Quantification of Microplastic Content in Surface Water and Sediment within Hudson River Tributaries and Marshes

A Final Report of the Tibor T. Polgar Fellowship Program

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ABSTRACT

The infiltration of microplastic (MP) pollution into aquatic ecosystems has been discovered in watersheds across the world. MPs have a variety of different origins, compositions, densities, shapes, and a high resistance to degradation. These properties allow for accumulation of MPs in major watersheds and make mitigation extremely difficult. Freshwater marshes are known to be a sink for sediment and certain pollutants, however, the role marshes play in MP accumulation is unknown. The main purpose of this study was to quantify and investigate differences in MP concentrations between marsh, tributary, and open water locations in the Hudson River watershed. The following four Hudson River marshes and their corresponding tributaries were sampled to investigate differences in MP content: Sleightsburg Marsh and Rondout Creek, Tivoli Bays and Saw Kill Creek, Fishkill Marsh and Fishkill Creek, and Constitution Marsh and Indian Brook. Surface water and sediment samples were analyzed from each sampling location to account for density differences in polymers present. The findings of this study indicate that Hudson River marshes act as a sink for MP pollution. Marsh samples contained a significantly higher average concentration of MPs in sediment (2.28 MPs/g MS) than tributary (0.27MPs/g MS) or open water samples (0.42 MPs/g MS) and the highest average surface water concentration (0.30 MPs/L) of all location types. Fishkill Creek and Sleightsburg Marsh contained the highest average MP concentrations between tributary and marsh sites, respectively. While development of mitigation strategies to eliminate microplastics from bodies of water has been proven nearly impossible without harming the ecosystem, the findings of this study highlight a need for elimination of microplastic use at the consumer level and prevention of infiltration at a regulatory level.

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INTRODUCTION

Microplastics (MPs) are composed of a variety of synthetic polymers and range between 0.1 μm and 5.0 mm in length. MPs can enter waterways as macroplastic waste or litter that overtime continue to fragment from the macroplastic to nanoplastic level and persist in aquatic ecosystems (Espinosa et al. 2016). The origin of these particles can vary greatly from fragmentation of macroplastic waste, such as water bottles to fragments of clothing composed of synthetic fibers, or to modern prefragmented MPs, such as microbeads found in facial cleansers and toothpastes. The New York State Attorney General's Office (2015) points out that manufactured microbeads and synthetic fibers are entering waterways through water treatment plants across the country that filter water through screens of 6.0 mm or larger in some cases and 1.5-6.0 mm in other cases. This creates a great concern due to the easy access of industrially engineered MPs into nearly all waterways.

Once introduced into aquatic ecosystems, MPs can have profound ecological impacts. MPs have been found to have major negative health effects for marine vertebrates and invertebrates, mainly by bioaccumulation in tissue. Ingestion of MPs by aquatic organisms including zooplankton, mollusks, crustaceans, aquatic worms, and vertebrates, such as fish, has been identified globally (Cole et al. 2013). Terrestrial and aquatic birds and mammals have also been found to contain MPs in their tissue and macroplastics in stomachs. MP ingestion in organisms can occur directly, through filter feeding or misidentification of plastics as food, and indirectly, through predation of organisms already containing plastics. The bioaccumulation of MPs in tissues of organisms allows these plastics to move through the food web and have larger effects on

species near the top. Fish, in particular, are highly affected by the toxicity of synthetic polymers which can damage or interfere with their endocrine, circulatory, immune, and muscular systems, as well as their livers, gills, gonads, and intestines (Espinosa et al. 2016). At the top of this food web, humans consume a wide variety of organisms worldwide, both aquatic and terrestrial, with the possibility of having MPs accumulated in their tissue. The blue crab (*Callinectes sapidus*) may be the best example of this in the Hudson River, as they are they are one of the most commonly caught and eaten species, found anywhere between the Troy Dam to New York Harbor (NYSDEC 2019). Striped bass (*Morone saxatilis*) is another example, while less commonly consumed when caught in the Hudson River, they spawn in the Hudson River each year and offspring can live up to two years in the river before entering the Atlantic Ocean (Hill et al. 1989).

The accumulation of the synthetic polymers is not the only point of concern for human health and the health of all other organisms. Many plastics are composed of toxic derivatives and are manufactured using potentially harmful chemicals. Certain polymers also have the ability to absorb ambient chemicals from the environment such as PAHs, DDT, chlordanes, and PCBs, which are known to persist in the Hudson River (Van et al. 2012). A large portion of these chemical groups have known toxicity to humans and other organisms, and MPs provide access into tissues of organisms causing potentially major health concerns (Espinosa et al. 2016). Mammals such as mice have been the focus of several new studies concerning MP polymer toxicity. Polystyrene microbeads of varying size have been identified to accumulate in the liver, kidneys, and gut of mice. This accumulation and exposure has led to impairment of energy transformation, disturbance of lipid metabolism, reduction of neurotransmission efficiency, and imbalances in

antioxidant defense systems (Deng et al. 2017). As the effects of MPs on human health are relatively unknown, studies using animal models can give a clearer perspective into the possible effects of MP accumulation in humans.

Buoyant MPs can flow more easily throughout waterways and denser MPs that have a greater ability to sink and accumulate in benthic sediment. Many current studies on MP accumulation in aquatic environments focus on types of polymers that are less dense and are easier to sample and identify; however, a study conducted by Hidalgo-Ruz et al. (2012) shows that the majority of researched MP polymers have average densities greater than 1.0 g/cm^3, meaning they will sink in fresh water. This shows that there is a need for investigation of certain plastic polymers below the surface water. Many of these polymers have densities that range just above 1.0 g/cm^3 which would easily allow them to be transported by water current. Sediment analysis will allow for the identification of the importance of marshes and tributaries on MP accumulation and transport in the Hudson River.

This project investigated MP content differences in surface water and sediment samples from tributaries, marshes, and adjacent open water of four target sites. MP content was compared between sites (four target marshes) or location types (tributary, marsh, open water) of the same sample type (surface water, sediment). Marshes are hypothesized to be a sink for MP pollution and have the highest MP contents in surface water and sediment. High density polymers are also hypothesized to be identified in marsh sediment, but not in tributary sediment. The hypothesis was tested that the largest watersheds and highest number of pollution discharge sites within the watershed would

have the highest MP content in both surface water and sediment regardless of location type.

METHODS

Site Selection

The following four marshes with corresponding tributaries were chosen for sampling based on location, ease of access, differences in land usage, ecological importance, and size of watershed. Figure 1 displays marsh locations of each site investigated in this study.

Tivoli Bays: Located in Dutchess County, NY, with Saw Kill Creek as the target tributary, Tivoli Bays was the largest marsh investigated in this study, spanning two miles along the east side of the river. It is also one of the more rural sites as there is little immediate urbanized land surrounding the marsh; however, the town of Tivoli is located northeast of the marsh and Bard College is southeast of the marsh. This site has a very high ecological importance and is home to many bird species including the bald eagle (*Haliaeetus leucocephalus*). This led to the site's designation as a New York State Important Bird Area and a New York Bird Conservation Area (NYSDEC 2018b). Sampling in Tivoli Bays marsh took place in Tivoli North Bay, due to inadequate sampling conditions in Tivoli South Bay, in which Saw Kill Creek discharges. Tivoli North Bay marsh sampling took place at the end of Cruger Island Road in Tivoli, NY (40º 00.527 N, 73º 54.527 W). The mouth of Saw Kill Creek is located on the southern end of the marsh and stretches through the towns and villages of Red Hook, Milan, Tivoli, Rhinebeck, and Annandale-on-Hudson. The Saw Kill Creek watershed includes

22 square miles of land which is primarily agricultural and residential (Saw Kill Watershed Community 2016). The sampling location for Saw Kill Creek was behind the parking lot of Bard College's Shafer House (42º 00.832 N, 73º 54.527 W). Open water sampling took place by boat about 20 m west of the train tracks that run north-south through the marsh, adjacent to the southern portion of the marsh (42º 01.125 N, 73º 55.689 W).

Fishkill Marsh: Fishkill Marsh, located in Beacon, NY, was the smallest marsh in this study; however, Fishkill Creek, Fishkill Marsh's main tributary source, has a very large watershed, encompassing about 193 square miles of land in both Dutchess and Putnam Counties. Although the city of Beacon, located directly north of this marsh, is subjecting the marsh to industrial and commercial land use consequences, very little urbanization in the form of residential neighborhoods has occurred to the south and east of the marsh, which is dominated by forests. Other major land uses within the watershed include recreational and agricultural use, making it the most diverse site (Burns et al. 2005). Sampling in Fishkill Marsh took place in front of a small wooden dock off of a trail to the west of Madam Brett Park in Beacon, NY (41º 29.215 N, 73º 58.683 W). Fishkill Creek Sampling took place on the north side of a small division of the creek within 100 meters of the parking lot of Madam Brett Park (41º 29.339 N, 73º 58.430 W). Due to shallow depths surrounding the mouth of the marsh, open water sampling took place approximately 300 meters southwest of the mouth in river accessed by boat (41º 28.810 N, 73º 59.473 W).

Sleightsburg Marsh: Located in Ulster County, NY, Sleightsburg Marsh is found on the southern side of Rondout Creek's mouth. Sampling at Sleightsburg Marsh took

place between the eastern end of Sleightsburg Park and a small island to its east (41º 55.216 N, 73º 58.257 W). The area around Sleightsburg Marsh is the most urbanized of the sites chosen with the City of Kingston adjacent to the marsh and mouth of the tributary. The major land uses are commercial and industrial making it the most heavily human impacted site. Rondout Creek is the largest tributary that was analyzed in this study and its watershed includes the Wallkill River which joins Rondout Creek before entering the Hudson River (Melendez et al. 2010). The combined Rondout-Wallkill watershed accounts for about 1,190 square miles of land in Ulster, Sullivan, Orange, and Sussex Counties. In order to obtain ample water flow and depth, sampling in Rondout Creek occurred upstream of the connection to Wallkill River, on the northwest side of the creek, about 200 meters southwest of the route 213 bridge in Rosendale, NY (41º 50.790 N, 74º 4.397 W). Open water sampling was performed by boat approximately 100 meters southeast of the small inlet utilized for Sleightsburg Marsh sampling (41º 55.169 N, 73º 57.808 W).

Constitution Marsh: Constitution Marsh in Putnam County is over 270 acres in area with high ecological importance similar to that of Tivoli Bays mainly due to the rich bird habitat it provides. It is home to the Constitution Marsh Audubon Center and Sanctuary including an education center. Sampling in Constitution Marsh took place on the northeast end of the boardwalk located northwest of the Audubon Center in Cold Spring, NY (41º 24.210 N, 73º 56.419 W). The surroundings of the marsh to the south and east are similarly rural to the brook, while the small town of Cold Spring to the north is the nearest urban area along with railroad tracks that pass through the marsh (NYSDEC 2018a). Indian Brook, the corresponding tributary, is the smallest of the tributaries that

was investigated and is surrounded mainly by forests with some residential homes and agricultural fields. Sampling in Indian Brook occurred off of Indian Brook Road about 50 meters east of the intersection with the Bear Mountain-Beacon Highway bridge, adjacent to a small abandoned brick building and a small walkway overpass in Garrison, NY (41º 50.770 N 74º 4.401 W). Open water samples were taken by boat about 20 meters west of the train tracks that run north-south through the marsh and directly west of the mouth to Indian Brook (41º 23.808 N, 73º 56.688 W).

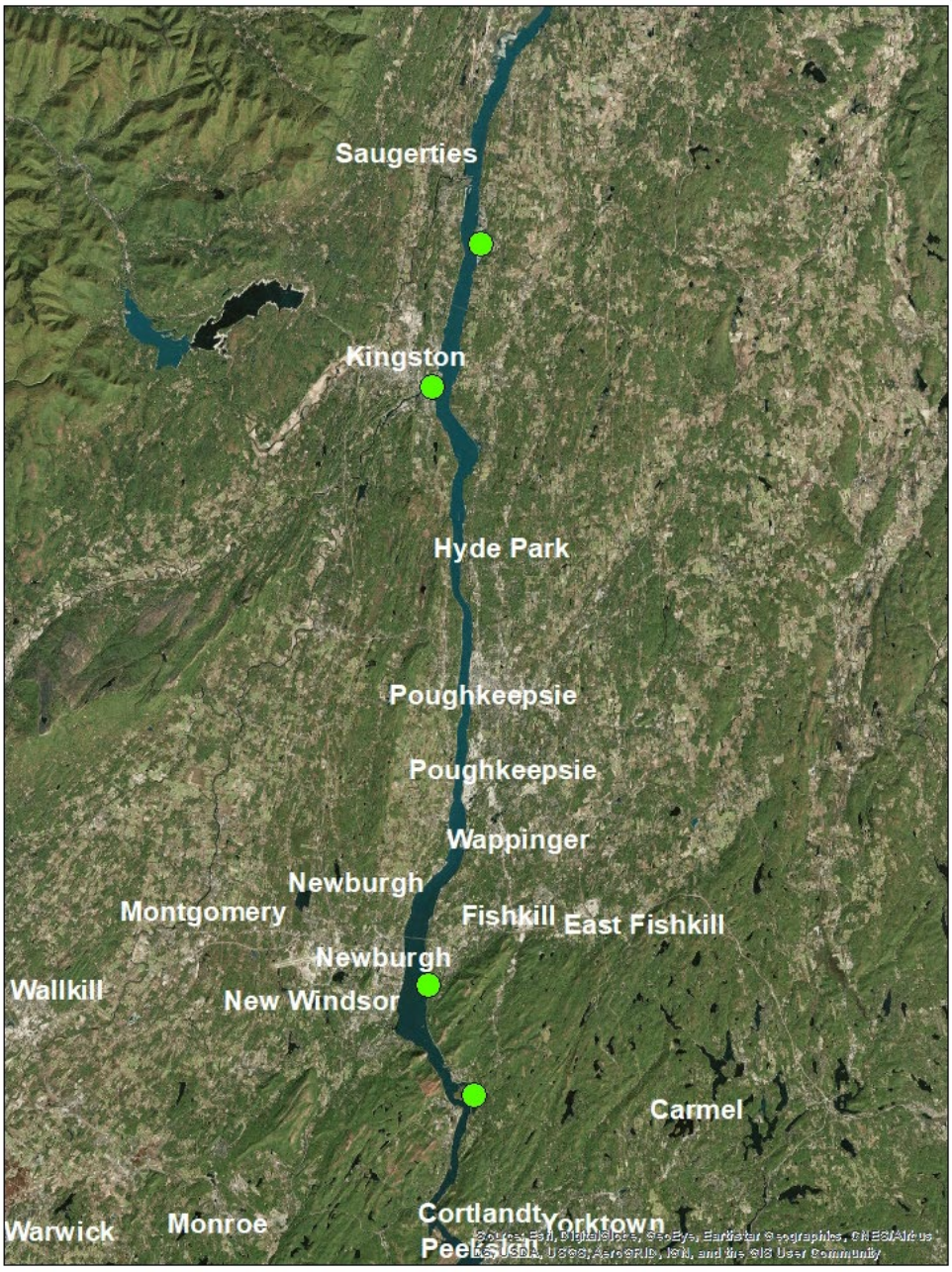


Figure 1. **Map of marsh locations of target sites:** Marsh locations of four major target sites displaying nearby towns and cities with populations greater than 18,000.

Sampling Set-up

Each of the tributary and marsh sampling sites were visited prior to sampling to ensure proper accessibility and water velocity. Tributary sampling took place far enough upstream in regions where the tides had no effect on the water velocity. Marsh sampling occurred in accessible areas between one and three hours after the most recent high tide to ensure ample water velocity downstream towards the river. All marsh and tributary sampling was performed twice on separate dates between 6/8/18 – 6/26/18 to allow for variations in weather conditions and water velocity.

Open water sampling took place aboard the Marist School of Science research vessel, which is a 28-foot pontoon boat with a square hatch in the bottom. Due to limitations with boat access, open water samples were only collected on one occasion for each site between 5/29/18 – 5/31/18 between the most recent high tide and the following low tide.

Sediment samples for each location were extracted within one meter of the surface water samples. For sampling consistency, all sediment samples in tributaries were also taken within one meter of the nearest stream bank. All sediment samples in marshes were also extracted at an exact location in which no water is present at low tide in order to investigate accumulation of MPs in the sediment. Open water sediment samples were taken directly below the location of the surface water sampling.

Site Characteristics

GPS coordinates of each sampling location were measured and recorded using a Garmin© Oregon® 550 portable GPS system. Each sampling location was characterized by surrounding land usage, major sources of pollution within each watershed, and visible

pollution in relation to the other target sites. Each site was given a ranking of 1-4 based on location type (tributary, marsh, open water) for visible pollution with 1 being most visibly polluted and 4 being the least polluted. Due to time limitations in relation to tides, water quality data could not be obtained as tributary and marsh sampling for the two northern most sites and the two southern most sites occurred on the same days to limit the use of fossil fuels in travel. As this study focuses on MP content at sampling locations, these factors were not believed to have a significant impact on the variance of findings.

Surface Water Sample Collection

For tributary and marsh sampling, an Aquatic Research Instruments Inc. © Standard Stream Drift Net (100 cm x 45 cm x 25 cm) with 333 μm mesh and detachable cod end was placed in the stream or marsh with the mouth of the net facing upstream. The net was secured by two metal poles and situated so that the top of the net was 2 cm or more out of the water and the bottom of the net was not in contact with the stream or marsh bed. The distance from the surface of the water to the top of the net was measured for each sample for later calculations of discharge. Open water sampling took place through a metal hatch in the bottom of the anchored vessel. The same drift net was deployed through the hatch and secured with two ropes so that the top of the net was 3 cm out of the water. The vessel was positioned so that the opening of the net was facing toward the marsh and surface water was flowing into the net.

For each sample the net was set up for 15 minutes of sampling before being removed from the water. Once removed from the water, the net was rinsed with deionized water towards the cod end and the resulting debris in the cod end was scraped out with a spatula and rinsed out into a labelled glass container for later analysis. Water velocity

was determined using a Swoffer Research Instruments© Current Velocity Meter (Model 2100) placed directly in front of the middle of the opening of the net. Current velocity readings were taken four times during sampling at minutes 0, 5, 10, and 15. These values were recorded in cm/sec and were averaged to account for abnormal flow conditions at any point during sampling and later used to calculate discharge of water through the net along with the net dimensions. A reading was recorded once the value had stabilized for at least 10 seconds. For open water sampling, waves and wakes created by other vessels may have introduced errors to the water velocity readings and discharge through the net.

Sediment Sample Collection

Sediment samples were extracted during the 15-minute surface water sampling. Open water sediment samples were obtained using an AMS © Ekman Dredge (15cm x 15cm x 20cm). The dredge was deployed off the side of the vessel and the collected sample was placed into a metal tray and transferred into a labelled 1 L glass container using a spatula and deionized water for later analysis. The dredge was deployed multiple times for certain samples that were not large enough to fill the container, ensuring a large sample volume. For tributary and marsh sediment samples, the dredge was also utilized; however, due to the amount of larger pebbles and stones in many samples, the dredge was ineffective and a shovel was used instead following the same protocol.

Sediment Density Separation

Once all sample collection was completed, benthic samples were wet sieved through a stacked arrangement of sieves with openings between 4.75 mm and 0.025 mm using deionized water. Sieved material larger than 4.75 mm and smaller than 0.025 mm was removed and the collected material within the desired size range was placed in a 600

mL beaker which was then placed in a drying oven at 80ºC for at least 24 hours. Sieving and drying were performed prior to weighing to normalize the samples to contain only dry particles of between 0.025-4.75 mm. Once dried, samples were weighed and those which contained large quantities of organic material were broken down to a smaller weight, noting the weight proportion to the original dried and sieved sample. These final samples then underwent density separation using a sediment-microplastic isolation (SMI) unit (Coppock et al. 2017). This was constructed using two 1' long pieces of 3" diameter PVC tubing connected by a PVC ball valve all secured using PVC glue and sealed on one end using a 3" diameter PVC coupling. The SMI unit was filled with a zinc chloride solution (515g $ZnCl_2$ per 1L H_20) with a density of 1.5 g/cm^3 to about 3-5 cm over the ball valve (approximately 1.5 L). A magnetic stirring bar was added to the bottom of the SMI unit and each sample was added prior to the addition of the zinc chloride solution. The unit was then placed on a magnetic stirring plate at a constant speed and was left for five minutes. The apparatus was then taken off the plate and left to settle for two minutes before being placed back on the plate for three consecutive 10 second stirs with 10 second pauses. After the final stir, the unit was left to settle for another 2 minutes. Once completed, the ball valve was closed and the resulting material and solution above the valve was poured and rinsed with the same zinc chloride solution into a 0.025 – 4.75 mm sieve with a 1 L beaker beneath it. The material within the sieve was transported into a labelled 600 ml beaker and placed in a drying oven at 80ºC for at least 24 hours. The remaining debris and solution in the SMI unit was poured through the cleaned 0.025 mm sieve into the same 1 L beaker where the solution could be reused as the process repeated for each benthic sample.

Wet Peroxide Oxidation

A modified NOAA Marine Debris Procedure for MP separation was followed to analyze water samples and sediment samples after density separation had been performed (Masura et al. 2015). All surface water samples were wet sieved with deionized water through the same 4.75 mm and 0.025 mm sieves as the benthic samples, discarding all material larger and smaller than this intended range. Samples were then placed in a drying oven at 80ºC for at least 24 hours. Once dried, certain samples containing large amounts of organics were weighed and only a portion of the sample was further analyzed with the weight proportion recorded. After this point all surface water and benthic samples were processed using the same methodology. All dried samples then underwent wet peroxide oxidation. A magnetic stirring bar was added to each 600mL beaker containing a specific sample. 20 mL of an aqueous 0.05M Fe(II) solution (7.5 g $FeSO_4 * 7H_2O$ and 3 mL concentrated H_2SO_4 per 500 mL of deionized water) and 20 mL of 30% hydrogen peroxide (H_2O_2) (Thermo Fisher Scientific ©) were then added to each beaker at room temperature and left for 5 minutes. The beaker was then placed on a hot plate, heated to 75ºC and stirred at medium speed for 30 minutes. If gas bubbles appeared, the beaker was removed from the hot plate until boiling had stopped and deionized water was added if boiling was vigorous. If organic material was still visible after 30 minutes, the process was repeated for a total of 80 mL of solution per sample. Once little or no organics were visible, the final mixture was sieved, rinsed with deionized water, and transported to a labelled 50 mL beaker. These final samples were dried for another 24 hours in a drying oven at 80ºC.

Microscope Separation and Quantification

Final samples were scraped out the 50mL beakers using a spatula onto petri dishes that were examined under a dissecting microscope at 10.5x – 40x magnification. Samples were spread out across the petri dishes using narrow-tipped forceps and methodically examined for MPs. Plastics were counted using a hand tally counter for the entire dish and the leftover material in the 50 mL beaker. Each sample was counted twice and the final counts were averaged. Larger plastics and unknown pieces of particulate matter suitable in size for use in infrared spectrometry were removed and placed in labelled glass vials.

Fourier Transform Infrared Spectrometry

Certain particulate matter was chosen for examination using Fourier Transform Infrared Spectroscopy (FTIR) to verify that the particle is composed of one or more synthetic polymers and to identify the polymer types. FTIR spectrums were created using a Nicolet™ iS™ 5-FT-IR Spectroscope that utilizes a high attenuated transverse reflection (ATR) unit with a ZnSe crystal. Each particle was placed on the plate and scanned over the range of 500 cm^{-1} – 4000 cm^{-1}, producing unique spectra. These were automatically compared to spectra of known compounds using Nicolet Software and the Marist library database which included the Hummel Polymer Samples library and the Nicolet Sampler library along with others, supplying the highest percentage matches to known compounds. Most synthetic fibers found in this study were not large enough to be identified using FTIR; however, certain fiber bundles were examined.

Data Analysis

MP content in surface water samples were calculated and represented in terms of number per liter of water discharged through the net for each sample. Discharge was calculated using the following equation:

$$Discharge\ (mL) = \frac{Net\ width\ (cm) * Net\ Height\ (cm) * Flow\ Rate\ (\frac{cm}{sec})}{Time\ Sampled\ (sec)}$$

Discharge was then converted from milliliters to liters of water. The average number of MPs was then divided by the calculated discharge in liters. If a sample volume was decreased due to removal of abundant organics, the corresponding discharge value was adjusted by the same ratio. MP content in benthic samples was calculated and represented in terms of number of MPs per gram of dried sediment between 0.025 – 4.75 mm in length, or microsediment (MS). Average MP counts for each sample were divided by the mass of the original dried and sieved sample.

Statistical Analysis

One-way analysis of variance (ANOVA) was performed using the SPSS v25.0 Statistical Package (2017) to test for differences in all comparable variables. Statistical analysis could not be performed for open water samples as only a single value of MP content was determined for surface water and sediment samples. A Student-Newman-Keuls (SNK) multiple-comparison test was used to determine differences among means at a probability level of $p \leq 0.05$.

RESULTS

Microplastic Content by Location Type

Average MP concentrations in surface water were not found to be significantly different based on location type; however, marshes contained the highest MP content (0.30 MPs/ L) while open water samples exhibited lower average concentrations (0.03 MPs/ L) (Figure 2).

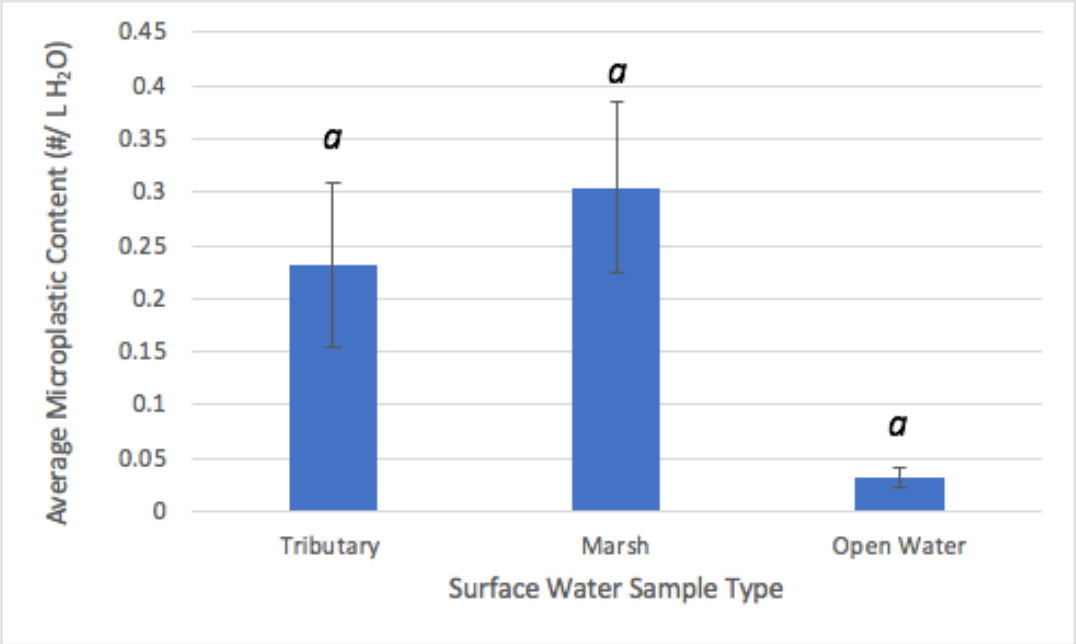


Figure 2. **Surface water microplastics by sample type:** Content of MPs (MPs/L) in surface water samples. The bar graphs represent MP content means ± SD of three measurements. Bar graphs with different letters (a and b) are significantly different at $\alpha \leq 0.05$ determined by SNK multiple comparison test.

Marsh samples were found to have significantly higher average MP concentrations in sediment (2.28 MPs/g MS) than tributaries or open water samples (p=0.05). Tributary and open water sediment samples contained average MP concentrations of 0.42 MPs/ g MS and 0.28 MPs/ g MS, respectively (Figure 3).

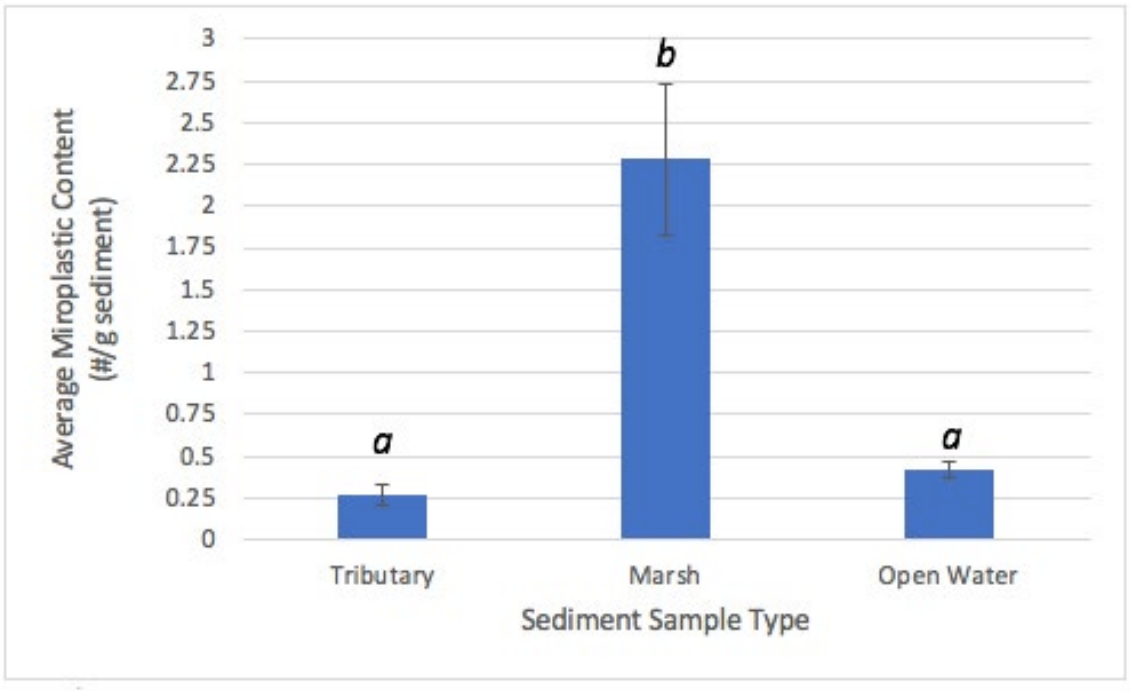


Figure 3. **Sediment microplastic contents by sample type:** Content of MPs (MPs/g MS) in sediment samples. The bar graphs represent MP content means ± SD of three measurements. Bar graphs with different letters (a and b) are significantly different at $\alpha \leq 0.05$ determined by SNK multiple comparison test.

Of the three major MP classifications, fibers were more abundant than either fragments or microbeads. Microbeads were the least abundant MP class examined in this study with only three microbeads identified from all samples. While less abundant than fibers, isolated fragments appeared in a variety of shapes, colors, and sizes.

Site Characterization

Site characterization performed during multiple visits to each site resulted in expectations that Rondout Creek and Sleightsburg Marsh would have the highest MP concentrations in each sampling category. The Rondout-Wallkill watershed encompasses 56 State Pollutant Discharge Elimination System (SPDES) outfalls, the greatest amount of all watersheds investigated. Both tributary and marsh location types for the Rondout watershed had the highest level of visible pollution of all sites. The Fishkill Creek

watershed was the only other watershed to contain SPDES outfalls, with 15 within the entirety of the watershed. Neither Saw Kill Creek nor Indian Brook watersheds contained SPDES outfalls; they had the least visible pollution in both tributary and marsh sites (Tables 1 and 2).

Tributary	Surrounding Land Use Type	Visible Pollution (1-4)	Number of SPDES Outfalls in Watershed	Watershed Size (mi^2)
Saw Kill Creek	Residential/Commercial	1	0	22
Indian Brook	Residential/Recreational	2	0	5
Rondout Creek	Commercial/Residential	4	56	1190
Fishkill Creek	Commercial/Industrial	3	15	193

Table 1. **Tributary site characteristics:** Characteristics of surrounding land area and watershed of tributary sampling sites.

Marsh	Surrounding Land Use Type	Visible Pollution (1-4)	Number of SPDES Outfalls in Watershed	Watershed Size (mi^2)
Tivoli Bays	Preserved/Recreational	2	0	22
Constitution Marsh	Preserved/Recreational	1	0	5
Sleightsburg Marsh	Commercial/Industrial	4	56	1190
Fishkill Marsh	Industrial/Recreational	3	15	193

Table 2. **Marsh site characteristics:** Characteristics of surrounding land area and watershed of marsh sample sites.

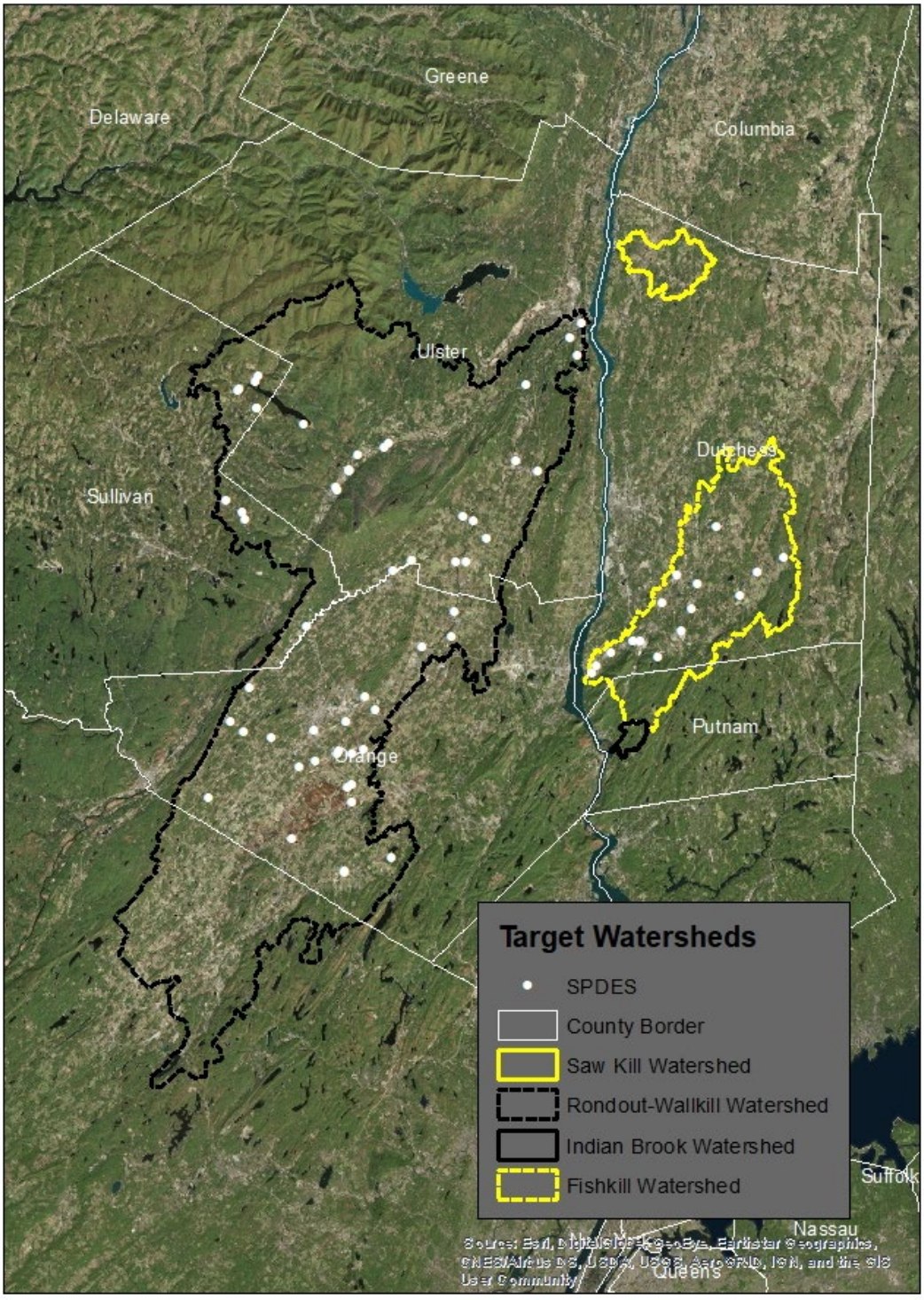


Figure 4. **Map of target watersheds and SPDES locations:** Target watersheds and the State Pollutant Discharge Elimination System (SPDES) outfalls within each watershed.

Tributary Microplastic Content

Fishkill Marsh was found to have the highest average MP concentrations in both sediment (0.45 MPs/g MS) and surface water (0.51 MPs/L) for tributary samples among all other sites. Surface water MP content in Fishkill Creek was significantly greater than all other sites, while Rondout Creek samples (0.34 MPs/L) had a significantly higher average concentration than Saw Kill Creek and Indian Brook. Tributary sediment sample concentrations were highly variable within each site, especially Indian Brook which produced a standard error of 0.21 MPs/g MS (Figure 5).

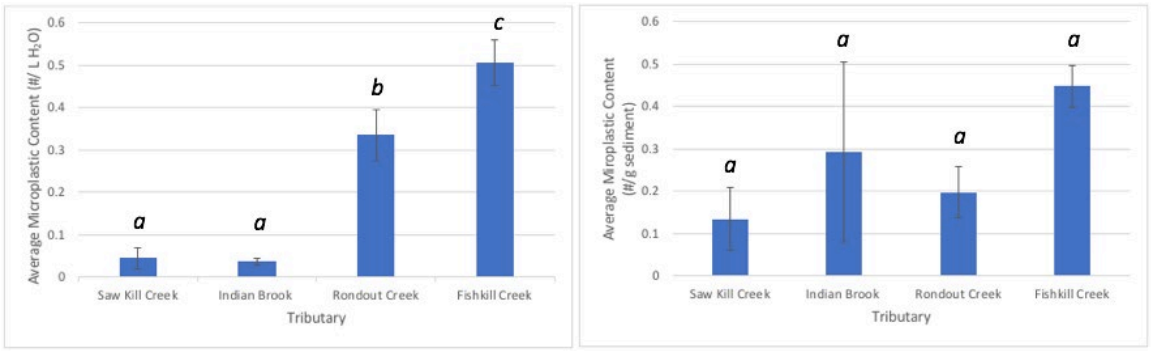


Figure 5. **Tributary microplastic contents by location:** Content of MPs (MPs/L and MPs/g MS) in tributary samples. The bar graphs represent MP content means ± SD of three measurements. Bar graphs with different letters (a and b) are significantly different at $\alpha \leq 0.05$ determined by SNK multiple comparison test.

Marsh Microplastic Content

Sleightsburg Marsh samples contained significantly greater average MP concentrations in surface water (0.66 MP/L) and sediment (4.13 MPs/g MS) than all other sites. No significant differences were found between surface water or sediment contents between the remaining three sites (Figure 6).

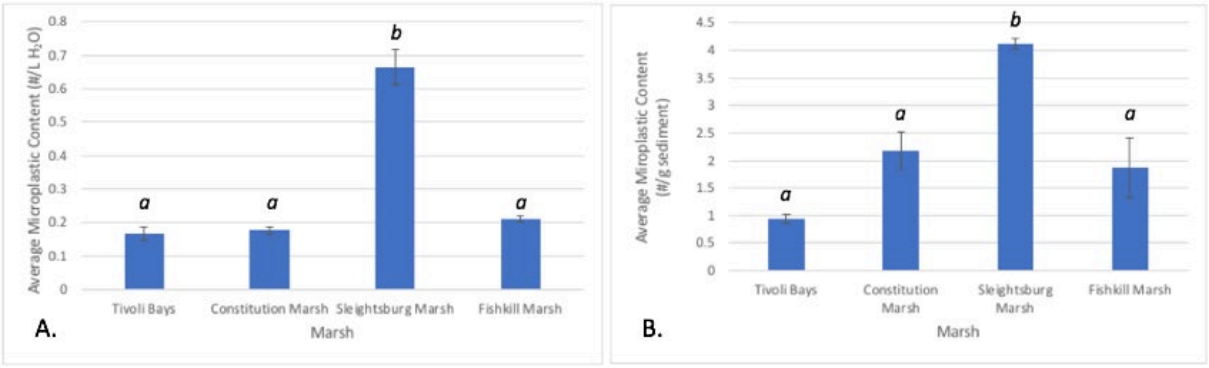


Figure 6. **Marsh microplastic contents by location:** Content of MPs (MPs/L and MPs/g MS) in marsh samples. The bar graphs represent MP content means ± SD of three measurements. Bar graphs with different letters (a and b) are significantly different at $\alpha \leq 0.05$ determined by SNK multiple comparison test.

Open Water Microplastic Content

Low variability was seen among open water surface water and sediment samples between sites. The highest MP content discovered in surface water samples was 0.054 MPs/L (Fishkill Marsh) and 0.56 MPs/g MS in sediment samples (Rondout Marsh) (Figure 7). Standard error could not be calculated due to low sample size (n=1).

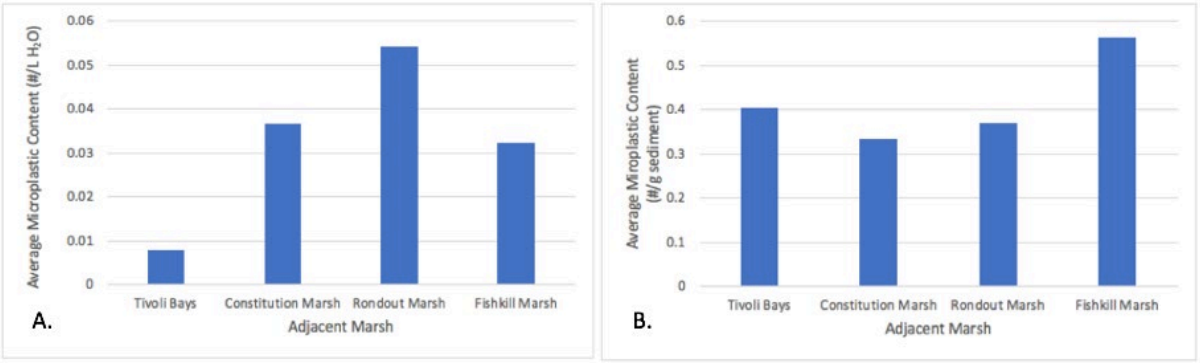


Figure 7. **Open water microplastic contents by location:** Content of MPs (MPs/L and MPs/g MS) in open water samples based on adjacent marsh.

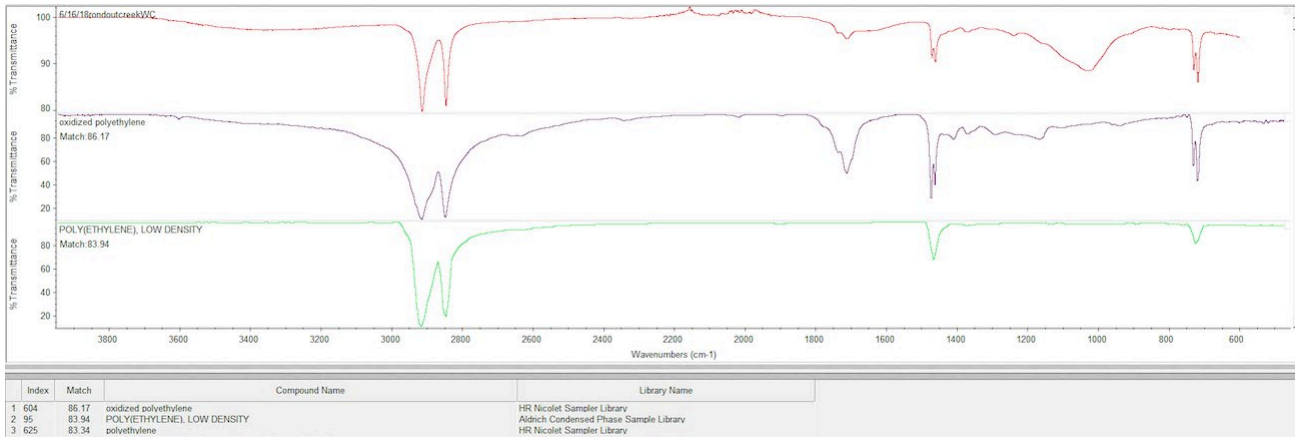
Infrared Spectroscopy

Of the 17 particles designated for identification through infrared spectroscopy, 16 particles resulted in matches greater than 50% to known polymers in the library database. 11 of these matches were found to be greater than 70% to their respective polymer. Of the 16 matches, nine were found in sediment and seven were found in surface water. Six different polymers were identified in this study with varying densities from 0.95-1.44 g/cm^3 (Table 3). Two spectra derived from examination of a particle from Rondout Creek tributary surface water and Constitution Marsh sediment are shown in Figure 8.

Polymer	Density (g/cm^3)	Number Identified in Surface Water	Number Identified in Sediment
Polyvinyl Chloride	1.38	1 (M)	2 (M)
Polyethylene	0.95	2 (T, T)	3 (M, M, OW)
Poly(vinyl stearate)	<1.0	1 (T)	1 (M)
Polyethylene Terephthalate	1.38	0	1 (M)
Polystyrene	1.04	2 (T,M)	2 (M,T)
Cellophane	1.44	1 (OW)	0

Table 3. **Polymers identified, abundance and densities:** Abundance of different polymers types identified using infrared spectroscopy and their relative densities (M, T, and OW represent whether the particle was found in a marsh, tributary, or open water sample, respectively).

A.



B.

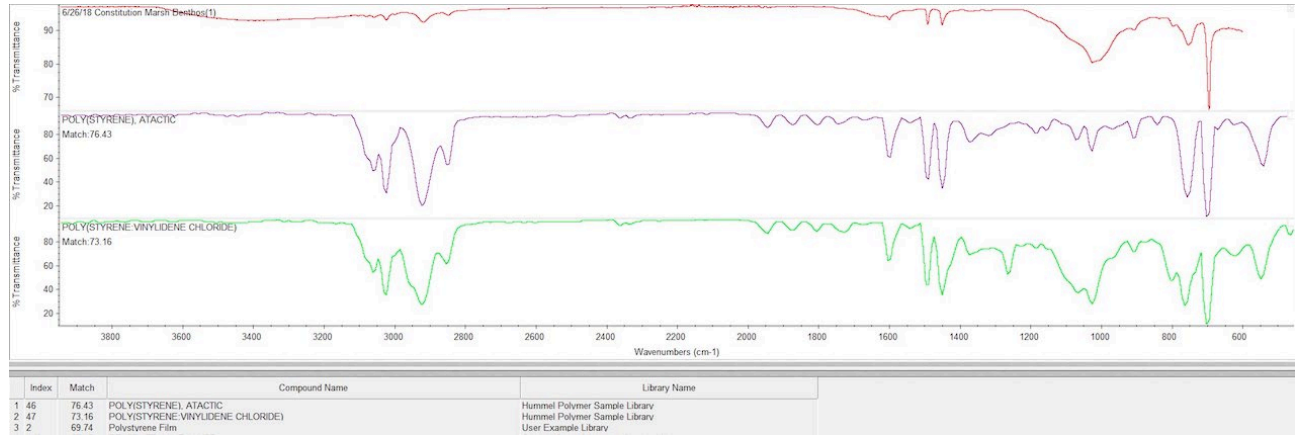


Figure 8. **FTIR spectra for two identified polymer particles:** Fourier Transform Infrared Spectrometry spectra of A) a particle sampled from surface water in Rondout Creek on 6/16/18 that produced an 86.17% match to oxidized polyethylene and B) a particle sampled from sediment in Constitution Marsh on 6/26/18 that displayed a 76.43% match to polystyrene.

DISCUSSION

Microplastic Content by Location Type

The findings of this study support the hypothesis that marshes may act as a sink for MPs. The marshes in this study contained significantly more MPs in sediment, with an average of 2.28 MPs/g MS, than either tributary or open water samples (Figure 3). Marshes were also found to have the highest average MP content across surface water samples; however, not significantly greater than tributary or open water MP contents. Surface water samples taken in open water were hypothesized to have the smallest MP concentration which is supported by this study as surface water content in open water was significantly lower than both marshes and tributary concentrations.

As only a small proportion of larger MPs were analyzed for polymer composition, the proportion of high-density plastics in marshes cannot be determined; however, both low-density polymers (polyethylene and poly(vinyl stearate)) and high-density polymers (polyvinyl chloride, polystyrene, and polyethylene terephthalate) were identified in marsh sediment. These results along with low MP concentrations in tributary sediment and the presence of high-density polymers in tributary surface water indicate a likely mechanism for the accumulation of high-density MPs in Hudson River marshes. As high-density plastics are discharged into tributaries, they are less likely to settle in streams with a constant velocity. Consequently, once these plastics travel downstream and reach the corresponding marsh, the water becomes stagnant or near stagnant and may allow plastics with a density greater than that of freshwater (1.0 g/cm^3) to sink and accumulate in the benthic zone. While the mechanism for low density polymer deposition is also unknown, the tidal influence on the marshes may play a key role by allowing these plastics to settle

during low tide and potentially become trapped by natural organic and inorganic material. Accumulation of MPs in salt marsh sediment has been identified in previous studies (Khan and Prezant 2018). As freshwater has a lower density than saltwater, the problem of accumulating MPs in sediment is amplified in freshwater mashes such as those in this study.

Microplastic Content by Site

The results of this study support the hypothesis that Sleightsburg Marsh would have the highest MP content in surface water and sediment. Sleightsburg Marsh contained significantly higher average MP concentrations in both surface water and sediment compared to the other three marshes. This can be explained by the large size of the watershed (1190 mi^2), the high number of SPDES outfalls found in the watershed, and the large amount of visible pollution at the site.

The findings fail to support the hypothesis that Rondout Creek would have the highest tributary MP concentrations in sediment or surface water. Fishkill Creek was found to have significantly higher concentrations than all other sites in surface water and the largest average MP concentration in sediment, although not significantly greater than any other site. Rondout Creek tributary samples were expected to contain the greatest MP content, largely due to the size of the Rondout-Wallkill watershed in comparison to the other target watersheds. A reason for the relatively low concentrations in comparison with Fishkill Creek could be the sampling location in Rondout Creek. Sampling in Rondout Creek took place upstream of its confluence with the Wallkill River in order to obtain proper water velocity, stream depth, and accessibility. By removing Wallkill River's contribution, the watershed sampled would only represent 405 mi^2 of the total

1190mi^2 watershed. This may account for the lower than expected MP concentrations in Rondout Creek tributary sampling.

Open water MP concentrations displayed very low variability between sites. This is likely due to the low sample size and the dilution of high microplastic concentrations in low discharge tributaries entering the high discharge Hudson River.

Putting the Hudson River in Perspective

Increases in the number of MP quantification studies worldwide and in the United States is allowing for comparisons of MP pollution between major watersheds around the world. The findings of this study show that the main stem of the Hudson River has an average surface water MP content of 0.03 MPs/L (Figure 2). A study which investigated regions of the Ottawa River in both Quebec and Ontario, Canada with varying land uses found an average of 0.10 MPs/L in surface samples near the shore, slightly higher than the average of this study (Vermaire et al. 2017). A different study in the United States examined MP content in surface water from 29 Great Lake tributaries which resulted in average concentrations of 4.2 MPs/m^3 or 0.0042 MPs/L in surface water (Baldwin et al. 2016). This finding is much lower than the average surface water MP content in the Hudson River tributaries investigated in this study. As more MP quantification studies continue to emerge, researchers will be able to create a more cohesive picture of the watersheds that are most subjected to MP pollution.

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