

QUANTIFYING AND SOURCE TRACKING MICROPLASTICS IN AN ESTUARINE
ENVIRONMENT

By

KENDI BAILEY

A thesis submitted to the

School of Graduate Studies

Rutgers, The State University of New Jersey

In partial fulfillment of the requirements

For the degree of

Master of Science

Graduate Program in Civil and Environmental Engineering

Written under the direction of

Nicole Fahrenfeld

And approved by

New Brunswick, New Jersey

October 2020

ABSTRACT OF THE THESIS

Quantifying and Source Tracking Microplastics in Estuarine Environment

By KENDI BAILEY

Thesis Director:

Nicole Fahrenfeld

The prevalence of microplastics in marine environments is well documented, but little is known of the accumulation patterns in estuarine environments and its land-based sources (i.e., wastewater effluents, and stormwater runoff). To investigate the behaviors of microplastics in estuarine environments, the samples were collected in the mouth of the Raritan River, NJ, along the river plume and the Hudson Raritan Bay targeting frontal zones, and into the ocean. Samples were collected during summer low flow and spring low and high flow conditions. To investigate the potential sources, samples were collected from various hydraulically connected stormwater outfalls and the influent and effluent of wastewater treatment plants (WWTPs). The focus of this study was on microplastics in the 500-2000 μm size range. The highest concentration of surface water was in the mouth of the Raritan during summer low flow. The concentrations of microplastics ranged from 0-2.75 MP/m^3 in the Raritan, 400-600 MP/m^3 in stormwater, and was frequently 0 MP/m^3 in wastewater effluent, suggesting stormwater may serve as

an understudied source. Polymers were characterized by attenuated total reflectance FTIR and polyethylene was the most prevalent type. Polymer types and concentrations were compared between the different waters and similarities between surface water, wastewater influent, and stormwater were found. Additionally, a linear correlation was found between the total concentration of particles in a sample following oxidation and density separation and its microplastic concentration for wastewater influent, surface water, and stormwater. If this correlation is also observed in other locations, it may serve as a method for rapid estimation of total microplastic by techniques that count total particles. These results have implications for understanding the behavior of microplastic in varying flow conditions and in frontal zones as well as reveal potentially important sources of microplastics in the estuarine environment.

Acknowledgements

Thank you to Dr. Bob Chant, Dr. Georgia Arbuckle-Keil, Dr. Gene Hall, for your collaboration and the allowance of use of your equipment. Thank you to New Jersey Sea Grant for supporting this project. Additional funding was proved by the Rutgers School of Engineering Fellowship. Thanks also to Will Boni, Katie Parrish, and Shreya Patil for lab support.

Table of Contents

ABSTRACT OF THE THESIS	ii
Acknowledgements	iv
1. Chapter (1): Broad Introduction.....	1
1-1- Background.....	2
2. Chapter (2): Introduction to Research, Methods, Results, and Discussion	4
2-1- Introduction.....	5
2-2- Materials and Methods	6
2-2-1- Sampling Methods.....	6
2-2-2- Extraction Methods.....	9
2-2-3- Chemical Analysis & Spectral Interpretation.....	10
2-2-4- Data Analysis	11
2-3- Results	12
2-3-1- Microplastic concentrations in surface and source waters	12
2-3-2- Microplastic composition in surface and source waters.....	15
2-4- Discussion	19
2-4-1- Microplastic in the Raritan river and estuary.....	19
2-4-2- Comparing microplastic in the Raritan river and estuary to different potential sources	22
2-5- Conclusions.....	23
3. Chapter (3): Broader Implications	25
3-1- Conclusion	26
References.....	27

Table of Figures

Figure 1 – Map of surface water sampling sites and salinity.....	6
Figure 2 – Map of stormwater sampling locations, stream gages, and precipitation stations..	8
Figure 3 - Stream gage height and hourly precipitation.	9
Figure 4 - Bubble plot showing sampling sites and microplastic concentration.	12
Figure 5 - Random forest regression model showing the factors and percent increase mean squared error.....	13
Figure 6 - Relationship between total concentration of particles per cubic meter and the microplastic concentration per cubic meter.	14
Figure 7 - Boxplots of microplastic concentrations	15
Figure 8 - Barchart of polymer types.....	16
Figure 9 - Polymer type composition.....	17
Figure 10 - Hierarchical cluster analysis of polymer type and concentration.	18

Table of Tables

Table 1 - WWTP sampling dates, amounts, types, design flow, and hydraulic connection to surface water sites.....	7
---	---

1. Chapter (1): Broad Introduction

1-1- Background

Due to plastic's low cost and convenience, plastic production has continued to rise over the last few decades.¹ It is estimated that over five trillion tons of plastic particles are floating at sea.² Plastic debris has significantly negative effects on marine life and seabird species, due to ingestion or other interaction.³ Plastic is of growing concern as a contaminant due to its chemical additives affecting the ecosystem as well as its transfer in the food chain.⁴

The size of the plastic plays an important role in its impact. Larger plastics can disrupt marine life and cause entanglements, while smaller particles can be mistaken for food. Large plastics greater than 5 mm can be referred to as macroplastics while particles smaller than 5 mm are microplastics. Microplastic can be categorized into two categories, primary and secondary. Primary microplastics are manufactured in small size such as the those in personal care products, while secondary microplastics are microplastics that were generated by the breaking of larger plastics and can consist of a range of polymers. The most common polymers found are polyethylene, polypropylene, polyester, polyethylene terephthalate, and polystyrene.⁵

The polymers are transported from rivers to oceans and there are widespread reports documenting microplastic in marine environment.⁶ Rivers have shown to be a significant contributor to the microplastic concentration in oceans.^{7, 8} The abundance of microplastics in rivers is necessary to further understand the transport into the marine environment. Rivers have several potential sources of microplastics including effluent from wastewater treatment plants which has been to be a source^{9, 10}, but studies indicate stormwater runoff as another potential source.^{10, 11}

Although microplastics in various surface waters have been documented, there is still a need for quantifying the aspects driving the presence, abundance, and distribution of microplastics in freshwater environments.¹² Comprehensive study involving microplastics in surface water and its potential sources such as wastewater and stormwater will aid in understanding the problem and further the ability to develop mitigation practices.

2. Chapter (2): Introduction to Research, Methods, Results, and Discussion

2-1- Introduction

Plastic debris are frequently observed in marine environments^{13, 14} and there is a rapidly growing concern about the threat it poses to those environments.^{15, 16} Microplastics (<5 mm) are small plastic particles that are often formed from larger particles and have spread throughout the world's seas and oceans.¹⁷ The spread of microplastics in marine environments poses concern regarding marine and human health.¹⁸ However, less is known about microplastic in estuarine environment and its sources of pollution.

Microplastics transport into rivers and oceans is a big point of interest. Plastic in river and coast environments has been reported.¹⁹ Studies have been done showing the influence of wastewater effluent on the river environment and its potential as a source.⁹ Sediments in stormwater retention ponds have also been investigated and suggested as a source when considering microplastic fate.²⁰ However, there have been few comprehensive studies involving surface water, wastewater, stormwater, limiting our understanding of the transport of microplastics.

The objectives of this study are to quantify microplastic concentration in surface water to see whether microplastic accumulates at frontal zones, to determine the effects of flow on the surface water plastic concentration, and to investigate potential sources of microplastics by quantifying microplastic concentration and clustering polymer types in wastewater influent, effluent, and stormwater. Based on polymer type, cluster analysis was performed to show similarities between samples. Moreover, correlations between total particle concentration and microplastic concentration were performed to provide insight to the relationship of total particles in a sample to the amount of microplastics.

2-2- Materials and Methods

2-2-1- Sampling Methods

Surface water sampling was performed on the Raritan River and in the Raritan/Hudson Bay (Fig. 1). Samples were collected by boat using plankton nets (mesh size 80 or 150 μm , Science First, Yulee, FL) in duplicate at each of three to six sampling locations on July 26, 2018 (low flow), April 11, 2019 (low flow), and April 16, 2019 (high flow). The nets were fixed to the back of the boat to collect floating particles by towing for 25 minutes at a speed of 2 knots. The volume passed through the net was either calculated using the speed of the boat, the time towed, and the net dimensions or via measurements from flow meters placed in the net opening (General Oceanics, Miami, FL). Sampling sites were selected to capture various salinities. One blank (net left open to air for the length of one tow) and one matrix spike (replicate net towed then spiked with polyethylene beads extracted from a personal care product), were collected at one site on each April 11, 2019 and April 16, 2019.

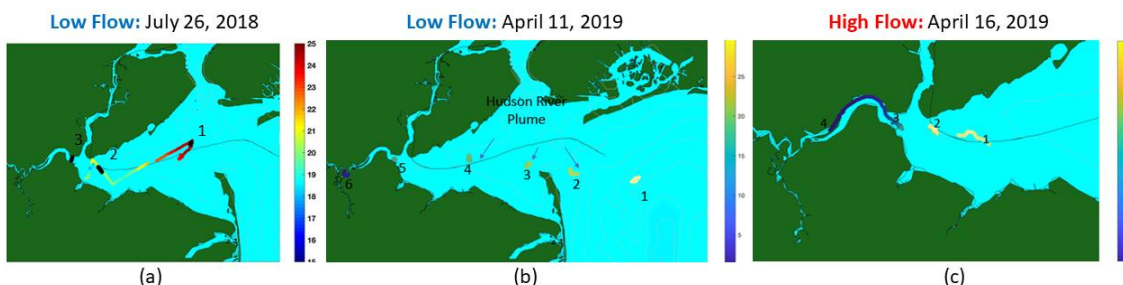


Figure 1 – This figure shows surface water sampling sites (a) July 26, 2018 (low flow) (b) April 16, 2019 (low flow) (c) April 16, 2019 (high flow). The colors represent surface salinity from low (blue) to high (dark red).

Four wastewater treatment plants (WWTPs) were sampled throughout New Jersey.

Either composite or grab samples were collected from wastewater treatment plants based upon availability (Table 1).

Table 1 - WWTP sampling dates, amounts, types, design flow, and hydraulic connection to surface water sites

ID	Sampling Date	Sample Volume (L)	Type	Flow (MGD)	Hydraulically Connected to study area
WWTP1	11/26/2018	3	24hr composite	16	Yes
WWTP2	9/03/2019	4	Grab	300	Yes
WWTP3	10/18/2019	4	Grab	3	No
WWTP4	12/04/2019	4	24hr composite	40	No

Stormwater samples were collected from three sites during heavy rain on October 16, 2019 (Fig. 2). Sample sites included two pipes carrying runoff from urban areas in Bayonne and New Brunswick NJ and one site carrying stormwater from a recreational area in Piscataway NJ (labelled City B, City N, and Field P, respectively). City B samples were collected as pump out of a storm drain and come from a combined sewer system. Field P and City N samples were taken from the pipe outfall and are part of the stormwater pipes in a region with separate sanitary systems. Five liters of stormwater were collected over the duration of a rainstorm with one liter taken every 10-45 min at a time per site (Fig 3). Rainfall and stream gage data were collected from the nearest stations for each sampling area. Rainfall data were taken from Rutgers New Jersey Weather Network²¹ and stream gage data taken from United States Geological Survey (USGS).²²

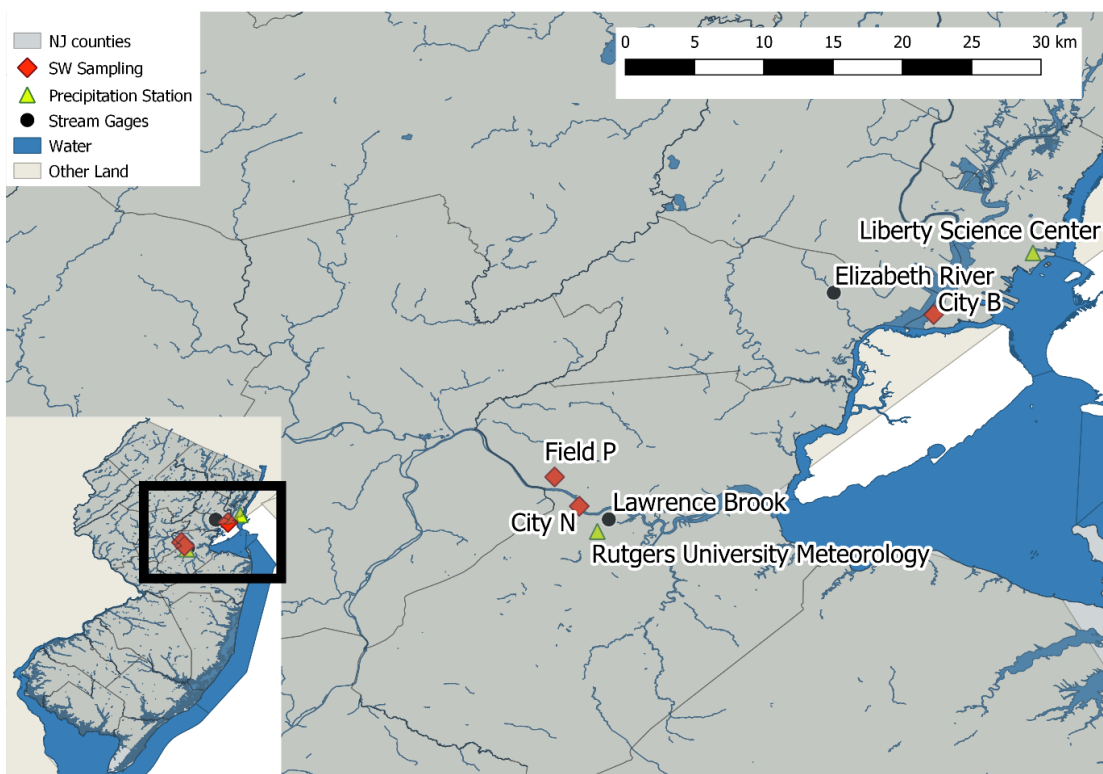


Figure 2 – Map of stormwater sampling locations, stream gages, and precipitation stations. Insert map shows study area location in New Jersey.

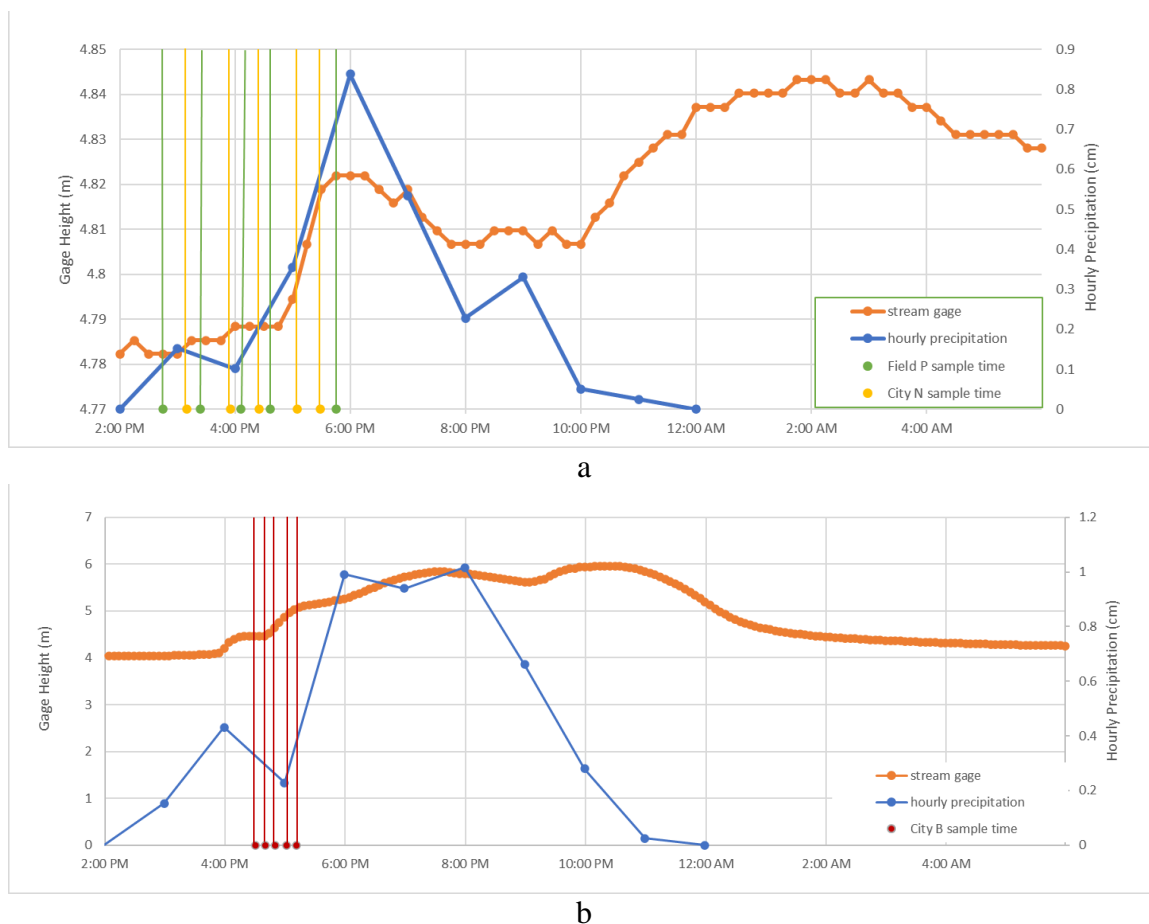


Figure 3 - Stream gage height and hourly precipitation data taken from the nearest stations for storm samples (a) Field P and City N, collected from Lawrence Brook stream gage in Weston Mills, NJ and precipitation from the New Brunswick, NJ (b) City B, collected from Elizabeth River stream gage in Elizabeth, NJ and precipitation from Jersey City, NJ.

2-2-2- Extraction Methods

Nets were rinsed with DI water and separated into size classes using a series of sieves (2000, 500, 250 μm size). Material retained on both the 2000 μm sieve size was discarded. Then, the materials from each remaining sieve were rinsed with DI water and transferred to glass beakers. The organic matter was oxidized by hydrogen peroxide and a catalyzed iron (II) solution.²³ Briefly, 20 mL of 0.05 M iron (II) solution was added to each beaker, followed by 20 mL of 30% hydrogen peroxide. The solutions were heated to 75°C on a hot plate and then stirred using a magnetic stir bar for 30 minutes before sodium chloride, 6 grams per 20 mL, was added to increase the mixture density. The

oxidized and NaCl treated samples were transferred to glass funnels with the ends capped by clamped surgical tubing for density separation. The funnels were covered with foil to prevent contamination and left overnight for settling. Settled materials were discarded and the floating particles were collected, rinsed with DI water, and transferred to glass petri dishes covered with a glass lid.

2-2-3- Chemical Analysis & Spectral Interpretation

The recovered particles in the 500-2000 μ m size range were analyzed using Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy on one of two instruments. (The 250-500 μ m size class was analyzed by K. Sipps.²⁴) The first instrument used was a Bruker Alpha spectrometer (Bruker Optics, Bellerica, MA) fitted with a DuroScope (Smith's Detection System, Danbury, CT) diamond or germanium ATR and equipped with a DTGS (Deuterated Triglycine Sulfate) detector. The other instrument used was a PerkinElmer Spectrum 100 FT-IR spectrometer (PerkinElmer Life and Analytical Sciences, Shelton, CT) equipped with a 3-reflection diamond ATR attachment and a DTGS detector. Particles were transferred to the ATR using tweezers for chemical analysis. Wavelengths were collected between 4000 and 600 cm^{-1} and 32 scans at 4 cm^{-1} resolution were performed per particle. For samples containing less than 80 particles, all were analyzed. For samples containing greater than 80 particles up to 119 particles were analyzed starting with visually identified microplastic. Microscope images were collected for select samples using a reflected light microscope (Stereo Zoom Microscope, Olympus, Japan) pictures were captured via cell phone camera. Spectra obtained from the FTIR were analyzed with visual inspection of peak patterns and confirmed using SiMPle (Systematic Identification of Microplastics in the

Environment).²⁵ SiMPle compares the IR spectra of their polymer database and assigns materials to them with accompanying probability scores. For this study, polymers with probability scores over 40% are counted as plastics and labelled by their polymer identification.

2-2-4- Data Analysis

Statistical analysis was performed using R (www.rproject.org). A Shapiro-Wilk test was used to test for normality of microplastic concentration data. Given that data were not normal, a Kruskal-Wallis test was applied to determine differences in concentration by sample source, followed by a posthoc pairwise.t.test with a Bonferroni correction for multiple comparisons. The same tests were used to compare the microplastic concentrations observed at different surface water sampling sites and dates. A random forest regression model (randomForest package) was used to determine the factors that affect the microplastic concentration after a permutational analysis of variance returned error. Correlation between the total concentration and the microplastic concentration per cubic meter was plotted as a linear regression and significance tested with a Spearman rank-order correlation test. Percentages of polymer types were found by separating the polymer hits into categories by polymer class. The categories used were polyethylene, polypropylene, polystyrene, polyester, rubber, vinyl copolymers, and other plastics. The polymer types and concentrations were compared between samples by creating a Bray-Curtis dissimilarity matrix of square root normalized data followed by cluster analysis with a SIMPROF test.

2-3- Results

2-3-1- Microplastic concentrations in surface and source waters

Microplastics were observed in each sample type (surface water, stormwater, wastewater). In surface water samples, microplastic concentrations were the highest in the river and lowest in the samples furthest out in the bay (Fig. 4). Differences were observed between the different sites/dates ($p=0.033$, Kruskal-Wallis), primarily due to the high observation at the mouth of the Raritan River during the July sampling event which was significantly higher than concentrations observed at all sites on the other sampling dates (all $p \leq 0.028$, posthoc pairwise.t.test). However, there were no differences observed between samples taken on the same day (all $p \geq 0.81$, posthoc pairwise.t.test). The relative percent difference between replicate samples ranged from 0-200% with an average of $94.8 \pm 84.2\%$. It is worth noting that the samples with higher relative percent differences (RPDs) were those with low MP concentration (i.e., <5 particles/cubic meter). For samples with >5 MP/cubic meter, RPD was $34 \pm 28\%$. The average recovery of microplastics in matrix spikes was 63.54 ± 12.1 . There were no microplastics observed in the field blank samples.

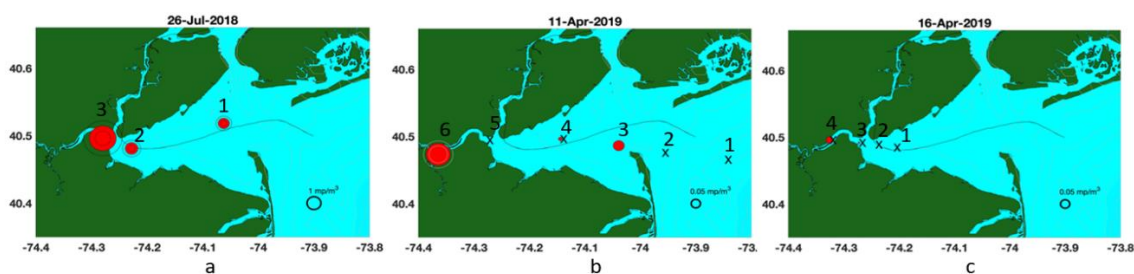


Figure 4 - Maps of the sampling area and bubble plots showing the average concentration of microplastics per cubic meter on each sampling date (a) July 26, 2018, low flow (b) April 11, 2019, low flow (c) April 16, 2019, high flow. When microplastics were observed in both replicate samples, the overlaid circles on the bubble plots indicate the high and low values and X's represent samples for which microplastics were not detected.

To understand the factors potentially driving the microplastic concentrations, a random forest regression was performed on salinity, standard deviation of salinity, flow, and date. This analysis indicated that the model explained 47.1% of the variance in the microplastic concentration data and that most significant factor in the surface water results was the date of the sampling (Fig. 5). The percent increase in mean square error for date is 15.6%. The significant factors were followed by standard deviation of salinity, a measure indicating how frontal the sampling location was, the flow, and the salinity (%IncMSE=7.90, 5.67, 3.53, respectively).

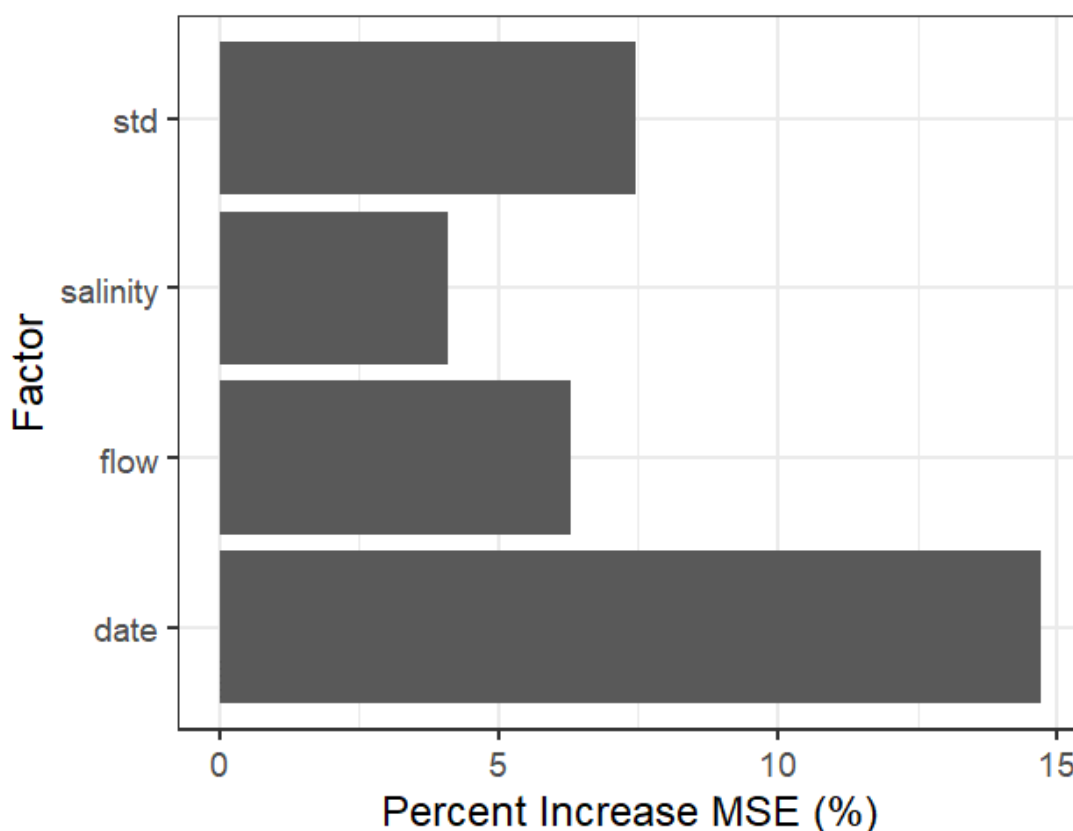


Figure 5 - Random forest regression model showing the factors and percent increase mean squared error. Std is the standard deviation of the salinity, showing how frontal the water is. These data explained 47.1% of the variance in the microplastic concentration for the surface water samples.

Next, to understand if microplastic observations were correlated with total particles present in the sample following wet peroxide oxidation, a correlation was tested between

the total concentration of particles and the microplastic concentration per cubic meter showing a significant positive correlation in surface water samples (Linear Regression: slope=0.56, $R^2=0.9798$, $p=2.58 \times 10^{-9}$, Spearman Rank, Fig. 6). The same correlation was tested on the data from all the samples showing positive correlation across all sampling types (Linear Regression: 0.35, $R^2=0.9346$, $p=6.33 \times 10^{-9}$, Spearman Rank, Fig. 6). Note, the field blanks for both the surface water and wastewater sampling did not have any microplastic particles, but the field blanks for the wastewater samples each had one non-microplastic particle. This low level of non-microplastic contamination did not appear to impact the correlation result.

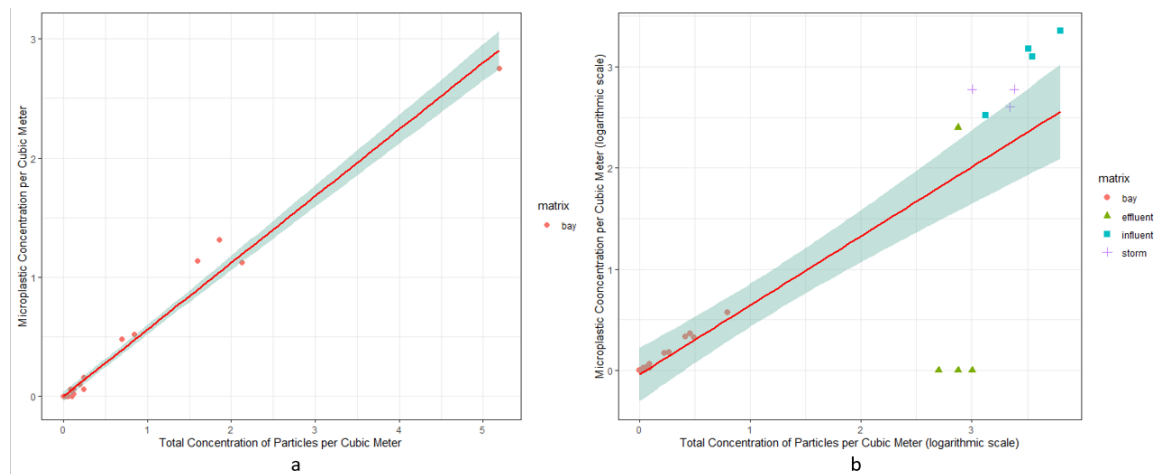


Figure 6 - Relationship between total concentration of particles per cubic meter and the microplastic concentration per cubic meter. (a) Surface water samples, the red line on the graph represents the linear regression and the shaded area around it represent a 95% confidence interval. (b) All sample types shown on a log(value+1) scale.

The wastewater influent had the highest concentrations of microplastic compared to wastewater effluent, stormwater, and surface water (all $p \leq 6.5 \times 10^{-5}$, posthoc pairwise.t.test with Bonferroni correction; Fig. 7). The wastewater influent also has the greatest range in concentrations, spanning two orders of magnitude. Wastewater effluent, stormwater, and surface water had similar concentrations of microplastics (all $p \geq 0.23$,

posthoc pairwise.t.test with Bonferroni correction) (Fig. 7). Although, the sample size for stormwater (N=3) was small and a larger sample size could possible result in significant difference in microplastic concentration compared the surface water (N=26); these matrices had median concentrations of 600 MP/m³ and 0.01 MP/m³, respectively.

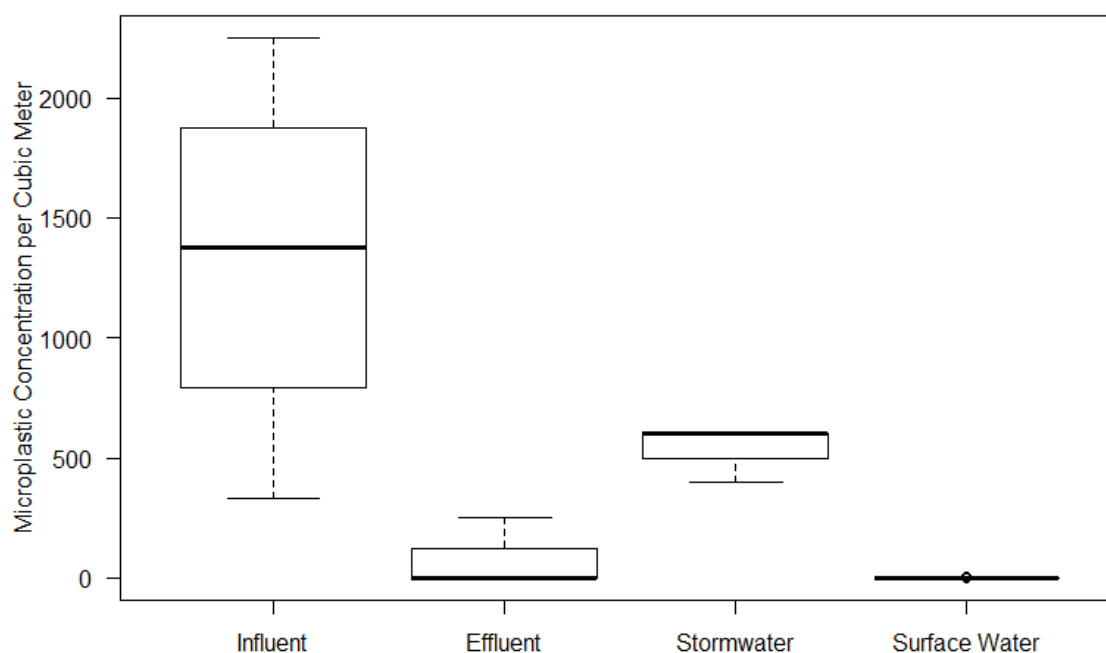


Figure 7 - Boxplots of microplastic concentration of wastewater influent (“influent,” N= 4), wastewater effluent (“effluent,” N=4), stormwater (N=3), and surface water (N=26).

2-3-2- Microplastic composition in surface and source waters

A variety of polymer types were identified via the SiMPle analysis, example spectra associated with select microparticles are shown in Fig. 8. Of the microplastics observed, the most commonly observed was polyethylene which represented $45.1 \pm 32.9\%$ of microplastics identified (all $p < 0.0003$, posthoc pairwise.t.test with Bonferroni correction) and was observed in 13/16 samples with microplastic (Fig. 9). Polymers including rubber (8/16 samples with microplastics), polypropylene (6/16), polystyrene (1/16), polyester

(2/16), and various vinyl copolymers (7/16) were also present. The vinyl copolymers consisted of ethylene ethyl alcohol, ethylene vinyl alcohol, styrene allyl alcohol, and styrene acrylonitrile. Polymers categorized as “other” included turf fibers, polyether, and polyvinyl stearate.

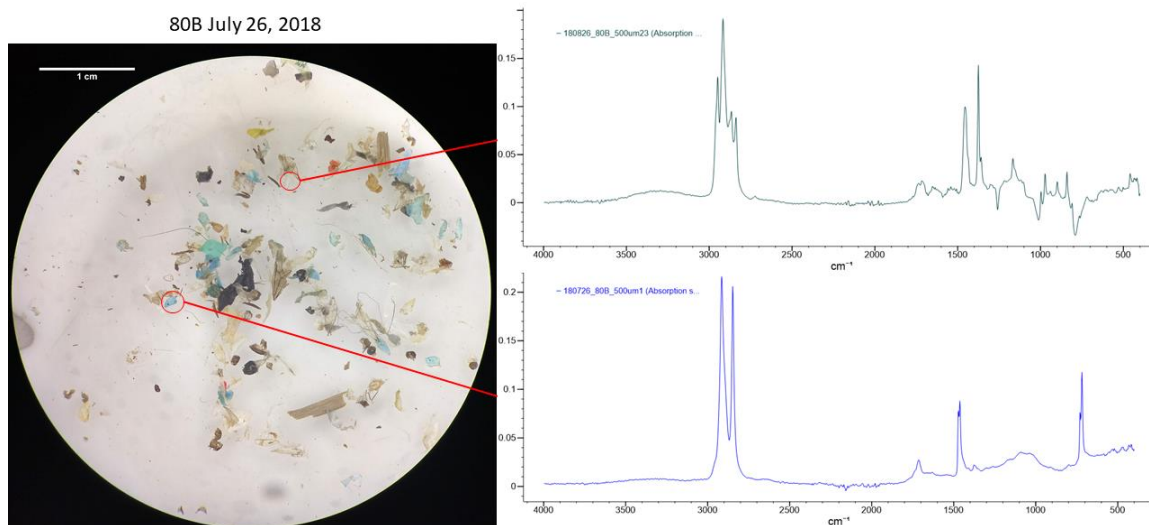


Figure 8 - Sample from July 26, 2018, site 1 showing examples of polypropylene (top) and polyethylene(bottom) plastics and their respective spectra.

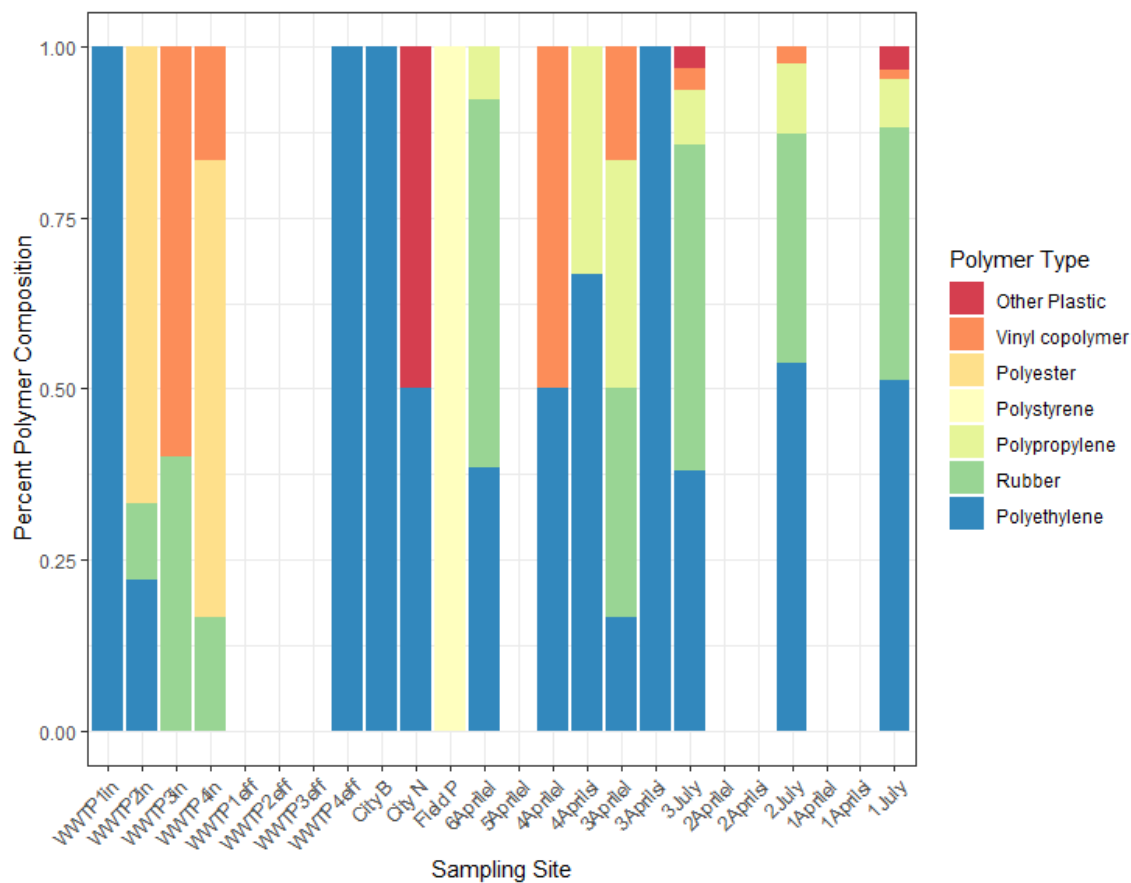


Figure 9 - The polymer type composition of each sample. Aprilel represents the April11, 2019 sampling date. Aprisi represents April 16, 2019

Cluster analysis was used to understand if there were patterns in the polymer type and concentration observed between the different sample types and locations. No clusters were significantly different (SIMPROF test, $p > 0.196$). Replicate surface water samples clustered with 30.6-71.4% similarity, which did not necessarily result in them forming clusters with the highest similarity to one another. Surface water samples from the low flow July 26, 2018 sampling formed a cluster with 59.1% similarity with one another and cluster with select samples from the April 11, 2019 low flow sampling at 30.6% similarity. Samples from Sites 3 and 4 on the low flow sampling clustered with wastewater influent from plants 2-3 with 42.0% similarity. The high flow April 16th samples with MP clustered with influent from WWTP1, effluent from WWTP4, and stormwater from City N and B with 63.4% similarity. Field P was the most distinct sample, consisting of only polystyrene with 0% similarity to the other samples.

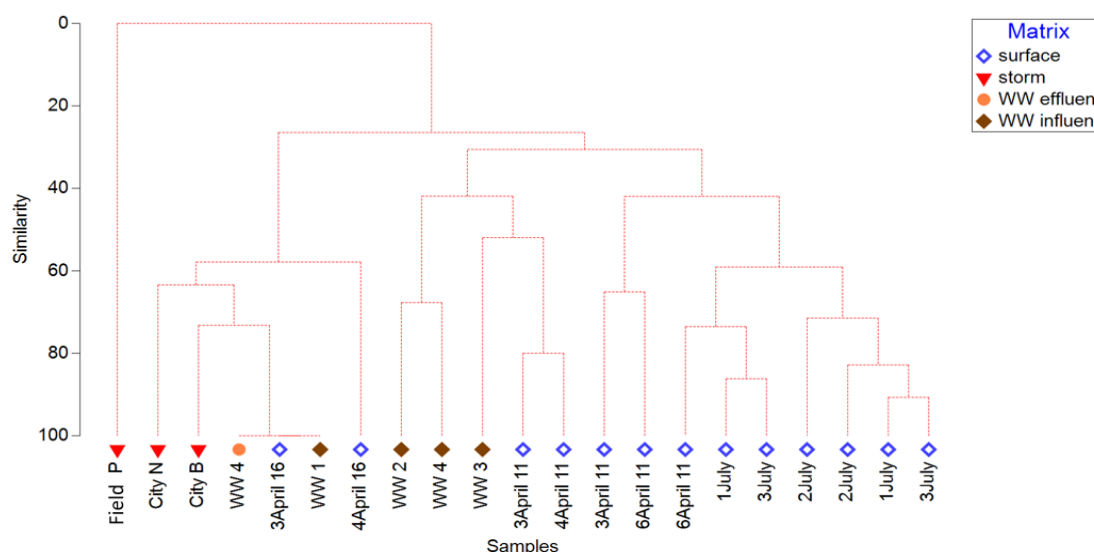


Figure 10 - Hierarchical cluster analysis of polymer type and concentration. Samples connected with red bars represent no significant differences (via SIMPROF test). Labels such as 3April 16 represents Site 3 collected on April 16, and so forth.

2-4- Discussion

2-4-1- Microplastic in the Raritan river and estuary

Microplastic concentrations between 0 and 2.75 MP/m³ were observed in surface waters collected from the mouth of the Raritan River out to the ocean. This is consistent with the range reported in a recent review of microplastics and nanoplastics in aquatic environments that concluded that the concentrations of macro and microplastics in lakes, rivers, and oceans would be between 10⁻³-10³ MP/m³.^{Ref 26} Likewise, the values found are consistent with studies of estuarine and coastal environments from the Raritan River,²⁴ Delaware Bay,²⁷ and the Adriatic Sea¹⁹ that reported values of 0.19-84 MP/m³.

The highest concentration of microplastic was found in the mouth of the Raritan River and in the river itself, as compared to the open ocean. A similar observation was reported in previous studies of microplastic size classes 300-5000 µm,^{Ref. 27} >500 µm,^{Ref 19} >125 µm^{Ref 28} in the river and ocean environment suggesting the river is a source that is diluted as it enters the estuary. Researchers that sampled multiple days saw date as a factor that influenced the microplastic concentration as well.^{27, 28} Our sampling plan was designed to capture whether microplastic accumulated at frontal zones where the freshwater from the river and ambient salt water of the ocean meet, given that this is where sediment accumulates²⁹ and therefore primary production is high. If microplastic concentrations were higher at frontal zones, then one may expect this to be a location of entry into the food web. Interestingly, in the size range studied here (500-2000 µm), there was no consistent accumulation in the frontal zones (site 2 on July sites 3,4,5 on April 11, 2-19; sites 2 and 3 on April 16, 2019). In the 250-500 µm size range, higher concentrations in

frontal zones was observed,²⁴ showing that the concentration data observed may not hold true across size classes.

There were generally no significant differences in samples taken on the same day with the exception of the mouth of the Raritan River during the July sampling event which was higher than all other concentrations observed. There were, however, noticeable differences between flow conditions where July (low flow) had microplastic concentration $1.22 \pm 0.826 \text{ MP/m}^3$, April 11 (low flow) had 0.35 ± 0.052 , and April 16 (high flow) had 0.01 ± 0.0214 . Kapp et al. also found that periods of low flow may accumulate microplastics³⁰ greater than $100 \mu\text{m}$ after sampling the Snake River, WY and revealing a negative correlation between microplastic concentration and velocity of water. In low flow conditions, the microplastic had higher concentrations as microplastic were not diluted by rain and runoff. Contrary to this study, researchers have found that in a tropical estuarine environment with a size above $45 \mu\text{m}$, concentrations are higher in high flow conditions³¹ where the flow serves to transport microplastic particles by direct runoff.

The most commonly observed polymer in the river and estuary was polyethylene which represented $45.1 \pm 32.9\%$ of microplastic identified. This finding is consistent with results from the paired analysis surface water samples in the $250\text{-}500\mu\text{m}$ size class conducted by Sipps,² where over 45% of the polymers identified were polyethylene. Rubber made up the next highest portion of polymers observed in the surface water $500\text{-}2000 \mu\text{m}$ size class, which was not reported by Sipps. But the other polymers observed (i.e., polypropylene, polystyrene, and polyester) were all present in both the $500\text{-}2000\mu\text{m}$ and $250\text{-}500\mu\text{m}$ size classes. The microplastic analyzed here were fragments, films, and

pellets but the observed morphologies were not quantitatively categorized. Note, fibers were observed in the samples but were not analyzed because of their small size and the chance of contamination.

There was a linear correlation between the total particle concentration remaining after the oxidation and density separation and microplastic concentration. The particles not classified as microplastic (i.e., manmade polymers) had high similarity to cellulose, natural fibers, cow fur, shells, and other natural materials. Notably, the wastewater effluent had several samples with a microplastic concentration of zero but that did contain other particles and therefore fell well outside of the regression confidence interval. The lower microplastic concentration may be due to sampling at a relatively small volume, or WWTPs being effective at removing microplastic. While some papers sample a small percentage of sample and scale up the results, little is known about the relationship between the total concentration of particles and the microplastic concentration in a sample. This result may indicate that total post-oxidation and density separation particle counting, and a regression could be used to estimate microplastic concentration in surface water, wastewater influent, and stormwater, but not wastewater effluent. Given that microplastic analysis with the techniques applied here is not high throughput, application of regression could help provide a first estimate of total microplastic concentration in such samples and help reduce analysis time. Of course, validation in wider set of locations would be needed to understand whether this regression is site-specific and further analysis following the regression analysis would still be needed to identify the types of polymers observed.

2-4-2- Comparing microplastic in the Raritan river and estuary to different potential sources

Microplastic collected from potential sources were collected and analyzed to understand if the observed polymer profiles were similar to those observed in the river and bay. The wastewater influent had the highest concentrations of microplastics while also having the greatest range in concentration (333-2250 MP/m³) compared to wastewater effluent, which frequently had a concentration of 0 MP/m³. This suggests that the treatment plants studied here appear to be generally effective at removing microplastics, which is consistent with a review of the occurrence and fate of microplastic in WWTP which concluded that treatment plants were efficient at removing 72-99.4% of microplastics.³² The stormwater concentrations were between 400 and 600 MP/m³. This is lower than a stormwater runoff study by Piñon-Colin that analyzed particles in a larger size range (i.e., greater than 25 µm) and found a range of 12,000-2,054,000 MP/m³ in runoff from residential, commercial, and industrial land usage.¹¹ Liu et al. sampled stormwater retention ponds for microplastic greater than 10 µm and found concentrations of 490-22,894 MP/m³ after looking at residential, industrial, and commercial areas.³³ The Piñon-Colin only did visual identification under microscope while this and the Liu study used FTIR analysis, therefore the higher greater microplastic concentration may be due to site-to-site differences or an overestimation due to error in visual identification(REF). The smaller size range of this study (500-2000µm) could be why it falls on the lower end or well below these ranges.

The polymer concentrations and profiles were compared between the sample types with cluster analysis. Stormwater from City B was collected near a parking lot in a residential

area and City N adjacent to a highway. These samples contained mainly polyethylene and clustered with 63.4% similarity to one another. Stormwater from Field P was collected in between three recreational artificial turf fields clustered at 0% similarity to all other samples and was the only sample from this study (stormwater, wastewater, surface water) to contain polystyrene. Other studies have observed higher quantities of polystyrene.^{11, 24, 34} This unique land use may explain why the results were so different from the other storm samples, although collection of more stormwater samples is suggested to fully capture the potential diversity of polymers it contains and potential linkages with land use.

Stormwater from City B and City N had 57.9% polymer similarity with surface water from April 11, 2016 and 26.5% similarity with and the rest of the surface water. This indicates that stormwater is a potential source of microplastic. Qualitatively, the surface water contained a colorful range of microplastic including bright blue and yellow fragments. WWTP particles were typically brown and orange fragments. Stormwater had brown and tan fragments.

2-5- Conclusions

In this study, microplastic were quantified and observed polymer types reported in surface water, wastewater influent, wastewater effluent, and stormwater to understand if and where microplastic accumulate and to provide insight into sources. The varied microplastic concentration in surface water by date suggests a relationship between date and/or flow, with the highest concentration observed during summer low flow conditions at the mouth of the Raritan River. More sampling dates at low and high would be needed this relationship to be validated. These results are for the 500-2000 μm size class and

were not all consistent with the smaller size class. Stormwater microplastic concentration and the clustering of polymer results with surface water samples indicate reveal it as a potential important source of surface water pollution. A higher number of stormwater samples with varying land usages would be needed to fully capture the contribution of stormwater. Additionally, this research found a linear correlation between the total concentration of particles and the microplastic concentration in a sample. Using a regression could reduce analysis time, but a broader set of locations would be needed to further determine this correlation and whether the correlation is site or source specific.

3. Chapter (3): Broader Implications

3-1- Conclusion

This study directs more research on the microplastic contamination in the estuarine environment. This is the first comprehensive study of microplastic concentration in the Raritan-Hudson Bay area. The similarities in polymer type between samples suggest their potential impact. It also demonstrates a linear correlation between total concentration and microplastic concentration which could potentially aid in microplastic concentration studies by reducing analysis time. Recommendations for next steps would be to conduct broader sampling. More surface water samples at low flow and high flow, as well as more stormwater samples with varying land-usages would be needed further investigate the connections found herein.

References

1. G. Gourmelon, Global plastic production rises, recycling lags, *Vital Signs*, 2015, **22**, 91-95.
2. M. Eriksen, L. C. Lebreton, H. S. Carson, M. Thiel, C. J. Moore, J. C. Borerro, F. Galgani, P. G. Ryan and J. Reisser, Plastic pollution in the world's oceans: more than 5 trillion plastic pieces weighing over 250,000 tons afloat at sea, *PloS one*, 2014, **9**, e111913.
3. C. J. Moore, Synthetic polymers in the marine environment: a rapidly increasing, long-term threat, *Environmental Research*, 2008, **108**, 131-139.
4. C. G. Avio, S. Gorbi and F. Regoli, Plastics and microplastics in the oceans: from emerging pollutants to emerged threat, *Marine Environmental Research*, 2017, **128**, 2-11.
5. A. Schwarz, T. Ligthart, E. Boukris and T. Van Harmelen, Sources, transport, and accumulation of different types of plastic litter in aquatic environments: a review study, *Marine Pollution Bulletin*, 2019, **143**, 92-100.
6. M. C. Blettler, E. Abrial, F. R. Khan, N. Sivri and L. A. Espinola, Freshwater plastic pollution: Recognizing research biases and identifying knowledge gaps, *Water Research*, 2018, **143**, 416-424.
7. L. C. Lebreton, J. Van Der Zwet, J.-W. Damsteeg, B. Slat, A. Andrady and J. Reisser, River plastic emissions to the world's oceans, *Nature Communications*, 2017, **8**, 15611.
8. S. Rech, V. Macaya-Caquilpán, J. Pantoja, M. Rivadeneira, D. J. Madariaga and M. Thiel, Rivers as a source of marine litter—a study from the SE Pacific, *Marine Pollution Bulletin*, 2014, **82**, 66-75.
9. S. Estahbanati and N. L. Fahrenfeld, Influence of wastewater treatment plant discharges on microplastic concentrations in surface water, *Chemosphere*, 2016, **162**, 277-284.
10. R. Sutton, S. A. Mason, S. K. Stanek, E. Willis-Norton, I. F. Wren and C. Box, Microplastic contamination in the San Francisco Bay, California, USA, *Marine Pollution Bulletin*, 2016, **109**, 230-235.
11. T. de Jesus Piñon-Colin, R. Rodriguez-Jimenez, E. Rogel-Hernandez, A. Alvarez-Andrade and F. T. Wakida, Microplastics in stormwater runoff in a semiarid region, Tijuana, Mexico, *Science of The Total Environment*, 2020, **704**, 135411.
12. D. Eerkes-Medrano, R. C. Thompson and D. C. Aldridge, Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs, *Water Research*, 2015, **75**, 63-82.
13. F. Galgani, A. Souplet and Y. Cadiou, Accumulation of debris on the deep sea floor off the French Mediterranean coast, *Marine Ecology Progress Series*, 1996, **142**, 225-234.

14. A. Cózar, F. Echevarría, J. I. González-Gordillo, X. Irigoien, B. Úbeda, S. Hernández-León, Á. T. Palma, S. Navarro, J. García-de-Lomas and A. Ruiz, Plastic debris in the open ocean, *Proceedings of the National Academy of Sciences*, 2014, **111**, 10239-10244.
15. C. Wilcox, E. Van Seville and B. D. Hardesty, Threat of plastic pollution to seabirds is global, pervasive, and increasing, *Proceedings of the National Academy of Sciences*, 2015, **112**, 11899-11904.
16. P. Villarrubia-Gómez, S. E. Cornell and J. Fabres, Marine plastic pollution as a planetary boundary threat–The drifting piece in the sustainability puzzle, *Marine Policy*, 2018, **96**, 213-220.
17. L. Van Cauwenberghe, A. Vanreusel, J. Mees and C. R. Janssen, Microplastic pollution in deep-sea sediments, *Environmental pollution*, 2013, **182**, 495-499.
18. M. Smith, D. C. Love, C. M. Rochman and R. A. Neff, Microplastics in seafood and the implications for human health, *Current Environmental Health Reports*, 2018, **5**, 375-386.
19. E. C. Atwood, F. M. Falcieri, S. Piehl, M. Bochow, M. Matthies, J. Franke, S. Carniel, M. Sclavo, C. Laforsch and F. Siegert, Coastal accumulation of microplastic particles emitted from the Po River, Northern Italy: Comparing remote sensing and hydrodynamic modelling with in situ sample collections, *Marine Pollution Bulletin*, 2019, **138**, 561-574.
20. F. Liu, A. Vianello and J. Vollertsen, Retention of microplastics in sediments of urban and highway stormwater retention ponds, *Environmental Pollution*, 2019, **255**, 113335.
21. Rutgers New Jersey Weather Network, Data Viewer, <https://www.njweather.org/data/hourly>).
22. USGS, Current Conditions for New Jersey: Streamflow, <https://waterdata.usgs.gov/nj/nwis/current/?type=flow>).
23. J. Masura, J. E. Baker, G. D. Foster, C. Arthur and C. Herring, Laboratory methods for the analysis of microplastics in the marine environment: recommendations for quantifying synthetic particles in waters and sediments, *NOAA Technical Memorandum NOS-OR&R-48*, 2015.
24. K. Sipps and G. Arbuckle-Keil, presented in part at the Hudson River Foundation Tibor Polgar Fellowship Presentation, Cary Institute for Ecosystem Studies, Millbrook, NY, August 21, 2019, 2019.
25. S. Primpke, M. Wirth, C. Lorenz and G. Gerdt, Reference database design for the automated analysis of microplastic samples based on Fourier transform infrared (FTIR) spectroscopy, *Analytical and Bioanalytical Chemistry*, 2018, **410**, 5131-5141.
26. O. S. Alimi, J. Farner Budarz, L. M. Hernandez and N. Tufenkji, Microplastics and nanoplastics in aquatic environments: aggregation, deposition, and enhanced contaminant transport, *Environmental Science & Technology*, 2018, **52**, 1704-1724.

27. J. H. Cohen, A. M. Internicola, R. A. Mason and T. Kukulka, Observations and Simulations of Microplastic Debris in a Tide, Wind, and Freshwater-Driven Estuarine Environment: the Delaware Bay, *Environmental Science & Technology*, 2019, **53**, 14204-14211.
28. N. Schmidt, D. Thibault, F. Galgani, A. Paluselli and R. Sempéré, Occurrence of microplastics in surface waters of the Gulf of Lion (NW Mediterranean Sea), *Progress in Oceanography*, 2018, **163**, 214-220.
29. P. J. Franks, Sink or swim: Accumulation of biomass at fronts, *Marine Ecology Progress Series. Oldendorf*, 1992, **82**, 1-12.
30. K. J. Kapp and E. Yeatman, Microplastic hotspots in the Snake and Lower Columbia rivers: A journey from the Greater Yellowstone Ecosystem to the Pacific Ocean, *Environmental Pollution*, 2018, **241**, 1082-1090.
31. A. Lima, M. Costa and M. Barletta, Distribution patterns of microplastics within the plankton of a tropical estuary, *Environmental Research*, 2014, **132**, 146-155.
32. G. Gatidou, O. S. Arvaniti and A. S. Stasinakis, Review on the occurrence and fate of microplastics in Sewage Treatment Plants, *Journal of hazardous materials*, 2019, **367**, 504-512.
33. F. Liu, K. B. Olesen, A. R. Borregaard and J. Vollertsen, Microplastics in urban and highway stormwater retention ponds, *Science of The Total Environment*, 2019, **671**, 992-1000.
34. N. Fahrenfeld, G. Arbuckle-Keil, N. N. Beni and S. L. Bartelt-Hunt, Source tracking microplastics in the freshwater environment, *TrAC Trends in Analytical Chemistry*, 2019, **112**, 248-254.