trawl net (335 μm). We found that MP concentrations in the water column >64 μm range from 20 to 130 p m^{-3} with over 90 % of the particles identified being <335 μm. MP concentrations based on trawl net sampling range from 0.02 to 221 p m^{-3} and are much more variable. For MP captured with the trawl net, median MP concentration was correlated with land cover for the tributary catchments and the highest MP concentrations were observed in urban streams during high streamflow.

Given our observations of increasing MP concentration associated with high stream discharge in urban streams and visual observations of plastics (micro and macro) moving during higher flows, we suspect that MPs from urban areas are mobilized, transported into the river network and move downstream in pulses. More work is needed to study how MP concentrations change during and in between run off events and how the mixing (or lack thereof) occurs when runoff from urban areas enters larger downstream tributaries.

In the case of trawl sampling, we found the level of effort required to quantify MP concentrations may not be reasonable given the probable substantial underestimation of MP presence when compared to other methods using a finer mesh. This study indicated >90 % of the MP particles >64 μm were in the size range of 64–335 μm and MP concentrations in bailing water samples were 35 to 375 times higher than in trawl samples depending on the sampling location. The large amount of organic matter (leaves, pollen, etc.) and sediment collected with most trawl samples (particularly during stormflow) required time consuming and expensive chemical and physical processing to separate the plastics from the natural materials. In addition, it is possible that plastic particles, particularly fibers, are lost during sample processing (i.e., net washdown, chemical digestion, etc.). Using a finer mesh size and sampling a smaller volume allows for less intensive processing and may provide a better estimate of the presence of MPs. However, collecting a substantially reduced volume of water may not capture all the MP shapes and polymer types present (Tamminga et al., 2022).

We echo the sentiments of many other researchers (e.g., Kapp and Yeatman, 2018; Lenaker et al., 2019) in calling for the development of standard procedures for MP collection, processing, and analysis. Variable sampling and analysis methods limit the comparability of results and contributes to uncertainty in quantifying the degree of MP pollution in the aquatic environment.

CRediT authorship contribution statement

J. Jack Kurki-Fox: Conceptualization, Methodology, Formal analysis, Visualization, Writing – original draft, Writing – review & editing. **Barbara**

A. Doll: Funding acquisition, Conceptualization, Methodology, Investigation, Supervision, Project administration, Writing – review & editing. **Bonnie Monteleone:** Investigation, Methodology, Writing – review & editing. **Kayla West:** Investigation, Writing – original draft, Writing – review & editing. **Gloria Putnam:** Funding acquisition, Conceptualization, Writing – review & editing. **Liam Kelleher:** Investigation. **Stefan Krause:** Funding acquisition, Writing – review & editing. **Uwe Schneidewind:** Investigation, Methodology, Writing – original draft, Writing – review & editing.

Data availability

Data will be made available on request.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgements

This research was funded by the National Atmospheric and Oceanic Administration Marine Debris Program (Grant Number - R/20-MD-01) with supplemental funding from North Carolina Sea Grant. We would like to thank Sound Rivers, Inc. for loaning kayaks and taking us out on their power boat to collect samples at Trent River, Contentnea Creek and the Neuse River at Fort Barnwell. U.S. would like to acknowledge funding from the German Research Foundation (DFG – grant number 403826296). S.K. would like to acknowledge funding from the Royal Society (INF\R2\212060) and Leverhulme Trust (RPG-2017-377 and RPG-2021-030). We would also like to thank Yasmin Yonan and Lee Haverson from the University of Birmingham for their help with analysis of the bail and sediment samples.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.scitotenv.2023.162940.

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