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Microplastics entering northwestern Lake Ontario are diverse and linked to urban sources

Jelena Grbić [a], Paul Helm [b, c], Samantha Athey [d], Chelsea M. Rochman [a, *]

[a] University of Toronto, Department of Ecology and Evolutionary Biology, St. George Campus, 25 Willcocks St, Toronto, Ontario, M5S 3B2, Canada
[b] Ontario Ministry of the Environment, Conservation and Parks, Environmental Monitoring and Reporting Branch, Toronto, ON, Canada
[c] University of Toronto, School of the Environment, Toronto, Ontario, Canada
[d] University of Toronto, Department of Earth Sciences, St. George Campus, Toronto, Ontario, Canada

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ABSTRACT

The sources of microplastics and other anthropogenic particles in freshwater are not well understood. The Greater Toronto Area, Canada's most populous urban area, offers a great study area for understanding the sources and pathways for microplastics to enter freshwater ecosystems. Here, we quantified and characterized microplastics and other anthropogenic particles from Lake Ontario surface waters and source waters (including stormwater runoff, agricultural runoff, and treated wastewater effluent) to better understand sources to the Great Lakes. Anthropogenic particle concentrations in lake samples were 0.8 particles L^{-1}. In source waters, average concentrations were relatively higher in stormwater and wastewater, with 15.4 particles L^{-1} and 13.3 particles L^{-1}, respectively, compared to 0.9 particles L^{-1} on average in agricultural runoff. Source waters revealed distinct signatures related to the morphologies of anthropogenic particles, e.g., fibers in wastewater. In addition, many upstream watershed characteristics were found to be significant predictors of anthropogenic particle concentration. Proximity to urban areas were positively correlated to anthropogenic particle concentrations. Future studies should focus on local source-apportionment to inform management and prevent further contamination of microplastics to freshwater ecosystems.

1. Introduction

Microplastics, plastic particles <5 mm in size, have been found in freshwater bodies across the world including on shorelines of lakes and rivers, benthic sediments, and surface waters (Eerkes-Medrano et al., 2015; Horton et al., 2017). Reported concentrations range from 0.00017 microplastics per liter (MP L^{-1}) in Lake Huron in the Laurentian Great Lakes to 100 MP L^{-1} in the surface waters of canals in Amsterdam (Leslie et al., 2017). Relative to the oceans, there have been less studies sampling freshwater ecosystems (Blettler et al., 2018). Moreover, methods of sampling, particle sizes included, and reporting units are generally inconsistent making it difficult to compare across locations (Hidalgo-Ruz et al., 2012; Dris et al., 2018). Still, based on the current body of literature, microplastic concentrations in surface waters have been found to be comparable and sometimes even higher in freshwater systems compared to marine (see Table S1).

Microplastics found in freshwater bodies can contaminate wildlife, including sportfish (Silva-Cavalcanti et al., 2017) and birds (Brookson et al., 2019). They have also been found to contaminate natural resources, such as drinking water (Pivokonsky et al., 2018), drawn from freshwater ecosystems. Concern has been raised about effects of microplastics to humans based on research showing exposure (Wright and Kelly, 2017; Rist et al., 2018; see Table S1 in Cox et al., 2019) and effects to aquatic biota (Rochman et al., 2016; Foley et al., 2018) and small mammals (Deng et al., 2017). Therefore, understanding the source of microplastics to the environment is of critical importance as it can inform mitigation to prevent future contamination and minimize the likelihood of further effects.

The most practical means to mitigate contamination and avoid any resulting harm is to know where the pollutant originates and "cut it off" at its source. Sources of microplastics include broken down litter, microbeads in personal care products, losses from plastic manufacturing and recycling, wear from textiles and tires, among others (Barnes et al., 2009; Lechner et al., 2014; Lechner and

* Corresponding author.
E-mail addresses: chelsea.rochman@utoronto.ca, chelsearochman@gmail.com (C.M. Rochman).

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Ramler, 2015; Dris et al., 2016; Duis and Coors, 2016; Amec Foster Wheeler and Infrastructure UK Limited, 2017; Boucher and Friot, 2017; Sommer et al., 2018). Key pathways delivering microplastics to freshwater systems have been identified as wastewater treatment plant (WWTP) effluent (Mason et al., 2016; McCormick et al., 2014; Murphy et al., 2016), sludge/biosolids (Magnusson and Norén, 2014), runoff from urbanized areas/impervious surfaces (Browne et al., 2011; Peters and Bratton, 2016), and atmospheric deposition (Dris et al., 2015). Studies have begun to examine sources and influences of pathways by relating watershed traits, hydrologic parameters, and weather patterns to microplastic concentrations (Barrows et al., 2018; Hitchcock and Mitrovic, 2019; Kataoka et al., 2019; Luo et al., 2019), and land-use regressions have been used to assess source influences for contaminants (Melymuk et al., 2013).

This study uses similar principles to better understand the sources of anthropogenic particles into a freshwater ecosystem, Lake Ontario of the Laurentian Great Lakes in North America, via urban and agricultural watersheds. We aim to understand whether land-use influences contamination by quantifying and characterizing microplastics and other anthropogenic particles (e.g. dyed cellulosic microfibers) in Lake Ontario surface waters and its source waters (agricultural runoff, stormwater runoff, and wastewater effluent). We set out to determine whether: (1) concentrations of microplastics and other anthropogenic particles in Lake Ontario and nearby rivers vary by upstream watershed characteristics; (2) the diversity of particle types vary by source waters; and (3) the background microplastic signal in Lake Ontario aligns with a specific type of source water.

The motivation for our work stems from the presence of microplastics in the Great Lakes and policy initiatives within Canada. Microplastics have been found in the Great Lakes within shoreline, riverine and beach sediments (Ballent et al., 2016; Corcoran et al., 2015; Dean et al., 2018; Zbyszewski et al., 2014; Zbyszewski and Corcoran, 2011), benthic lake sediments (Corcoran et al., 2015), surface waters of lakes and tributaries (Baldwin et al., 2016; Eriksen et al., 2013), and in the St. Lawrence River (Castañeda et al., 2014). The federal government has taken an interest in microplastics with its recent ban on microbeads from personal care products (Government of Canada, 2018) implemented in the summer of 2018. Additionally, the Ocean Plastics Charter spearheaded by Canada during its 2018 presidency of the G7 calls upon "collaborating on research on the sources and fate of plastics" (G7 4f 2018). The reduction of microplastics to waters such as the Great Lakes has garnered attention by jurisdictions in Canada and the United States, including the International Joint Commission (IJC, 2016), the Province of Ontario's Great Lakes Protection Act and Great Lakes Strategy (MECP, 2015; MECP, 2016), and NOAA's Marine Debris Program (NOAA, 2019).

2. Methods

2.1. Study region: Northwestern Lake Ontario

Lake Ontario, one of the five Laurentian Great Lakes, is situated at the end of the Great Lakes Watershed feeding directly into the St. Lawrence River leading to the Atlantic Ocean. Lake Ontario straddles Canada and the United States, and on the Canadian side has 104 subwatersheds draining into it with an area of 38,472 km^2. Located along Lake Ontario's shores in the northwest is the Greater Toronto Area (GTA), home to Canada's largest urban area with a population of 6.3 million residents (City of Toronto, 2019). Agriculture is also prevalent in the upper portions of the watersheds that contain the GTA, with 19,266 farms providing $12 billion CAD to Canada's economy (FAO, 2019).

Sampling of WWTP effluent, urban stormwater runoff, and agricultural runoff was conducted to obtain information on microplastic and other anthropogenic particle abundance and character, providing source information. Lake waters adjacent to Toronto, which receive river and wastewaters, were also sampled for comparison (Fig. 1). All samples were collected between July 28th and October 14th, 2015.

2.2. Sample collection

Final WWTP effluent was collected from three treatment plants in the region, referred to as WWTP A, WWTP B and WWTP C. Three 24-h composites (4 L volume) were sampled on three separate days from each plant using automated ISCO 6712 samplers to collect 167 mL each hour. Urban stormwater runoff samples were collected from three urban rivers (Etobicoke Creek, Humber River and Don River) and the agricultural watershed samples were collected from three small streams downstream of agricultural areas (Elgin West, Bruce Creek and Little Rouge). Stormwater and agricultural runoff samples (4 L each) were collected in triplicate during wet weather over the course of one day using a stainless steel bucket with polypropylene rope from a bridge, and transferred to an amber glass Winchester bottle. Lake water samples consisted of 10 L grab samples taken from four sites in Lake Ontario off Toronto: one in the plume of the Humber River, one in the plume of WWTP B, one in Humber Bay, and one in Toronto Harbour near the mouth of the Don River/Keating Channel. Three replicates were collected at each lake site using the stainless steel bucket off the side of a monitoring vessel and transferred to clean polyethylene bags in a plastic bucket.

For all sampling events, one field blank was sampled from one location for each of the four types of samples to account for any procedural contamination. Field blanks were sampled in an identical fashion to the samples, but with reverse osmosis (RO) water from the laboratory.

All sample bottles were washed with soap and water and triple-rinsed with RO water prior to sampling. The stainless steel bucket was rinsed three times with site water prior to sampling to prevent cross-contamination. Samples were taken back to the Ministry of the Environment, Conservation and Parks laboratory for processing, while quantification and characterization occurred at the University of Toronto.

2.3. Sample processing and analysis

Upon return to the laboratory, all samples were filtered through a 10 μm polycarbonate filter (142 mm diameter; EMD Millipore™ Isopore™) via a stainless steel filter holder (MilliPore Sigma) and stored sealed in a clean glass petri dish. The filtrate was collected and the water volume was measured using a graduated cylinder and recorded. For every set of 10 samples filtered, a laboratory blank with RO water was included to account for any procedural contamination in the laboratory.

Samples and blanks were subjected to further clean-up via a density separation technique. Each large sample filter was placed into a clean glass jar with a plastic lid containing ~550 mL of RO water then agitated in an ultrasonic bath (Fisher Scientific M Series 120V) for 1–2 h. The filter was then removed and rinsed, and the remaining water with the sample particles was sieved down to 25 μm and transferred to a clean glass separatory funnel with ~170 mL of filtered saturated calcium chloride solution ($CaCl_2$, $\rho = 1.4$ g/L). The funnel was shaken for ~20 s, then left for 1–3 days to allow for adequate separation. If during separation substantial material was observed sticking to the side of the glass funnel, the bottom of the sample was released on the second day, shaken for

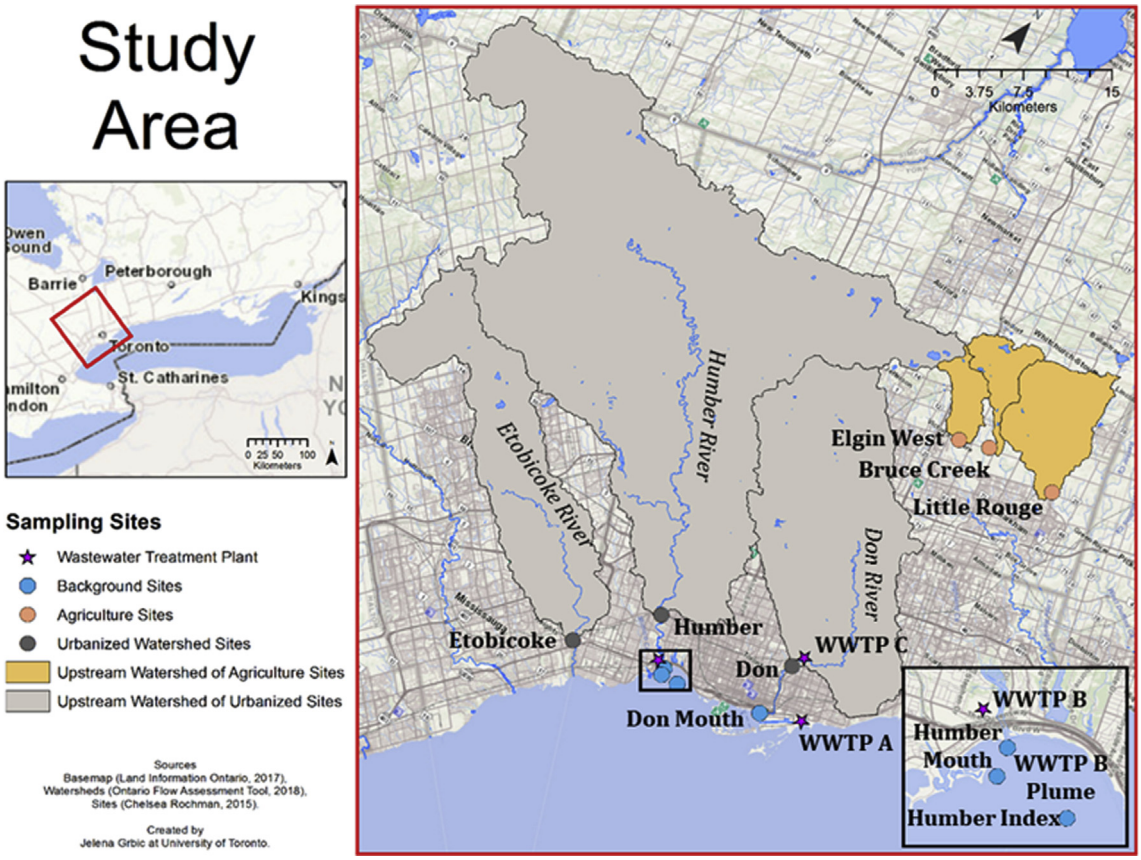

Fig. 1. Study area watersheds and sites of sample collection. Urbanized watershed sites correspond to "Stormwater (SW)", agriculture sites correspond to "Agriculture (AG) ", background sites correspond to "within lake (LAKE)", and wastewater treatment plant sites correspond to "wastewater treatment plant effluent (WWTP)".

~20 s, and left for another day to separate. After separation, the dense material in the bottom of the funnel was released and discarded. The remaining sample was then separated into two size fractions, 25–125 μm and >125 μm, by stacking a 125 μm sieve on top of a 25 μm one, and pouring the solution through those, making sure to have a collection pan to catch the $CaCl_2$ for proper disposal. Each size fraction was then filtered onto individual 10 μm polycarbonate filters (47 mm diameter) and stored in a clean glass petri dish.

The >125 μm size fraction was evaluated for this study. Particle counting and characterization by shape and color was completed with a stereomicroscope first with a black background, to look for clear/white particles, and then with a white background for colored particles. All personnel were trained in the same manner, and the first three samples completed were evaluated by the trainer for inconsistencies. Counting guides (Shaw Institute, n.d.), examples from publications (Helm, 2017), and past sample sets, were all used for training. Particles were grouped into twelve shape categories: foam, fiber, fiber bundle, fragment, commercial fragment, film, pellet, sphere, paint, tire/road wear, sud (soap-like hard fragments that fell apart when probed but were chemically identified to be of anthropogenic origin), and gel. They were also grouped by basic colors (e.g. red, yellow), silver, gold, multi colored and an additional category of clear-blue due to the existence of numerous clear fibers with blue patches. All particles were counted and characterized by color/category. For measurements of length and width, a maximum of 20 particles of each color/category combination (e.g., blue fiber) were picked manually off the filter (due to time constraints) with forceps and placed onto double sided sticky tape to be imaged and measured using ImageJ software. Characterization of each picked particle was confirmed by two researchers to check consistency. The sum of particles in relevant field and lab blank samples were subtracted by color category to account for contamination.

A subset of the particles from all samples were chemically identified. Given the large number of particles counted and time considerations, we chose a representative 10% (by color/category) to be chemically identified across all samples (except for blanks where all non-fibers were identified). Our final results presented for chemical identification were blank subtracted by color-category-chemical for all non-fibers. For fibers, this subtraction was not necessary because the fibers in the blank were subtracted first by color-category, and then the remaining 10% of fibers in the samples were chemically identified. The chemical identification was completed using micro-Raman spectroscopy (HORIBA Raman Xplora Plus) for particles unable to be handled with forceps. Chemical identification with Raman was done in LabSpec6 software using a 785 nm (range 50–2000 cm^{-1}) or 532 nm (range 50–4000 cm^{-1}) laser with primarily a 100x long working distance microscope objective (and occasionally 50x objective) with a filter ranging from 0.1% to 100%, gratings of 600 or 1200 grooves/mm, 1 or up to 10 s for acquisition time, 2, 4, 6, 8, or 10 number of accumulations, a confocal hole diameter of 100 μm or 300 μm, and a confocal slit width of 50 or 100 μm. When acquiring spectra, parameters would be optimized to inhibit poor resolution, fluorescence, and other issues. This results in particles having a different suite of parameters (for example, the 785 nm would provide a better spectrum for darkly colored particles). The spectral library used was BioRad KnowItAll Raman Spectral Library of which certain databases were more extensively used, including Bio-Rad Sadtler (e.g. Polymers & Monomers (Basic); Polymers &

Processing Chemicals), HORIBA Scientific (e.g. Forensic), and Wiley (e.g. Sigma-Aldrich Library of Raman Spectra). For particles able to be handled with forceps, Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR FTIR; Bruker Alpha II) with a diamond internal reflection element and OPUS/3D software was used for chemical identification with 24 background and sample scans, and a spectral range wavenumber of 400 to 4000 cm^{-1}. The spectrum was matched to built-in Bruker libraries and the Primpke et al. (2018) library. For both Raman and FTIR, a spectral match generally fell between 80 and 98%, with a few exceptions made based on personal judgement. Chemical confirmation indicated anthropogenic particles were visually identified successfully at an average success rate of 93% across source types when excluding particles not able to be chemically identified, and 77% on average across source types assuming those unable to be chemically identified were non-anthropogenic.

2.4. Contamination control

Several laboratory practices were implemented to avoid contamination of samples with plastic and other anthropogenic material. All materials used during extraction and analysis were washed and scrubbed with soap using a seaweed sponge (VWR, Natural Wool Sponge 470001–406), rinsed three times with tap water followed by three times with RO water, and dried in an oven or wiped with a Kimwipe then blown with air to rid of Kimwipe fibers. Laboratory air was cleaned using a HEPA Air Purifier (Alen BreatheSmart FIT50), benches cleaned daily, and cotton lab coats worn by those extracting and counting particles. Samples were kept covered to prevent contamination from the air. Plastic use was minimized, or accounted for via lab and field blanks as noted above.

2.5. Data analysis

We used nonmetric multidimensional scaling (nMDS) to examine patterns of assemblage structure of microplastics (i.e., by category, color/category, and polymer type) among sources and with microplastics found in the lake. We used plastic categories (i.e., shapes), plastic category/color and polymer types to make separate two-dimensional ordinations. nMDS plots were run using Euclidean distances. We excluded one WWTP sample from all plots because it was an outlier. We used the function 'metaMDS' in the vegan community ecology package (Oksanen et al., 2008) in R.

Bivariate regressions were conducted using R software to examine whether upstream watershed characteristics influenced the quantity of particles in surface waters. We took into account model assumptions including residual normality (by examining histograms and qq-plots), and log-transformed all the data. The following predictor variables were included: watershed traits (population density, sum of road length, plastic industry, slope, end-of-life vehicle yards), and watershed land cover (urban, green, water, agriculture). This relationship was also assessed with these same characteristics but within a riparian zone. The water quality of rivers can be influenced at the full watershed or riparian zone scale (Sliva and Williams, 2001; Tran et al., 2010). Beacon Environmental Ltd (2012) evaluated studies for buffer zone width that attenuate pollutants from entering waterways and the maximum recommended width was 90 m, so to be conservative we chose 100 m. Predictor variables were chosen based on their likelihood to contribute plastics to the environment. Data sources for predictors can be found in Table S3, with maps of plastic industries in Fig. S1, population in Fig. S2, and land cover in Fig. S3.

3. Results

3.1. Anthropogenic particles in source waters

The average concentrations (±stdev) of microplastics and other anthropogenic particles per sample type are 13.3 ± 15.5 particles L^{-1} in wastewater effluent, 0.9 ± 1.3 particles L^{-1} in agricultural runoff, 15.4 ± 7.9 particles L^{-1} in stormwater runoff, and 0.8 ± 0.7 particles L^{-1} in the lake (Fig. 2; see Tables S4 and S5 for values). On average, the particle lengths and widths are 1.2 ± 1.0 mm and 0.07 ± 0.1 mm in wastewater effluent, 0.5 ± 0.5 mm and 0.2 ± 0.2 mm in agricultural runoff, 0.9 ± 0.9 mm and 0.2 ± 0.2 mm in stormwater runoff, and 1.0 ± 0.9 mm and 0.3 ± 0.2 mm in the lake, respectively (for more information on lengths and widths see Figs. S4–S5, Table S6). Particle categories are shown in Fig. 3 for each watershed type. Fibers are the dominant category in wastewater treatment plant effluent (90% relative abundance), and to a lesser extent in stormwater runoff (41%). Tire and road wear particles made up 22% of particles in stormwater, and were not found in other sample types. Categories in agricultural runoff and lake samples are diverse with no overwhelmingly dominating category. Colors of the particles are summarized for each sample type in Fig. S6. The dominant color for agriculture, stormwater, and lake samples is clear/white (accounting for half) while wastewater effluent is more mixed with 32% blue, 24% clear/white, 13% clear-blue and various colors remaining. Detailed results by sample type and location are provided in Figs. S7–S18 of the Supporting Information. The chemical identification of the anthropogenic particles is shown in Fig. 4. Wastewater effluent and lake samples have less diversity of chemical types then agriculture and stormwater runoff.

3.2. Relationships among sample types

The nMDS plots yielded a pattern whereby sources (stormwater, wastewater and agricultural runoff) grouped when run with anthropogenic particles grouped by categories (2D stress = 0.004;

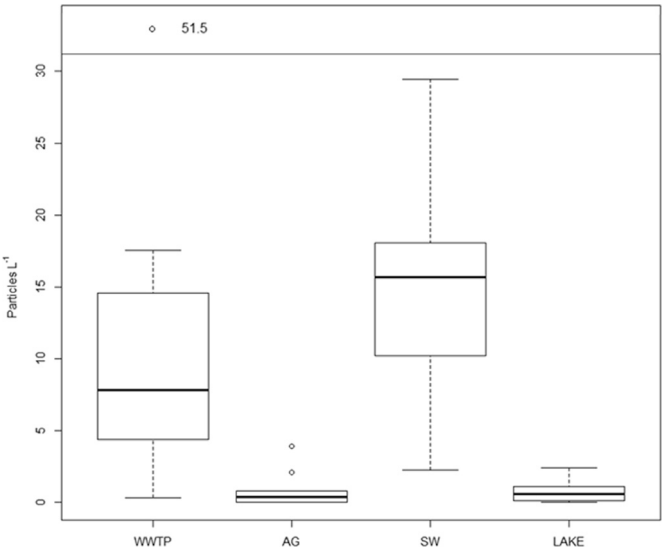

Fig. 2. Boxplot showing microplastics and other anthropogentic particles for each source type and within-lake after subtraction of anthropogenic particles in the blanks by color/category. The middle black bar indicates the median. Each box spans the first (25th percentile) to third quartile (75th percentile) with the box representing 50% of the data, and whiskers extend to minimum and maximum values not exceeding 1.5 times the interquartile range. Any outliers are represented by open circle dots, and any outliers outside the bounds of the y-axis have their value written next to them.

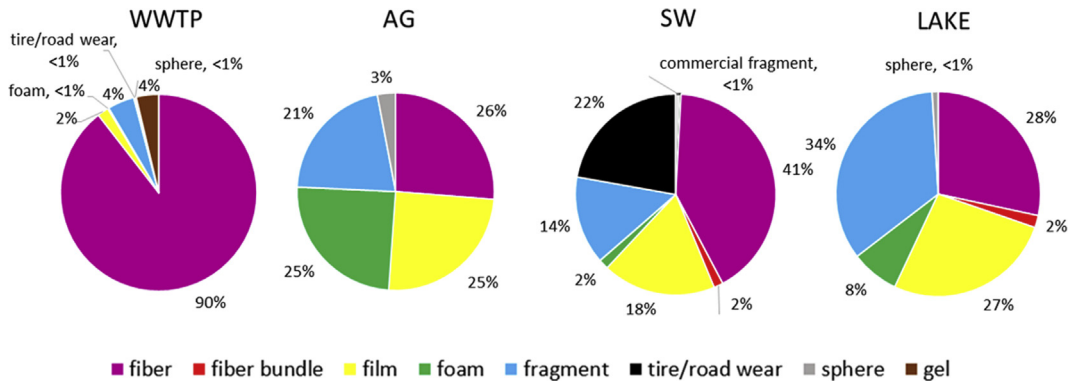

Fig. 3. Anthropogenic particle categories across source types and within-lake.

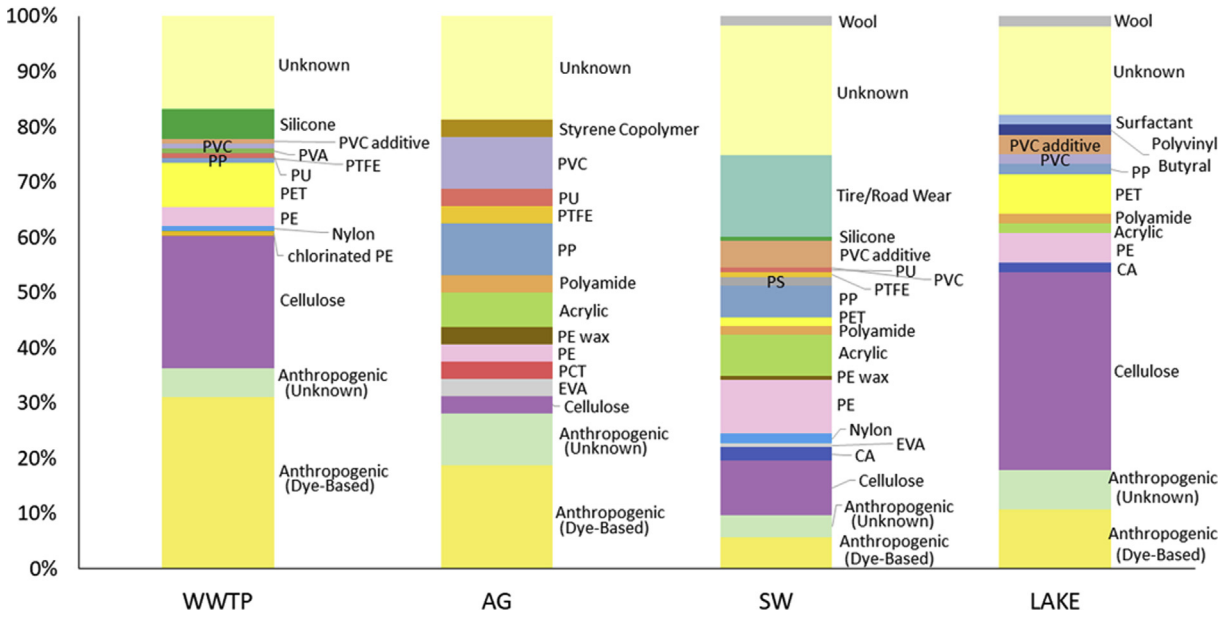

Fig. 4. Chemical identification results for all anthropogenic particles chemically analyzed in wastewater effluent, agricultural runoff, stomwater runoff and within-lake. Anthropogic (unknown) defines a particle that is visually identified to be anthropogic (based on homogeneous, and generally bright, coloring and hardness when physically probed) but no spectrum or clear chemical composition was able to be obtained via FTIR or Raman Spectroscopy from the particle. Anthropogenic (dye-based) defines a particle that has a chemical signal of an anthropogenic dye.

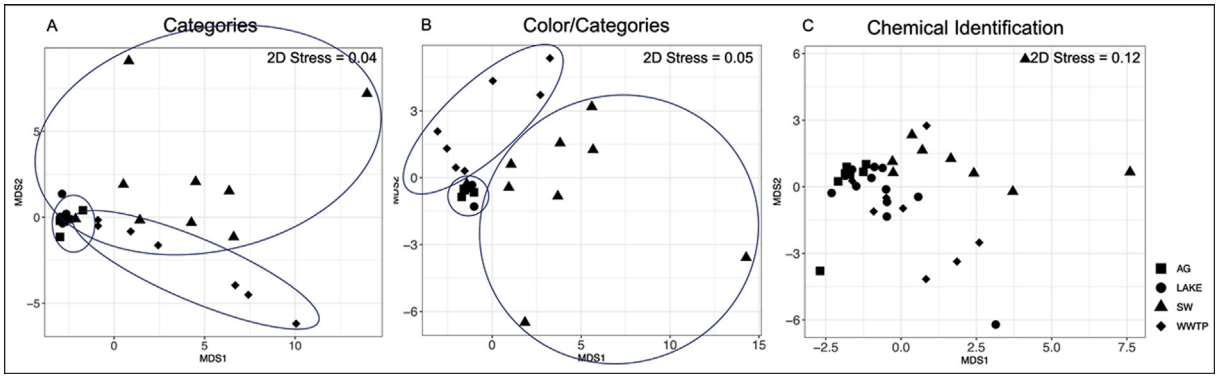

Fig. 5. Non-metric multidimentional scaling (nMDS) ordination plot for anthropogenic particle assemblages grouped by categories (A), color/categories (B) and chemical identification types (C). Blue circles show the grouping patterns among sources (Agricultural runoff - squares, strom water -triangles and WWTP - diamonds). Anthropogenic particle assemblages in the lake are depicted as filled dots. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

Fig. 5a) and color/category (2D stress = 0.05; Fig. 5b). When particles were grouped by chemical identification, groupings are not existent (2D stress = 0.13; Fig. 5c). For categories and color/category, where groupings by source are apparent, the anthropogenic

particle assemblages in surface waters from the lake group most with agriculture, followed by stormwater (Fig. 5a and b).

3.3. Relationships with watershed characteristics

At the upstream watershed scale, eight of the nine predictor variables had statistically significant bivariate relationships with mean particle L^{-1} (Table S7). Although plastic industry had the highest explained variation with 79%, there were no plastic industries upstream of agricultural watersheds and so the graph lacks data between the two extremes along the x-axis (see Fig. 6 bottom right) suggesting the results should be taken with caution. The predictors indicative of urbanized areas like population density and urban percent have the next highest explained variation (Fig. 6). Detailed results for the riparian zone and particle concentration regression models can be found in the Supporting Information (Table S8). Overall, there are little differences between these and the upstream watershed regressions.

4. Discussion

Overall, we found microplastics and other anthropogenic particles in all sample types and across all locations. We found that the characteristics of particles associated with different source waters was unique for wastewater treatment plant (WWTP) effluent and stormwater runoff. WWTP effluent was dominated by fibers, whereby stormwater runoff had the unique component of black rubbery particles that resembled tire and road wear particles. We also found that concentrations of microplastics and other anthropogenic particles in Lake Ontario streams were correlated with urbanization in the region.

4.1. Wastewater effluent

Our results demonstrate that WWTP effluent is a key pathway for microplastics and other anthropogenic particles to enter Lake Ontario. The average concentration of anthropogenic particles in wastewater effluent, 13.3 ± 15.5 particles L^{-1}, is higher than concentrations found in nine of eleven studies (see Table S2). However, further sampling should be done to determine a more precise estimate as our study showed a high variability amongst replicates (e.g. as low as 0.3 particles L^{-1} and as high as 4.4 particles L^{-1} in WWTP A) and had a small sample set.

Microfibers comprised 90% on average of the particles released through wastewater effluent. Other studies have also found fibers to be the predominant category type in wastewater effluent (Browne et al., 2011; Mason et al., 2016; Prata, 2018). The make-up of the fiber colors in wastewater effluent in this study are: blue (clear-blue and blue make up 50%), clear/white (make up 25%), and dark (black and grey make up 16%) (Fig. S19). Most of the blue fibers were chemically identified as indigo/indigo carmine or cellulose (~87%). One source of these fibers to waste water is from the washing of blue denim jeans (McQueen et al., 2017). Denim jeans are made of cotton (one type of cellulosic material) textile dyed with indigo to make blue denim (Wolf, 2011). The remaining fibers were a mix of cellulose, polyester, and other synthetic fibers (e.g. polyurethane, a material used in spandex). Roughly half of the fibers found were not identified as a polymer type because dyes masked the underlying chemical composition of the fiber (Fig. S20). A significant source of these fibers to wastewater is the washing of garments and other textiles (Boucher and Friot, 2017; Yang et al., 2019). Other potential sources are materials flushed down toilets, such as wet wipes and feminine hygiene products that may contain plastics like polyester (Munoz et al., 2018). Additionally, the treatment plants sampled receive sewer overflows (water from urban runoff during high flows), and so direct littering of textiles or fiber shedding into the atmosphere that has settled into the system can also be sources.

Amongst the remaining non-fiber particles, we found sixteen 'gel' particles in effluent from WWTP A and B. The subset of these that were chemically identified were all silicone polymers. One silicone particle was also found in the Don River, downstream of WWTP C. Other studies have found silicone in surface water (Hendrickson et al., 2018), fish (Biginagwa et al., 2016), and sediment (Ballent et al., 2016). Silicone polymers are made up of a silicone-oxygen backbone and not a carbon backbone like the classical petro-based polymers. Some typical applications of them include breast implants, cookware, hair conditioners, and more

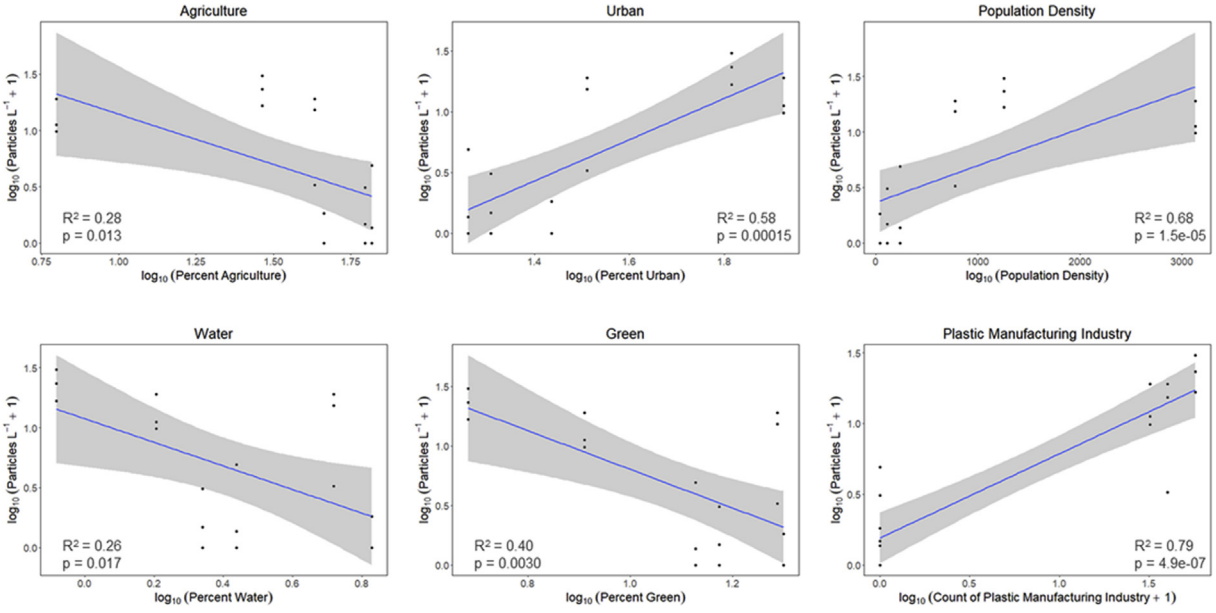

Fig. 6. Bivariate regression graphs and corresponding R-square values of microplastic abundance plotted aginst predictors.

(Verschoor et al., 2016). Ballent et al. (2016) identified silicone in Lake Ontario sediments, noting that silicone is among the polymeric materials produced in Canada (CIAC, 2014), and suggesting that silicone polymers also settle in Lake Ontario sediment. We find here that wastewater effluent is a pathway to which these polymers enter the watershed, however there are likely additional pathways given the multiple sources discussed.

4.2. Agricultural runoff

Agricultural runoff had the lowest concentration of anthropogenic particles compared to the other source types. Of those anthropogenic particles that were found, they cannot be fully attributed to agricultural uses as the upstream watersheds were not entirely made up of agricultural fields (Elgin West had 63% agricultural land and 20% urban area, Bruce Creek had 46% agricultural and 27% urban area, and Little Rouge had 65% agricultural and 18% urban area).

The use of plastic materials for agricultural practices, termed plasticulture, is a potential source of microplastics from agricultural fields (Rochman, 2018). For example, irrigation is employed in Ontario (Statistics Canada, 2016; OMAFRA, 2019a), and a commonly used polymer for irrigation pipes is PVC and LDPE/HDPE (Andrady, 2003), which we did find in our samples. Another example are greenhouse films, made from PE or EVA copolymers (Andrady, 2003). Both polymers were present in the Little Rouge samples and greenhouses were present upstream based on the land cover data. There are many applications of plastic in agriculture (e.g. nursery pots, tile drainage) and a diversity of chemical types as well, so detailed sampling would need to be done to confirm and assess the contribution of each to microplastics abundance.

Sewage sludge is applied to agricultural fields in Ontario (OMAFRA, 2019b), and found from other studies to be a major sink for microplastics from wastewater effluent with >95% being diverted from the final effluent (Murphy et al., 2016; Talvitie et al., 2017). However, based on spatial data of “non-agricultural source material” (NASM) from 2019 which includes sewage sludge (OMAFRA, 2019b), the agricultural watersheds sampled in this study did not have sewage sludge applied to them and so may not be a source of microplastics in our samples.

4.3. Urban stormwater runoff

Urban areas are significant hotspots for microplastics (Baldwin et al., 2016; Hitchcock and Mitrovic, 2019; Luo et al., 2019; Wang et al., 2017) and our study illustrates that urban centers are important contributors of microplastics to Lake Ontario. From our samples, the diversity of chemical types in stormwater runoff (Fig. 4) suggests a high diversity of sources including plastic industries, littering, roads, and wastewater effluent.

Although it is not fully clear the contribution of plastic manufacturing industry to microplastic abundance in the watersheds sampled, it is still a source that should be considered. A considerable number of plastic manufacturing and recycling industries are located in southern Ontario (Ballent et al., 2016; this study Figs. S1 and S2) and, of all provinces and territories, Ontario has the largest GDP for plastics and rubber manufacturing (Innovation, Science, and Economic Development Canada, 2017, 2018). Microplastic particles with characteristics consistent with manufacturing and recycling processes (flash, trimmings) are indicated to be present in Toronto area waters and sediments (Helm, 2017; Ballent et al., 2016). In other studies on the Great Lakes, commercial fragments and pellets have been found in environmental samples (Ballent et al., 2016; Corcoran et al., 2015; Helm, 2017; Zbyszewski et al., 2014). Corcoran et al. (2015) found the most common type of microplastics to be pellets at a Humber Bay beach site. Due to the low volumes sampled, we did not collect any pellets and found only a small number of fragments indicated to be generated from commercial activities (~1%). It is thus less clear whether there are specific chemical types or categories that can be linked back to the industrial sources. The commercial fragments were found in Etobicoke Creek and chemically identified as polyethylene and polyethylene methacrylate, suggesting that any manufacturers producing these polymers could be spilling these plastics into the watershed. This watershed has the largest number of plastic manufacturing industries (approximately 56) of all watersheds in Lake Ontario.

Litter (materials intentionally discarded to the environment) and debris (materials lost by wind from properties, recycling, etc.) are sources of anthropogenic materials to the environment that is more prevalent in urban areas. Litter could not be included in regression models due to lack of data on the distribution of litter/debris across watersheds. However, based on shoreline clean-up data from the GTA (Table S9), litter and debris are likely contributors to the abundance of microplastics as these materials break up in the environment. The top item found is often cigarette butts, made with cellulose acetate and we did find cellulose acetate in the stormwater samples. All other polymeric chemicals that make up the debris items listed in Table S9 were found in our samples, such as polypropylene and polyethylene. More detailed sampling will be necessary to assess the degree to which these litter and debris items contribute to microplastic abundance in urban waters.

Microfibers made up the highest proportion (41%) of categories in stormwater samples. Studies of surface waters within urban areas generally find fibers to be the predominant category (88% fibers, Luo et al., 2019; ~70% fibers, Baldwin et al., 2016; ~100% fibers, Dris et al., 2015; 89% fibers, Leslie et al., 2017; 53–96% fibers, Wang et al., 2017; ~70% fibers, Su et al., 2016). There are many avenues in which microfibers could be making their way into the streams including the shedding of clothing/textiles, litter/debris, and building materials (Carr, 2017). An additional source may be microfibers from sewage sludge, since a large portion of the watershed upstream of the Humber River and Etobicoke Creek samples are agricultural (43% and 29%) where NASM was applied.

Total road length and end-of-life vehicle yards were also significantly and positively correlated to particle concentrations indicating that the more roads there are, the greater the concentration of anthropogenic particles. This is evidenced by the stormwater samples that had black particles in them which we believe to be tire and road wear particles (TRWP). TRWPs are generated from the use of tires over time, and particles from the road surface (e.g. crack sealer) generated by frictional wear (Kreider et al., 2010; Panko et al., 2019). Most of them could not be identified due to Raman Spectroscopy limitations with black particles. Of the few that could be identified, two were found to be Vine Black or ‘carbon’ with Raman, while one was identified with FTIR as Copolymer Ethylene-Vinyl Acetate (EVA) Rubber. Carbon black is used as a filler to car tires, adding strength and longevity, and makes up 20–35% of a general passenger car tire by weight (Koenig, 1999; Wagner et al., 2018). EVA rubber is used in many applications and so the source is unclear (PHS, 2015). Of the particles that could not be identified via spectroscopy, they are assumed to be from tires based on their rubber-like texture and elongated/sausage-like shape (Kreider et al., 2010; Dannis, 1974), though they could be a mixture of TRWP. We found the most black particles in the Etobicoke Creek samples (65 compared to Humber with 19 and Don with 8), which as mentioned earlier had the greatest amount of manufacturing industry, but is also home to the Toronto Pearson International Airport that services 1,100 planes per day (Airports Authority, 2019; Kole et al., 2017).

4.4. Relationships between anthropogenic particles from source waters and Lake Ontario surface waters

Nearshore Lake Ontario waters adjacent to the GTA receive microplastics and other anthropogenic particles from the dominant pathways of wastewater effluent and stormwater runoff. However, based on our nMDS results (Fig. 5), the stormwater runoff and wastewater effluent did not group with lake samples, suggesting that particle fate processes can rapidly alter the character of microplastics present in the system, especially in surface water where these samples were collected. Sediments clearly are a repository of microplastics entering the Lake Ontario system (Ballent et al., 2016; Corcoran et al., 2015). As stormwater runoff, carrying a range of particle and chemistry types at high energy, enters the system and flow energy drops, the characteristics of the particle load will change with more dense or biofouled plastics settling. More buoyant particles, e.g. those with lower densities and lower surface area to volume ratios (less surface for fouling relative to volume/density) will tend to stay at the surface where our samples were collected (Kooi et al., 2018). Similarly, municipal wastewater effluent is discharged near the lake bottom through diffusers. Particles such as fibers, with relatively high surface area to volume ratios and polymers with densities just above 1 g cm^{-3} (polyamide) and 1.2–2.3 g cm^{-3} (polyester) (Hidalgo-Ruz et al., 2012), are more likely to remain in the water column or deposit to sediment then rise to the surface, altering the particle distribution observed when sampling at the surface. Although collected at different times, samples taken from the plume of WWTP B in the lake had lower particle numbers (0.5 particles L^{-1}) compared to WWTP B plant effluent (27.9 particles L^{-1}) due to dilution, and the percentage of fibers were also lower in the plume compared to the effluent.

5. Conclusions

Urban areas were found to contribute significant amounts of microplastics and other anthropogenic particle contamination to Lake Ontario. Tire wear and/or asphalt sealant particles coming from roadways as well as fibers from a variety of sources are entering Lake Ontario via stormwater and treated wastewater effluent. Although we did find relationships with our regression analyses, this work was exploratory given our limited overall sample size (N = 18; n = 3 for each location sampled) and spatial coverage (3 sites per sample type). We recommend future studies with a higher resolution of spatial and temporal coverage.

To mitigate microplastics and anthropogenic particles entering the environment, decision-makers may begin by working to better understand and prevent these sources. In particular, point sources like plastic manufacturing industries should be considered in future monitoring efforts. Nonpoint sources amongst urban areas are more difficult to monitor, however, there exist some solutions to mitigating particle releases such as permeable pavements or bioretention cells on or near roadways that can be put in place to trap particles before they enter a river or lake (Kole et al., 2017; Gilbreath et al., 2019). In addition, educational programs that work to prevent littering can be implemented. A great example of an educational initiative is Operation Clean Sweep by the American Chemistry Council (2019) working to educate companies about limiting any plastics releases to the environment. Finally, in wastewater effluent we found mostly fibers, which can be prevented from entering wastewater treatment plants. McIlwraith et al. (2019) tested two microfiber-capturing technologies in washing machines and found that both reduce microfibers in effluents. The results of this study can be used to inform local policy by using scientific data to guide best management practices and future mitigation strategies.

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Declaration of competing interest

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

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.watres.2020.115623.

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