



Sources and sinks of microplastics in Canadian Lake Ontario nearshore, tributary and beach sediments



Anika Ballent^{a,*}, Patricia L. Corcoran^a, Odile Madden^b, Paul A. Helm^c, Fred J. Longstaffe^a

^a Department of Earth Sciences, University of Western Ontario, 1151 Richmond St. N., London, ON, N6A 5B7, Canada

^b Museum Conservation Institute, Smithsonian Institution, 4210 Silver Hill Rd., Suitland, MD, 20746, USA

^c Environmental Monitoring and Reporting Branch, Ontario Ministry of the Environment and Climate Change, 125 Resources Rd., Toronto, ON, M9P 3V6, Canada

ARTICLE INFO

Article history:

Received 31 March 2016

Received in revised form 8 June 2016

Accepted 9 June 2016

Available online 21 June 2016

Keywords:

Microplastics

Lake Ontario

Sediments

Raman spectroscopy

Nearshore

Watershed

ABSTRACT

Microplastics contamination of Lake Ontario sediments is investigated with the aim of identifying distribution patterns and hotspots in nearshore, tributary and beach depositional environments. Microplastics are concentrated in nearshore sediments in the vicinity of urban and industrial regions. In Humber Bay and Toronto Harbour microplastic concentrations were consistently > 500 particles per kg dry sediment. Maximum concentrations of ~28,000 particles per kg dry sediment were determined in Etobicoke Creek. The microplastic particles were primarily fibres and fragments < 2 mm in size. Both low- and high-density plastics were identified using Raman spectroscopy. We provide a baseline for future monitoring and discuss potential sources of microplastics in terms of how and where to implement preventative measures to reduce the contaminant influx. Although the impacts of microplastics contamination on ecosystem health and functioning is uncertain, understanding, monitoring and preventing further microplastics contamination in Lake Ontario and the other Great Lakes is crucial.

© 2016 Elsevier Ltd. All rights reserved.

1. Introduction

Studies concerning plastics contamination of marine environments began in the 1970s (e.g. Carpenter and Smith, 1972; Colton et al., 1974), and since that time, investigations have shown that plastic waste is consistently found in aquatic environments including beaches, ocean surface waters, deep-sea sediments, freshwater lakes, and tributaries (e.g. Eriksen et al., 2013; Van Cauwenberghe et al., 2013; Vianello et al., 2013; Cózar et al., 2014; Turra et al., 2014; Eerkes-Medrano et al., 2015). Contamination of aquatic environments with plastics has become a global issue as a result of low recycling rates, designs that do not include the post-consumer stage of the product, and lack of policies that support a circular plastics economy (Neufeld et al., 2016).

Microplastics, defined as plastic particles < 5 mm long (NOAA, 2015), are either manufactured for use in applications such as cosmetics, personal care products, industrial abrasion processes and synthetic fabrics (Fendall and Sewell, 2009; Eriksen et al., 2013; Sundt et al., 2014), or are generated by the degradation of larger plastic products (Carpenter and Smith, 1972; Sundt et al., 2014). In a recent study, microbeads, many of which were comparable to particles isolated from cosmetic products, comprised an estimated 58% of microplastics < 1 mm in size collected from the surface waters of the Great Lakes (Eriksen et al.,

2013). Several countries, including Canada and the United States, have since begun the process of banning the sale of cosmetic products containing microplastics. Polyethylene (PE) and polypropylene (PP), often used in the production of cosmetic microplastics, have densities less than that of fresh water, but have nonetheless been regularly identified in submerged sediments (Claessens et al., 2011; Vianello et al., 2013; Corcoran et al., 2015). The study of microplastics in sediment is therefore needed for a comprehensive understanding of microplastics contamination in the Laurentian Great Lakes.

Microplastics pollution has been reported from Great Lakes surface waters (Eriksen et al., 2013), along shorelines (Zbyszewski and Corcoran, 2011; Zbyszewski et al., 2014; Corcoran et al., 2015) and in offshore lake bottom sediments (Corcoran et al., 2015), but its presence in subsurface sediments of nearshore regions and tributaries is still largely unknown (Driedger et al., 2015). Allan et al. (2013) modeled current environmental stressors affecting the Great Lakes and found that cumulative stress levels were greatest in nearshore regions and generally decreased with distance from the shore. Only one investigation concerning microplastics pollution in Lake Ontario sediments has been published to date (Corcoran et al., 2015), despite it being the terminal lake within the Great Lakes system. In addition, the lake is surrounded by highly urbanized and industrialized regions, particularly along the northern shore, which have been associated with the accumulation of plastic debris (e.g. Barnes et al., 2009; Turra et al., 2014). We herein provide a regional investigation of the abundance and depositional patterns of microplastics in nearshore, tributary and beach

* Corresponding author.

E-mail address: 4anikab@gmail.com (A. Ballent).

sediments along the Canadian shoreline of Lake Ontario in an effort to provide: (i) a baseline for future monitoring, (ii) a means to assess potential sources of microplastics to the lake, and (iii) a distribution map of current microplastics hotspots.

Microplastics in benthic ecosystems pose an environmental threat primarily because organisms that feed on the benthic community may potentially ingest microplastics. Littoral and profundal fish species in large temperate lakes have diets that consist primarily of benthic organisms, and in Lake Ontario ~92% of fish and ~96% of invertebrate species are found in littoral habitats (Vadeboncoeur et al., 2011). The majority of aquatic species in Lake Ontario are closely connected to nearshore benthic habitats, and microplastics contamination of these sediments may be directly affecting the health of the lake ecosystem at many trophic levels. Although plastics are not classified as hazardous waste in Canada, certain plastic products, such as polycarbonate CD-ROM discs and polyurethane foams commonly used in furniture, are manufactured from hazardous derivatives (Lithner et al., 2009). Additives such as polybrominated diphenyl ethers (PBDEs; e.g. flame retardants) (Lithner et al., 2011; Rochman et al., 2014) and plasticizers such as Bisphenol-A are also often included to change the physical properties of the plastics (Oehlmann et al., 2009). Plasticizers have been shown to have negative impacts on the hormonal systems of invertebrates, fish and amphibians (Oehlmann et al., 2009). Conclusive evidence for the transfer of associated hazardous compounds from plastics to organisms is lacking, but several studies have suggested correlations between plastics ingestion and compromised physiological function (e.g. Teuten et al., 2009; Wright et al., 2013; Syberg et al., 2015). An additional threat of microplastics is their role as colonization surface habitats for bacteria or other organisms, which may lead to the invasive transport of microbial communities (e.g. Ye and Andradý, 1991; Zettler et al., 2013; Harrison et al., 2014; McCormick et al., 2014; Nauendorf et al., 2016).

A comprehensive overview provided by Eerkes-Medrano et al. (2015) highlights our limited understanding of microplastics contamination in freshwater systems. Rivers and urban tributaries, however, have been shown to be major transport pathways for microplastics and macroplastics, plastics >5 mm (Moore et al., 2011; Gasperi et al., 2014; Lechner et al., 2014; Rech et al., 2014; Zhao et al., 2014; Corcoran et al., 2015; Naidoo et al., 2015). Whereas buoyant materials are transported on surface waters (Gasperi et al., 2014), non-buoyant materials are transported along the tributary bed (Moore et al., 2011; Morrill et al., 2014). Microplastic debris loads can be introduced into tributaries via non-point spill and litter sources as well as point sources such as effluent pipes (Lechner and Ramler, 2015), storm water drainage outlets (Armitage & Rooseboom 2000) and possibly wastewater treatment plants, particularly during combined sewage overflow and bypass events during heavy precipitation conditions (MacDonald and Podolsky, 2009). Rech et al. (2014) and Corcoran et al. (2015) showed that macroplastic and microplastic debris loads carried by rivers are also deposited along river banks, suggesting that rivers are both depositional and erosional zones for anthropogenic debris.

2. Setting and methods

2.1. Setting

Lake Ontario drains an area of slightly >64000 km² and is the terminal lake in the Laurentian Great Lakes chain (Fig. 1). Prevailing wind patterns in the Toronto region from November to February are mainly NW to WSW, and gradually shift to ENE-dominated from March to October. The western end and the northwestern shore of the lake are characterized by several urban and industrial regions, including the cities of Hamilton, Mississauga and Toronto, with populations of 0.52, 0.71 and 2.62 million, respectively. Plastics manufacturing in Canada is concentrated in Southern Ontario (Statistics Canada, 2012). According to a 2014 statistical report of the Canadian Chemical Industry (CIAC), production of synthetic resins, fibres and rubbers included PE, ethylene vinyl acetate,

polystyrene (PS), polyvinyl chloride (PVC), polyacrylamides, polyethylene terephthalate (PET), nylons, latex emulsions, polyesters, silicones and butyl and halobutyl rubbers (CIAC, 2014, p. 34). High-density resins comprised 16% and PE comprised 80% of Canadian synthetic resin/rubber exports by weight in 2013 (CIAC, 2014, p. 35). In total, ~3500 kt of PE were produced in 2013 (CIAC, 2014, p. 34).

2.2. Sample collection

Nearshore, tributary and beach sediments were sampled using a combination of sediment trap, core and grab sampling techniques in order to obtain as many data points as possible. The original objective was to collect all nearshore samples using a Glew gravity corer, but this method proved to be especially challenging as a result of the high wave action in Lake Ontario. The Ontario Ministry of the Environment and Climate Change (MOECC) donated Shipek grab samples, in addition to passive sediment trap samples that they had collected from Lake Ontario (Nearshore Index and Reference sites, Great Lakes Nearshore Monitoring Program). Tributary sediment was best sampled using a petite ponar grab that could be lowered from a standing position. Beach sediment was sampled using a split spoon corer, as it was originally thought that depth below the surface could be related to microplastics abundance. However, given the highly variable hydrodynamic conditions that take place on beaches, we have chosen to represent all sediment depths at each beach as a whole. The use of various sampling methods enabled a greater spatial resolution, but temporal (annual and seasonal) constraints were not possible. Sample names, dates, sampling instruments, depositional environments, locations, and water depths are detailed in Table 1.

A total of 33 nearshore samples were collected (Table 1; Fig. 1). Five nearshore sediment samples were collected using a Glew gravity corer in August 2014. The PVC cores measured 6.5 cm in diameter, and ranged between 6 and 15 cm thick. Immediately after recovery, the gravity cores were extruded into 1 cm intervals ($N \leq 15$) and stored in sealed PE bags. Twenty-five samples were collected by the MOECC from the Canadian shoreline of Lake Ontario and the proximal St. Lawrence River in August 2012 and July 2014 using a Shipek grab sampler with a square opening of 20 cm and a half-cylindrical cup with a radius of 10 cm (Wildco, Yulee, FL). Three replicate grab samples were collected from each station, homogenized in a metal tray and transferred into 0.5 L PET collection bottles. Three additional nearshore samples were collected by the MOECC from sediment traps in November 2014. The traps comprised an array of four acrylic cylinders, secured at approximately 2 m above the lake bed, and were allowed to collect sediment for 6 months.

Tributary sediment samples from Red Hill Creek, Etobicoke Creek, Humber River and Don River (Fig. 1) were obtained with a 16 × 14.5 cm hand-held, stainless steel Petite Ponar sediment grab (Wildco, Yulee, FL). Sample locations were constrained foremost by accessibility and second by the presence of sediment depositional zones. At each of seven sample locations, 2 grab sample replicates were combined in a metal tray and were spooned into 0.5 L PET collection bottles.

Sediment was also sampled from five east and south facing beaches along the north-western shore of Lake Ontario in June 2015: Beachway Park, Bronte Beach, Marie Curtis Park, Sunnyside Beach and Woodbine Beach (Fig. 1). Much of the northern shore of Lake Ontario has been built up with large boulders or is inaccessible due to privatization of lands, which limited sample sites to public sandy beaches. Using a stainless steel split spoon corer with a height of 30 cm, two cores were collected from each beach at approximately 2 m and 6 m from the waterline, representing the proximal and distal foreshore, respectively. The foreshore sediments are regularly submerged with seasonal changes in water level as well as during storm surges. The corer was equipped with an inner, segmented PVC core, each segment measuring 10 cm long. Upon opening the core, each segment was covered with a PE cap. All proximal foreshore sites, except at Marie Curtis Beach, were

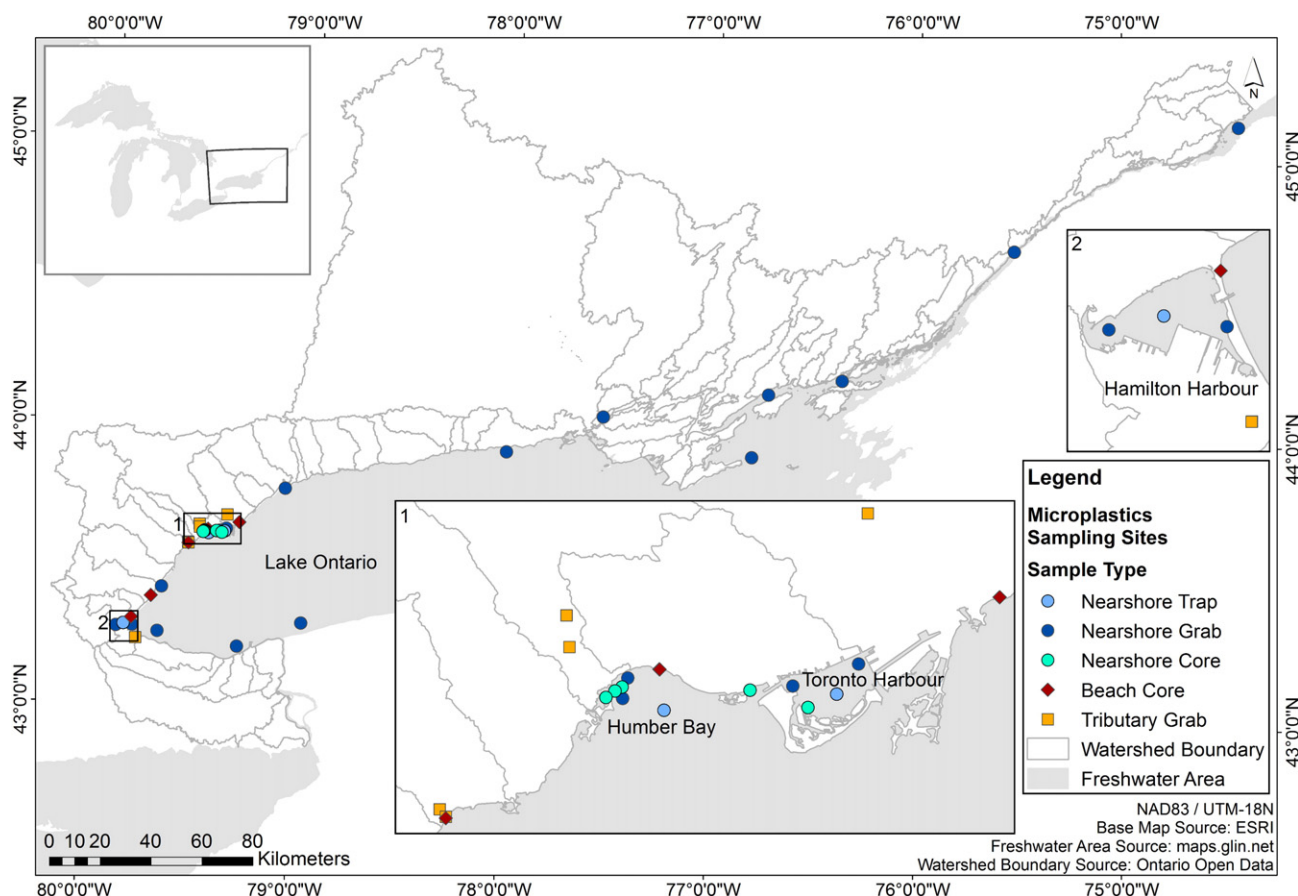


Fig. 1. Sampling sites by depositional environment and instrument type for which microplastics in sediments in Lake Ontario and the St. Lawrence River were analyzed. Watershed boundaries indicate the regions that drain directly into Lake Ontario and the St. Lawrence River.

limited to a sampling depth of 20 cm due to the high water content below that depth. All samples were kept cool until returned to the laboratory where they were stored at $-25\text{ }^{\circ}\text{C}$ until analysis.

2.3. Microplastic quantification

The sediment samples were dried at $70\text{ }^{\circ}\text{C}$ and weighed. All samples, except those collected by gravity core, were sieved using a Taylor sieve shaking apparatus with sieve mesh sizes of 5.6 mm, 2.0 mm, and 0.063 mm for 5 min at 60 Hz. Consolidated sediment samples with high clay fractions were first wet sieved through a 0.063 stainless steel sieve, then dried and weighed again to calculate the fine fraction. Following sieving, each fraction was weighed, the $>2\text{ mm}$ and $>5\text{ mm}$ fractions were visually examined for microplastic, and the $>0.063\text{ mm}$ fraction was transferred through a sample splitter. Half of the $>0.063\text{ mm}$ fraction was used for density separation. All samples were processed using a sodium polytungstate (SPT) density separation technique. Each sample was combined with SPT, (1.5 g cm^{-3}), magnetically stirred for 2 min and then transferred to a glass separation funnel to settle. After draining the non-buoyant material, the buoyant material was drained into a polycarbonate/polyester $0.053\text{ }\mu\text{m}$ sieve, rinsed thoroughly with filtered deionized water, transferred to a second separation funnel containing 500 mL of filtered deionized water, and then allowed to settle. The resulting non-buoyant and buoyant fractions were consecutively drained through a polycarbonate/polyester $0.053\text{ }\mu\text{m}$ sieve and transferred to glass vials. Samples were dried at $70\text{ }^{\circ}\text{C}$ and were covered until visual processing. Samples collected using the gravity corer were not split or sieved; the microplastic-containing fraction was separated by decanting and filtering through VWR® Grade 114 qualitative fast flow $25\text{ }\mu\text{m}$ filter paper.

Microplastics were visually identified using a Nikon SMZ1500 stereo microscope at magnifications ranging from $15\times$ to $225\times$. With decreasing particle size, the ability to identify a particle as plastic becomes reduced due to fewer visual and textural clues as discussed by Lenz et al. (2015) and Song et al. (2015). Even though particles at the lower end of the size limit defined by the filter or sieve can be magnified sufficiently, lower observation limits are constrained by the ability to distinguish synthetic particles from other particles using colour (bright, non-natural colors are easier to detect), presence of shiny lustre (often associated with plastics) and other visual and textural cues. In addition, the higher the magnification, the more time is needed to process a sample. In light of these limitations, the lower size limit of visual identification of plastics is estimated to be $\sim 0.25\text{ mm}$. Microplastic particles were counted and sorted by type into 3 categories: fibres, fragments and spherical beads. All particles were photographed using a Nikon digital camera DXM1200F connected to the microscope.

Throughout the sampling and laboratory analysis, precautions were taken to minimize contamination of the samples from airborne microplastic particles. Containers holding samples were kept covered with aluminum foil throughout the process except during periods when the samples were drying in the closed oven. The laboratory surfaces were routinely wiped down and all beakers, trays, containers, funnels, tools and sieves were thoroughly washed and rinsed with filtered deionized water before and after each use and were stored with openings covered in aluminum foil. Metal and glass containers and tools were used in all analyses, except for a polycarbonate/polyester mesh sieve. Sampling containers used in the field were plastic; however, precautions were taken that all materials were either cleaned prior to use or were new and unopened containers. Clothing worn by researchers were of natural fibres and in the laboratory, white cotton

Table 1
Summary of sediment samples by name, site location description, depositional environment, sampling instrument type, date, geographic coordinates and underwater depth. A depth of zero is assigned to beach samples taken above the lake water level. Microplastic abundance is reported as particles per kg of dry sediment; N kg^{-1} . The fine fraction (clay and silt sized particles) is reported as the percent of sediment $<63 \mu\text{m}$. Abbreviations: Hb: harbour; Rv: river; Cr: creek; STP: sewage treatment plant outfall.

Sample	Site	Environ.	Type	Year	Month	Lat. (°)	Long. (°)	Depth (m)	N kg^{-1}	% sed. $<63 \mu\text{m}$
S-7481	Six Mile Cr	Nearshore	Grab	2012	Aug	43.320	-78.979	18	320	6.79
S-7486	Port Dalhousie	Nearshore	Grab	2012	Aug	43.228	-79.283	19	290	92.0
S-7491	Stoney Cr	Nearshore	Grab	2012	Aug	43.268	-79.671	22	70	24.4
S-7541	Oakville	Nearshore	Grab	2012	Aug	43.426	-79.661	21	1360	78.9
S-7546	Humber Bay	Nearshore	Grab	2012	Aug	43.623	-79.447	15	280	59.0
S-7553	Toronto Hb	Nearshore	Grab	2012	Aug	43.632	-79.370	9	3210	96.7
S-7501	Pickering	Nearshore	Grab	2012	Aug	43.794	-79.085	20	230	4.40
S-7506	Chub Point	Nearshore	Grab	2012	Aug	43.953	-78.012	21	140	4.23
S-7514	Trenton	Nearshore	Grab	2012	Aug	44.088	-77.544	3	800	31.4
S-7509	Prince Edward	Nearshore	Grab	2012	Aug	43.958	-76.812	21	430	81.7
S-7521	North Channel	Nearshore	Grab	2012	Aug	44.181	-76.735	24	780	97.4
S-7526	McDonnell Bay	Nearshore	Grab	2012	Aug	44.234	-76.375	4	120	15.8
S-7531	Prescott	Nearshore	Grab	2012	Aug	44.698	-75.532	3	40	1.41
S-7536	Lake St. Francis	Nearshore	Grab	2012	Aug	45.137	-74.416	12	80	5.84
S-3025	Humber Bay, index	Nearshore	Grab	2014	Jul	43.623	-79.447	15	230	46.6
S-3026	Humber Rv, mouth	Nearshore	Grab	2014	Jul	43.633	-79.464	8	730	3.47
S-3027	Humber Bay, STP	Nearshore	Grab	2014	Jul	43.626	-79.466	8	2550	71.2
S-3028	Toronto Hb, index	Nearshore	Grab	2014	Jul	43.632	-79.370	9	1590	91.6
S-3029	Don Rv, mouth	Nearshore	Grab	2014	Jul	43.642	-79.361	9	1250	96.2
S-3030	Toronto Hb, west	Nearshore	Grab	2014	Jul	43.633	-79.390	7	2790	82.0
S-HB14	Humber Bay	Nearshore	Grab	2014	Jul	43.623	-79.447	15	50	66.4
S-TH14	Toronto Hb	Nearshore	Grab	2014	Jul	43.632	-79.370	9	530	92.6
S-3031	Hamilton Hb, index	Nearshore	Grab	2014	Jul	43.289	-79.836	24	130	N/A
S-3032	Hamilton Hb, west	Nearshore	Grab	2014	Jul	43.281	-79.872	13	210	N/A
S-3033	Hamilton Hb, SE	Nearshore	Grab	2014	Jul	43.285	-79.794	22	160	N/A
T-258	Hamilton Hb, index	Nearshore	Trap	2014	Nov	43.289	-79.836	24	260	90.0
T-2047	Humber Bay, index	Nearshore	Trap	2014	Nov	43.623	-79.447	15	2210	97.0
T-1364	Toronto Hb, index	Nearshore	Trap	2014	Nov	43.632	-79.370	9	750	96.0
G-HB1	Humber Bay	Nearshore	Core	2014	Aug	43.630	-79.466	6	1240	77.9
G-HB2	Humber Bay	Nearshore	Core	2014	Aug	43.629	-79.469	4	990	88.4
G-HB3	Humber Bay	Nearshore	Core	2014	Aug	43.626	-79.473	4.5	3470	91.7
G-TH1	Toronto Harbour	Nearshore	Core	2014	Aug	43.631	-79.409	2.5	4270	36.7
G-TH2	Toronto Harbour	Nearshore	Core	2014	Aug	43.627	-79.383	5	670	66.2
P-DR1	Don Rv	Tributary	Grab	2015	Jun	43.691	-79.360	0.18	480	23.3
P-HR1	Humber Rv	Tributary	Grab	2015	Jun	43.652	-79.493	0.23	100	0.28
P-HR2	Humber Rv	Tributary	Grab	2015	Jun	43.642	-79.491	0.26	1740	51.8
P-EC1	Etobicoke Cr	Tributary	Grab	2015	Jun	43.587	-79.545	0.09	1210	27.7
P-EC2	Etobicoke Cr	Tributary	Grab	2015	Jun	43.585	-79.542	2.5	27,830	0.00
P-RC1	Red Hill Cr	Tributary	Grab	2015	Jun	43.240	-79.774	0.35	100	22.7
P-RC2	Red Hill Cr	Tributary	Grab	2015	Jun	43.240	-79.774	0.11	40	1.01
C-BW1	Beachway Park	Beach	Core	2015	Jun	43.312	-79.800	0	60	0.09
C-BW2	Beachway Park	Beach	Core	2015	Jun	43.312	-79.800	0	60	0.09
C-BB1	Bronte Beach	Beach	Core	2015	Jun	43.392	-79.710	0	20	0.04
C-BB2	Bronte Beach	Beach	Core	2015	Jun	43.392	-79.710	0	70	0.03
C-MC1	Marie Curtis Park	Beach	Core	2015	Jun	43.584	-79.542	0	50	0.06
C-MC2	Marie Curtis Park	Beach	Core	2015	Jun	43.584	-79.542	0	190	0.09
C-SS1	Sunnyside Beach	Beach	Core	2015	Jun	43.637	-79.450	0	470	0.05
C-SS2	Sunnyside Beach	Beach	Core	2015	Jun	43.637	-79.450	0	250	0.09
C-WB1	Woodbine Beach	Beach	Core	2015	Jun	43.666	-79.299	0	170	0.03
C-WB2	Woodbine Beach	Beach	Core	2015	Jun	43.666	-79.299	0	50	0.05

laboratory coats were worn. During analysis, doors to the corridors were kept closed whenever possible. To test for airborne microplastic contamination levels during sample processing in the laboratory, petri dishes (cleaned and microscope inspected) were set in the working space of each lab room and the drying oven for 2 h, immediately followed by visual inspection with the same stereo microscope used for sediment sample analysis. Two replicate tests were conducted for each space.

2.4. Polymer identification

In order to determine the relative abundance of various polymer compositions, microplastic fragments and beads were randomly selected for analysis by Raman spectroscopy and X-ray fluorescence spectroscopy (XRF) at the Museum Conservation Institute at the Smithsonian Institution. Raman spectroscopy was conducted with a NXR Fourier-transform Raman module coupled to a 6700 Fourier transform infrared spectrometer (Thermo Electron Corporation, Madison, WI, USA). The

FT-Raman module was equipped with a continuous wave near infrared ND:YVO₄ excitation laser (1064 nm), a germanium detector cooled with liquid nitrogen and a CaF₂ beam splitter. Laser power was chosen empirically to maximize signal-to-noise ratio (SNR) without damaging the sample, and ranged from 0.01–0.07 W across a 50 μm round laser spot. Spectra comprised a co-addition of 64–2048 scans collected at 8 cm^{-1} resolution across 98–3994 cm^{-1} Raman shift. The performance of the spectrometer was checked against a reference scan of polystyrene and recalibrated as necessary each day of analysis. Raman spectra were plotted with OMNIC™ software (Thermo Scientific, Madison, WI, USA) and compared to commercial spectral libraries¹ and custom libraries prepared by the Smithsonian's Museum Conservation Institute. All spectra were analyzed using the automated search function of the

¹ HR FT-Raman Polymer Library (copyright 1997–2001, 2004 Thermo Electron Corporation by Nicolet Raman). HR Pharmaceutical Excipients FT-Raman Library (copyright 1999, 2004 Thermo Electron Corporation for Marcel Dekker, Inc.). FDM Retail Adhesives & Sealants (Fiveash Data Management, Inc., Madison, Wisconsin, USA)

software and also visually before identification was finalized. Of the 6331 plastic particles identified in the sediment samples, a total of 90 particles were analyzed by Raman spectroscopy. Using a random number generator, up to twelve particles were selected from three tributary samples and two 1 cm intervals from each of the five nearshore gravity core samples. Particles selected by the random number generator that could not be successfully analyzed (i.e. the material was too dark or thin) were replaced by those associated with the next randomly generated number. Fibres were excluded due to their insufficient diameter and volume. Some samples were also analyzed by X-ray fluorescence spectroscopy (XRF) to confirm the presence of chlorides in suspected polyvinyl chloride plastics. The instrument used was a Bruker Artax 400 μ XRF spectrometer equipped with a Rh-tube, a poly-capillary lens with a $\sim 100 \mu\text{m}$ focal spot and a Peltier-cooled Si-drift detector. The excitation voltage ranged between 25 and 50 kV and the current ranged between 490 and 492 μA .

2.5. Geographic spatial analysis

Population density and plastics-related industries were mapped on a watershed basis to gain insight into the relative levels of urban and industrial waste that may be expected to enter the lake through tributaries along the shoreline of Lake Ontario. Esri® geographic information software ArcGIS was used to calculate and map these two variables and to map the spatial variation of microplastics. Geographic shapefile datasets for the primary-level watershed boundaries (areas draining to Lake Ontario and the St. Lawrence River) and quaternary-level watershed boundaries (river and coastal stream catchment basins) were retrieved from the Government of Ontario Open Source Data Catalogue and Land Information Ontario. The datasets were used to generate a shapefile for quaternary-level watershed boundaries in which only those watersheds that drain into Lake Ontario and the St. Lawrence River were included, and in which all watersheds include a portion of the Lake Ontario or St. Lawrence River shoreline (Fig. 1). Multiple drainage points per watershed were permitted where small coastal creeks were located and for which separate quaternary-level watersheds were not delineated.

Canadian 2011 Census data obtained from Statistics Canada were used to determine the approximate human population of each watershed. Wastewater treatment plants proximal to the Ontario shoreline of Lake Ontario and St. Lawrence River were plotted using facility addresses. Storm drain outlets and combined sewer overflow outfalls along the tributaries and lake shore are densely located, particularly in urban regions. The abundance of outfalls would be expected to correlate well with population levels on the scale of the study, as indicated by a map showing storm drain outfalls along Taylor Creek, tributary of the Don River (City of Toronto, 2006). They are therefore not individually mapped in this study. Plastics-related industry contact addresses were collected from ThomasNet, an online supplier discovery and product-sourcing directory. Through the search engine, businesses with descriptions or names containing the word 'plastic' were selected, and verified to be in the plastics industry by qualitative analysis of the description. Results were constrained to suppliers located in Ontario, Canada and categorized according to type: manufacturer, distributor and service. All businesses were considered equally in counting the number of businesses located in each watershed. For businesses with multiple locations, all locations in Ontario were included. The search was not exhaustive, and the list of locations used in this study may be incomplete; however, registration in the ThomasNet directory is free and includes a large number of plastics-related businesses. Geographic locations of microplastics samples ($N = 51$), recorded using a handheld Geographic Positioning Device (GPS), were formatted into a point feature shapefile. Datasets were converted within ArcGIS to a common projected coordinate system used for this project: North American Datum 1983, Universal Transverse Mercator, Zone 18 North (NAD83/UTM-18N). Spatial analysis was completed primarily in vector space, but drainage area

and population were calculated in raster space at a resolution of 100 m. Plastics-related industry counts were calculated using a spatial join function.

3. Results

3.1. Microplastics abundance

A total of 6331 particles were visually identified as microplastics. Microplastics abundance for each sample site was normalized to particles per kg of dry sediment ($N \text{ kg}^{-1}$, dw) using the initial mass of the dried sediment sample (Table 1). Microplastics were identified in every sediment sample, and abundances varied between 20 and 27,830 kg^{-1} (Fig. 2). Maximum microplastics abundance was found at site P-EC2, at the mouth of Etobicoke Creek. The sample was primarily composed of algae, and therefore the extrapolated total number of microplastics is exceptionally high due to the low mass of the dried algae. Additional results and analyses presented here exclude this data point unless specifically noted. On average (not including P-EC2), microplastics abundance was 760 kg^{-1} . In the sample processing lab, the drying oven and microscopy lab airborne contamination levels were 2, 3 and 1.5 fibres h^{-1} of exposure, respectively on the scale of a standard glass Petri dish (area: $A = 64 \text{ cm}^2$). During processing, extreme caution was taken to minimize sample exposure. Contamination of the sediment samples with fibres may have occurred during the drying stages of sample preparation during which sample containers ($A = 2\text{--}315 \text{ cm}^2$) were exposed for up to 24 h.

Nearshore sediments contained on average the greatest abundance of microplastics (980 kg^{-1}), followed by tributary sediments with 610 kg^{-1} and beach sediments with 140 kg^{-1} (Fig. 3a). Microplastics in nearshore sediments were most concentrated in Humber Bay and Toronto Harbour. Microplastic abundances of $>1000 \text{ kg}^{-1}$ were found only at sites in the Greater Toronto Area (GTA) and offshore of Oakville (sample S-7541), west of Toronto. Microplastics abundance, as recorded in the sediments sampled from the gravity core, generally decreased within the top 2 g cm^{-2} of sediment accumulation, but microplastics were found at all sampled depths up to 15 cm (equivalent to 11.2 g cm^{-2} accumulated sediment mass) below the sediment surface (Fig. 4a). Nearshore sediments collected with the gravity cores had relatively high microplastic concentrations compared to the trap and grab samples; average microplastic abundance for gravity core, trap and grab samples were 2130 kg^{-1} , 1070 kg^{-1} and 730 kg^{-1} , respectively.

Microplastics abundance in tributary sediments appears to display variability on small spatial scales (Fig. 2, Table 1). For example, in Humber River and Etobicoke Creek, downstream sites contained microplastic counts one to two orders of magnitude greater than sites within 1 km upstream. Abundances of microplastics in beach samples appear to decrease with greater distance from Toronto (Fig. 4c). Microplastic contamination loads in Lake Ontario are comparable to those reported in similar studies from around the world, as summarized in Table 2.

3.2. Microplastic morphology

Microplastics in nearshore depositional zones were almost exclusively $<2 \text{ mm}$ in size. Microplastics $>2 \text{ mm}$ were found only in one nearshore sediment sample in Toronto Harbour (sample S-3030). Plastic particles $>2 \text{ mm}$ were slightly more common in tributary sediments with 84 particles at site P-EC2 and 1 particle at site P-RC2; overall, 4% of the microplastics found in tributary samples were $>2 \text{ mm}$ in size. Approximately 8% of plastics in beach samples were $>2 \text{ mm}$, the majority of which were found at Marie Curtis and Sunnyside (Fig. 5a) beach sites and at the mouth of Etobicoke Creek (sample P-EC2).

Fragments and fibres were the dominant morphologies for microplastics $<2 \text{ mm}$ across all depositional zones, with beads being a minor component (Fig. 3b). Fragments (including films) and beads (industrial pellets) were the most common microplastics $>2 \text{ mm}$. Fibres

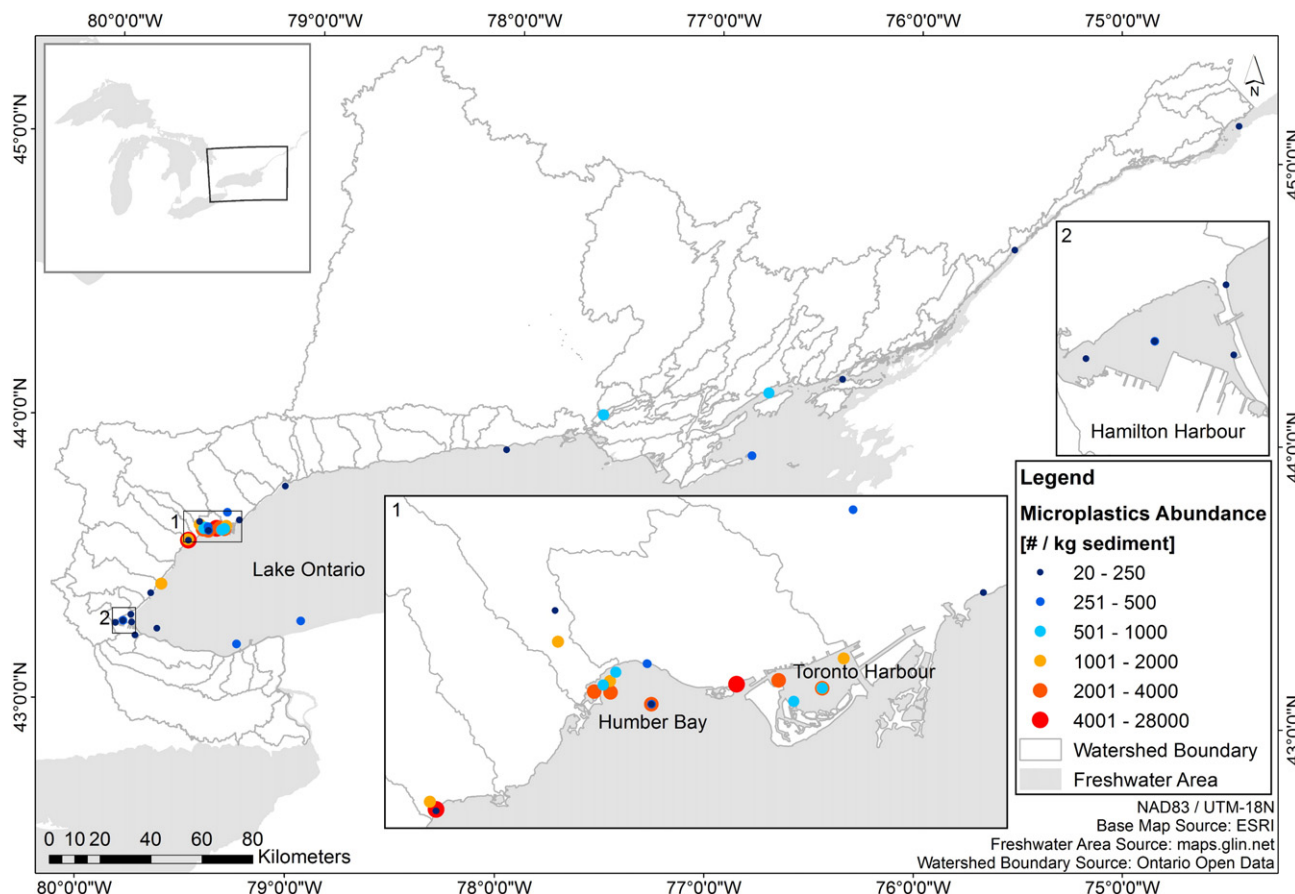


Fig. 2. Microplastics abundance normalized to particles $N\text{ kg}^{-1}$ sediment (dry weight, dw), for 50 study sites in Lake Ontario. The inset shows the Greater Toronto Area in detail.

were most abundant in nearshore samples and least abundant in tributary samples. Beads were found in all depositional environments, but were not found in the sediment traps.

In general, microplastics were of variable colour, texture, grade of degradation, size and shape. Fibres were highly regular in diameter along their entire length and varied in colour and length from tens of microns to several millimeters (Fig. 5b). Irregularly shaped, bulbous to wispy fragments with smooth surfaces and translucent diaphaneity were common (e.g. Fig. 5c, f). Beads were mainly spherical, translucent, amber or black, and sometimes cracked or fragmented (Fig. 5c, far right column). Oblong, helical forms composed of rigid, opaque material were common in the tributary and nearshore sediments, particularly in Etobicoke Creek (Fig. 5d). These particles had smooth clean surfaces and did not appear fragmented. In a conservative classification, we estimate that at least 4% of all microplastics were of this form. At Etobicoke Creek, however, these particles made up ~30% of all fragments <2 mm. Non-rigid, black, opaque particles appearing as amorphous chunks or long thin helical twists accounted for 7% of microplastics collected in the study (Fig. 5e).

3.3. Polymer composition

Of 90 suspected microplastics analyzed using Raman spectroscopy, 60 (67%) were positively identified as synthetic polymers. An additional five particles could not be identified but were found to contain phthalates, which are plasticizers, and toluidine red, a pigment commonly used for plastic products. Three samples were identified as non-plastic. These particles, mistaken for microbeads, were identified as quartz and calcium carbonate and were likely well-rounded sand grains. Thirty-one percent of the analyzed particles were identified as PE, 10% as PS and 4% as polyurethane (PU) (Fig. 6). Polypropylene

(PP), PVC, and polystyrene sulfonate (PSS) each made up 3% of the analyzed particles. Other polymers including PET, polymethyl methacrylate (PMMA), polyvinyl/vinyl acetate copolymer, PMMA-PS copolymer or mixture, acrylonitrile butadiene styrene (ABS), nylon, phenoxy/epoxy resin, and polymethylsiloxane (silicone) were identified (Fig. 6). Twenty-two samples remain unidentified. Microplastic counts were not adjusted to reflect the plastic to non-plastic ratio of the Raman analysis results due to the low percentage (1.4%) of particles analyzed.

Several patterns relating plastic morphology and composition were recognised. Fragments identified as PE were consistently characterized by translucent diaphaneity and irregular wispy and bulbous forms, also noted by Corcoran et al. (2015). The black opaque rubbery particles could not be identified using Raman spectroscopy due to their tendency to combust even at very low laser power. This problem was also noted by Lenz et al. (2015); however, their analyses of similarly described particles suggested that they originate from black tire rubber. Yellow, translucent, rigid fragments were commonly identified as PU. Several of the smooth, spherical, transparent, amber-red beads (Fig. 5c, bottom right) were identified as polystyrene sulfonate (PSS).

3.4. Watershed analysis

A total of 66 watersheds were analyzed for their population and abundance of plastics-related industries. The Don River watershed had the greatest population, whereas the Toronto Urban Catchment watershed had the highest population density with ~7380 people km^{-2} (Fig. 7). Both of these watersheds empty into the Toronto Harbour. There are approximately 20 major wastewater treatment plants along the Canadian shore of Lake Ontario and the upper St. Lawrence River (Fig. 7), which could contribute plastic debris to the lake. With regards to industry intensity, Etobicoke Creek contains the largest number of

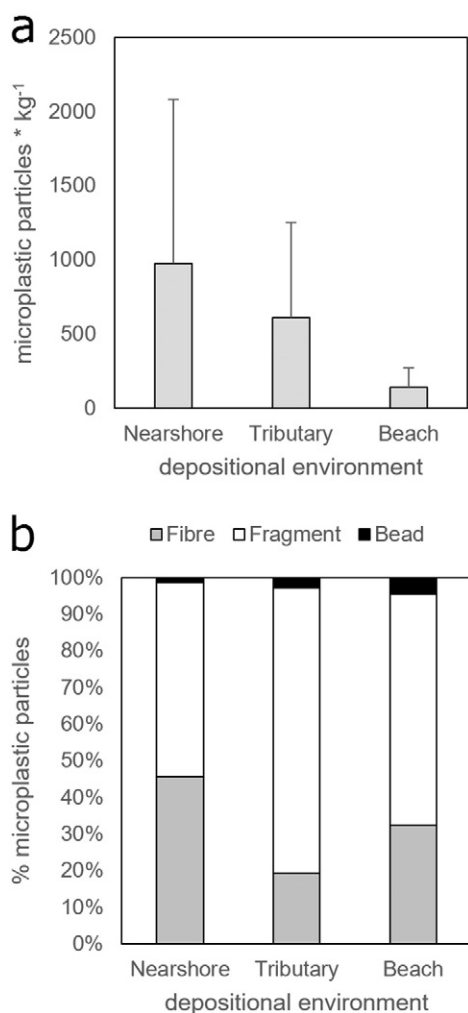


Fig. 3. (a) Microplastics (<2 mm) abundance, $N\text{ kg}^{-1}$ sediment (dw), for beach, tributary and nearshore sediments of Lake Ontario averaged (error bars indicate standard deviation) across depositional environment. (b) The relative abundance of fibres, fragments and beads averaged across beach, tributary and nearshore samples. Samples collected from the St. Lawrence River are considered as nearshore samples.

plastic product manufacturers, distributors and service businesses combined, at 62 business facilities. There is a clear clustering of the plastic industry in the Greater Toronto Area extending towards the Hamilton Region (Fig. 8). Several watersheds did not include any plastic industry facilities, as identified through the ThomasNet directory.

4. Discussion

4.1. Lateral trends in deposition

The intense microplastics contamination in samples from the Greater Toronto Region may be attributed to the high population density and industrial activity in the watersheds draining into this region. The Etobicoke Creek, Mimico Creek, Humber River, Toronto Urban Catchment, and Don River watersheds have a combined population of 3.4 million, which accounts for 40% of the total population of all watersheds draining into Lake Ontario, in Canada. Likewise, half of the plastics production facilities in the study region are located in the same five watersheds. Higher resolution sediment sampling along the northwest shore of Lake Ontario may reveal a clearer trend between microplastics abundance and watershed population- and industry-density. For the same reason, accounting for sewage and storm outlets as point sources of microplastics by sampling consistently near these outlets is suggested for future studies.

The high concentrations of microplastics in Toronto Harbour and Humber Bay may also be influenced by the morphology of the shoreline at those locations. It has been shown that deposition of microplastics in bottom sediments occurs in low energy environments, such as harbours and lagoons, where fine particles supplied by fluvial and anthropogenic outputs can settle (Claessens et al., 2011; Vianello et al., 2013). Average circulation patterns in Lake Ontario as modeled by Beletsky et al. (1999) show that in both summer and winter, currents in the vicinity of Toronto Harbour move along the shore from southwest to northeast. We expect that the peninsula located just west of Humber Bay protects the southeast shore of Humber Bay and the Inner Toronto Harbour from severe waves during the dominant anticyclonic surface water circulation during the summer and winter in the northwestern basin of Lake Ontario (Beletsky et al., 1999). Similarly, the Toronto Islands may reduce water flow velocity in the Inner Toronto Harbour and Humber Bay during easterly long-fetch storm events. The relative abundance of microplastics in this region may result from the lower frequency of re-suspension and transport events associated with weaker hydrodynamic forcing. Although the “harbouring effect” may allow greater accumulation of microplastics contamination, it is only one of many variables affecting the spatial variability of plastic debris. For example, Hamilton Harbour has relatively low microplastic contamination levels in comparison to what would be expected given the coastal morphology of the harbour. This indicates that microplastics in sediments are foremost dependent on source loads.

The dense concentration of microplastics at the mouth of Etobicoke Creek compared to upstream sediments is consistent with reduced boundary shear stress, the driving force of particle motion in a transport fluid, as tributaries widen and flatten into the lake. In a marine model study, strong unidirectional flows associated with internal waves and storm events were needed to transport non-buoyant plastic particles down-slope in a submerged environment (Ballent et al., 2013). As theoretically applied to Lake Ontario, microplastics should be transported by rapid flow in tributaries and during storm events and deposited as turbulence and bottom currents subside, for example, at the mouths and banks of tributaries. Our results show, however, that microplastics are also found in tributary sediments where higher flow regimes dominate, and in nearshore, open environments where sediments are exposed to erosion and large-scale transport. Further research is needed to understand the similarities and differences between the transport mechanics of microplastics and other sedimentary particles such as clastic grains, clays and organic aggregates in aquatic environments.

Microplastic contamination levels may also be influenced by the presence of obstructing structures, variations in topography, and areal extent of the watershed. Reduced flow rates due to obstructing structures or flatter topography may be associated with increased microplastic deposition upstream, thereby reducing microplastics abundance at the river mouth. Several of the watersheds in the study are amalgamated river systems, many of which have control structures such as dams, weirs, reservoirs and lakes. The input locations of microplastics should be considered in geographic relation to the topographic and anthropogenic features of the tributary. Several questions to be addressed by future investigations of microplastics transport through tributaries are: What distances are microplastics being transported before being deposited? What are the minimum flow velocities and shear stresses found in tributaries and how much do these values vary over the length of a tributary? Where in the tributaries are shear stresses sufficient to transport microplastic? What percentage of the plastics found in the sediments were originally positively buoyant?

Spatial variability on scales of tens to several hundreds of meters was exhibited in the Toronto Harbour and Humber Bay region where sample sites were close and where multiple samples were collected from the same site. Tributary site P-EC2, for example, had two orders of magnitude more microplastic particles than the beach sediments within 100 m away at Marie Curtis Park, and one order of magnitude more microplastics than sediments only 350 m upstream. Similarly, the four

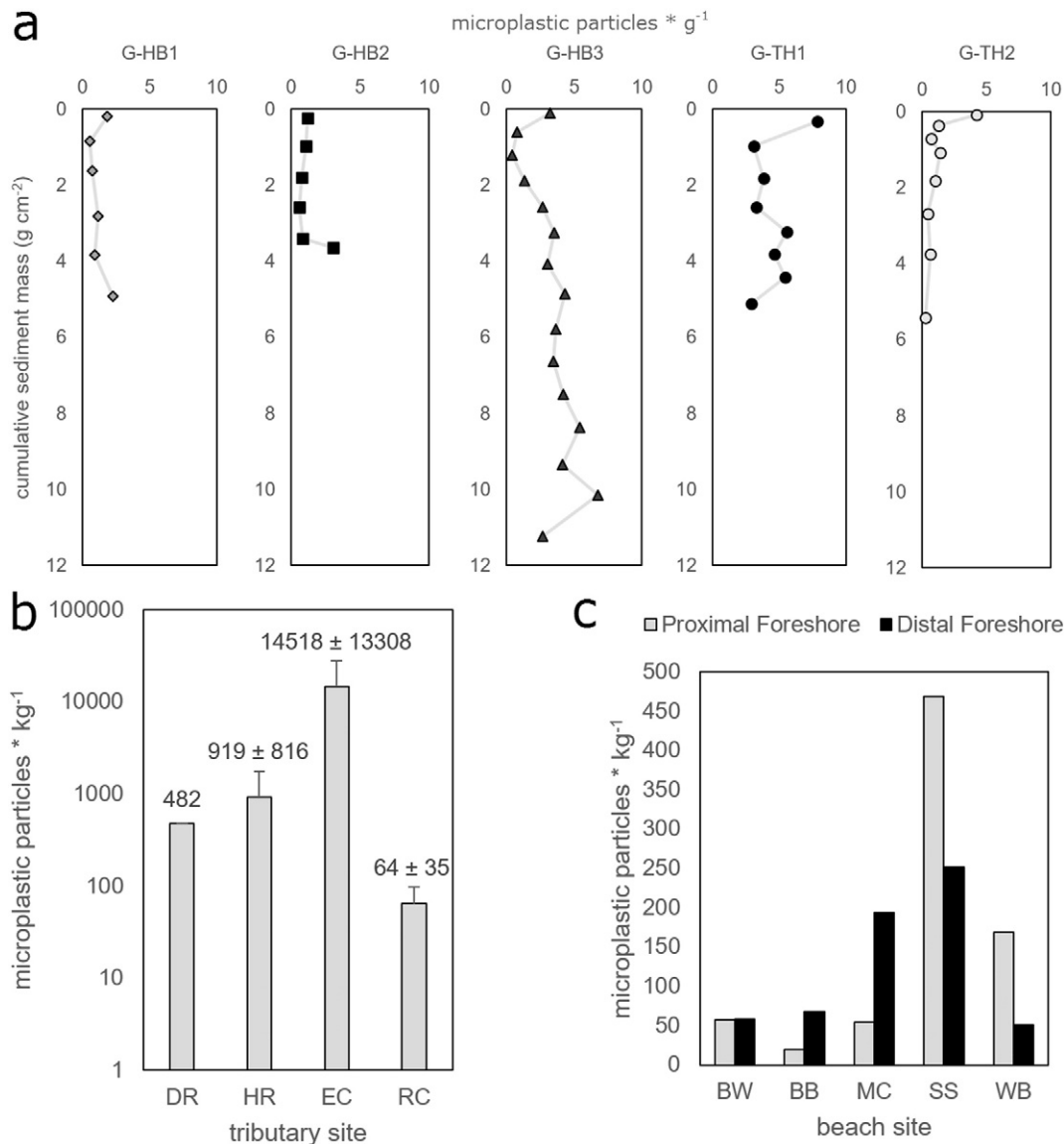


Fig. 4. (a) Microplastics (<2 mm) abundance, $N g^{-1}$ sediment (dw), plotted against cumulative sediment mass ($g cm^{-2}$), dw, for nearshore sediments of Humber Bay and Toronto Harbour as sampled by gravity core. Cumulative sediment mass (CSM) is a function of the core radius (r), sediment mass of the core interval (m), and depth of interval in cm (d): $CSM = \sum_{i=1}^d \frac{m_i}{\pi r^2}$. (b) Microplastics (<2 mm) abundance, $N kg^{-1}$ sediment (dw), averaged (error bars indicate standard deviation) for tributaries draining into Lake Ontario including Don River (DR), Humber River (HR), Etobicoke Creek (EC) and Red Hill Creek (RC). In each tributary (except DR), two proximal sites were sampled. (c) Microplastics (<2 mm) abundance, $N kg^{-1}$ sediment (dw), at Beachway (BW), Bronte (BB), Marie Curtis Park (MC), Sunnyside (SS) and Woodbine (WB) beaches. One proximal and one distal foreshore sample from each beach was collected along a transect perpendicular to the waterline. Proximal and distal sites are denoted with a '1' and '2', respectively, in the sample name as listed in Table 1.

separate grab and trap samples taken from the Humber Bay Index station (S-7546 and S-HB14, S-3025, T-2047) along the Toronto waterfront had microplastic counts between 40 and 2210 kg^{-1} highlighting the temporal variability and meter-scale spatial variability of samples collected from the same station. The observed variability is possibly reflective of the turbulent and random nature of fluid flows and surface characteristics such as substrate type, topography, roughness and presence of vegetation (e.g. Vianello et al., 2013; Corcoran et al., 2015).

4.2. Vertical trends in deposition

The nearshore gravity core samples provide insight into the vertical variability of microplastics in lake bottom sediments where plastic concentrations are possibly the highest in Lake Ontario (Fig. 4a). Microplastic abundance was extrapolated according to sediment weight, and therefore the relative abundance of microplastics in the

top 2 cm can be attributed to the greater content of water and natural organic material in the upper unconsolidated layer.

Sediment accumulation rates of $\sim 1.7 mm yr^{-1}$ are estimated for the nearshore environment of the western basin of Lake Ontario based on pollen dating of *Ambrosia* (first occurrence 120 years B.P.) as calculated by Rukavina (1976). The deepest gravity core, which penetrated to a depth of 15 cm, may therefore represent the last ~ 90 years. However, the increase in water content in the unconsolidated sediment of the upper layer points to a much shorter time period. Furthermore, frequent resuspension of surface sediments in nearshore (depth < 40 m) lake environments by storm events (Klump et al., 2000) can resuspend material on scales equal to those deposited annually in lake basins within a period of days, as shown for Lake Michigan (Eadie et al., 1996; Schwab et al., 2000). Material resuspended by these events may be confined to the nearshore in the presence of a coastal plume (Mortimer, 1988; Hall, 2008). Further research is needed to constrain the timescales of

Table 2

A summary of average microplastics contamination in various marine and freshwater sediments, worldwide, is given. Microplastics contamination is reported as average particle abundance per kg dry sediment, $N \text{ kg}^{-1}$ (dw).

Study	Study area	Depositional environment	Avg. $N \text{ kg}^{-1}$ (dw)
Turra et al. (2014)	Sao Paulo, Brazil	Marine Beach	0.1 ^a
Dekiff et al. (2014)	Germany	Marine Beach	2 ^b
Van Cauwenberghe et al. (2015)	Belgium	Marine Beach	6
Browne et al. (2010)	UK	Marine Beach	~60 ^{a,b}
Claessens et al. (2011)	Belgium	Marine Beach	95 ^b
This study	Ontario, Canada	Lacustrine Beach	140
Costa et al. (2010)	Brazil	Marine Beach	310 ^{a,b}
Mathalon and Hill (2014)	Halifax, Canada	Marine Beach	5000
Claessens et al. (2011)	Belgium	Marine Harbour	165 ^b
Naidoo et al. (2015)	Durban, S. Africa	Marine Harbour	1165 ^{a,c}
Vianello et al. (2013)	Venice, Italy	Marine Lagoon	1500 ^b
Frias et al. (2016)	Portugal	Marine Nearshore	55
Claessens et al. (2011)	Belgium	Marine Nearshore	90 ^b
This study	Ontario, Canada	Lacustrine Nearshore	980
Corcoran et al. (2015)	Ontario, Canada	Lacustrine Offshore	352
This study	Ontario, Canada	Tributary	760 ^d

^a Using an average sediment density of 1600 kg m^{-3} (Fettweis et al., 2007).

^b Modified from Van Cauwenberghe et al. (2015) Table 1.

^c Using a 1.25 average wet/dry ratio (Van Cauwenberghe et al., 2015).

^d Not including site P-EC2.

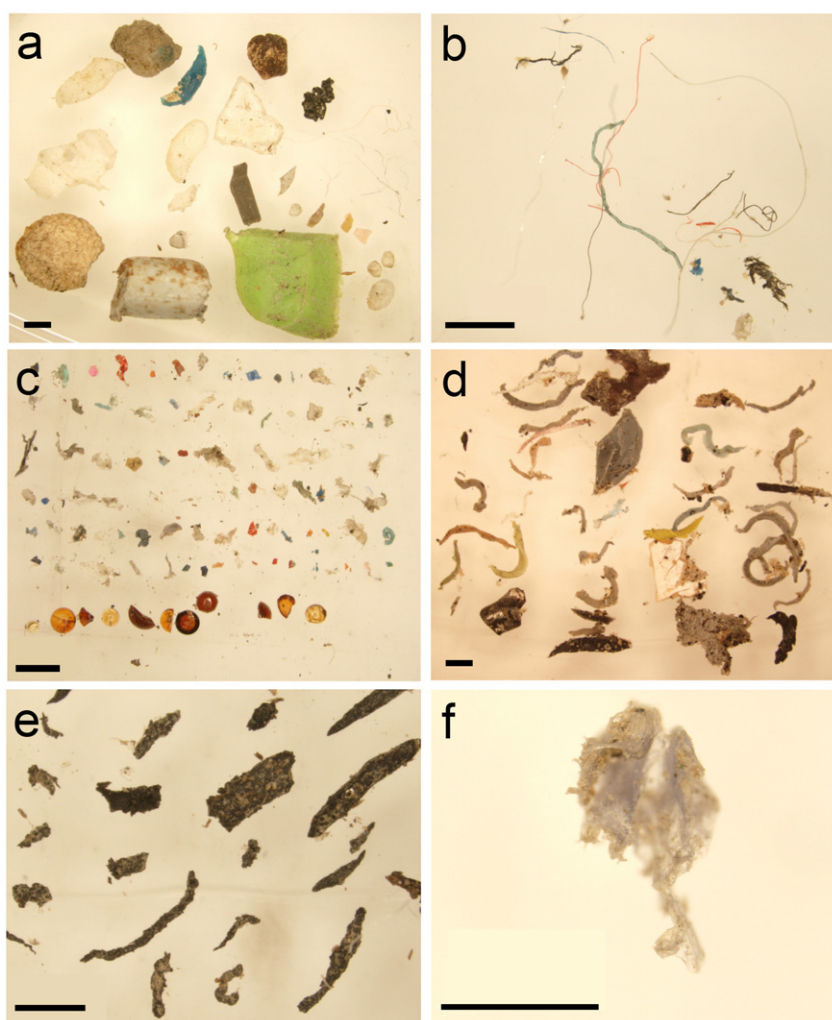


Fig. 5. Examples of microplastics identified in sediment samples from tributaries, beaches and the nearshore lake bottom of Lake Ontario. All scale bars are 1 mm. (a) Macro- and microplastic fragments, fibres, foams and pellet isolated from the upper 10 cm of proximal foreshore sediments at Sunnyside Beach. (b) Microplastic fragments and fibres isolated from nearshore sediment in Toronto Harbour as collected in a sediment trap (sample T-1364). (c) Microplastics found in grab sediments (sample S-3027) in Humber Bay, including hexagonal glitter ($N = 1$, top row) and whole and fragmented PSS beads ($N = 11$, bottom row), among other fragments of unidentified source. (d) Microplastics from Etobicoke Creek. Long helical fragments may be derived from deflashing processes used for finishing injection moulded plastic products. (e) Examples of black, opaque fragments with rubber-like consistency found in Humber Bay. (f) Microplastic fragment exhibiting bulbous to wispy form and isolated from Toronto Harbour (sample G-TH1) at a depth of 1–2 cm below the sediment surface.

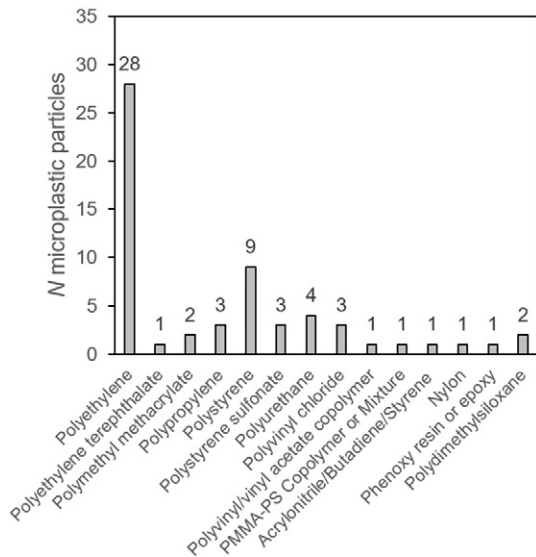


Fig. 6. Synthetic polymers and compounds which were identified in the FT-Raman spectroscopic analysis of particles isolated from Lake Ontario nearshore and tributary sediments. Of ninety particles analyzed, 60 were plastic in composition, 3 were non-plastics (e.g. quartz, calcium carbonate), 5 were plastic-associated compounds (e.g. phthalates, toluidine colourant), and 22 could not be identified.

microplastics transport and deposition in transient nearshore and more permanent offshore basins. Microplastics in offshore basin sediments of Lake Ontario were reported to extend to a maximum of 8 cm below the sediment surface (Corcoran et al., 2015), which is consistent with a lower sediment accumulation rate compared with that of the nearshore locations studied here.

4.3. Physical characteristics and transport behaviour

The density and shape of microplastic particles may also impact distribution patterns identified in Lake Ontario. Plastics range in density from ~ 0.8 to 1.4 g cm^{-3} , which is less than the average density of mineral sediments ($1.6\text{--}2.7 \text{ g cm}^{-3}$, (Fettweis et al., 2007; Hidalgo-Ruz et al., 2012)). Theoretically, PE and PP particles should float because their densities are lower than that of freshwater, however, PE was the most common type of plastic among the Raman analyzed samples. Plausible mechanisms for the deposition of low-density polymers in submerged sedimentary environments include net density increase of microplastic particles by biofouling (e.g. Ye and Andradý, 1991; Andradý, 2011; Zettler et al., 2013; McCormick et al., 2014), adsorption of natural substances to the surface (Frias et al., 2016), inclusion of inorganic fillers during manufacturing (Corcoran et al., 2015) and faecal express (Cole et al., 2013; Setälä et al., 2014; Zalasiewicz et al., 2015). Inorganic fillers were not identified in any of the Raman spectra of the particles identified as PE and PP in this study, however, many microplastics in our study, particularly those with irregularly shaped, textured or degraded surfaces, appeared to have clay-like particles adhered to their surfaces. Microplastic particles made of PE and PP and with greater surface area to volume ratios, such as fibres and irregularly shaped fragments, are expected to have lower settling velocities and lower shear stress values needed to initiate particle motion than microplastic particles of high-density polymer types and mineral sediments. They may therefore be transported at lower flow and turbulence levels and be more readily transported offshore, consistent with the findings of Corcoran et al. (2015). Denser microplastics may behave more similarly to mineral sediments and be more constrained to nearshore areas.

Comparisons of microplastic types recovered from samples of different sedimentary environments is challenging because of the variations in sampling methods. Simply comparing abundances, as normalized to sediment mass, the high proportion of fibres to fragments in the nearshore sediments compared to the tributary sediments may suggest

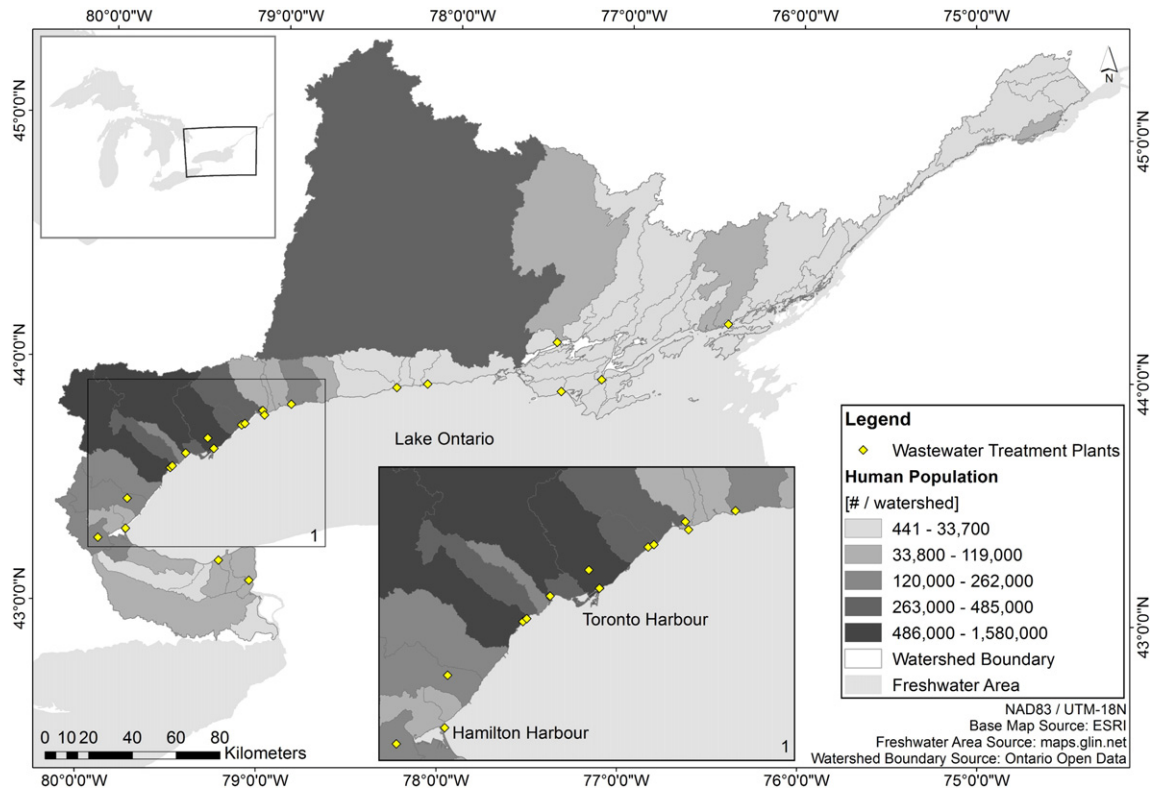


Fig. 7. Human population map for watersheds draining into Lake Ontario and the St. Lawrence River. Locations of wastewater treatment plants proximal to the shoreline are included.

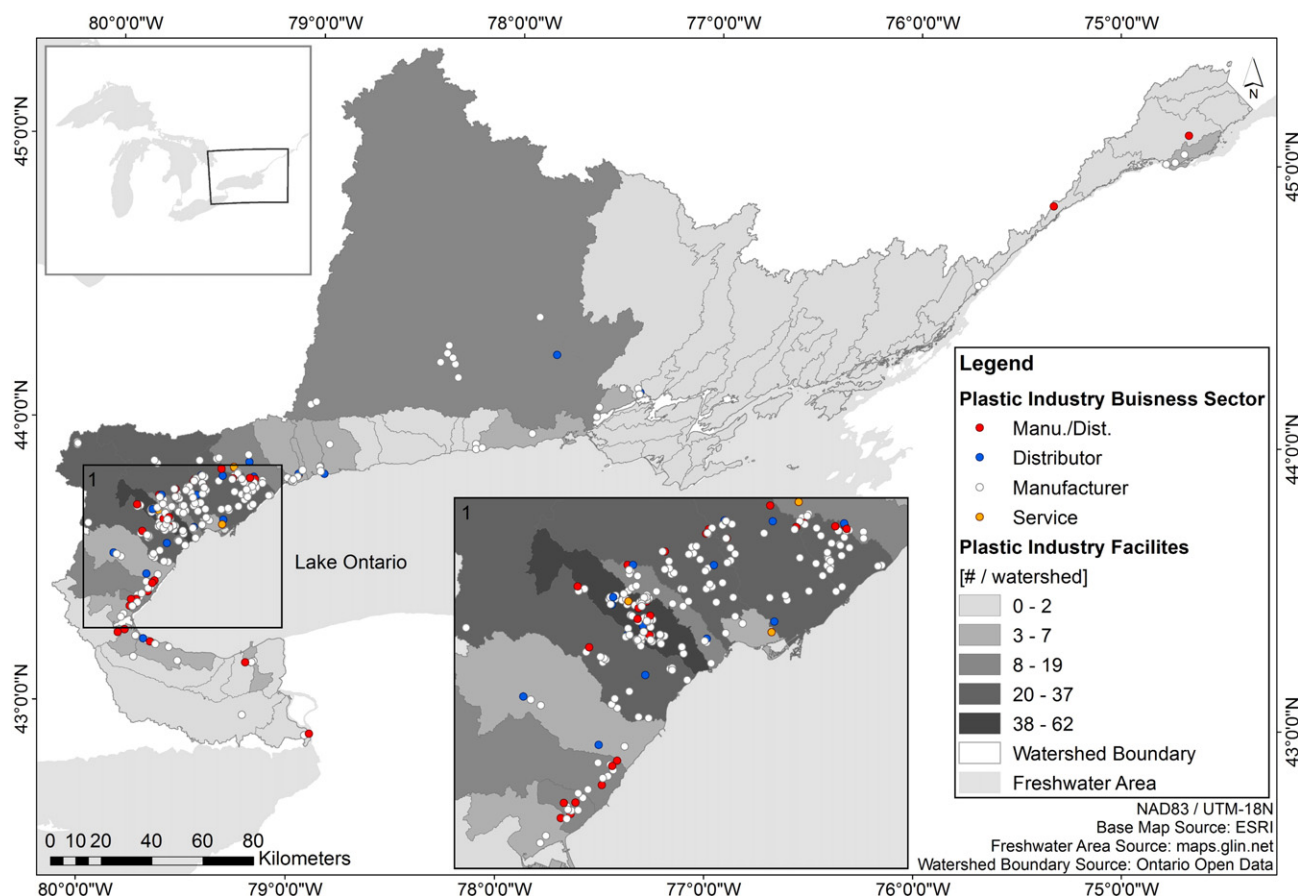


Fig. 8. Locations of plastics-related manufacturing, distributing and service facilities within the watersheds draining into Lake Ontario and the St. Lawrence River.

that fibres are transported through suspension for greater distances than fragments, which may have higher settling velocities or are transported as bedload. Sediment traps, which collect particles falling out of suspension from the overlying water column, contained almost exclusively fibres. The overall low proportion of microbeads in all environments contrasts with the surface water results of Eriksen et al. (2013), suggesting that microbeads remain suspended in the water column as a result of their low density. Notwithstanding, the low sampling resolution combined with the use of multiple sampling techniques make these observations speculative. More thorough analysis of microplastic morphology and composition may reveal trends regarding which types of plastics are most easily transported to depth in an aquatic environment.

4.4. Potential sources

Our results indicate that microplastics in coastal sediments of Lake Ontario likely originate in proximal watersheds and are likely transported to the site of deposition through tributaries. Future studies of microplastics in sediments directly adjacent to storm water, wastewater treatment plant, and combined sewer outfalls may reveal a clearer trend regarding how much plastic is contributed by these sources, and how microplastics abundance in the sediment varies with distance from outfalls. Assigning particular origins to the microplastics is challenging due to their small size, fragmented nature, and the unknown range of possible sources. A speculative discussion of the potential sources of microplastics contamination in Lake Ontario follows.

Polyurethanes are commonly used in the production of foams for furniture, as well as in adhesives such as construction glue products, surface coatings and sealing applications. The black, opaque fragments with rubber-like consistency (Fig. 5e) may originate from vehicle tires

as suggested by Lenz et al. (2015). The natural wear down process of tires during driving may contribute small particles such as those seen in our study. These particles could easily be washed from roads to storm drains during rain events. Similarly, the shredding of used tires for recycling purposes referred to as crumb rubber, as defined by Regulation 347: General Waste Management under the Environmental Protection Act, Revised Statute of Ontario, 1990, may also contribute <2 mm particles. Fibrous microplastics are thought to originate from the production, washing and the natural aging of textiles, such as synthetic clothing and carpets (e.g. Browne et al., 2011).

The amber-colored beads (Fig. 5c, bottom row) identified to contain PSS may be polystyrene resin beads that are commonly used as an ion exchange medium for water purification and softening, as well as in various medical and industrial applications (Dardel, 2016). The beads represent a source of microplastics not yet discussed in the literature. Microbeads have recently become an environmental focus in the scientific and political realms with the result of new legislation. The Microbead-Free Waters Act, adopted in the United States in 2015, bans the manufacture of microbead-containing cosmetic products by July 2017. In Canada, microbeads manufactured for use in cosmetic products may be added to the List of Toxic Substances in Schedule 1 of the Environmental Protection Act of 1999. This ban would not, however, address the majority of the beads identified in the sediments, assuming they are indeed used for non-cosmetic purposes. It is possible, however, that many of the irregularly shaped particles in our samples which were categorized as fragments, originate from cosmetic products. Leslie (2014) reports that microplastics used in cosmetics, such as facewashes and toothpastes, range in shape from spherical to amorphous, suggesting that 'microbeads' are not limited to bead morphologies.

The oblong, helical fragments (Fig. 5d) could originate from finishing processes during the manufacture of injection-moulded plastics. A

common finishing process, termed deflashing, involves the removal of extraneous material, flash, from the seams and edges of solidified products where resin may have leaked into voids between the mould halves (SME, 2016). The shaving-like particles identified in our samples could potentially be the waste flash particles resulting from this process. A study by Lechner and Ramler (2015) identified an industrial point source of microplastics along the Danube River in Austria. According to their investigation, the allowable plastic loads in wastewater of the manufacturing plant was 30 mg L^{-1} , which translates to the equivalent of almost 95 tons of plastic waste per year, as calculated for flow rates of 100 L s^{-1} . Considering that plastics are not a regulated constituent of waste water in Ontario under the Ontario Environmental Protection Act, R.S.O. 1990, it is possible that substantial loads of microplastics are being released by manufacturing and moulding facilities and draining directly into Lake Ontario.

5. Conclusions and outlook

The spread and quantity of microplastics found in nearshore, tributary and beach sediments of Lake Ontario suggest that this contaminant may be entering the food web through ingestion by benthic fauna and higher-trophic organisms such as birds and fish. The wide range of polymers and particle morphologies represented in Lake Ontario sediments reflects various sources, potentially traced to industrial, transportation, construction and consumer activities. Reducing the influx of microplastics contamination will similarly require a range of measures addressing the various sources, for example, continued improvement and monitoring of waste management programs in cities and in industrial settings, such as Operation Clean Sweep, as well as an accelerated transition to a circular plastics economy (Neufeld et al., 2016). We suggest future monitoring of microplastics in the sediments of Lake Ontario and feeding tributaries, particularly in the GTA region, as well as a more detailed investigation of the input locations of microplastic along the tributaries and lake shoreline to further improve strategies targeting contamination reduction.

Acknowledgments

This work was funded under the Great Lakes Strategy / Canada-Ontario Agreement with Respect to the Great Lakes program (Project ID # 2206). We would like to thank Danielle Cocchetto and Tim Howe for assisting with field work, as well as our editor, Charles Sheppard, at the Marine Pollution Bulletin and reviewers for their constructive feedback and assistance in improving this manuscript.

References

Allan, J.D., McIntyre, P.B., Smith, S.D.P., Halpern, B.S., Boyer, G.L., Buchsbaum, A., Burton Jr., G.A., Campbell, L.M., Chadderton, W.L., Ciborowski, J.J.H., Doran, P.J., Eder, T., Infante, D.M., Johnson, L.B., Joseph, C.A., Marino, A.L., Prusevich, A., Read, J.G., Rose, J.B., Rutherford, E.S., Sowa, S.P., Steinman, A.D., 2013. Joint analysis of stressors and ecosystem services to enhance restoration effectiveness. *Proc. Natl. Acad. Sci. U. S. A.* 110 (1), 372–377. <http://dx.doi.org/10.1073/pnas.1213841110>.

Andrady, A.L., 2011. Microplastics in the marine environment. *Mar. Pollut. Bull.* 62 (8), 1596–1605. <http://dx.doi.org/10.1016/j.marpolbul.2011.05.030>.

Armitage, N., Rooseboom, A., 2000. The removal of urban litter from stormwater conduits and streams: Paper 1 - The quantities involved and catchment litter management options. *Water SA* 26 (2), 181–187.

Ballent, A., Pando, S., Purser, A., Juliano, M.F., Thomsen, L., 2013. Modeled transport of benthic marine microplastic pollution in the Nazare Canyon. *Biogeosciences* 10 (1), 1–14. <http://dx.doi.org/10.5194/bg-10-1-2013>.

Barnes, D.K.A., Galgani, F., Thompson, R.C., Barlaz, M., 2009. Accumulation and fragmentation of plastic debris in global environments. *Philos. Trans. R. Soc. London, Ser. B Biol. Sci.* 364, 1985–1998.

Beletsky, D., Saylor, J.H., Schwab, D.J., 1999. Mean circulation in the Great Lakes. *J. Great Lakes Res.* 25, 78–93.

Browne, M., Galloway, T.S., Thompson, R.C., 2010. Spatial patterns of plastic debris along estuarine shorelines. *Environ. Sci. Technol.* 44 (9), 3404–3409. <http://dx.doi.org/10.1021/es903784e>.

Browne, M.A., Crump, P., Niven, S.J., Teuten, E., Tonkin, A., Galloway, T., Thompson, R., 2011. Accumulation of microplastic on shorelines worldwide: sources and sinks. *Environ. Sci. Technol.* 45 (21), 9175–9179.

Carpenter, E.J., Smith Jr., K.L., 1972. Plastics on the Sargasso Sea surface. *Science* 175, 1240–1241.

Chemical Industry Association of Canada (CIAC), 2014. 2014 Statistical Review (http://canadianchemistry.ca/library/uploads/Statistical-Review-2014_ENG.pdf) pp. 34–35.

City of Toronto. (2006). Taylor Creek Outfalls and Closed Landfill Sites. Map scale: 1 : 38000. Retrieved from www1.toronto.ca on May 29, 2016.

Claessens, M., De Meester, S., Landuyt, L.V., De Clerck, K., Janssen, C.R., 2011. Occurrence and distribution of microplastics in marine sediments along the Belgian coast. *Mar. Pollut. Bull.* 62 (10), 2199–2204. <http://dx.doi.org/10.1016/j.marpolbul.2011.06.030>.

Cole, M., Lindeque, P., Fileman, E., Halsband, C., Goodhead, R., Moger, J., Galloway, T.S., 2013. Microplastic ingestion by zooplankton. *Environ. Sci. Technol.* 47 (12), 6646–6655. <http://dx.doi.org/10.1021/es400663f>.

Colton, J.B., Burns, B.R., Knapp, F.D., 1974. Plastic particles in surface waters of the northwestern Atlantic. *Science* 185 (4150), 491–497. <http://dx.doi.org/10.1126/science.185.4150.491>.

Corcoran, P.L., Norris, T., Ceccanese, T., Walzak, M.J., Helm, P.A., Marvin, C.H., 2015. Hidden plastics of Lake Ontario, Canada and their potential preservation in the sediment record. *Environ. Pollut.* 204, 17–25.

Costa, M.F., Ivar do Sul, J., Silva-Cavalcanti, J.S., Araújo, M.C.B., Spengler, A., Tourinho, P.S., 2010. On the importance of size of plastic fragments and pellets on the strandline: a snapshot of a Brazilian beach. *Environ. Monit. Assess.* 168, 299–304. <http://dx.doi.org/10.1007/s10661-009-1113-4>.

Cózar, A., Echevarría, F., González-Gordillo, J.I., Irigoien, X., Ubeda, B., Hernández-León, S., Palma, A.T., Navarro, S., García-de-Lomas, J., Ruiz, A., Fernández-de-Puelles, M.L., Duarte, C.M., 2014. Plastic debris in the open ocean. *Proc. Natl. Acad. Sci. U. S. A.* 111, 10239–10244. <http://dx.doi.org/10.1073/pnas.1314705111>.

Dardel, F., 2016. Ion exchange. Retrieved from <http://dardel.info/IX/index.html> (on February 1, 2016).

Dekiff, J.H., Remy, D., Klasmeyer, J., Fries, E., 2014. Occurrence and spatial distribution of microplastics in sediments from Norderney. *Environ. Pollut.* 186, 248–256. <http://dx.doi.org/10.1016/j.envpol.2013.11.019>.

Driedger, A.G.J., Dürr, H.H., Mitchell, K., Cappellen, P.V., 2015. Plastic debris in the Laurentian Great Lakes : a review. *J. Great Lakes Res.* 41 (1), 9–19. <http://dx.doi.org/10.1016/j.jglr.2014.12.020>.

Eadie, B.J., Schwab, D.J., Leshkevich, G.L., Johengen, T.H., Assel, R.A., Holland, R.E., Hawley, N., Lansing, M.B., Lavrentyev, P., Miller, G.S., Morehead, N.R., Robbins, J.A., Van Hoof, P.L., 1996. Anatomy of a recurrent episodic event: a winter-spring plume in southern Lake Michigan. *EOS Trans. Am. Geophys. Union* 77, 337–338.

Erkes-Medrano, D., Thompson, R.C., Aldridge, D.C., 2015. Microplastics in freshwater systems: a review of the emerging threats, identification of knowledge gaps and prioritisation of research needs. *Water Res.* 75, 63–82.

Eriksen, M., Mason, S., Wilson, S., Box, C., Zelliers, A., Edwards, W., Farley, H., Amato, S., 2013. Microplastic pollution in the surface waters of the Laurentian Great Lakes. *Mar. Pollut. Bull.* 77 (1–2), 177–182.

Fendall, L.S., Sewell, M.A., 2009. Contributing to marine pollution by washing your face: microplastics in facial cleansers. *Mar. Pollut. Bull.* 58 (8), 1225–1228. <http://dx.doi.org/10.1016/j.marpolbul.2009.04.025>.

Fettweis, M., Du Four, I., Zeelmaekers, E., Baeteman, C., Francken, F., Houziaux, J.-S., Mathys, M., Nechad, B., Pison, V., Vandenberghe, N., Van den Eynde, D., Van Lancker, V., Wartel, S., 2007. Mud Origin. Characterisation and Human Activities (MOCHA) Final Scientific Report Belgian Science Policy Office (59 pp.).

Frias, J.P.G.L., Gago, J., Otero, V., Sobral, P., 2016. Microplastics in coastal sediments from Southern Portuguese shelf waters. *Mar. Environ. Res.* 114, 24–30. <http://dx.doi.org/10.1016/j.marenvres.2015.12.006>.

Gasperi, J., Dris, R., Bonin, T., Rocher, V., Tassin, B., 2014. Assessment of floating plastic debris in surface water along the Seine River. *Environ. Pollut.* 195, 163–166. <http://dx.doi.org/10.1016/j.envpol.2014.09.001>.

Hall, E., 2008. Hydrodynamic Modelling of Lake Ontario. Queen's University (146 pp. <http://hdl.handle.net/1974/1556>).

Harrison, J.P., Schratzberger, M., Sapp, M., Osborn, A., 2014. Rapid bacterial colonization of low-density polyethylene microplastics in coastal sediment microcosms. *BMC Microbiol.* 14 (232), 1–15. <http://dx.doi.org/10.1186/s12866-014-0232-4>.

Hidalgo-Ruz, V., Gutow, L., Thompson, R.C., Thiel, M., 2012. Microplastics in the marine environment: a review of the methods used for identification and quantification. *Environ. Sci. Technol.* 46 (6), 3060–3075.

Klump, J.V., Edgington, D.N., Waples, J.T., Szmania, D.C., Brown, B.E., Orlandini, K.A., 2000. Sampling methods and approaches using radionuclide tracers in the study of sediment resuspension and cross margin transport in nearshore of the Laurentian Great Lakes. *Int. J. Sediment Res.* 18 (2), 1–12.

Lechner, A., Ramler, D., 2015. The discharge of certain amounts of industrial microplastic from a production plant into the River Danube is permitted by the Austrian legislation. *Environ. Pollut.* 200, 159–160.

Lechner, A., Keckeis, H., Lumesberger-Loisl, F., Zens, B., Krusch, R., Tritthart, M., Glas, M., Schludermann, E., 2014. The Danube so colourful: a potpourri of plastic litter outnumbers fish larvae in Europe's second largest river. *Environ. Pollut.* 188, 177–181. <http://dx.doi.org/10.1016/j.envpol.2014.02.006>.

Lenz, R., Enders, K., Stedmon, C.A., Mackenzie, D.M.A., Nielsen, T.G., 2015. A critical assessment of visual identification of marine microplastic using Raman spectroscopy for analysis improvement. *Mar. Pollut. Bull.* 100 (1), 82–91. <http://dx.doi.org/10.1016/j.marpolbul.2015.09.026>.

Leslie, H.A., 2014. Review of Microplastics in Cosmetics. Institute for Environmental Studies, VU University of Amsterdam (33 pp.).

Lithner, D., Damberg, J., Dave, G., Larsson, K., 2009. Leachates from plastic consumer products—screening for toxicity with *Daphnia magna*. *Chemosphere* 74 (9), 1195–1200. <http://dx.doi.org/10.1016/j.chemosphere.2008.11.022>.

- Lithner, D., Larsson, A., Dave, G., 2011. Environmental and health hazard ranking and assessment of plastic polymers based on chemical composition. *Sci. Total Environ.* 409 (18), 3309–3324. <http://dx.doi.org/10.1016/j.scitotenv.2011.04.038>.
- MacDonald, E., Podolsky, L., 2009. Flushing out the Truth: Sewage Dumping in the Great Lakes. Ecojustice, Toronto, Ontario, Canada (Retrieved from <<https://www.ecojustice.ca/wp-content/uploads/2014/11/Flushing-Out-the-Truth-2009.pdf>> on 1 June 2016).
- Mathalon, A., Hill, P., 2014. Microplastic fibres in the intertidal ecosystem surrounding Halifax Harbour, Nova Scotia. *Mar. Pollut. Bull.* 81 (1), 69–79. <http://dx.doi.org/10.1016/j.marpolbul.2014.02.018>.
- McCormick, A., Hoellein, T.J., Mason, S.A., Schlupe, J., Kelly, J.J., 2014. Microplastic is an abundant and distinct microbial habitat in an urban river. *Environ. Sci. Technol.* 48, 11863–11871.
- Moore, C.J., Lattin, G.L., Zellers, A.F., 2011. Quantity and type of plastic debris flowing from two urban rivers to coastal waters and beaches of Southern California. *J. Integr. Coast. Zone Manag.* 11 (1), 65–73.
- Morritt, D., Stefanoudis, P.V., Pearce, D., Crimmen, O., Clark, P.F., 2014. Plastic in the Thames: a river runs through it. *Mar. Pollut. Bull.* 78 (1–2), 196–200. <http://dx.doi.org/10.1016/j.marpolbul.2013.10.035>.
- Mortimer, C.H., 1988. Discoveries and testable hypotheses arising from coastal zone color scanner imagery of southern Lake Michigan. *Limnol. Oceanogr.* 33 (2), 203–226. <http://dx.doi.org/10.4319/lo.1988.33.2.0203>.
- Naidoo, T., Glassom, D., Smit, A.J., 2015. Plastic pollution in five urban estuaries of KwaZulu-Natal, South Africa. *Mar. Pollut. Bull.* 101 (1), 473–480. <http://dx.doi.org/10.1016/j.marpolbul.2015.09.044>.
- National Oceanographic and Atmospheric Administration (NOAA), 2015A. Marine Debris Program: Types and Sources. Retrieved from <http://marinedebris.noaa.gov/discover-issue/types-and-sources> (on 3 December 2015).
- Nauendorf, A., Krause, S., Bigalke, N.K., Gorb, E.V., Gorb, S.N., Haeckel, M., Wahl, M., Treude, T., 2016. Microbial colonization and degradation of polyethylene and biodegradable plastic bags in temperate fine-grained organic-rich marine sediments. *Mar. Pollut. Bull.* 103, 168–178. <http://dx.doi.org/10.1016/j.marpolbul.2015.12.024>.
- Neufeld, L., Stassen, F., Sheppard, R., Gilman, T. (Eds.), 2016. The New Plastics Economy—Rethinking the Future of Plastics 36 pp. Retrieved from <http://www.ellenmacarthurfoundation.org/publications>.
- Oehlmann, J., Schulte-Oehlmann, U., Kloas, W., Jagnytsch, O., Lutz, I., Kusk, K.O., Wollenberger, L., Santos, E.M., Paull, G.C., Van Look, K.J.W., Tyler, C.R., 2009. A critical analysis of the biological impacts of plasticizers on wildlife. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* 364 (1526), 2047–2062. <http://dx.doi.org/10.1098/rstb.2008.0242>.
- Rech, S., Macaya-Caquilpán, V., Pantoja, J.F., Rivadeneira, M.M., Jofre Madariaga, D., Thiel, M., 2014. Rivers as a source of marine litter—a study from the SE Pacific. *Mar. Pollut. Bull.* 82 (1–2), 66–75. <http://dx.doi.org/10.1016/j.marpolbul.2014.03.019>.
- Rochman, C.M., Lewison, R.L., Eriksen, M., Allen, H., Cook, A., Teh, S.J., 2014. Polybrominated diphenyl ethers (PBDEs) in fish tissue may be an indicator of plastic contamination in marine habitats. *Sci. Total Environ.* 477, 622–633.
- Rukavina, N., 1976. Nearshore sediments of Lakes Ontario and Erie. *Geosci. Can.* 3 (3), 185–190.
- Schwab, D.J., Beletsky, D., Lou, J., 2000. The 1998 coastal turbidity plume in Lake Michigan. *Estuar. Coast. Shelf Sci.* 50 (1), 49–58. <http://dx.doi.org/10.1006/ecss.1999.0531>.
- Setälä, O., Fleming-Lehtinen, V., Lehtiniemi, M., 2014. Ingestion and transfer of microplastics in the planktonic food web. *Environ. Pollut.* 185, 77–83. <http://dx.doi.org/10.1016/j.envpol.2013.10.013>.
- Society of Manufacturing Engineers (SME), 2016. Plastics finishing. Fundamental Manufacturing Processes Study Guide (Retrieved from <http://www.sme.org/ProductDetail.aspx?id=74589> on February 21, 2016).
- Song, Y.K., Hong, S.H., Jang, M., Han, G.M., Rani, M., Lee, J., Shim, W.J., 2015. A comparison of microscopic and spectroscopic identification methods for analysis of microplastics in environmental samples. *Mar. Pollut. Bull.* 93 (1–2), 202–209.
- Statistics Canada, 2012. Industry Canada: Industry Profile for the Canadian Plastic Products Industry. Accessed <https://www.ic.gc.ca/eic/site/plastics-plastiques.nsf/eng/p101383.html> (on November 9, 2015. Last modified: January 9, 2012).
- Sundt, P., Schulze, P.-E., Syversen, F., 2014. Sources of Microplastic-Pollution to the Marine Environment. Norwegian Environment Agency Retrieved from <http://www.miljodirektoratet.no/Documents/publikasjoner/M321/M321.pdf>.
- Syberg, K., Khan, F.R., Selck, H., Palmqvist, A., Banta, G.T., Daley, J., Sano, L., Duhaime, M.B., 2015. Microplastics: addressing ecological risk through lessons learned. *Environ. Toxicol. Chem.* 34 (5), 945–953. <http://dx.doi.org/10.1002/etc.2914>.
- Teuten, E.L., Saquing, J.M., Knappe, D.R.U., Barlaz, M., Jonsson, S., Björn, A., Rowland, S.J., Thompson, R.C., Galloway, T.S., Yamashita, R., Ochi, D., Watanuki, Y., Moore, C., Viet, P.H., Tana, T.S., Prudente, M., Boonyatumanond, R., Zakaria, M.P., Akkhang, K., Ogata, Y., Hirai, H., Iwasa, S., Mizukawa, K., Hagino, Y., Imamura, A., Saha, M., Takada, H., 2009. Transport and release of chemicals from plastics to the environment and to wildlife. *Philos. Trans. R. Soc. Lond. B Biol. Sci.* 364 (1526), 2027–2045. <http://dx.doi.org/10.1098/rstb.2008.0284>.
- Turra, A., Manzano, A.B., Dias, R.J.S., Mahiques, M.M., Barbosa, L., Balthazar-Silva, D., Moreira, F.T., 2014. Three-dimensional distribution of plastic pellets in sandy beaches: shifting paradigms. *Sci. Rep.* 4 (4435), 1–7. <http://dx.doi.org/10.1038/srep04435>.
- Vadeboncoeur, Y., McIntyre, P.B., Vander Zanden, M.J., 2011. Borders of biodiversity: life at the edge of the world's large lakes. *Bioscience* 61 (7), 526–537. <http://dx.doi.org/10.1525/bio.2011.61.7.7>.
- Van Cauwenbergh, L., Vanreusel, A., Mees, J., Janssen, C.R., 2013. Microplastic pollution in deep-sea sediments. *Environ. Pollut.* 182, 495–499. <http://dx.doi.org/10.1016/j.envpol.2013.08.013>.
- Van Cauwenbergh, L., Claessens, M., Vandegehuchte, M.B., Janssen, C.R., 2015. Microplastics are taken up by mussels (*Mytilus edulis*) and lugworms (*Arenicola marina*) living in natural habitats. *Environ. Pollut.* 19, 10–17. <http://dx.doi.org/10.1016/j.envpol.2015.01.008>.
- Vianello, A., Boldrin, A., Guerriero, P., Moschino, V., Rella, R., Sturaro, A., Da Ros, L., 2013. Microplastic particles in sediments of lagoon of Venice, Italy: first observations on occurrence, spatial patterns and identification. *Estuar. Coast. Shelf Sci.* 130, 54–61. <http://dx.doi.org/10.1016/j.ecss.2013.03.022>.
- Wright, S.L., Thompson, R.C., Galloway, T.S., 2013. The physical impacts of microplastic on marine organisms. *Environ. Pollut.* 178, 483–492.
- Ye, S., Andradý, A.L., 1991. Fouling of floating plastic debris under Biscayne Bay exposure conditions. *Mar. Pollut. Bull.* 22 (12), 608–613. [http://dx.doi.org/10.1016/0025-326X\(91\)90249-R](http://dx.doi.org/10.1016/0025-326X(91)90249-R).
- Zalasiewicz, J., Waters, C.N., Ivar do Sul, J., Corcoran, P.L., Barnosky, A.D., Cearreta, A., Edgeworth, M., Gałuszka, A., Jeandel, C., Leinfelder, R., McNeill, J.R., Steffen, W., Summerhayes, C., Wagemann, M., Williams, M., Wolfe Alexander, P., Yonah, Y., 2015. The geological cycle of plastics and their use as a stratigraphic indicator of the Anthropocene. *Anthropocene* <http://dx.doi.org/10.1016/j.ancene.2016.01.002> (in press).
- Zbyszewski, M., Corcoran, P.L., 2011. Distribution and degradation of fresh water plastic particles along the beaches of Lake Huron, Canada. *Water Air Soil Pollut.* 220 (1–4), 365–372. <http://dx.doi.org/10.1007/s11270-011-0760-6>.
- Zbyszewski, M., Corcoran, P.L., Hockin, A., 2014. Comparison of the distribution and degradation of plastic debris along shorelines of the Great Lakes, North America. *J. Great Lakes Res.* 40 (2), 288–299.
- Zettler, E.R., Mincer, T.J., Amaral-Zettler, L., 2013. Life in the “plastisphere”: microbial communities on plastic marine debris. *Environ. Sci. Technol.* 47, 7137–7146. <http://dx.doi.org/10.1021/es401288x>.
- Zhao, S., Zhu, L., Wang, T., Li, D., 2014. Suspended microplastics in the surface water of the Yangtze Estuary System, China: first observations on occurrence, distribution. *Mar. Pollut. Bull.* 0–6. <http://dx.doi.org/10.1016/j.marpolbul.2014.06.032>.