Influence of Wastewater Treatment Plant Discharges on Microplastic Concentrations in Surface Water

By

Shirin Estahbanati

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ABSTRACT OF THE THESIS

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By Shirin Estahbanati

Thesis Director:

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The abundance of microplastic particles in the marine environment is well documented, but less is known about microplastics in the freshwater environment. Wastewater treatment plants (WWTPs) do not effectively remove microplastics allowing for their release to the freshwater environment. To investigate concentration of microplastic in fresh water and the impact of WWTP effluent, samples were collected upstream and downstream of four major municipal WWTPs on the Raritan River, NJ. Microplastics were categorized into three quantitative categories (500-2000 µm, 250-500 µm, 125-250 µm), and one semi-quantitative category (63-125 µm). Then, microplastics were classified as primary (manufactured in small size) or secondary (derived from larger plastics) based on morphology. The concentration of microplastics in the 125-250 and 250-500µm size categories significantly increased downstream of WWTP. The smaller size classes, often not quantified in microplastic studies, were in high relative abundance across sampling sites. While primary microplastics significantly increased downstream of WWTP, secondary microplastic was the dominant type in the quantitative size categories (66-88%). Interestingly, no correlation between microplastic and distance downstream was observed. These

results have implications for understanding the fate and transport of microplastics in the freshwater environment.

Acknowledgements

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1. Chapter (1): Broad Introduction

1-1- Background

Diverse applications of plastic and low production cost caused an increase in the plastic production during the last decades (PlasticsEurope 2013). Studies showed that 10% of the plastic ends up in global oceans (Thompson 2006). Plastic compromises 75% of the marine debris and pose a top environmental issue beside the climate change (Gregory and Ryan 1997). Plastic debris are emerging contaminant due to adverse impact on human ability to conserve biological diversity in future (Sutherland et al. 2010). Plastic particles found in marine habitats from benthic to pelagic of all oceans (Barnes et al. 2009). The impact of plastic debris on marine species depends on plastic size. Large plastic particles, such as plastic bag, uptake by marine lives while small plastic debris, such as small pellet, pose a serious risk to marine species. Microplastic defines as plastic particle smaller than 5 mm.

Microplastic categories into primary, manufactured in small size, and secondary, derived by breaking larger particles. Origin of primary microplastic includes plastic in scrubber, cosmetic product, feedstock pellets, and synthetic fibers in clothes. Secondary microplastic consists of polyester, acrylic, and polyamide generated by breaking large plastics. The secondary microplastic are likely to stay for a long time in the freshwater, natural water body, modified water body, and artificial water body (Eerkes-Medrano et al. 2015). Although microplastic abundance and impact in the marine environment have been subject of several studies since 1970 (Carpenter et al. 1972), there is a gap in knowledge about microplastic concentration in the freshwater environment

Widespread of microplastic in freshwater environment has been reported. For example, microplastic abundance in the Danube River (Lechner et al. 2014), and Lake

Hovsgol (Free et al. 2014) were reposrted. The potential impacts of human activities on microplastic spatial pattern has been indicated in studies to address the contamination sources. For instance, the pellets and flakes found in the Danube River was linked to the closer proximity to the plastic production site (Lechner et al. 2014) and the abundance of secondary microplastic in Lake Hovsgol suggested an origin of the derivation from household items (Free et al. 2014).

The rate of microplastic derivation in the aquatic environment, marine and freshwater, is unknown. Obviously physical forces, such as storms and wave actions, in the various aquatic bodies are different. Consequently, the rate of plastic derivation is different in freshwater and marine environment (Andrady 2011).

Scanning microscope has been applied to address degradation patterns of microplastic (Zbyszewski et al. 2014). Secondary microplastics are derived due to the mechanical, oxidative, and biological degradation (Zbyszewski et al. 2014). Degradation patterns of microplastics are important to provide insight into the sources of microplastic pollution in the environment (Ballent et al. 2012).

Microplastioc abundance in the freshwater environment depends on number of factors including human population, density of urban centers, water resistance time, volume of the water body, waste management methods, and closer proximity to WWTP effluent discharges (Free et al. 2014, Zbyszewski et al. 2014, Moore et al. 2011, Eriksen et al. 2013).

Given the link between microplastic abundance and WWTP effluent discharges, microplastics which are not removed via settling steps of WWTPs cause the microplastic transport into the freshwater environment. It has been suggested that sampling from upstream and downstream of WWTP discharges will reveal significant

information about the influence of WWTPs on microplastic patterns in the freshwater environment (Eerkes-Medrano et al. 2015).

Although, the microplastic present in rivers have been documented (Moore et al. 2011), the impact of rivers on microplastic pollution in the marine environment is not established yet. Therefore, the role of rivers as a microplastic transport pattern into the marine environment needs to be considered. Several international organizations such as European Union's Water Framework Directive (Directive2000/60/EC 2000) and Marine Strategy Framework Directive (Directive2008/56/EC 2008) advanced integrated management of freshwater and marine environment to improve global water environment. It seems more research needs to be done to provide enough information for international organizations to take appropriate actions

2. Chapter (2): Introduction to the research, Experiments Description, Results and Discussion

2-1- Introduction

Worldwide plastic production has been growing since 1950 (PlasticsEurope 2013). Consequently, millions of tons of plastics enter oceans and landfills each year (Gourmelon 2015). Researchers have found all oceans have been affected by plastic pollution (Free et al. 2014). Plastics entering aquatic environments have a wide size distribution from micrometer to meter size range (Hidalgo-Ruz et al. 2012). Microplastics are defined as plastic particles smaller than 5 mm (Sadri and Thompson 2014), derived from larger particles (secondary microplastics) or manufactured in small size (primary microplastics) (Hidalgo-Ruz et al. 2012). In the United States it is estimated that 8 trillion microplastic beads enter the aquatic environment daily (Rochman et al. 2015). Due to slow rates of plastic degradation, microplastics persist in the environment (Roy et al. 2011). The presence and consequences of microplastics in the marine environment have been studied since 1970 (Carpenter et al. 1972). However, less is known about microplastic abundance in the freshwater environment (Yonkos et al. 2014).

Accumulation of microplastic in lakes (Eriksen et al. 2013, Faure et al. 2012), estuaries (Sadri and Thompson 2014), and rivers (Lechner et al. 2014, McCormick et al. 2014) has been reported. WWTP effluent is one of the sources of microplastics in the freshwater environment (McCormick et al. 2014, Magnusson and Norén 2014, Carr et al. 2016). Microplastics are not removed via settling in the primary and secondary steps of wastewater treatment (Eerkes-Medrano et al. 2015). WWTP effluent resulted in an increase in the concentration of microplastic in Chicago River (McCormick et al. 2014). However, other studies have not determined the cumulative impact of WWTP effluents along a river. Further, most studies focus on plastics

larger than 330 µm, overlooking smaller size classes which are potentially important sources of microplastic pollution in the freshwater environment.

The objective of this study was to investigate the abundance of microplastic and the impact of municipal WWTP effluents on the microplastic concentration in the Raritan River. In this study, the presence of microplastics <330 µm is reported for the first time. Based on morphology, microplastics were categorized into primary and secondary groups to address sources of microplastic contamination. Moreover, correlations between distances downstream and microplastic concentration were performed to provide insight into the fate and transport of microplastic in the river environment.

2-2- Materials and Method

2-2-1- Sampling

Sampling was performed on the Raritan River, located in central New Jersey (NJ), US (Figure 1). The river basin covers 2850 km^2 and provides water for drinking, irrigation, agriculture, recreation, and industry. The River has two branches, north and south, that meet then flow into the Raritan Bay. The primary land use of the river main stem is urban and suburban, (51.3%) and the primary land use of the south and north branches are agricultural and forest (61.31%) (Newcomb et al. 2000). More than 10 municipal WWTPs discharge into the Raritan River, five of which are major (>1 MDG). The Millstone River is a major tributary to the Raritan River and has several minor and one major WWTP. Samples were collected upstream and downstream of three major municipal WWTPs located upstream of head-of-tide (selected based on ease of access for sampling): two discharging into south Branch (WWTP-A1 with design flow 2.3 MGD and A2 with design flow 3.8 MGD), one into

the north branch (WWTP-B, design flow 5 MGD). Samples were also collected on the main branch upstream of the intersection of with the Millstone River (with 4 minor WWTP and 2 major WWTP-D,E, design flow 13 and 3.5 MGD) and downstream of this intersection and one WWTP discharging into the main branch (WWTP-C, design flow 23 MGD) of the river. This site will be referred to as WWTP-M/C. A background site was selected on the south Branch (Background) as a control without WWTP discharge upstream. Sampling was performed during baseflow.

Table 1-WWTP discharge by sampling location

Name	Branch	Design flow (MGD)
Background	North	NA
WWTP-A1	North	2.3
WWTP-A2	North	3.8
WWTP-B	South	5
WWTP-C	Main	23
WWTP-D	Millstone	13
WWTP-E	Millstone	3.5

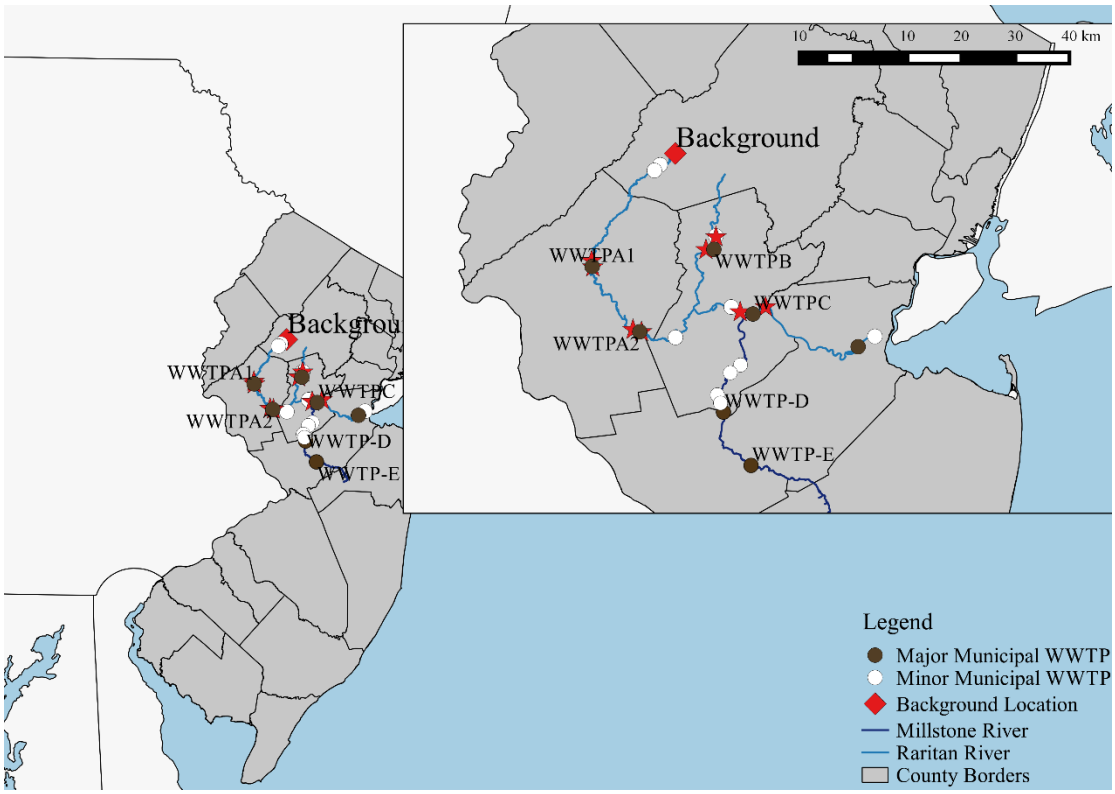

Figure 1- Map of sampling locations. Sampling was performed up and downstream of major municipal WWTP (>1 MGD)

Samples were collected during baseflow with plankton nets (0.2 m diameter, 0.51 m long) with 153 µm mesh size (Fieldmaster, Lenexa, Kansas) in duplicate in October and November 2015 (Figure 2). The nets were fixed perpendicular to flow on the river surface, with half of net opening submerged to collect floating particles. The water velocity was estimated at the sampling locations by the float method and verified using a pygmy meter (USGS Model 6200 AA, Columbus, Ohio). Samples were collected for 1 h. Sampling was performed downstream first, then upstream of a given WWTP, with paired samples collected within 3-72 h of one another. The volume of sample collected was calculated by taking the product of river surface velocity, cross sectional area of the submerged portion of the net opening, and sample collection time. Nets were transferred to the lab for analysis. Field blanks were performed by pouring Deionized (DI) water (5×10^{-3} m^3) through the net in the field, then leaving the net open and exposed to air for 1 h. Matrix spike duplicates were performed in the field by adding 1 g of personal care product containing polyethylene to the net after sampling but prior to microplastic extraction.

Figure 2- Net sampling (Downstream of WWTP-C)

2-2-2- Extraction of microplastics

The contents of each net were rinsed with DI water (0.25 m^3) three times into a series of sieves (4000, 2000, 500, 250, 125, and 63 µm aperture size). Material captured on the largest two size categories of sieves was discarded. Then, the contents of each sieve were rinsed with DI water, transferred to a 200 mL beaker, and dried overnight at 90°C. The organic content of each sample was oxidized by hydrogen peroxide catalyzed by iron (II) (Baker et al. 2015). Iron (II) solution (20 mL, 0.05 M) was added to each beaker, following by 20 mL hydrogen peroxide. The solutions were heated to 75°C for 30 min after which sodium chloride was added to increase the mixture density. Then, the solutions were transferred to a funnel to facilitate density separation, covered with foil, and left overnight for settling (Figure 3). Settled

materials were discarded and floating particles were rinsed with DI water and transferred to a glass petri dish.

Figure 3-Experimental Steps (A) Wet Peroxide Oxidation of Organic Material, (B) Density Separation of microplastic particles

Recovered particles were visualized under a reflected microscope (Stereo Zoom Microscope, Olympus, Japan). For the 500 µm size category, plastics were counted directly. Due to the high abundance of particles in the 63, 125, and 250 µm size categories, the area of each petri dish was divided into an 80 block grid (29.3mm^2), and random grid blocks (20-30 blocks) were counted per sample. The total number of microplastics was calculated by scaling up the number of counted microplastics based on the surface area of grids counted. This method was found to accurate within 1.7-9.6% compared to counting the total number of microplastics directly (Figure 5 and Figure 6). During visualization, the microplastic particles were categorized as primary and secondary microplastic based on visual inspection of particle morphology. Morphology of the plastic particles collected in the field was compared to plastic particles extracted from a variety of personal care products containing

polyethylene (Figure 4). The concentration of microplastics in field samples was determined by dividing the number of microplastics counted by the volume of sample collected (the product of the cross sectional area of the submerged net opening, river velocity, and length in time of sample collection).

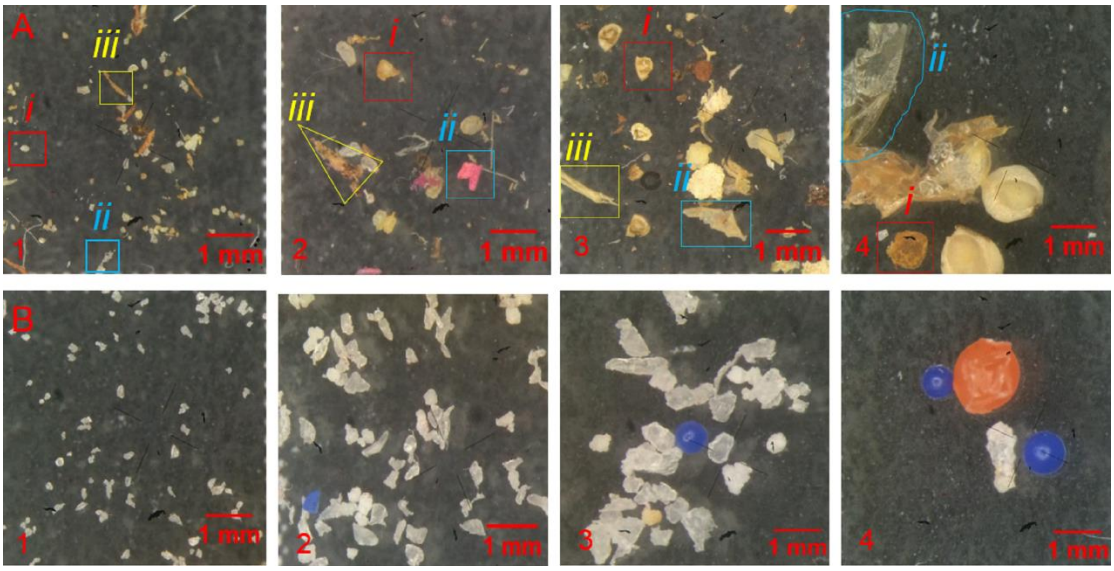

Figure 4- (A) Microplastics recovered in samples in the 1) 63-125 µm size category, 2) 125-250 µm size category, 3) 250-500 µm size category, and 5) 500-2000 µm size category. (B) Microplastics recovered from personal care products in the 1) 63-125 µm size category, 2) 125-250 µm size category, 3) 250-500 µm size category, and 5) 500-2000 µm size category. Examples of different particles classifications are labeled i) primary microplastic, ii) secondary microplastic, and iii) non-microplastic particles excluded during the counting step.

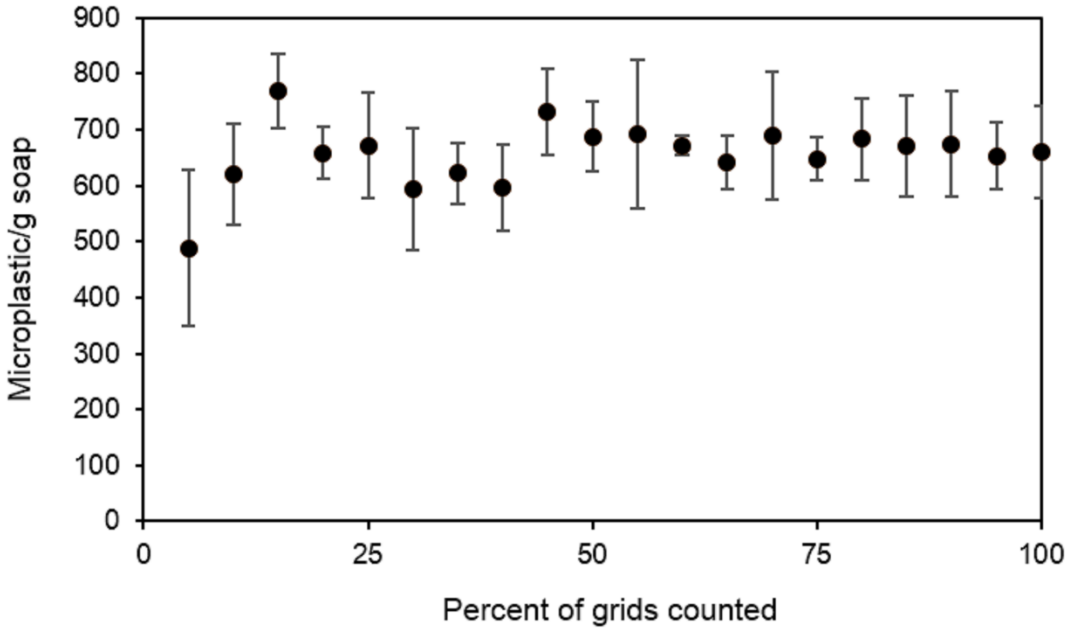

Figure 5- Number of microplastic per gram of soap versus percent of grids counted (soap sample)

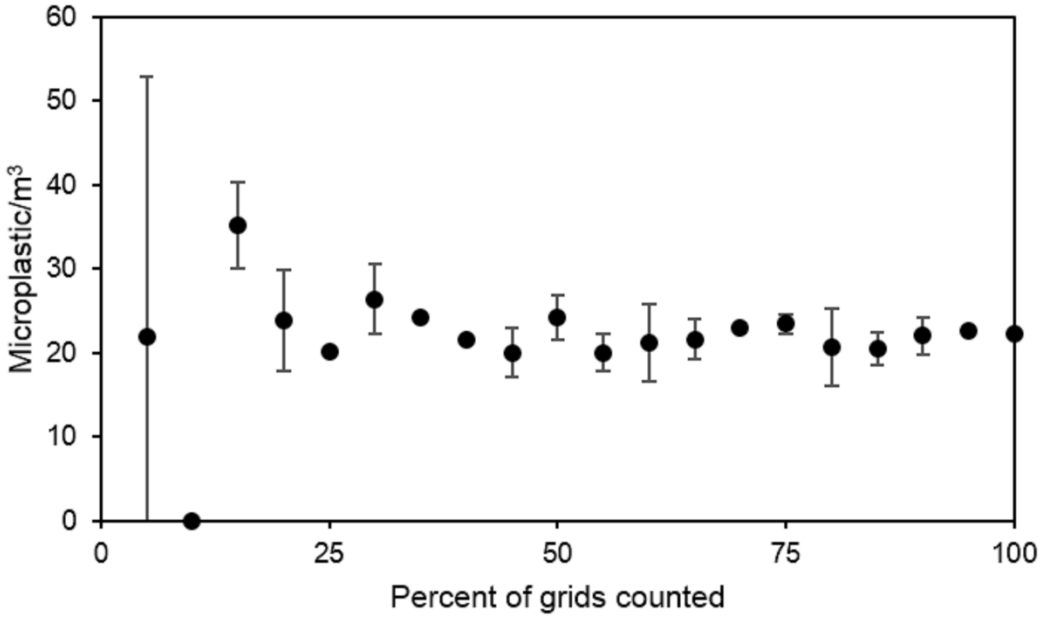

Figure 6- Number of microplastic per gram of soap versus percent of grids counted (in a field sample with low number of microplastic)

A Student's t-test was applied for normal and a Wilcox Rank Sum test for non-parametric data to compare (a) the total concentration of microplastics upstream and downstream of each WWTP for a given size category, (b) the concentration of primary and secondary microplastics in each size category, and (c) concentration of primary microplastics in each size category across all WWTPs. Correlation between microplastic concentration and distance downstream was tested for the South and Main Branch of the River using linear regression in Excel (Microsoft, Silicon Valley, California). A Kruskal-Wallis test with a post-hoc pairwise t-test with a Bonferroni correction for multiple comparisons was performed for to compare the concentration of microplastics in the four size categories across all sampling sites.

2-3- Results

Microplastics were observed in all samples and size categories, including those collected at the background site (Figure 7). Microplastic concentrations increased downstream of WWTP-A1, A2, and M/C in the 125 μm size category (p=0.024-

0.048), and for WWTP-A2 and M/C in the 250 µm size category (p=0.0012-0.0052) compared to upstream samples. No differences were observed in concentration of microplastics in samples collected downstream of the WWTP discharge compared to samples collected upstream for the 63 and 500 µm size categories (p=0.075-0.67). The 500 µm size category was the least abundant size class across all sampling sites (p=0.0014-0.013). There was significantly more microplastics observed in the 125µm size category than the 250 µm size category across all sampling sites (p= 0.0088). The average relative percent differences for field replicates were 44.9% for the 63 µm, 19.8% for the 125 µm, 26.2% for 250 µm, and 27.4% for 500 µm size categories. The average recovery of microplastics in matrix spikes was 45.1% for 63 µm, 75.1% for 125 µm, 97.5% for 250 µm, and 54.4% for 500 µm size category. Microplastics observed in the blank samples were 19.4 times lower than observed in any river sample at upstream of the WWTP –A1and 3 times lower than observed in at the background location.

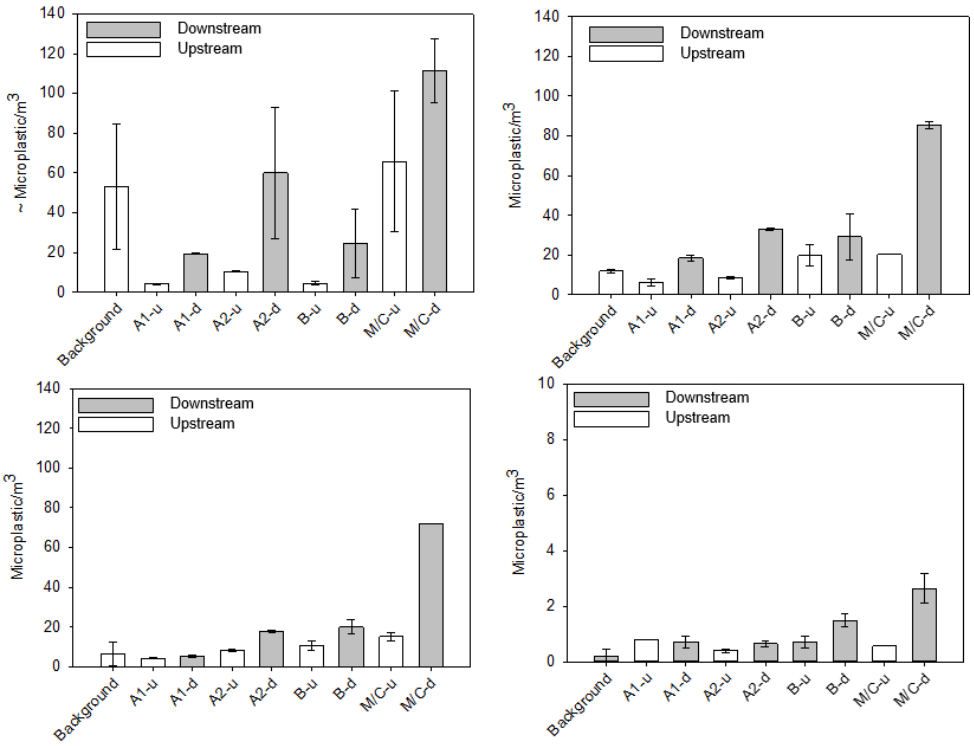

Figure 7- Concentration of microplastics in a. 63-125 µm, b. 125-250 µm, c. 250-500 µm, and d. 500-2000 µm size categories upstream (white) and downstream (gray) of WWTPs. Concentrations for 63um size category is semi-quantitative because the net used for sampling had an aperture of 153 µm. Error bars represent standard deviation of field duplicates. P value for significant differences observed comparing upstream and downstream concentrations for a given WWTP and size category are labeled, p< 0.05 are marked with *, p< 0.01 are marked with *

Microplastics were categorized as primary and secondary plastics based on visual inspection of morphology (Figure 8). Comparing across all size categories, secondary microplastics were more abundant than primary microplastics in 125, 250 and 500 µm categories (p=0.038, 0.0039, and 0.0038, respectively). The average percent of secondary microplastics was 42.4% for the 63 µm, 73.1% for the 125 µm, 66.9% for the 250 µm, and 87.9% for the 500 µm size category. Comparing upstream and downstream samples for all WWTPs, the concentrations of primary microplastics increased downstream of WWTPs in the 63, 125, and 250 µm size categories (p=0.0078, 0.0078, and 0.023, respectively).

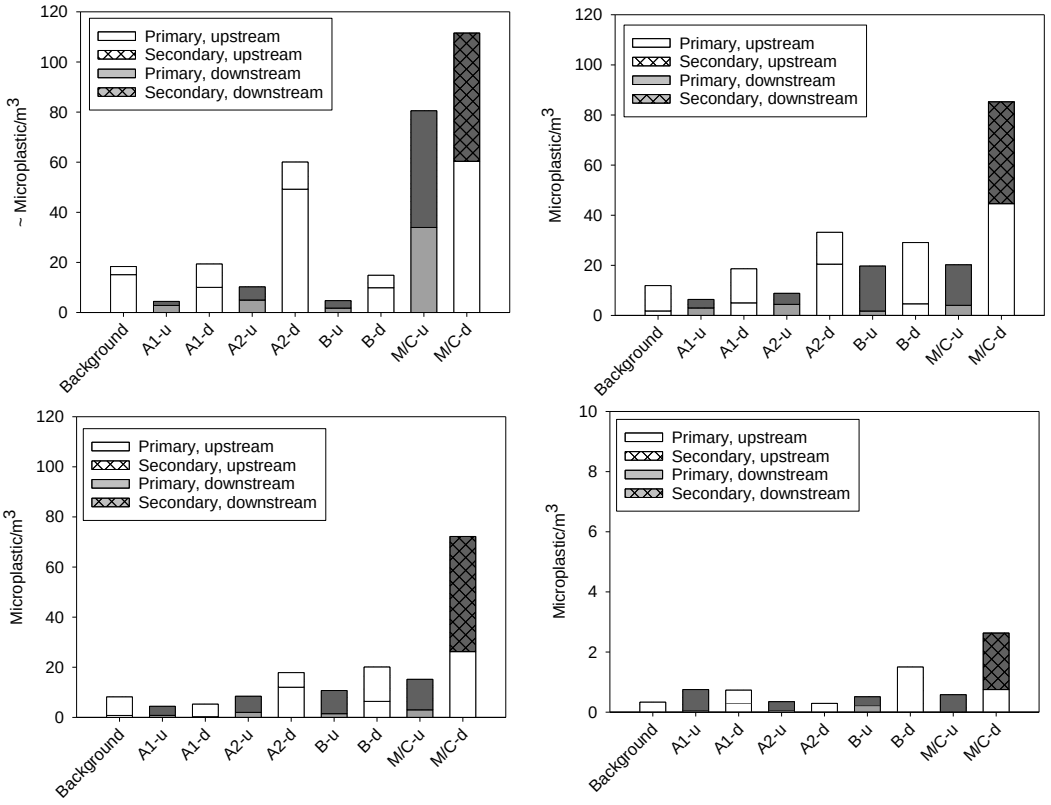

Figure 8- Concentration of primary and secondary microplastics in a. 63-125 µm, b. 125-250 µm, c. 250 µm-500 µm, and d. 500-2000 µm size categories upstream and downstream of WWTPs. Concentrations for 63um size category is semi-quantitative because the net used for sampling had an aperture of 153um. Percent of Primary microplastics shown above bars

No correlation was observed between distance from Raritan Bay and the total concentration of microplastics (slope=-1.82, R2=0.42, Figure 10) nor for the concentration of microplastics in the 125-2000µm size categories (slope=-1.14, R2=0.46, Figure 9). The lack of correlation is because the microplastic concentrations decreased between the sample collected downstream of a given WWTP and the next upstream sampling location. The two curves represent the regression confidence interval with 5% deviation from linear regression. For example, downstream of WWTP-A1 microplastic concentration was 43.9 microplastics/m3 and 19.3 km downstream (at the upstream sampling location for WWTP-A2) microplastic concentration was 27.8 microplastics/m^3.

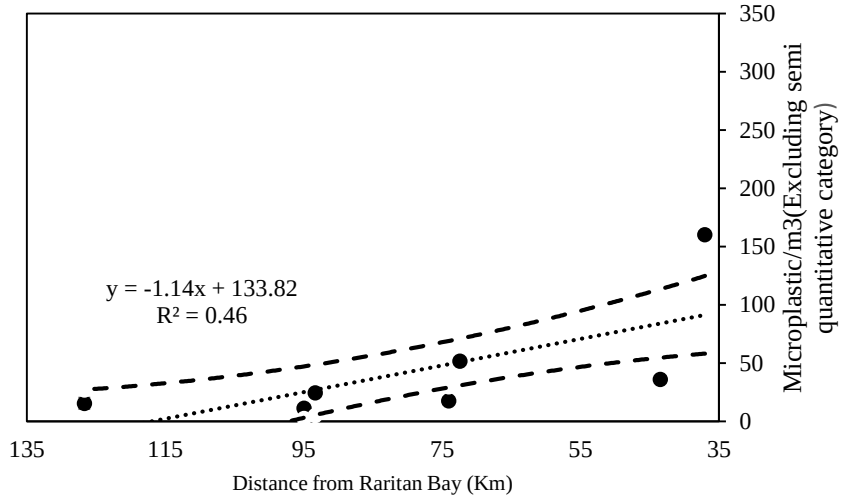

Figure 9- Concentration of microplastics versus distance from Raritan Bay. Error bars represent standard error on duplicate field samples. The solid line represents linear regression and dotted lines represent 95% confidence intervals.

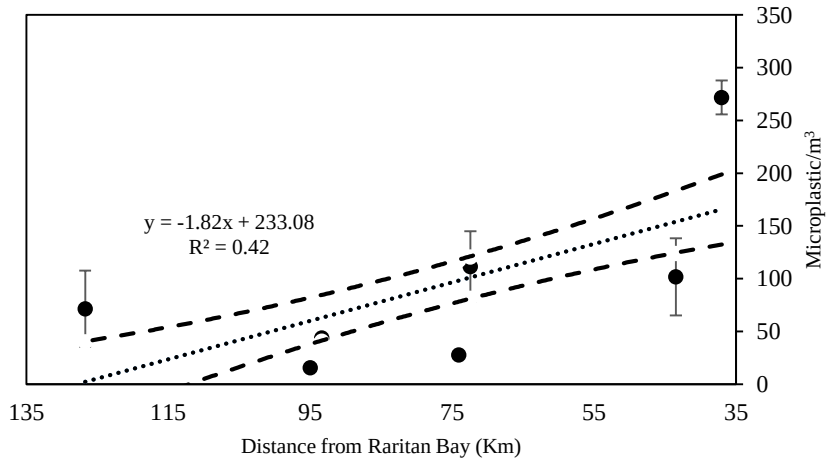

Figure 10- Concentration of microplastics versus distance from Raritan Bay. Error bars represent standard error on duplicate field samples. The solid line represents linear regression and dotted lines represent 95% confidence intervals.

2-4- Discussion

This study provides insight into the impact of wastewater treatment plant discharges on the prevalence of a wide size distribution of microplastics in the freshwater environment. Increases in microplastic concentrations were observed for the 125-250µm and 250-500µm size categories downstream of select wastewater treatment plants on the Raritan River. This result is consistent with results of McCormick et al. (2014) who observed microplastic concentrations (including fibers, which were not

quantified in this study) increased downstream of a WWTP on the Chicago River. WWTPs are known sources of microplastics in the freshwater environment given their incomplete removal during wastewater treatment (Magnusson and Norén 2014). It is noteworthy that increases in microplastic concentrations for WWTP C/M integrate the impacts of several minor WWTP along the Millstone in addition to WWTP-C and WWTP-D and E.

Interestingly, the microbeads in the 500µm category, which have received considerable attention (Lechner et al. 2014, Eriksen et al. 2013), were in low abundance compared to other microplastic types. At the background location on the Raritan River microplastic was observed with concentrations 3.8 times less than the most contaminated sampling location (downstream of WWTP-C) but 4.6 times greater than the site with the lowest plastic concentration, upstream of WWTP-A1. This indicates sources of microplastic other than WWTP are present in the river. Excluding semi quantitative size category, concentration of microplastic at the background location was generally lower than the microplastic abundance downstream of the WWTPs.

Given that several major WWTP are located along the Raritan River, the concentration of microplastics as a function of downstream distance was investigated. While microplastic concentrations were greatest at the furthest downstream sampling point (WWTP-C), a strong correlation between distance downriver and microplastic concentration was not observed. Microplastic concentrations decreased between any given WWTP downstream sampling site and the next closes upstream sampling site (e.g., WWTP-A1 downstream and WWTP-A2 upstream). Uptake by biota (McCormick et al. 2014, Barnes and Milner 2005), dilution, settling (Wagner et al. 2014, Castañeda et al. 2014), and/or skimming of microplastic particles during

transport could account for this observation. It is also possible that temporal variations in microplastic concentration obscure the trend given that samples for different locations were collected up to one week apart. The presence of microplastics at the furthest downstream sampling location indicates that the Raritan River is likely a source of microplastics in the receiving estuary. Widespread observation of microplastics in the New York/New Jersey Harbor estuary was recently reported (NY-NJBaykeeper 2016). Therefore, our results indicate that rivers serve as a source of the microplastics in the marine environment as suggested by Eerkes-Mederano et al. (Eerkes-Medrano et al. 2015)

Table 2- Comparison of microplastics observed in this study to select other studies

Location	Freshwater upstream of WWTP (No,/m3)	Freshwater Downstream of WWTP (No,/m3)	Freshwater, unspecified (No,/m3)	Marine water (No,/m3)	Study units	Net mesh size (µm)	Sampled size range	Volume/ Distance Sampled	Reference
Raritan River **	50.5±35.4	71.7±60.2			No./m3	153	125-2000 µm	1.3-13.5 m3	This study
Chicago River	1.9±0.8	17.9±11.0			No./m3	333	333-2000 µm	Not Reported	(McCormick et al. 2014)
Danube River			3.2×10-2±4.7		Items 1000 m3	500	<2mm, 2-20 mm	Maximum 1 km	(Lechner et al. 2014)
Swedish west coast waters				102,550	No./m3	80	500-2000 µm	5-19 km	(Norén 2007)
South California Shore Long Beach California				3.9	No./m3	333	< 4.7 mm	0.5-1 km	(Lattin et al. 2004)
				7.3	No./m3	333	<4.7 mm	0.5-1 km	(Moore et al. 2002)
North Pacific Ocean				2.2	No./m3	333	<4.7 mm	5-19 km	(Moore et al. 2001)
Hovsgol Lake			14.2×10-2***		Items km-2	333	355-999 µm 1-4.7 mm >4.7 mm	0.4-8.5 km	(Free et al. 2014)
Laurentian Great Lakes			70.7×10-5		Particle km-2	333	355-999 µm 1-4.7 mm >4.7 mm	1.94-4 km	(Eriksen et al. 2013)
Tamar estuary			0.028		Items/m3	300	<1 mm 1-3 mm 3-5 mm >5 mm	4.86 km	(Sadri and Thompson 2014)

****Units were converted from particles per area to particles per volume, **63-125 µm were counted in samples, but not included here because net mesh size was greater than size class, *** concentration per area was converted to NO./m^3 by ividing to reported numbers to the height of the applied net***

Comparison of results among microplastic studies is complicated due to the variations in sampling techniques (i.e., size classes targeted), plastic categories quantified (e.g., primary, secondary, beads, and/or fibers), and units used in reporting results (Hoellein et al. 2014). Notably, some researchers report microplastic abundance based on number of microplastics per volume of collected samples [e.g., (Lechner et al. 2014)],

while others report the microplastic concentration based on surface area of field sampling [e.g., (Eriksen et al. 2013)]. Nonetheless, microplastic concentrations observed in this study were generally greater than other freshwater studies and within the range reported for marine studies (Table 1). For all comparisons of the concentration of microplastic across studies discussed here, only particles in the 125-2000 μm size class for the Raritan River are considered so that comparisons are quantitative. Further, conversions from particles per unit area reported by other researchers were converted to particles per unit volume for consistency of units. The concentration of microplastic in Raritan river was higher than other studies of microplastic in Chicago river (McCormick et al. 2014) and Danube River (Lechner et al. 2014). The concentrations of microplastic observed in this study were less than the maximum value in the marine environment (Norén 2007), but microplastic concentrations were higher than concentrations for ocean studies along the Southern California shore, Southern California's coastal water, and North Pacific Ocean (Lattin et al. 2004). The microplastic concentration in the river was higher than the concentration in the Hovsgol and Laurentian Great lakes (Free et al. 2014, Eriksen et al. 2013) and the Tamar estuary (Sadri and Thompson 2014). The higher concentrations observed in this study are likely to due to the smaller net mesh sized used here than in most other studies because the smaller size classes were in higher relative abundance in our study. It is also possible that converting from particles per area to particles per volume for other studies under estimated the concentrations reported given that it was assumed the nets were fully submerged

To the authors' knowledge, this is the first study of the distribution of microplastic smaller than 355 μm in the fresh water environment. Other researchers concentrated on quantifying larger microplastics: 355-900 μm in Hovsgol Lake (Free et al. 2014),

500-2000 μm in Danube River (Lechner et al. 2014), and 300-1000 μm in Tamar Estuary (Sadri and Thompson 2014). Microplastics in 63 and 125 μm size categories dominated the personal care products tested in the lab (constituting 34.4% and 45% of the microplastics in the tested cosmetic product). Because the plankton net used in this study had a mesh size of 153μm, the particles collected on the 63 μm sieve should be considered semi-quantitative as particles of in this size category can pass through the net. Despite this, the 63 μm size category was the most abundant in 6 out of 9 of our sampling locations, and in the remaining 3 locations 125 μm size category was the dominant category. Sampling with nets with smaller mesh size is recommended to quantify this size category given results for the extraction of personal care products and the semi-quantitative field data presented here indicate this size class may be the dominant size category. Visually differentiating and chemically confirming the composition of these particles presents challenges but may be worthwhile nonetheless because these smaller microplastics provide more specific area for adsorption of contaminants and growth of biofilm. Both sorption of hazardous organic contaminants (Moore 2008) and biofilm growth (Hoellein et al. 2014) have been reported on microplastic surfaces.

Microplastics measured in the Raritan River were classified as primary or secondary to provide insight into the potential source. Secondary microplastics result from the fragmentation of larger pieces of plastic as opposed to from the use of small plastic particles in personal care products. The increasing concentration of primary microplastics downstream of the all WWTPs in >63, 125, and 250 μm categories highlights the role of WWTPs as a source of primary microplastics. The presence of primary microplastics at the background location indicates that WWTP effluent was

not the only source and/or may be indicative of inaccuracies in this visual class categorization. However, across all sampling sites in the >125, 250, and 500 μm size classes, secondary microplastics were present at higher concentrations. Secondary microplastics are formed by biological degradation, photodegradation, chemical deposition, and physical breakdown of larger pieces of plastics (Andrady 2011). The sources of secondary microplastics are varied and may include cigarettes, plastic bags, and tires (Hoellein et al. 2014). Other studies have categorized microplastics based on different characteristics such as chemical composition (e.g. polypropylene, polystyrene) (Morét-Ferguson et al. 2010), shape (e.g. color, texture) (Corcoran et al. 2015), size (Eriksen et al. 2013), and type (e.g. food wrappers, tobacco packing) (Morritt et al. 2014), therefore direct comparisons are not currently feasible. Current legislation in the US focuses on phasing out the production of personal care products containing non-degradable microplastics less than 5 mm in size (EnergyCommerceCommittee 2015) by July 2018. In addition, the Netherlands, Austria, Belgium and Sweden have supported bans on the production of microplastics used in detergents and cosmetic products (Simon 2014). This action would be expected to decrease the release of primary microplastics in WWTP impacted waters and may decrease the levels of secondary microplastics formed from the primary microplastic particles in personal care products.

2-5- Conclusions

This study demonstrated the spatial pattern of primary and secondary microplastics in the Raritan River. The results of this study indicated that microplastic concentration, particularly primary microplastics, was increased downstream of WWTP outfalls. Additionally, the presence of microplastics at the background location showed that

WWTPs are not the only source of microplastic contamination in the river. Correlations between distance from the Raritan Bay and concentration of microplastic indicated other fate and transport processes are driving microplastic concentrations between WWTP outfalls including potentially microplastic digestion by biota, settling, skimming, and dilution. To the author's knowledge, this is the first report of the abundance of microplastic in small size categories (125-2000 μm quantitatively, and 63-125 μm semi-quantitatively). The high concentrations observed for the smaller size categories indicate these are potentially important in the freshwater environment, especially given their high surface areas.

3. Chapter (3): Broader Implications

3-1- Conclusion

The results of this study direct more research on the microplastic contaminant in the freshwater environment. The biological impact of microplastic pollution in the marine environment suggests potential impact of this pollutant in the freshwater environment. Hydrophobic microplastic particles adsorb organic contaminants and are a surface for biofilm in growth and serve to transport these pollutants into marine life. Recommendation for next step includes analysis of microbial community on the surface of microplastics to address biological impact of this contaminant in the freshwater environment. Moreover, this work highlighted the widespread of microplastic in small size categories for the first time. Therefore, applying nets with small mesh aperture is useful to study microplastic concentration in smaller size categories quantitatively. In addition, this research clearly suggests WWTP effluents as point sources of microplastic discharge in the river environment. Therefore, estimation of influent and effluent concentration of microplastic is suggested to give a clear picture of WWTP impact on microplastic spatial pattern.

4. Appendix

4-1- QA-QC Sampling

Figure A. 1-QA-QC sampling (A) Raritan River, (B) D & R Canal

4-2- Matrix Spiked Experiments

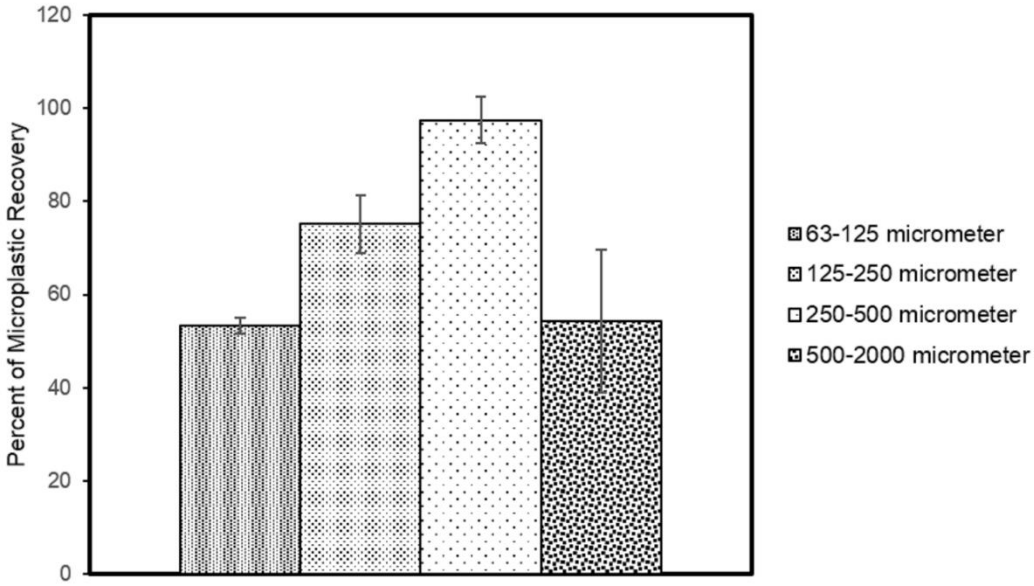

Figure A. 2--Matrix spikes sample recovery, Donaldson Park Samples

4-3- QA-QC Experiments

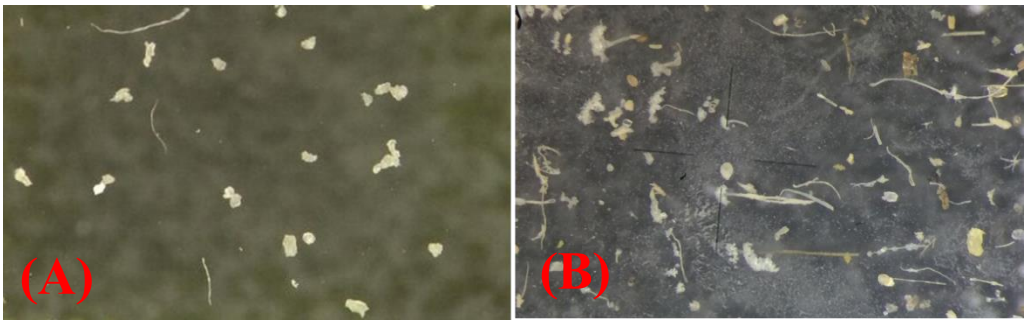

Figure A. 3-- Microplastic versus spiked sample (A) microplastic in a soap sample, and (B) spikes sample

Table A. 1-QA-QC test for the counting of the grids (High Concentration)

% of the grids	# microplastic	STDEV
5.00	488.22	139.08
10.00	619.86	90.55
15.00	770.01	66.96
20.00	658.62	45.89
25.00	672.03	94.79
30.00	593.58	108.62
35.00	621.90	54.52
40.00	597.11	77.37
45.00	731.37	77.04
50.00	687.90	63.11
55.00	692.74	132.59
60.00	672.09	17.57
65.00	641.92	49.06
70.00	688.97	113.85
75.00	647.60	38.14
80.00	683.07	72.99
85.00	671.83	90.24
90.00	675.05	94.22
95.00	653.28	60.43
100.00	660.67	82.68

Table A. 2- QA-QC test for the counting of the grids (High Concentration)

% of the grids	# microplastic	STDEV
5.00	21.90	30.97
10.00	0.00	0.00

15.00	35.24	5.11
20.00	23.85	5.95
25.00	20.22	0.00
30.00	26.37	4.14
35.00	24.16	0.00
40.00	21.57	0.00
45.00	20.03	2.93
50.00	24.28	2.64
55.00	20.02	2.18
60.00	21.18	4.66
65.00	21.62	2.45
70.00	23.01	0.55
75.00	23.44	1.11
80.00	20.65	4.61
85.00	20.51	1.93
90.00	22.03	2.26
95.00	22.55	0.00
100.00	22.25	0.41

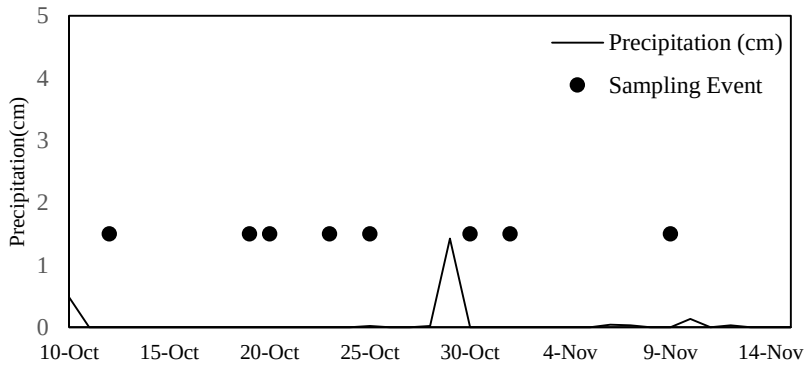

Figure A. 4-Sampling was performed during base-flow. Precipitation during the month of sampling is shown.

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