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# Anthropogenic particles in natural sediment sinks: Microplastics accumulation in tributary, beach and lake bottom sediments of Lake Ontario, North America

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# Abstract

Surface waters of the Great Lakes are known to be contaminated with microplastics, however, microplastics in the sediments of the region are poorly documented. This study provides a baseline of micro- and macro-plastics contamination in nearshore, tributary and beach sediments of Lake Ontario and the upper St. Lawrence River. Microplastics were quantified and characterized by morphology and composition using visual identification and Raman spectroscopy. Microplastics are most concentrated in nearshore sediments in the vicinity of urban and industrial regions. Concentrations in Humber Bay and Toronto Harbour consistently measured > 500 particles per kg dry sediment, and maximum concentrations of ~28,000 particles per kg dry sediment were quantified at Etobicoke Creek. Sourced from consumer and industrial activity, abundant plastics in Lake Ontario coastal environments are unnatural persistent contaminants warranting urgent action for the protection of benthic fauna and ecosystem health.

# Keywords

Plastics, microplastics, Lake Ontario, sediments, riparian, Toronto, Humber Bay, Hamilton Harbour, Raman spectroscopy, ArcGIS, polyethylene

# Acknowledgments

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# Relationship to published works

The following published manuscripts and abstracts, as well as posters and oral presentations contain text, data and figures that have also been used in this manuscript. The texts in this manuscript have been revised and modified, however some passages in the following documents have been included here verbatim.

Ballent, A. Corcoran, P., Madden, O., Helm, P., Longstaffe, F. (2016). Sources and sinks of microplastics in Canadian Lake Ontario nearshore, tributary and beach sediments. *Marine Pollution Bulletin*, http://dx.doi.org/10.1016/j.marpolbul.2016.06.037, in press.

Ballent, A., Corcoran, P., Helm, P., Longstaffe, F., Madden, O. (2016). Microplastics in sediment of Lake Ontario, Canada: Potential sources and sinks. 59th Annual Conference on Great Lakes Research, Guelph, Ontario, June 2016. Abstract, Oral Presentation.

Ballent, A., Corcoran, P., Helm, P., Marvin, C.: Microplastics in sediment of Lake Ontario, Canada: Potential sources and sinks. Envirocon 2016, University of Western Ontario, London, Ontario, March 2016. Oral Presentation.

Ballent, A., Corcoran, P., Helm, P., Marvin, C., Longstaffe, F. (2016). Abundance, Sources and Sinks of Microplastic in Lake Ontario Sediments, Canada. Fallona Family Interdisciplinary Showcase, December 2016. Poster.

Ballent, A., Corcoran, P., Helm, P.: Microplastic Accumulation in Beach and Lake Bottom Sediments of Lake Ontario, North America. 58th Annual Conference on Great Lakes Research, Burlington, Vermont, May 2015. Abstract, Oral Presentation.

Ballent, A., Ceccanese, T., Corcoran, P., Longstaffe, F., Helm, P., Marvin, C.: Microplastics in Lake Ontario Sediments. Invited talk given at Lake Ontario Evenings: Microplastics Edition in Toronto, Ontario.

All of the above works were written or presented by the first author, A. Ballent, who also conducted the majority of field work, laboratory analysis and data analysis. P. Corcoran supervised this study and contributed additionally by planning the research, conducting field work, revising texts, and securing funding for this work. P. Helm supplied samples, assisted with field work, provided the gravity corer and revised texts. F. Longstaffe assisted with field work and revising texts. C. Marvin provided samples. O. Madden assisted with laboratory analysis and revised texts. T. Ceccanese assisted with field work and laboratory analysis.

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# Chapter 1

# 1 Introduction

The Laurentian Great Lakes provide large surrounding populations with significant recreational and ecosystem services in both Canada and the United States of America; however, these services and resources are jeopardized by urban and industrial activity. A multitude of environmental stressors including eutrophication, invasive aquatic species, climate change and various anthropogenic contaminants have been identified as threats to the integrity of the Great Lakes system (Allan et al., 2013).

This study focuses on one particular stressor: microplastic debris contamination. Microplastics are generally defined as any piece of plastic debris ≤ 5 mm in the largest dimension (Barnes et al., 2009; Ryan et al., 2009; Thompson et al., 2009). Microplastics have only recently been documented in the Great Lakes, and the existing studies focus mainly on larger size beach debris (Zbyszewski & Corcoran, 2011; Zbyszewski et al. 2014; Corcoran et al., 2015; Hoellein et al., 2015) and surface water contamination (Eriksen, Mason, et al., 2013). This thesis investigates the abundance, morphology, composition and distribution of microplastic debris in tributary, beach and near-shore sediments of Lake Ontario.

## 1.1 The current state of microplastics research

In 1974, Colton et al. documented microplastic debris as a widespread aquatic contaminant in the northwestern Atlantic Ocean; however, significant attention from the scientific community began to expand only in the 2000s with the identification of the widespread accumulation of plastics in the North Pacific Ocean gyre (Moore et al., 2001) and in the western North Atlantic Ocean gyre (Law et al., 2010; Morét-Ferguson et al., 2010). Since then, investigation of plastics pollution has encompassed most aquatic environments, however, freshwater systems and benthic environments are not thoroughly studied.

Since the 1960s, the industrial production of commercial plastic has increased exponentially, with global production levels reaching 311 million tonnes per year in 2014 (PlasticsEurope, 2013; PlasticsEurope, 2015, Fig. 1.1).

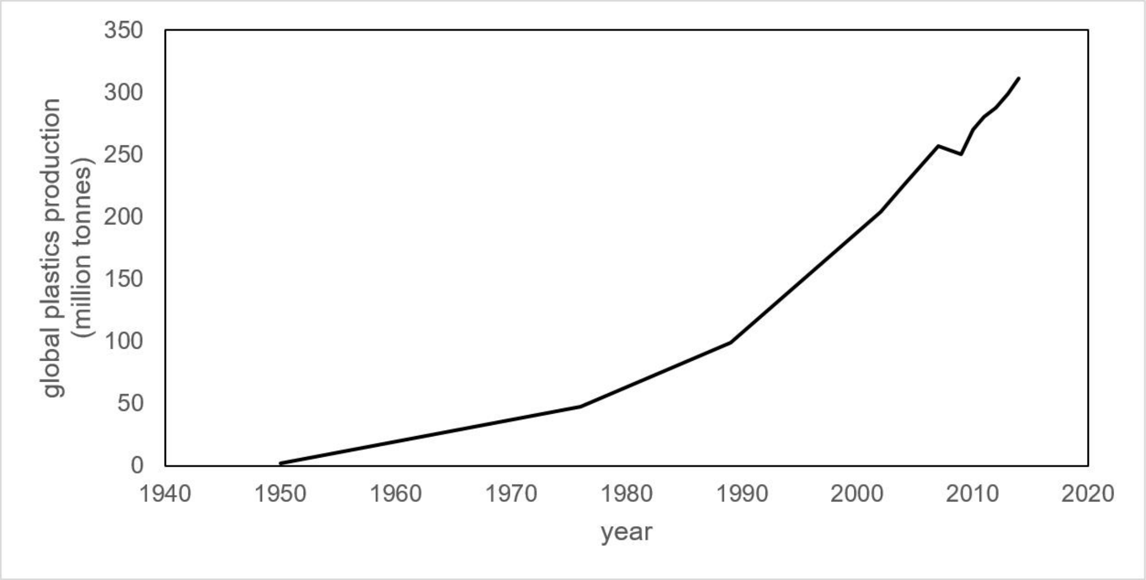

**Figure 1.1** Global plastics production in millions of tonnes from 1950 to 2014 (Data from PlasticsEurope, 2013; PlasticsEurope, 2015).

Petroleum-based plastic products have become ubiquitous in the modern urban lifestyle as a cost-effective replacement for traditional materials such as glass, paper, metal, ceramic and natural fibres. Major advancements in the medical, food, transport, technological, automotive, construction and cosmetic industries have been driven by the innovation and use of plastics (Neufeld et al. 2016). The scale of the plastics industry, low recycling rates, poor product designs that do not account for the post-consumer stage of the product, insufficient recovery systems, and a lack of policies in support of a circular plastics economy (Neufeld et al., 2016) have led to microplastics contamination becoming a global issue by creating a system where plastics production is greater than plastics recovery and use, with a substantial fraction being lost to the environment (Jambeck et al., 2015). For example, packaging accounts for ~26 % of global plastics use, of which only 14% is recycled; recovered plastics account for only 5% of the initial value of the packaging industry (Neufeld et al., 2016). A circular plastics economy would attempt to close the supply chain by increasing recovery of plastics and reducing virgin plastics production (Neufeld et al., 2016), with a side-effect of limiting waste lost to the environment.

Synthetic polymers are generally resistant to biological decay (Tokiwa et al. 2009), however, mechanical forces, photo-degradation, thermo-oxidative degradation and hydrolytic degradation (breakdown in the presence of water) cause embrittlement and fragmentation of plastic through the reduction of the molecular weight of the polymer (Andrady, 2011). These processes contribute to the generation of microplastic particles from products that are littered or otherwise enter the environment (Andrady, 2011). Other sources of microplastic particles include the manufacture of microbeads which are used in personal care products (Gregory, 1996; Andrady, 2011) and as sand-blasting medium (Andrady, 2011), the spillage of virgin industrial pellets used for the production of plastic goods (SPI and ACC, 2015), and the loss of fibres from fishing gear and synthetic fabrics such as carpet, fleece and other clothing (Browne et al., 2011).

The dispersal of non-point source plastic litter in the terrestrial environment ultimately leads to its transport by surface runoff through tributaries and storm drains (Moore et al., 2011; Lechner et al., 2014; Rech et al., 2014; Lechner & Ramler, 2015) into freshwater bodies (Eriksen, Mason, et al., 2013; Free et al., 2014) and marine environments (Morét-Ferguson et al., 2010; Eriksen, Maximenko, et al., 2013; Law et al., 2014). Buoyant plastic accumulates in the neustonic zones of lakes and exposed sediments in freshwater systems (Zbyszewski & Corcoran, 2011; Zbyszewski et al. 2014; Corcoran et al. 2015) and also in oceanic gyres (e.g. Cózar et al., 2014), beach sediments (e.g. Liebezeit & Dubaish, 2012; Dekiff et al., 2014; Mathalon & Hill, 2014) and abyssal sediments (e.g. Claessens et al., 2011; Van Cauwenberghe et al., 2013; Vianello et al., 2013) of marine systems. Our understanding of the fate of non-buoyant plastics in the environment is lacking. The few studies that have examined microplastics in marine sediments give evidence for wide-spread dispersal (e.g. Claessens et al., 2011; Vianello et al., 2013; Mathalon & Hill, 2014; Alomar et al., 2016).

Recent research suggests that microplastics contamination in beach and near-shore sediments may negatively impact coastal ecosystems (e.g. Vianello et al., 2013; Mathalon & Hill, 2014). Organisms of many trophic levels, including several benthic organisms and benthic feeders, have been shown to ingest or otherwise take up microplastic and associated chemicals with severe consequences to the healthy functioning of the organisms' physiological systems (e.g. Browne et al., 2013; Besseling et al., 2014; Watts et al., 2014; Avio et al., 2015; Besseling et al., 2015; Nobre et al., 2015).

With respect to the Laurentian Great Lakes, plastic debris has been found on both the beaches (Zbyszewski & Corcoran 2011; Zbyszewski et al. 2014; Corcoran et al. 2015) and in surface waters with particularly high microplastic abundances in southern Lake Erie (Eriksen, Mason, et al., 2013). Lake Ontario is the basin of lowest elevation within the Laurentian Great Lakes freshwater system and drains into the North Atlantic Ocean via the St. Lawrence River. The drainage basin of Lake Ontario is highly urbanized and industrialized in certain regions, specifically, in the corridor between Lake Huron and Lake Ontario. As such, Lake Ontario is expected to be prone to high levels of plastic pollution. Microplastics in the offshore sediments of Lake Ontario extended to a maximum of 8 cm below the sediment surface at two sites, one off the northern shore near Pickering and the other off the southern coast on the Niagara Bar (Corcoran et al., 2015). Detailed investigation into the abundance and distribution of microplastic on a system wide scale in the sediments of Lake Ontario had not been conducted prior to the present investigation.

## 1.2 Study objectives

The regional abundance and depositional patterns of microplastics in the nearshore lake-bottom, tributary and beach sediments of Lake Ontario and the upper St. Lawrence River are analyzed along the coastline of the province of Ontario. Distribution patterns and major sinks of non-buoyant sedimentary microplastics, are contrasted with variations in watershed population and the plastics industry on a regional scale using ArcGIS. The objectives of this study are to (i) provide a baseline for future monitoring of microplastics abundance in Lake Ontario coastal sediments, (ii) provide a means to assess potential sources of microplastics to the lake and (iii) scientifically support the efforts of political and non-governmental organizations in changing public and industrial mindsets towards single-use plastics.

Anticipated sinks for microplastics, semi-permanent to permanent depositional zones that allow for accumulation of microplastic particles, include environments where turbulence is low enough for plastic particles and other organic debris such as decaying plant material to settle. Near-shore regions such as harbours, coves and protected shorelines where flows are restricted are expected to have greatest accumulations of microplastic debris. Greatest abundances on beaches are expected to be found along the backshore and downwind margins where obstacles such as vegetation and retaining walls facilitate the collection of buoyant debris during storm and high water events. Microplastics are expected to be most abundant in urban and industrial regions with decreasing numbers with increasing distance from tributaries and urban point source outlets.

# Chapter 2

# 2 Context

Various sizes and terminologies have been used to describe plastics contamination as outlined by Rocha-Santos & Duarte (2014). In the present study, the description of microplastics given by the National Oceanic and Atmospheric Administration (NOAA, 2016) is used. Microplastics are plastic particles that have been fragmented to or were manufactured at a size < 5 mm. Plastics debris > 5 are referred to as ‘macroplastics’.

## 2.1 Plastic: a modern material

Plastics comprise a broad category of materials that are composed of polymers; macromolecules that can be processed and shaped. A wide range of organic molecules, monomers, are used to produce polymers of repeating units. Conventional plastics are produced from organic substances, such as crude oil, by a process of distillation of the source material followed by polymerisation and processing. During distillation, the crude oil (or other source substance) is heated by which certain components of the substance become vaporized and are separated from the starting material. In the case of natural gas and crude oil, hydrocarbon molecules such as ethane and propane are broken into ethylene in a heating process termed ‘cracking’. The monomer molecules, e.g. ethylene and propylene, are joined into long chains of repeating units in catalyzed reactions called polymerisation reactions. Large masses of the resulting long polymer chains, e.g. polyethylene, polypropylene, form the plastic material in two main ways. Thermoplastics are those plastics made up of polymer types which coalesce by only “intermolecular attractions” (Byrdson, 1999, p. 23), not chemical bonds. Thermoplastics are plastic materials that can be melted, moulded and re-solidified repeatedly. Thermosets, in contrast, are plastic materials made up of polymers which upon formation, form irreversible chemical bonds between polymers, generally as a catalyzed reaction. Thermosetting plastics cannot be melted and reprocessed after initial production (Byrdson, 1999). Most types of plastic used in consumer goods, and expected to be found in environmental samples, are thermoplastics and therefore can be recycled. Polyurethanes, polyesters, epoxies and vulcanized rubbers are common thermosets.

Raw plastic material is often produced in the form of pellets (granules) for transport purposes and for consistent heating and flow of plastics in extrusion and injection moulding production processes (Byrdson, 1999). The raw plastics are combined with organic and inorganic compounds, termed additives, to alter the physical properties of the plastic material. Additives comprise fillers, plasticizers, lubricants, flame-retardants, colorants, substances which prevent aging of the plastic, substances to improve properties for blowing extrusion processing, substances that promote crosslinking between polymers, and photo-degrading agents (Byrdson, 1999).

There are thousands of different types of plastic (Byrdson, 1999), however, these are composed of a relatively small number of distinct of synthetic polymers. Aliphatic polyolefins, have the simplest structure; for example, polyethylene (PE) is composed of $CH_2$— repeating units. Polystyrene (PS) plastics are processed into a variety of forms including PS which is produced as solid, non-expanded material, closed-cell extruded foam (e.g. Styrofoam), and expanded PS commonly used for the production of single-use cups and plates. Polyamides comprise a wide array of Nylons. Other types of thermoplastics include polyacetals, polycarbonates, polyvinyl chloride (PVC) and polyvinyl acetate (PVA) and most polyesters including polyethylene terephthalate (PET). Silicones, most polyurethanes, epoxide resins and some polyesters are thermosetting plastics. Acrylics such as poly (methyl methacrylate) (PMMA), may be either thermoplastic or thermosetting.

Plastics can also be classified according to density. The density of a substance or object can affect how it is transported through the environment, which is of interest when investigating contaminant dispersal. The density of plastic materials depends on the molecular structure and crystallization properties of the polymer; i.e. the mass of the atoms in the molecule and the way that the molecules and polymers are arranged in space (Byrdson, 1999). The density of a polymer is increased with longer chain lengths and with reduced branching of chains. For example, PE density ranges between 0.89 and 0.97 g $cm^{-3}$ depending on the amount of branching of the polymers; in low-density polyethylene (LDPE) polymers are linear but branch repeatedly, whereas high-density polyethylene (HDPE) polymers are unbranched and packed together more tightly

(Byrdson, 1999; Morét-Ferguson et al., 2010). Polypropylene (PP), LDPE and HDPE are the three types of plastic that are less dense than water (Table 2.1), and are expected to be found primarily in the surface compartments of aquatic systems. Most other types of plastic including solid PS, Nylon, PVC and PET are more dense than water (Table 2.1), and are therefore expected to be found only in the benthic environment of aquatic systems. The addition of additives, such as air inclusions and mineral fillers, which are often incorporated into plastics can also alter the density of plastic materials.

**Table 2.1** Common plastics with abbreviations, density range, for 25° C and common uses. Each polymer is identified by type: thermosetting (TS) or thermoplastic (TP).

| **Plastic Name** | **Abbreviation** | **Density ($g\ cm^{-3}$)** | **Common uses** | **Type** |
|---|---|---|---|---|
| Polypropylene | PP | 0.85 – 0.92 | Packaging, textiles | TP |
| Polyethylene | PE | 0.89 – 0.97 | Packaging, plastic bags | TP |
| Polystyrene | PS | 1.04 – 1.08 | Single use cutlery | TP |
| Acrylonitrile butadiene styrene | ABS | 1.06 – 1.08 | Lego | TP |
| Nylon 6 | Nylon | 1.15 | Clothing, electronics | TP |
| Polymethyl methacrylate | PMMA | 1.18 | Lenses, cases | TP |
| Polyvinyl acetate | PVA | 1.19 | Elmer’s glue | TP |
| Polyurethane | PU | 1.20 | Foams, seals, wheels | TS |
| Polycarbonate | PC | 1.20 – 1.22 | CD-ROM | TP |
| Polyvinyl chloride | PVC | 1.6 – 1.41 | Construction, packaging | TP |
| Polyethylene terephthalate | PET | 1.38 – 1.41 | Water bottles, clothing | TP |

## 2.2 Trends in plastics manufacturing – globally and in Canada

The global production of plastics, including thermosetting and thermoplastic resins and excluding some types of fibres, increased from 1.7 million tonnes in 1950 to 311 million tonnes in 2014 (PlasticsEurope, 2013; PlasticsEurope, 2015; Fig. 1.1). In the 1950s, the development of the Ziegler-Natta reactions, which use catalysts for controlled polymerization, allowed for the development of high-density plastics including high-density PE (HDPE) and PP. Other developments around the same time, included the invention of high-impact polystyrene, acrylonitrile butadiene styrene (ABS), and polycarbonates (Byrdson, 1999). These advancements allowed for the rapid commercialization of plastics. Discoveries of new plastics are still occurring, particularly of special purpose plastics and new catalyzing reactions such as the metallocene catalyst polymerization of PE which can produce extremely high molecular weight PE.

Plastics manufacturing in Canada currently accounts for ~2% of the global total (Government of Canada, 2013). According to two statistical reports published by the Canadian Chemical Industry (CIAC, 2014; CIAC, 2015), production of synthetic resins, fibres and rubbers included PE, ethylene vinyl acetate, PS, PVC, polyacrylamides, PET, nylons, latex emulsions, polyesters, silicones and butyl and halobutly rubbers. The manufacturing companies associated with the CIAC are BASF Canada; Dow Chemical Canada ULC; Imperial Oil, Products & Chemicals Division; Lanxess Inc.; Nalco Canada Co. (An EcoLab Co.) and NOVA Chemicals Corporation. Shipment (total manufacturing revenue) values of synthetic resins and rubbers combined increased from ~6.5 to 10.8 billion CAD between 2009 and 2014. Exports and imports were valued almost equally (~4 - 8 million CAD yr$^{-1}$) and both increased from 2009 to 2014. CIAC member companies operated out of ~100-150 establishments, employing between ~4.9 and 6.9 million people between 2009-2014 (CIAC, 2015).

Approximately 55% (~6 billion CAD) of the production of synthetic resins, rubbers and fibers occurred in the province of Ontario in 2014, the most recent year for which a CIAC statistical report has been published (CIAC, 2015). The largest aggregation of the CIAC production facilities in Ontario is located in Sarnia, on the southern shore of Lake Huron, with the second largest aggregation located in the ‘Golden Horseshore’, which is the highly urbanized region along the NW shores of Lake Ontario. The demand for plastic products is driven by three main economic sector end-use markets in Canada: packaging (39%), construction (33%), automotive (14%). (Government of Canada, 2013). The plastic type which is produced at the highest volume annually in Canada as of 2011 is PE, derived most commonly from petroleum products (Government of Canada, 2013). Polyethylene production by CIAC member companies between the years 2009-2014 was consistently above 3 Mt; ~3.5 Mt and ~3.4 Mt, respectively for 2013 and 2014 (CIAC, 2015).

## 2.3 Plastics degradation

The degradation of plastic waste into smaller pieces allows for widespread distribution of microplastics and makes plastics available to smaller organisms. Small particles are more susceptible to changes in density and to adsorption of contaminants, as a result of their large surface area to volume ratio, and are thus possibly more ecologically hazardous than intact plastic items and macroplastics. Plastics are generally resistant to biodegradation and aging processes due to the high molecular weight of synthetic polymers. Polymers must be cleaved into molecules of lower molecular weight to be assimilated into living cells or mineralized into bioavailable nutrients such as $CO_2$ or $H_2O$ (Lucas et al., 2008).

Plastics are more susceptible to abiotic depolymerisation processes driven mainly by mechanical stress, increases in temperature and UV radiation, which take place in combination with the chemical alteration of the polymer strands by oxidation (presence of $O_2$ or $O_3$) or hydrolysis (presence of water) (Lucas et al., 2008; Andrady, 2011). The depolymerisation processes, whether driven by abiotic or biotic factors, are sustained by the formation of free radicals (atoms with a vacant space in the valence shell of the electron orbitals), which can attack the bonds within the polymer to cleave it (Lucas et al., 2008).

The main chemical aging process affecting plastics is photo-oxidation. Photo-oxidation of plastics is a process by which UV radiation reacts with chromophores or other groups in the molecular structure of the plastic or added compounds. This results in polymer chain breakage and the generation of free radicals, as described by Singh & Sharma (2008). The radicals bind with oxygen and initiate a propagation reaction. Termination of the propagation reaction occurs when the free radicals react with each other, cross-linking the polymers (Byrdson, 1999). The use of additives, such as metals, can enhance the photodegradability of plastics by increasing the adsorption of UV-radiation and the formation of destructive reaction products, i.e. free radicals (Brydson, 1999). Photo-oxidation results in the reduction of the molecular mass of the polymer, embrittlement, discolouration and fracturing of the plastic material (Byrdson, 1999). Embrittled plastics are subject to fragmentation by mechanical stresses due to reduced strength and flexibility of the material (Singh & Sharma, 2008; Andrady, 2011). This has major implications for the spread and distribution of plastic debris throughout the environment, as smaller particles are more easily dispersed by natural forces including water and air. A thorough review of the types, mechanisms and methods of plastic degradation is given by Singh & Sharma (2008).

Some types of plastic (e.g. cellophane) are biodegradable in the natural environment (Byrdson, 1999), but those synthetic plastics that are currently most commonly produced, including PE, PS, PP and PMMA, are not considered biodegradable in the natural environment (Byrdson, 1999; Lucas et al., 2008). The invention of degradable plastics has increased in recent years, however, most types require specific circumstances (e.g. the presence of certain microbes; a specific temperature range) for full biodegradation to take place (Eubeler et al., 2010). Studies on the degradation of plastics in various environments including soil (Ohtake et al., 1995; Mumtaz et al., 2010; Devi et al. 2015), marine sediments (Nauendorf et al., 2016) and seawater (O'Brine & Thompson, 2010) have been conducted, but report variable timescales of degradation. Roy et al. (2008) suggest that LDPE containing photodegrading additives is susceptible to biodegradation on shorter time scales, and report biodeterioration, biofilm development, and molecular weight loss of ~8% occurring over a period of 2 weeks.

Microplastic particles take a variety of forms including fragments, pellets, beads and fibres. Fragments are derived from larger plastic debris as a result of mechanical erosion and aging processes. Fragments of solid, foam, film and sheet plastics have been found ubiquitously in marine and freshwater environments (e.g. Cole et al., 2011; Eerkes-Medrano et al., 2015). Pellets, a common form of raw plastic material, generally range in size from 1 - 10 mm in diameter and have a variety of morphologies, ranging from flat discs, to roughly spherical beads, to cylinders with flat, pinched or bulbous ends. Pellets may be spilled during transport by ship, train and truck, from the production facility to the processing facility, and also in facilities during production (SPI & ACC, 2015). Pellets have been identified in environmental water and sediment samples for decades (Colton et al., 1974; Ashton et al., 2010; Moreira et al., 2015). Microplastics that are manufactured as small beads generally < 1 mm in size, are termed 'microbeads.'

Microbeads are often used as abrasives in cosmetic and personal care products and in other applications such as sandblasting or deflashing (Hidalgo-Ruz et al., 2012; Eriksen, Mason, et al., 2013). Microbeads, as used in cosmetics, refer to particles with a range of sizes, polymer composition, and shapes ranging from spherical to irregular (Leslie, 2014). Fibres are produced from the production and natural wear of textiles including synthetic clothing and carpeting and other products such as rope and lines.

## 2.4 Plastics in the environment

Investigations of plastics contamination in many aquatic environments including beaches, ocean surface waters, deep-sea sediments, freshwater lakes, and tributaries, as well as throughout terrestrial environments are now published (e.g. Eriksen, Mason, et al., 2013; Vianello et al., 2013; Van Cauwenberghe et al., 2013; Cózar et al., 2014; Townsend & Barker, 2014; Turra et al., 2014; Eerkes-Medrano et al., 2015), however, studies pertaining to freshwater and benthic environments are less abundant in comparison to those of oceanic and surface water environments.

### 2.4.1 Sources of microplastics debris

Although the consumption of plastics has increased exponentially since the 1950s improvements in recovery and recycling technologies are lacking. Recent pressure has been placed on manufacturers to adopt ‘extended producer responsibilities’ policies, in which producers account for the entire life-cycle of a product, including recovery and recycling costs. This strategy was developed by Thomas Lindhqvist in 1990, who outlines the concept and implementation strategies in an open access doctoral dissertation published in 2000 (Lindhqvist, 2000).

In addition to the persistence and “throw-away” design of plastic products, municipal recovery and recycling systems are absent in much of the world, and often have low participation rates where they do exist. Once entered into the environment, littered plastics have been shown to disperse through waterways, such as rivers, tributaries and storm drains and to accumulate in beach sediments (Liebezeit & Dubaish, 2012; Dekiff et al., 2014; Mathalon & Hill, 2014; Zbyszewski et al., 2014), lakes (Eriksen, Mason, et al., 2013; Free et al., 2014), ocean surface waters (Morét-Ferguson et al., 2010; Eriksen, Maximenko, et al., 2013; Cózar et al., 2014; Law et al., 2014;) and benthic sediments (Claessens et al. 2011; Van Cauwenberghe et al. 2013; Vianello et al. 2013).

Data collected by volunteers for the Adopt-a-Beach and Great Canadian Shoreline Cleanup events in 2012 show that beach debris on Great Lakes shorelines were >90% recreational and smoking related items, and ~1-3% water-way activity related items (Driedger et al., 2015). Plastic household items and recreational items, such as food, take-out and confection packaging, single use beverage and product bottles and cutlery, make up a large portion of aquatic debris (Driedger et al., 2015). Plastic waste material, even if properly disposed of by the consumer can still be released into the environment during waste management process, from collection, transport and sorting by municipal organizations, to long-distance transport of bales which are often shipped across seas for recycling. Industrial spillage of raw plastics (granules) during transportation and within factories is another potential source of plastic debris (SPI & ACC, 2015). Agriculture may be another significant source of plastics as pellets are used for mulching and feed and films are used for covering fields and packaging products (Cunnningham et al., 1972; Espí et al., 2006).

Consumer cosmetic and personal care products (e.g. facewashes, toothpastes, lipsticks body washes, sunscreens) (Fendall & Sewell, 2009; Eriksen, Mason, et al., 2013; Leslie 2014; Sundt et al., 2014) are also sources of microplastics. The microplastics in these products have been found in high concentrations in the surface waters of the Great Lakes (Eriksen, Mason, et al., 2013). Both observational and model-based studies indicate that local industry and waste management are significant factors controlling the abundance of microplastic pollution in freshwater and marine environments (Free et al., 2014; Turra et al., 2014; Jambeck et al., 2015).

### 2.4.2 Microplastic debris in freshwater systems

Studies pertaining to microplastic debris in freshwater systems show that microplastics can be transported from urban areas through rivers to lakes, bays and oceans (Moore et al., 2011; Hoellein, Rojas, et al., 2014; Rech et al., 2014). A comprehensive overview of plastics contamination in freshwater systems (Eerkes-Medrano et al., 2015) discusses sampling techniques and factors affecting plastic abundance and dispersal in freshwater systems, sources of plastics, and ecological consequences of microplastics. A second review (Dris, Imhof, et al., 2015) focuses on methodologies for sampling and analyzing microplastics in freshwater environments, comparing existing methods and recommending ways in which future research methods could be conducted to provide the most replicable and comparable data. These reviews reveal the absence of studies investigating plastics contamination in submerged lake sediments.

Rivers, particularly urban tributaries, are depositional sites as well as major transport pathways for microplastics and macroplastics (Moore et al., 2011; Gasperi et al., 2014; Lechner et al., 2014; Rech et al., 2014; Zhao et al., 2014; Corcoran et al., 2015). Plastics are transported on surface waters (Gasperi et al., 2014) and along the tributary bed (Moore et al., 2011; Morritt et al., 2014) depending on the buoyancy of the material. Microplastic debris types previously identified in tributaries comprise industrial (pellets) and urban waste (Moore et al., 2011; Lechner et al., 2014; McCormick et al., 2014). Debris can be introduced into tributaries via point sources (effluent pipes, drainage outlets, wastewater treatment plants) and non-point sources (dumping, spills and litter). Rech et al. (2014) and Hoellein et al. (2014) showed that macroplastic debris loads carried by rivers are also deposited along river banks, suggesting that rivers are both depositional and erosional zones for anthropogenic debris. Sampling techniques have involved both water and sediment sampling, but generally one or the other. Most water sampling studies have targeted surface waters, however, two studies (Moore et al., 2011; Morritt et al., 2014) included subsurface waters. Sediments have generally been sampled from exposed river banks and bars; however, a study by Hoellein et al. (2014) sampled the benthic sediments of the North Shore Channel of the Chicago River for debris > 1 cm in size.

Studies of microplastics in tributary waters have included the Los Angeles River, San Gabriel River and Coyote Creek in Southern California (Moore et al., 2011), the Thames River in the UK (Hoellein et al., 2014), the Danube River in Austria (Lechner et al., 2014), the North Shore Channel of the Chicago River in the USA (McCormick et al., 2014), the Seine River in France (Gasperi et al., 2014; Dris, Gasperi, et al., 2015), the rivers of Chesapeake Bay in the USA (Yonkos et al., 2014), and the Yangtze River in China (Zhang et al., 2015). In the Yangtze River, Zhang et al. (2015) investigated the abundance and composition of microplastics in the surface waters of the mainstream and four tributaries behind the Three Gorges Dam. They identified PE, PP and PS microplastic particles, in the size range 112 $\mu$m – 5 mm, at spatial densities of 0.19 x $10^6$ to14 x $10^6$ $km^{-2}$.

Studies of microplastics in tributary sediments have been less common. On the banks of the Elqui, Maipo and Bio-bio Rivers in Chile, Rech et al. (2014) investigated debris >1.5 cm in size. Wagner et al. (2014) published a review of microplastics contamination in freshwater environments and reported microplastics abundances of 34 - 64 particles $kg^{-1}$ dry sediment in the sediments of the Elbe, Mosel, Neckar and Rhine Rivers, however, they did not include information regarding sampling location or whether the sediments were riparian or benthic. In the St. Lawrence River, which drains the Laurentian Great Lakes from the eastern end of Lake Ontario, Casteñada et al. (2014) reported microplastics at maximum concentrations of 398,000 particles $m^{-2}$ in the river sediments. The authors found the greatest concentrations in the effluent channel of the Gentilly-2 Nuclear Power Plant. The collected particles, however, were not spectroscopically identified, and were only assumed to be polymers based on appearance, melting point (113.7°C) and differential scanning calorimetry.

Lake surface waters have been investigated in at least three studies including Lake Geneva in Switzerland (Faure et al. 2012), Lakes Superior, Huron and Erie of the Great Lakes in North America (Eriksen, Mason, et al., 2013) and in Lake Hovsgol in Mongolia. Respective mean extrapolated microplastics spatial concentrations were 48,000 $km^{-2}$, 43,000 $km^{-2}$ and 20,000 $km^{-2}$. Subsurface waters were investigated in one study of Lake Märalen in Sweden (Landbecker, 2012), for which fibrous anthropogenic particles were reported at concentrations of 0-28 particles $m^{-3}$. Fibrous particles were observed in water pumped from a depth of 0.5 m below the surface, however, successful spectroscopic identification was not achieved due to the small size of the particles (> 20 $\mu$m in diameter, < 3000 $\mu$m in length) and the fibres were assumed to be natural fibres, such as wool and cotton, due to their slack texture.

Studies of plastic debris in and on lake shore sediments include Lake Huron of the Great Lakes (Zbyszewski & Corcoran, 2011), Lake Geneva in Switzerland (Faure et al. 2012), Lake Garda in Italy (Imhof et al., 2013), Lakes Erie and St. Clair of the Great Lakes (Zbyszewski et al., 2014), Lake Michigan of the Great Lakes (Hoellein et al., 2014; Hoellein et al., 2015), and Lake Ontario of the Great Lakes (Corcoran et al., 2015). All but the first study in the list (See Section 2.3.4) are discussed in the review papers by Eerkes-Medrano et al. (2015) and Dris, Imhof, et al. (2015).

### 2.4.3 Microplastic debris in sediments

Microplastics studies targeting aquatic environments can be categorized by habitat (e.g. freshwater or marine), but also by compartment (e.g. neustonic, pelagic or benthic). The majority of studies focus on the neustonic compartment of tributaries, lakes and oceans, however, many types of plastic have densities greater than water. Plastics are therefore expected, and have been found, in sedimentary environments such as beaches (e.g. Zbyszewski et al., 2014), the abyssal ocean floor (e.g. Van Cauwenberghe et al., 2013), lake bottom sediments (Corcoran et al., 2015) and tributary sediments (Castañeda et al., 2014; Hoellein et al., 2014; Rech et al., 2014; Wagner et al., 2014; Corcoran et al., 2015).

The transport mechanism and pathways of plastic debris in the abyssal benthic zones of the ocean are generally unknown. One possible mechanism includes benthic layer transport from the source (coastal or offshore) via bedload transport, saltation and suspension (Ballent et al., 2013). This type of transport mechanism could explain the presence in the deep sea of plastic objects with a negative buoyancy in seawater. Tidal, offshore and turbidity currents may play a role in the transport of negatively buoyant plastics from coastal to abyssal and profundal zones of the oceans and large lakes as described by Zalasiewicz et al. (2016). Originally buoyant microplastics could be transported to depth by increases in the net particle density caused by assimilation of particles with more dense matter, for example with faecal express of ingested plastics (Cole et al., 2013; Setälä et al., 2014; Zalasiewicz et al., 2016), assimilation in marine snow (Zalasiewicz et al., 2016; Lagarde et al., 2016), biofouling (e.g. Ye and Andrady, 1991; Andrady, 2011; Zettler et al., 2013; McCormick et al., 2014), and adsorption of natural biological and mineral substances to the surface (Zalasiewicz et al., 2016; Frias et al., 2016).

Several studies report relatively high abundances of microplastic in the bottom sediments of low energy environments such as harbours and lagoons, where fine particles supplied by fluvial and anthropogenic outputs can settle. For example, in the Belgian coastal zone, microplastic particles were found in significantly higher concentrations in harbours as compared to off-shore and beach sediments (Claessens et al., 2011). The authors also investigated the depositional history of microplastic on Belgian beaches, finding decreasing abundance with depth. In the Lagoon of Venice, Italy, bottom sediments sampled using a box corer, contained on average ~1500 microplastic particles per kg of dry sediment (Vianello et al., 2013). Vianello et al. also observed a correlation between the hydrodynamic characteristics of the sample site and microplastic abundance. A similar study published in 2014 by Mathalon & Hill reports microplastic fibre concentrations of ~20-80 fibres per 10 grams of sediment in the intertidal zone of Halifax Harbour in Canada. The Great Lakes also exhibit low-energy environments within harbours, coves and along shores where constructed barriers such as jetties and seawalls protect shores.

In terms of microplastics in beach sediments, a study by Dekiff et al. (2014) reported homogenous distributions of microplastic <1 mm at concentrations of 1-3 particles per kg sediment over distances of 500 m in the North Sea East Frisian Islands, Germany. A unique study conducted in Sao Paulo, Brazil investigated the abundance of pellets in beach sediments on a 3-dimensional scale, quantifying microplastic at depths down to 2 m with results suggesting that less than 10% of plastics are found within the top 5 cm of sediment, as would be expected under constant sedimentation rate conditions (Turra et al., 2014). Turra et al. also reported a correlation between the proximity of industrial plants and microplastics abundance. In another study, Free et al. (2014) investigated plastics abundance on the shores and surface waters of the remote Lake Hovsgol, in Mongolia, where neustonic microplastic abundances were reported to be similar to those in the Great Lakes (Eriksen, Mason, et al., 2013). Examination of the types of microplastic revealed the complete absence of pellets and microspheres, a phenomenon attributed to the lack of industry in the area. These two studies indicate that local industry and waste management are significant factors in regulating microplastic pollution in freshwater and marine environments.

Beach plastics in Hawaii were more abundant at the high-tide line than at the berm (storm wave extent), where on average 1.9 g plastic per l sediment, and 0.2 g plastic per l sediment were observed, respectively (McDermid & McMullen, 2004). In a similar study of beach plastics on the island of Fernando de Noronha, in the Equatorial Western Atlantic Ocean off the coast of Brazil, plastics debris was significantly more abundant on windward beaches compared to leeward beaches, suggesting that beach orientation with respect to the prevailing wind direction has an effect on the distribution of plastics washing ashore (do Sul et al., 2009). The authors noted that plastics manufacturing industry was absent on the island, suggesting that industrial pellets originated from distal sources.

### 2.4.4 Microplastic debris studies in the Great Lakes

Studies report microplastic pollution in the Great Lakes surface waters (Eriksen, Mason, et al., 2013), shorelines (Zbyszewski & Corcoran, 2011; Zbyszewski et al., 2014; Corcoran et al., 2015) and offshore bottom sediments (Corcoran et al., 2015) and nearshore bottom sediments (Ballent et al., 2016), but microplastics contamination in the subsurface sediments of the coastal regions of the Great Lakes is still largely unknown (Opfer 2012, p. 50; Opfer 2013, p. 24; Driedger et al. 2015).

The first study of plastics in the Great Lakes was conducted by Zbyszewski & Corcoran in 2011 who investigated microplastic abundance on the shorelines of Lake Huron. Sampling techniques involved quadrat and transect surveys of visible microplastics, including pellets, fragments and foam pieces. They reported greatest concentrations at the southern-most beach, Sarnia Beach, where abundances of 408 pieces/m$^2$ were quantified, which they attributed to proximity to the plastics industry activity coupled with the dominant cyclonic surface circulation of the lake. Fourier Transform Infrared (FTIR) spectroscopy of pellets and fragments revealed that the dominant polymers were PE and PP. One PET fragment was also identified. Surface textures on pellets and fragments, described as flaking, pits, grooves, gauges and fractures, were suggested to be oxidative and mechanical weathering artifacts.

A single study investigating microplastic concentrations in the surface waters of Lake Superior, Lake Huron, and Lake Erie reported average spatial densities of ~43,000 microplastic particles km$^{-2}$. Maximum concentrations of almost 0.5 billion particles km$^{-2}$ were located in the eastern part of Lake Erie (Eriksen, Mason, et al., 2013). Fragments, foams, films, fibres and pellets < 1 mm made up 80% of all plastic particles collected; only 2% were > 4.75 mm. This suggests that floating plastics debris is primarily made up of microplastics, rather than large intact plastic objects. Eriksen, Mason, et al., (2013) also observed that many of the pellet-shaped particles < 1 mm in sizer were not polymers but aluminum silicates (coal fly ash), and that others were very similar to microplastic particles present in common brands of facewash. In a more recent investigation of microplastics in the surface waters of tributaries and the nearshore of Lake Ontario and Lake Erie, particle concentrations were found to be an order of magnitude higher than offshore concentrations reported by Eriksen, Mason, et al. (2013). The greatest abundances were 6.7 million particles per km$^2$, as measured in urban regions near Detroit and Windsor in Lake Erie, and near Humber Bay and Toronto Harbour in Lake Ontario. Fragments and fibres were the most abundant morphologies, but notable contributions of foam particles and industrial cuttings were also reported (Helm et al., 2016).

Another study published by Zbyszewski et al. (2014) compared microplastic debris on the shorelines of Lake St. Clair, Lake Erie and Lake Huron The authors observed plastic pellets, fragments and foam particles at average spatial densities of 4.25 particles m$^{-2}$ and noted high spatial variability between sample sites at all three lakes. The highest spatial densities of 34 microplastics particles m$^{-2}$ were observed at Sarnia Beach on the southern shore of Lake Huron. Of the sample sites on Lake Erie and Lake St. Clair shorelines, the highest spatial densities observed were 3.7 particles m$^{-2}$ at Presque Isle and 8.4 particles m$^{-2}$ at Grosse Pointe.

In the same year, Hoellein et al. (2014) investigated anthropogenic litter abundances along three 400 m long, 50 m wide transects on Lake Michigan beaches near Chicago, and along three 70-100m stretches of the riparian and benthic zones on the North Channel of the Chicago River. All types of anthropogenic litter, including metal, fabric, paper, plastic and glass items > 2 cm were collected; microplastics abundances were not investigated. Plastics were most common in riparian zones and least common in the benthic zone of the river, by percentage of total litter abundance.

In another study of anthropogenic litter on the shores of Lake Michigan, Hoellein et al. (2015) used data published by the Adopt-a-Beach volunteer cleanup program to summarize debris characterization on five beaches. Debris (plastics and other materials) was collected by volunteers, and was primarily food and smoking-related. Debris abundance was positively and linearly correlated with volunteer hours, and also with county population density (Hoellein et al., 2015). Debris abundance was not related to other measured environmental factors of catchment area, percentage of built up area, tourism and recreation GDP, or beach popularity as measured by the Flikr score, suggesting that debris was mainly littered by beach-goers or washed onto the beach from distal sources. The authors concluded that determining sources of litter was not possible and that riverine sources were minor. This study, however, only investigated large intact recognizable debris, and did not focus purely on plastics. The authors also noted that several of the beaches in the study were regularly cleaned during the summer months.

Microplastics pollution in Lake Ontario has received little attention despite the fact that it is furthest downstream within the Great Lakes system and that it is highly urbanized and industrialized. Corcoran et al. (2015) investigated shoreline, riparian and offshore sediments and was the first study to include data of microplastics in bottom lake sediments. A stretch of shoreline in Humber Bay Park West and a section of the Humber River riparian bank were analyzed triweekly for accumulation of microplastics. Particles in both locations comprised mainly industrial pellets, but also fragments, intact items and foam particles. At the Humber Bay shoreline site consecutive triweekly accumulation rates were 26.5 particles $m^{-2}$ and 13.4 particles $m^{-2}$, and pellets deposited on the Humber River bank indicate that the Humber River is a notable source of microplastic contamination to the lake. Two core samples of sediment accumulation depths of 30 cm were analyzed for microplastics. The cores were taken from the Niagara Bar at a water depth of ~ 66 m and from the north-central part of the lake at a water depth of ~ 182 m. Microplastics were present to a depth of 8 cm below the sediment surface in both locations, and generally decreased with depth in the sediment. Microplastics were analyzed visually and with FTIR spectroscopy, revealing that the particles were of various color and morphology, including angular, rounded and wispy, and were mostly composed of PE (*N*=16). Some particles were PP (N=6) and nitrocellulose (N=3). Inorganic matter, including calcium carbonate, silica and mica were identified with several, though not all particles. The authors interpreted the association of these inorganic substances to be mineral fillers included in the plastics during manufacture, or to be minerals adsorbed or otherwise attached to the surface of the plastics. In 2016, Ballent et al. published a study of microplastics in the nearshore, tributary and beach sediments of Lake Ontario, which contains information presented in this thesis.

A literature review of microplastics in the Great Lakes (Driedger et al. 2015) provided a general summary of the current situation of microplastics contamination research and monitoring as conducted by the volunteer based Adopt-a-Beach program and Great Canadian Shoreline Cleanup programs.

### 2.4.5 Ecological implications of microplastics contamination

Microplastics in benthic ecosystems pose an environmental threat primarily because benthic fauna and 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). As such, 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. Aquatic fauna for which ingestion of microplastics has been shown to occur include demersal and pelagic fish (Neves et al., 2015; Phillips & Bonner, 2015; Rummel et al., 2015), deposit- and filter-feeder benthic invertebrates (Setälä et al., 2015), farmed and wild bivalves (Mathalon &

Hill, 2014; Van Cauwenberghe & Janssen, 2014), lugworms (Browne et al., 2013; Van Cauwenberghe et al., 2015) and freshwater waterfowl (English et al., 2015). Biginagwa et al. (2015) studied plastics ingestion in predatory Nile Perch and omnivorous Nile Tilapia, common fish caught in Lake Victoria, Tanzania. The authors observed plastic debris contamination in drainage ditches near the lake and noted that the surrounding regions were densely populated. Of the fish examined, 20% (*N*=4) contained plastics (PE, PU, PET, PE/PP copolymer and silicone as confirmed by FTIR spectroscopy) in their gastro-intestinal organs.

Ingestion of microplastics can be associated with detrimental physiological consequences, including inflammatory responses at the tissue level in mussels (von Moos et al. 2012), liver toxicity in fish (Rochman, Hoh, et al., 2013), increased mortality in lugworms (Browne et al., 2013) and reproductive repercussions in zooplankton (Besseling et al., 2014). Ingested microplastic particles can move through trophic systems, for example in planktonic food webs (Setälä et al., 2014) and from mussels to crabs (Farrell & Nelson, 2013).

In Lake Ontario, several species of littoral and stream-dwelling benthic organisms and benthic feeders may be at risk of ingesting microplastics. Invertebrates such as the quagga and zebra mussels are recent invasive species in the Great Lakes and may be prone to ingestion of microplastics. Marine invertebrates such as the filter feeding blue mussel *Mytilus edulis* and the deposit feeding lug worm *Arenicola marina* have been shown to ingest microplastics during feeding in the natural environment and in microcosm experiments (Van Cauwenberghe et al., 2015). In an analysis of microplastic ingestion by *M. edulis* in the coastal waters of China, both fibres and fragments were found to be ingested (Li et al., 2016).

In the tributary and coastal waters of Lake Ontario, examples of bottom feeding fish species that may be subjected to microplastics ingestion include various species of carp (*Hypophthalmichthys nobilis*, *Mylopharyngodon piceus*, *Ctenopharyngodon idella* and *Hypophthalmichthys molitrix*), Logperch (*Percina caprodes*), Round Goby (*Neogobius melanostomus*) and Tubenose Goby (Proterorhinus marmoratus), Channel Catfish

(*Ictalurus punctatus*), Flathead Catfish (*Pylodictis olivaris)* Northern Hog Sucker (*Hypentelium nigricans*), and Redhorses (*Moxostoma sp*.) (Eakins 2016). These species are warm-water benthic fish common in the riverine and lacustrine environments of the southern Great Lakes and include invertivores, detritivores, herbivores and carnivores. Studies regarding plastics ingestion by the above species have not yet been published, however, preliminary results from an experimental feeding study through the Ontario Ministry of the Environment and Climate Change reveal that plastics are ingested and beads and pellets are most likely consumed and retained (Munno et al., 2016). The authors report ongoing research investigations of field studies regarding ingestion by common fish species in Lake Ontario nearshore and tributary environments of Humber Bay, Hamilton Harbour and Toronto Harbour, but do not include preliminary results except for an apparent susceptibility to the retention of fibres (Munno et al., 2016). Lake trout and other benthic feeding pelagic fish could also be exposed to microplastic through ingestion of prey with microplastic retained in the gut. The diet of lake trout (*Salvelinus namaycush*) has shifted to include more round goby since the species was introduced to Lake Ontario in the 1990s (Dietrich et al., 2006), and a study of fish diet in Lake Michigan suggests that the energy pathways of pelagic and profundal fish species are transferring away from a pelagic diet and towards a nearshore benthic pathway, due to the expansion of the dreissnenid mussel (Turschak et al., 2014). The transfer of microplastics may not be limited to fish and invertebrates in the Great Lakes as there is evidence for benthic feeding Round Gobies becoming a dominant prey for double crested cormorants (*Phalacrocorax auritus*) colonies in the upper St. Lawrence River (Johnson et al., 2015), eastern Lake (Johnson et al., 2015), and in Hamilton Harbour (Somers et al., 2003). Microplastics were ingested and some particles were retained for over 24 hours by fish in a feeding experiment using fish caught in the coastal waters of Lake Ontario (Munno et al., 2016), suggesting that there is the possibility that microplastics are moving to higher trophic levels in the Great Lakes. Preliminary results of *in situ* ingestion of microplastics in Lake Ontario nearshore fish species indicate that microplastic fibres were most prevalent compared to other morphologies in the GI tracts of sampled fish (Munno et al., 2016).

Plastics are not classified as hazardous waste in Canada, perhaps as a result of the intrinsically inert qualities of polymers such as PE and PP (Rochman, Browne, et al., 2013). Certain plastic products, however, are manufactured from hazardous derivatives such as polycarbonate CD-ROM discs and polyurethane foams commonly used in furniture (Lithner et al., 2009). Additives such as polybrominated diphenyl ethers (PBDEs; e.g. flame retardants) (Lithner et al., 2011; Rochman, Lewison, 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). Lithner et al. (2009) tested the effect of plastic consumer item leachates, of which the polyvinyl chloride and polyurethane leachates were most toxic to the freshwater arthropod, *Daphnia magna*. 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).

Microplastic loads in the Danube River have been shown to be on the same order of magnitude by count as fauna of the same size (Lechner et al., 2014), suggesting that the scale of microplastics pollution may be sufficient to fundamentally alter trophic systems of tributaries and larger water bodies by imitating food sources of organisms in the lowest trophic levels. Microplastics may also be facilitating changes in microbial communities, acting as non-stationary colonization surface habitats for bacteria or other organisms adhering to the plastics (e.g. Ye & Andrady, 1991; Zettler et al., 2013; Harrison et al., 2014; McCormick et al., 2014; Nauendorf et al., 2016).

Plastics may be classified as carcinogenic, hormone disrupting, or toxic, due to manufacture from hazardous derivatives and/or additives such as polybrominated diphenyl ethers (PBDEs) i.e., flame-retardants (Lithner et al., 2011; Rochman, Lewison, et al., 2014) or because of the adsorption of environmental pollutants such as persistent organic pollutants and trace metals such as Pb and Cd (Browne et al., 2013; Rochman, Hentschel, & Teh, 2014). However, there is no conclusive evidence that adsorbed toxins are transferred to an organism upon ingestion. Some studies suggest that ingestion of plastic particles leads to the disruption of the physiological systems of organisms (Browne et al., 2013; Van Cauwenberghe et al., 2015). In the case that toxins are transferred to the tissues of organisms, there is the possibility that plastics facilitate bioaccumulation of associated pollutants in higher trophic level organisms.

Overall, while research pertaining to the ecological implications of microplastics is still ongoing and there are many questions still to be answered, there is sufficient evidence that microplastics contamination of aquatic environments needs to be stemmed in order to protect the quality of these systems which are valued for the ecological, recreational and commercial services that they provide.

## 2.5 Methodologies commonly used in studies of microplastics in sediments

### 2.5.1 Collection methods

Methods for the collection of submerged and exposed sediments for the investigation of microplastics contamination have varied across studies. Surveys of macrodebris lying on seafloor or river bed sediments are commonly conducted by bottom trawling and diving (in submersibles, scuba or snorkeling), video taken by autonomous underwater vehicles (Spengler & Costa, 2008; Mordecai et al., 2011) and by wading in shallow waters (Hoellein et al., 2014). Surveys of macrodebris in exposed beach and riparian sediments are traditionally conducted by transect or quadrat surveys (e.g. Hoellein et al., 2014; McCormick et al., 2014; Hoellein et al., 2015) although newer methods have incorporated webcam imagery (Kataoka et al., 2012). Collection of microplastics deposited in exposed sediments has involved transect (e.g. Liebezeit & Dubaish, 2012; Moreira et al., 2015), quadrat (e.g. Turra et al., 2014) and core sampling (Carson et al., 2011; Claessens et al., 2011) or a combination of techniques (Zbyszewski and Corcoran, 2011; Zbyszewski et al., 2014; Corcoran et al., 2015).  Investigation of microplastics in submerged sediments or of particles < 1 mm in size, however, requires retrieval of sediment for laboratory analysis. In the literature, submerged sediments have been collected with box cores (Corcoran et al., 2015), van Veen grabs (Browne et al., 2011; Claessens et al., 2011) and Peterson and Petite Ponar grabs (Castañeda et al., 2014).

### 2.5.2 Sample processing methods

The separation of microplastics from sediments is often aided with a sort of density separation, particularly where targeted particles are < 1 mm and not identifiable with the naked eye. Density separation of low-density plastics was conducted using seawater as the separation fluid at a large scale in the field for large quantities of beach sediment in a study of the 3-dimensional distribution of pellets > 1mm on beaches in Brazil (Turra et al., 2014). For high-density plastics, separation mediums of higher densities generally > 1.43 g $cm^{-3}$ are needed (Imhof et al., 2012). Solutions of sodium chloride (Hidalgo-Ruz et al., 2012), zinc chloride (Imhof et al., 2012; Mathalon & Hill, 2014; Dris, Imhof et al., 2015), sodium iodine (Claessens et al., 2013) and sodium polytungstate (Corcoran et al., 2009; Corcoran et al., 2015) have been used. Methods used for removing the supernatant containing microplastics from the sample are consistently ill-described (Hidalgo-Ruz et al., 2012). Decanting and removal of floating particles by picking with forceps is likely less efficient as particles may be missed and stick to the containers walls (Hidalgo-Ruz et al., 2012). In order to overcome this issue, several devices have been invented to increase recovery rates in sediment density separation processes. An instrument, named the Munich Plastic Sediment Separator (MPSS) was developed by Imhof et al. (2012), achieved a recovery efficiency of 95.5% for microplastics < 1 mm of a range of densities of 0.8-1.43 g $cm^{-3}$. The separation column was constructed of an aeration column with a motor-powered stirrer and overlying skimming chamber. Compared to the MPSS, a simple decanting method for plastic retrieval after stirring and aeration resulted in an average recovery rate of ~40% by weight for particles < 1 mm. A similar column elutriation technique developed by Claessens et al. (2013) was highly efficient with recoveries of 100% of microspherules and 98% of fibres.

A review of identification and quantification methods written by Hidalgo-Ruz et al. (2012) describes methodologies used for marine microplastics. A recent report published by NOAA outlines sample processing methods for water, sediment bed and beach samples (Masura et al. 2015). As the study of microplastic pollution develops, many experiments and publications aim to refine and standardize research methods to address issues related to sampling and analysis of microplastic. Commonly recognized is the necessity of minimizing contamination of samples during laboratory analyses, particularly by airborne plastic fibres (e.g. Dekiff et al. 2014; Mathalon & Hill 2014). Recommendations include reducing exposure of samples to air by keeping containers closed, keeping all tools, surfaces, and containers clean, wearing clothing of natural fibres, and reducing drafts and excessive exposure from corridors, and conducting controls for environmental contamination in the laboratory (Woodall et al., 2015).

### 2.5.3 Quantification methods

The quantification of microplastics separated from sediments is normally conducted manually using stereomicroscopes (Hidalgo-Ruz et al., 2012). Studies have shown, however, that visual analysis is not a reliable method for the identification of microplastics and that spectroscopic analysis is needed for reliable quantification of microplastics (e.g. Eriksen, Mason et al., 2013; Song et al., 2015). In a study of microplastics in the surface waters of the Great Lakes, surface electron scanning and energy dispersive x-ray spectroscopy revealed that on average 20% of the particles suspected to be plastic by visual identification were in actuality aluminum silicates and likely fly ash particles (Eriksen, Mason et al., 2013). Song et al. (2015) report that microplastic fragment quantification was underestimated and fibre quantification was overestimated using a stereo microscopic analysis compared to Fourier-transform infrared (FTIR) spectroscopic analysis, suggesting that visual identification of microplastic samples is not reliable. Synthetic and natural fibers were reported to have similar appearance, and fragments < 1 mm were often not identified by visual examination.

### 2.5.4 Compositional analysis methods

Spectroscopy is a common technique used to determine the types of polymers and materials present in sediment samples (e.g. Corcoran et al., 2009; Cooper and Corcoran, 2010; Zbyszewski & Corcoran, 2011; Zbyszewski et al., 2014; Frias et al., 2016). Spectroscopy is the study of the interactions between matter and electromagnetic radiation. In theory, three types of interaction can be described when a photon encounters a molecule or other type of particle. The first, termed Rayleigh scattering, is an elastic scattering by which the incoming photon is adsorbed and is emitted with the same energy. The second, termed Stokes shift, is an inelastic scattering by which the energy of the incoming photon is decreased because some of the energy is transferred to the molecule changing its vibrational state. The third type, termed Anti-stokes shift, is also an inelastic scattering, but where the incoming photon is adsorbed by a molecule which is already in increased energy vibrational state. The interaction causes the molecule to return to the normal vibrational state and the vibrational state energy is transferred to the emitted photon, which, as a result, has a greater energy relative to the incident photon. The shift in energy, Raman shift, of the incident light is dependent on the vibrational, rotational and other low frequency modes of the molecule. The second and third types of interaction are referred to as Raman scattering. Only about 0.001% of incident light interacting with a particle is scattered inelastically; the majority of the incident light is scattered elastically.

Raman spectroscopy is an analytical technique in which the Raman, i.e. inelastic, scattering of light by interaction with a molecule is detected to reveal information about the structure and properties of the molecule. It can be employed for the identification a wide variety of organic and inorganic substances and is well-suited to identification of polymers and other components of plastics. Several studies have used Raman spectroscopy to aid in the identification of microplastic particles (e.g. Imhof et al., 2012; Cregut et al., 2014; Lenz et al., 2015).

Modern Raman spectroscopic technique relies on the use of a monochromatic laser, generally in the near infrared (NIR), visible or near ultraviolet (NUV) range, a filter to remove the Rayleigh scattered light, and an instrument which detects the incoming Raman scattered light. The use of a monochromatic laser light source allows for all Rayleigh scattered light to be completely filtered out and the Raman shift to be accurately measured relative to the laser light. Several advanced types of analytical instruments involving Raman spectroscopy have been developed; here two common types which differ in the methods by which the Raman signal is detected, and which are used in this study, are further discussed.

Dispersive Raman is a technique which uses a grating, a device with finely etched grooves, to spread the Raman scattering spectrum of a sample across the range of wavelengths making up the spectrum, similar to the way in which a prism sorts incoming visible light across a larger area, organizing the light rays by wavelength. The Raman scattered light is detected by a silicon charge coupled detector (CCD) which converts the electromagnetic radiation into an electrical signal which can be read by a computer and displayed as a plot. Dispersive Raman spectroscopy is particularly useful for analyzing small particles, achieved by using in combination with a confocal aperture. Lasers which emit light in the visible range are used with dispersive Raman spectroscopy, with higher energies (i.e. shorter wavelengths, blues) giving a stronger signal and also higher probability of fluorescence (Thermo Fisher Scientific Inc., 2008).

Fourier Transform Raman (FT-Raman) spectroscopy is an alternative technique which uses much lower laser energies, generally in the near infrared range, in order to overcome the effect of fluorescence at higher laser energies. In FT-Raman technique a device called an interferometer is used to convert Raman scattered light into an interferogram signal during analysis. An interferogram is a pattern formed by the interference of multiple waves, e.g. Raman scattered electromagnetic light waves. The interferogram is transferred to an infrared signal by a material which responds to infrared light, such as Geranium or the semiconductor, indium gallium arsenide (InGaAs). The resulting electrical signal of the interferogram is converted to the Raman spectrum using the Fourier Transform algorithm (Thermo Fisher Scientific Inc. 2008).

The measured light intensities are plotted against the wavenumber, commonly in units of $cm^{-1}$ which indicate the energy difference between the laser light and the Raman scattered light. The resulting substance specific spectrum is the cumulative energy intensity detected for each wavenumber, i.e. the energy distribution of inelastic light scattered by the sample upon illumination with a monochromatic laser. The energy intensity which is relative to the amount of material present (Thermo Fisher Scientific Inc. 2008), is arbitrary and is commonly unlabeled or labeled with ‘Raman intensity’.

Another type of spectroscopy commonly used to analyze synthetic polymers is Fourier transform infrared (FTIR) spectroscopy. It is an analytical procedure in which a substance can be identified from the unique absorbance or emission spectrum of infrared radiation across a large range of wavelengths that is transmitted through a sample. It is useful in the identification of polymers as it can provide information about the molecular structure of the material as well as about the level of oxidation of the material (Löder & Gerdts, 2015). Comparison of the fingerprint region of the infrared spectrum to spectra of known materials allows for the identification of the polymer, whereas higher frequencies of the infrared spectrum signal functional group vibrations through which the presence of certain types of photo-oxidation products can be identified (Cooper, 2012).

Raman spectroscopy is useful for the analysis of microplastics, however, there are several limiting factors. Analysis can be completed without sample preparation or contact with the sample, allowing for preservation of the sample. Run times range from as little as several seconds to several minutes, with longer run times improving the resolution of the spectra. In addition, thick materials can be analyzed as the technique does not rely on the penetration of light through the sample, as in infrared spectroscopy (Lenz et al., 2015). Conversely, thin particles may give poor spectra due to lack of volume and low Raman scattering signal. Technological advancements have allowed for laser spot sizes of < 1 μm allowing for very small particles of plastic and fibres to be analyzed; however, instruments with larger spot sizes limit the size of particles measured. Symmetric, non-polar bonds produce stronger Raman scattering than polar bonds, which are better analyzed with FTIR spectroscopy.

Limitations of Raman spectroscopy arise for fluorescent materials, as the intensity of fluorescent light emitted upon illumination with laser light is often much higher than the Raman scattered light, masking the spectrum of the other substances in the material (Fredericks, 2012). (Lenz et al., 2015) reported the effect of pigment additives on the Raman spectra of variously colored particles of industrially supplied ABS plastic. Whereas blue, black and white colored particles had spectra similar to pure ABS, the spectra of red and yellow particles were strongly masked to a degree at which the spectra could not be positively identified. Other additives, such as black carbon in rubbers and titanium dioxide as a mineral filler and UV-degradation inhibitor were encountered. In these examples, the fillers did not effect signal quality but ability to match materials to those with known spectra was negatively affected as additional peaks were present and could potential obscure peaks needed to confidently identify a polymer. Dark colored materials also pose challenges as such materials absorb much of the light energy of the laser, and often have the tendency to combust even at very low laser power (Lenz et al., 2015).

Song et al. (2015) reported negative effects on FT-IR spectrum quality of microplastics from weathering and surface contaminations, and Lenz et al. (2015) reported similar effects in Raman analysis. Biofouling and adherence of mineral particles to the surfaces of microplastic particles, particularly of those with textured surfaces, has been regularly mentioned in the literature (e.g. Artham et al., 2009; Reisser et al., 2014). Lenz et al. (2015) show that the presence of biological organic matter on the surface of a particle masked the Raman spectrum particularly in the fingerprinting region, hindering spectral analysis, matching and polymer identification, and suggesting the importance of taking measures to clean particles before analysis and to use uncoated spots on particles for compositional identification.

Spectral libraries are generated from analysis of pure substances. The spectra of certain types of polymers have been shown to diverge from those of the unaltered material with progressive degradation and exposure to UV radiation (Lenz et al., 2015). In the study by Lenz et al. (2015), PE, PVC, PA and PET plastics were subjected to UV exposure under air, freshwater and saltwater conditions to investigate Raman spectral changes due to weathering. PE and PVC polymers were most strongly affected, with decreases in the intensity of characteristic peaks. In PVC plastics exposed to over 1600 simulated midday sun hours of UV exposure, the characteristic peaks in the fingerprinting range at 693 and 637 cm$^{-1}$ (C-Cl bonds) were no longer observable compared to particles exposed to ~700 and fewer simulated midday sun hours, and two additional peaks at 1139 and 1540 cm$^{-1}$ (C=C bonds) appeared.

Spectroscopic analysis is a time-consuming procedure often requiring sample preparation of individual particles, scanning, and manual spectral analysis by an expert. In addition, studies have shown that correct visual identification of plastic particles decreases with smaller particles (Lenz et al. 2015; Song et al. 2015) Improvements in the automation of spectral analysis may allow for increased accuracy and greater amounts of particles to be analyzed in studies of microplastics. Some attempts at improving spectral analysis efficiency have already been made. FTIR spectrometers coupled with attenuated total reflectance (ATR) capabilities allows for larger surfaces to be scanned in a single run (Cooper, 2012). Some studies have used this technique to scan filter papers, on which microplastics were retained from samples, to determine the presence and types of plastic present (e.g. Vianello et al., 2013; Song et al., 2015). Another recent study, investigated the applicability of thermal decomposition to the determination of PE, and its degradation properties, in environmental solid samples (Dümichen et al., 2015).

In this study, X-ray fluorescence (XRF) is used as an alternative compositional analysis tool to confirm the presence of chlorides in suspected polyvinyl chloride plastics, as well as to look for inorganic fillers. XRF is an application which detects the presence of elements (typically heavier than silicon) in a sample by measuring the fluorescence energy released when a sample is bombarded by X-rays. XRF has not been used in microplastics identification studies, as present in the literature however, it has been used in applications involving plastics, for example in industry for quality control and manufacturing purposes (Mans et al., 2007) and in forensics (Roux and Lennard 2006).

# Chapter 3

# 3 Regional setting

The Laurentian Great Lakes are situated on the North American continent across the Canadian-USA border. The five lakes have a combined watershed of ~770,000 km$^2$ and make up the largest freshwater system in the world (Larson & Schaetzl, 2001). The five lakes—Superior, Michigan, Huron, Erie, and Ontario—are connected by a series of rivers, and cover an elevation change of 109 m. As the terminal lake within the system, Lake Ontario outflows to the North Atlantic Ocean through the St. Lawrence River. Lake Ontario is the smallest lake by surface area, covering 19000 km$^2$.

The Great Lakes basins were formed by repeated glacial scouring during the late Cenozoic (Larson & Schaetzl, 2001). Geological and biological deposits evidence at least six glacial advances and retreats having occurred between ~10 and 78 ka, during the most recent, Wisconsonian, glaciation (Richmond & Fullerton, 1986).

## 3.1 Lake Ontario and the St. Lawrence River

This study focuses on the nearshore, tributary and beach zones of Lake Ontario and the upper St. Lawrence River along the Canadian shoreline which lies within the province of Ontario. The working definition for the nearshore zone in this study refers to the coastal region of the lake where the lake bottom is between 0-25 m below the water surface. Along the perimeter of Lake Ontario, the nearshore region generally extends < 7 km offshore, making up ~10% of the total area of the lake (Rukavina, 1976). Toronto Harbour, Humber Bay and Hamilton Harbour, which are focus points in this study, are within the nearshore zone. The tributary zone, as referred to in this study includes the benthic and riparian zones of input tributaries, from small coastal streams to large riverine systems. Tributary sediment investigation was constrained to the near-lake region (< 10 km from the tributary mouth on the lake) for input streams, however, the entire direct drainage area of the lake and upper river is included in geographical investigations of population and industry levels of the region. The upper St. Lawrence River, from Lake Ontario to the eastern extent of the province of Ontario is ~ 1 km wide at the narrowest sections and up to 20 m deep along much of the central axis (Paturi et al., 2012). The sediments sampled in the St. Lawrence are considered together with the nearshore samples because of the large scale of the river and the lack of a defined transition point between the lake and river. The beach environments considered in this study are constrained to the sandy shoreline on the northwestern shore of the lake.

### 3.1.1 Geology of the Lake Ontario region

The surficial sediments of the lake are described as mainly glacial deposits and soft sediments eroded from the surrounding regions (Rukavina, 1976). Post glacial sediments are primarily sourced from eroding shorelines, as opposed to stream discharge and the erosion of glacial sediments, based on grain size distribution. Sediments at the west end of the lake near Hamilton City may be sourced from easterly cross-lake storm events, whereas sediments in Toronto and Wellington are more likely sourced from shoreline erosion (Rukavina, 1976). Although the bed-load transport component of stream discharge was shown to be a negligible factor in sediment supply and transport to the lake (Ongley, 1973), fine-grained fractions may be attributed to the suspended load of tributaries (Kemp & Harper, 1976). Silt and clay-sized sediments may also be sourced from the winnowing, transport and re-deposition of bottom sediments during storm events, as is suggested to occur in offshore zones (Halfman et al., 2006).

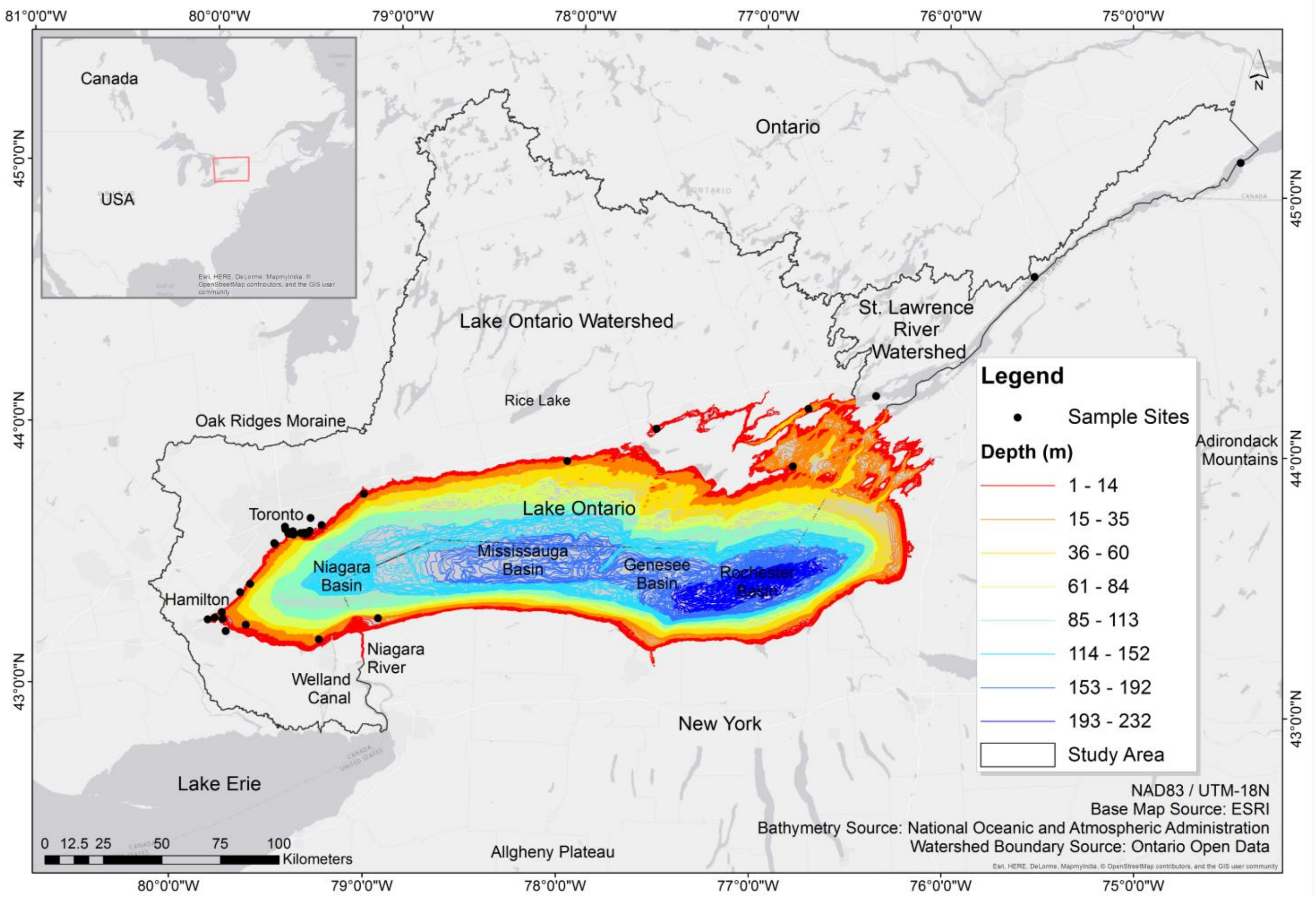

**Figure 3.1** Bathymetry of Lake Ontario and watersheds draining directly to Lake Ontario and the upper St. Lawrence River from within the province of Ontario.

Sedimentation rates in near shore areas of the western basin of Lake Ontario are estimated to be ~ 1.7 mm $yr^{-1}$ based on pollen dating of Ambrosia (Rukavina, 1976). Alternatively, sediment accumulation rates as calculated from sediment bed thickness and the age of the lake, are 0.3, 0.4, 0.5 and 0.7 mm $yr^{-1}$ at Toronto, Niagara, Wellington and Hamilton, respectively. Offshore depositional basin sedimentation rates calculated from $^{210}Pb$ dating are between 0.9 - 4.3 mm $yr^{-1}$ (0.03 – 0.08 g $cm^{-2}$ $yr^{-1}$) with mixing depths up to ~50 mm (1 g $cm^{-2}$) (Wong et al., 1995). Similar palynological data for offshore sedimentation rates based on Ambrosia pollen dating ranged between 0.3 – 2.2 mm $yr^{-1}$ (0.009 - 0.1 g $cm^{-2}$ $yr^{-1}$) (Kemp & Harper, 1976). Both palynological and radiometric dating of offshore sediments indicate higher sedimentation rates in the offshore zones compared to the nearshore depositional zones.

### 3.1.2 Hydrology of Lake Ontario and the St. Lawrence River

Lake Ontario directly drains an area of approximately 64,000 $km^2$, half of which is within the province of Ontario. The St. Lawrence River is the sole outflow point of Lake Ontario, and itself drains an area of ~4900 $km^2$ within the province of Ontario. The primary inflow route to Lake Ontario is the Niagara River which drains Lake Erie and supplies roughly 50% of the suspended sediment load of Lake Ontario (Kemp & Harper, 1976). The Welland Canal is a shipping corridor between Lakes Erie and Ontario through which microplastic contamination may spread. The watershed of Lake Ontario is bounded by the Adirondack Mountains to the east and the Allegheny Plateau to the south. The Oak Ridges Moraine, which runs parallel to the northern shore between the Niagara Escarpment to the west and Rice Lake to the east, defines the drainage catchment area of the north west end of the lake. The Trent River waterway extends ~175 km north of the central part of the lake. Along the St. Lawrence River, the direct drainage area is confined to within ~40 km to the north (Fig. 3.1).

Flow influx into the lake constitutes approximately 273 $km^3$ $yr^{-1}$, on average as calculated from a retention time of 6 years and a lake volume of 1640 $km^3$. Lake Ontario outflows are monitored at the Moses-Saunders Power Dam, regulated by the International St. Lawrence River Board of Control (ISLRBC). Flow rates ranged between ~5000-9000 $m^3$ $s^{-1}$ between the years 2011 and 2015 (ISLRBC, 2016a). Seasonal weather variations in water levels are dependent on evaporation rates, influxes from Lake Erie through the Niagara River and regional precipitation levels (ISLRBC, 2016b). Water level peaks are observed during the spring months due to snow melt and low evaporation rates, and minimum water levels are observed during the late fall and early winter when evaporation rates are highest (ISLRBC, 2016b). Watershed influx levels are related to drainage area; the Niagara River is the largest drainage flux into Lake Ontario at ~5,800 $m^3 s^{-1}$ (Hornlein et al., 2004, p. 97). In comparison, some of the larger watersheds in the Toronto region have much smaller discharge rates; the Humber River average total flow is 6 $m^3 s^{-1}$ (TRCA, 2008, p. 16) and the Don River average total flow is 4 $m^3 s^{-1}$ (TRCA, 2009, p. 10). The Trent River, which is the largest watershed in the study region has an average flow of 140 $m^3 s^{-1}$ measured at the Glen Miller Generating Station (IESO, 2016).

Annual water level fluctuations in Lake Ontario are < 2 m (Gronewold et al., 2013). Localized increases and decreases in water levels can be driven by lake scale storm-induced standing waves called seiches (ISLRBC, 2016b). Storm events in Lake Ontario are primarily easterly, generally parallel to the major axis of the lake, with the long fetch allowing for severe storm waves to build up in the west (Rukavina, 1976). Surface water circulation within the lake is predominantly cyclonic in the summer and winter months, with an anticyclonic system along the north-west shore between Toronto and Prince Edward County (Beletsky et al., 1999). A more recent investigation of Lake Ontario water circulation patterns reveals that depth averaged summer circulation is characterized by greater flow velocities in the nearshore zones compared to offshore (Hall, 2008). Westward along-shore currents were simulated in both the north and south coastal regions in the west half of the lake in 2006, and were consistent with the circulation models suggested by Beletsky et al. (1999). Rao & Murthy (2001) report stronger along shore current velocites (max 30-40 cm $s^{-1}$) than cross shore current velocities (max 10-20 cm $s^{-1}$) as measured using an array of moored current meters and Lagrangian drifter experiments. The strong coastal currents described for Lake Ontario explain the patchy and relatively thin postglacial sediment layer in the nearshore zone described by Rukavina (1976). Offshore and onshore wind patterns causing upwelling and down-welling vertical water structures, respectively, have been observed in Lake Ontario, however, whether and how sediment transport is affected by such coastal regimes is not clear (Rao & Murthy, 2001).

## 3.2 Human geography of Southern Ontario

The Canadian shoreline, from the Niagara River outflow on the western end of the southern shore along the northern shore to the outflow of the St. Lawrence River, is characterized by heavy industrialization and several urban regions and the Toronto megacity. Due to high population densities in the Greater Toronto Area, we expect greater accumulations of microplastics in the near shore, tributary and beach sediments of this region.

### 3.2.1 Human population

The western end and the northwestern shore of Lake Ontario are characterized by several urban and industrial regions, including the cities of Hamilton and Toronto, with populations of 0.52 and 2.62 million, respectively. In addition, the Regional Municipality of Peel is located adjacent to western Toronto, and comprises the cities of Mississauga, Brampton and Caledon. Mississauga and Brampton are the second and third largest cities in the Golden Horseshoe region (3rd and 4th largest in Ontario, after Toronto and Ottawa). The combined population of the Region of Peel as of 2011, was 1.3 million.

### 3.2.2 Industrial activity

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, PS, PVC, polyacrylamides, PET, nylons, latex emulsions, polyesters, silicones and butyl and halobutly 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, ~3,500 kt of PE were produced in 2013 (CIAC, 2014, p. 34). Plastics-related industrial activity is often confidential and not shared publicly, complicating investigation into annual production volumes.

### 3.2.3 Recent policy developments concerning plastics

In response to increased public awareness of the proven and potential harmful effects of plastics, organizations and governments have been acting to reduce the flux of plastics contamination into the Great Lakes environment. In the USA the manufacture, sale and import of cosmetic and personal care products containing plastic beads < 5 mm in size was recently banned through the Microbead-Free Waters Act of 2015. In Canada, the governmental association Environment Canada is in the process of considering a similar ban, but for plastic particles < 2 mm in size, through the addition of such plastics beads on the Toxic Substances List of the Environmental Protection Act of 1980. As per current discussion, medical products would be exempted from the ban, as well as products and applications not included in the personal care and cosmetics industry, for example, industrial abrasives and printing media (Pettipas et al. 2016). Microbeads, however, only comprise a fraction of the microplastics load entering the environment: 58% of microplastics <1 mm in surface waters of Great Lakes as reported by Eriksen et al. (2013). Pettipas et al. (2016) provides a review of current regulations on macroplastics and microplastics and discusses potential future options for Canadian policy developments aimed at reducing plastic waste.

Organizations such as Stewardship Ontario and Recycling Council of Ontario are working together with providers to improve recycling rates and waste diversion from landfill. For example, 5 grocery companies have transferred to using only labeled PET polymer type rigid, clear packing clamshells in store packaging of food items in effort to increase the PET recycling stream and provide a marketable supply to recycling companies.

## 3.3 Municipal solid waste management in Ontario, Canada

Although many objects can be repurposed or reused, plastics made up 11% of the waste stream on average across all coastal countries, with an estimated 275 million metric tonnes for the year 2010 (Jambeck et al., 2015). Canada had an urban population of ~21 million in 2012 as calculated by the World Bank, and generated ~2.3 kg of municipal solid waste per capita per day, an estimated 4% of which was plastic (Hoornweg &

Bhada-Tata, 2012, p. 80). The human population in the Golden Horseshoe region was ~8.7 million in 2011 (Statistics Canada, 2013). Assuming similar waste generation levels as calculated by the World Bank and that 2% of the waste generated becomes littered, ~5,800 tonnes of plastics may have been littered in the Golden Horseshoe region in 2011. Littered plastic waste, due to its buoyancy and light weight characteristics, can be washed or wind-blown into tributary systems leading downstream or directly into nearby waterbodies. It can be expected that a significant amount of plastic waste enters Lake Ontario, each year due to this process. The municipal solid waste management systems for three of the largest municipalities in the Golden Horseshoe region are discussed in further detail.

In Toronto, solid residential waste management is organized to include several waste diversion streams for materials that can be reused or recycled. Apart from the Blue Bin recycling program, diversion streams account for compostable wastes (the Green Bin program), electronics, large appliances, hazardous wastes, tires. The Blue Bin recycling program accepts most metal containers and plastic items including foamed polystyrene and films such as bags and overwrap, except black plastics, laminated materials such as chip bags and squeeze tubes, multi-material items such as toys, compact-discs, electronics, and fibrous items such as clothing. Residential waste produced in Toronto decreased from 2007-2014 from ~500,000 tonnes to ~380,000 tonnes at the same time as diverted materials increased from ~370,000 to 420,000 tonnes. Total waste tonnage during this period decreased by ~65,000, while the percentage of the total tonnage that was diverted increased from 42 to 53% (City of Toronto, 2016).

Solid waste collection and management for the Cities of Mississauga, Brampton and the Town of Caledon are organized collectively by the Region of Peel municipality. Solid waste collection in the Region of Peel is similar to that of Toronto; organics, yard waste, and recyclables are collected in separate waste streams. The Blue Bin recycling waste stream includes most plastics as well as paper, glass and metal packaging items. Accepted plastics include most food and household product containers as well as films, bags and foamed polystyrene. The most recent data regarding waste generation and diversion rates are statistics for 2010, when ~20% of the total waste stream was diverted through the Blue Bin recycling program (Regional Municipality of Peel, 2012). Specific percentages or tonnages for plastic waste were not found.

In the City of Hamilton, the solid waste collection and management system comprises organics, yard waste, and recycling waste diversion streams that operate alongside the non-diverted landfill stream. Acceptable plastic items include most food packaging items including bags, films and foamed polystyrene. According to a report published by the City of Hamilton in 2013, plastics made up 8.6% (~18,700 tonnes) of the total 216,000 tonnes of generated residential waste in 2010 (City of Hamilton, 2012). An estimated average diversion rate for plastics was 30%, suggesting the potential for improvements in the amount of plastic items that could be recycled. Between 2002-2010, total annual waste generated was approximately halved, from 226,000 tonnes to 111,000, and percentage of diverted waste doubled from 21% to 49%.

# Chapter 4

# 4 Methodology

A total of 50 sediment samples were collected from the nearshore, tributaries and beaches along the Canadian shoreline of Lake Ontario. Samples were processed using a density separation technique to isolate organic material from inorganic sediments. Additional beach quadrat and transect surveys of visible plastic debris were conducted on five beaches and four tributary banks along the Canadian shoreline of Lake Ontario. Visual and spectroscopic analyses were employed to identify microplastic abundance and composition. Geospatial analysis was conducted with GIS software to explore relationships between microplastics data and geographic data of the lake and the surrounding region.

## 4.1 Sample collection

Nearshore, tributary and beach sediments were sampled using sediment trap, core and grab sampling techniques (Appendix A). In addition, beach surveys including transect and quadrat type geometries were conducted to investigate visible (> 1 mm) microplastic and macroplastic contamination of sandy beaches (Appendix C-G).

### 4.1.1 Nearshore sediments

A total of 25 nearshore lake-bottom sediment samples were collected from 21 stations (Nearshore Index and Reference sites, Great Lakes Nearshore Monitoring Program, Ontario Ministry of the Environment and Climate Change) along the length of the Canadian shoreline of Lake Ontario in the summer months of 2012 and 2014 (Fig. 4.1). Samples were collected using a Shipek sediment grab with a 400 $cm^2$ square opening and a half cylindrical cup of radius 10 cm (Wildco, Yulee, FL). Three replicate grabs were collected at each station, homogenized in a metal tray and transferred into 0.5 L PET collection bottles. Sediments were sampled from the nearshore regions of Six Mile Creek, Port Dalhousie, Stoney Creek, Hamilton Harbour (*N*=3), Sixteen Mile Creek in the town of Oakville, Humber Bay (*N*=3), Toronto Harbour (*N*=3), Pickering, Chub Point, Trenton, Prince Edward County, the North Channel, McDonnell Bay, Prescott, Lake St. Francis (clockwise along the lake perimeter starting from the southern shore, Fig. 4.1).

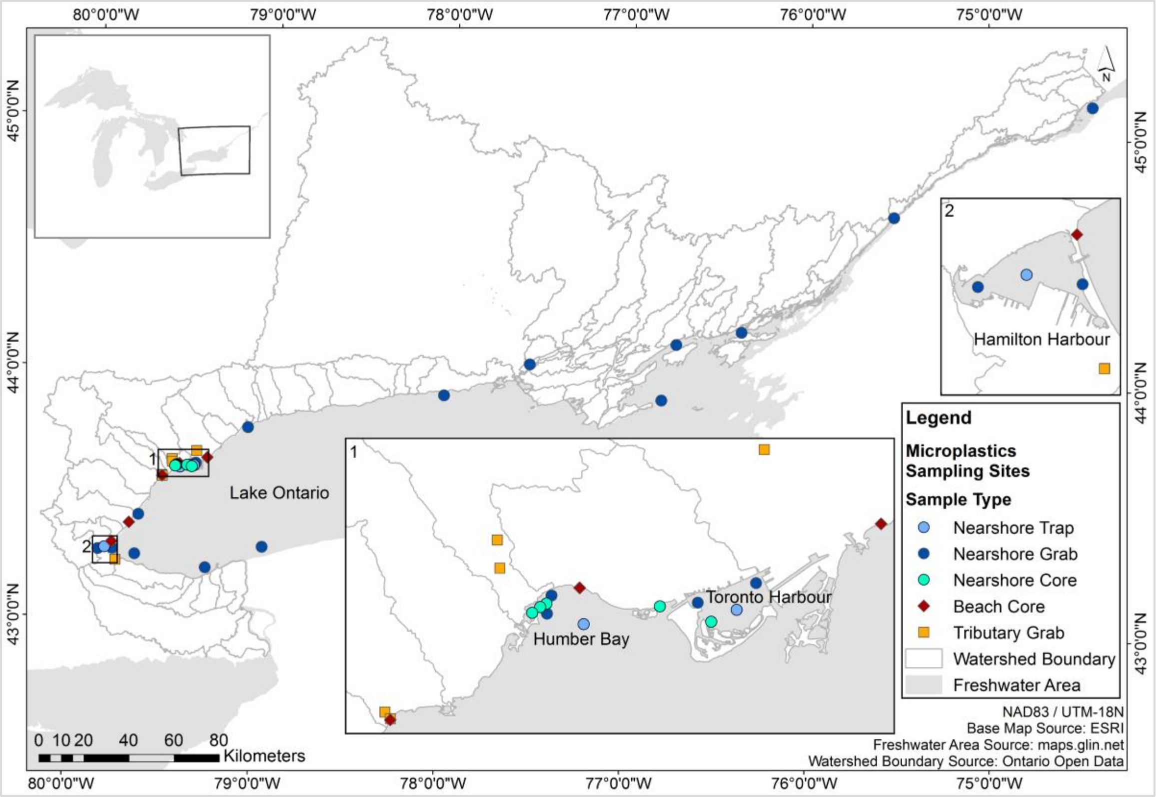

**Figure 4.1** Sediment sampling locations in the nearshore, tributary and beach depositional zones of Lake Ontario and the upper St. Lawrence River.

Sediment traps (*N*=3), each an array of four PVC cylinders, were deployed in Humber Bay, Toronto Harbour and Hamilton Harbour in May 2014 and retrieved November 2014 (Fig 4.1). Traps were secured at approximately 2 m above the lake bottom sediment. Three cylinders were analyzed for microplastics and the fourth for sediment grain size distribution.

Five additional nearshore sediment samples were collected using a Glew gravity corer. Two were collected in Toronto Harbour, one in the walled mooring harbor adjacent to Coronation Park and one in the Toronto Inner Harbour next to Muggs Island. Three cores were collected in Humber Bay along the shoreline of Humber Bay Shores Park. The PVC corer measured 6.5 cm in diameter, and sediment cores ranged between 6 and 15 cm in depth. Core depth variation is attributed to sampling difficulties including high wave action during sampling as well as sediment consistency. Cores were capped, stored upright, immediately extruded into 1 cm intervals and stored in sealed polyethylene bags. All samples were kept cool until return to the laboratory where they were stored at -25 °C until analysis. The glass transition temperature is the temperature at which plastics harden and stiffen, below which, no further transitions are expected

The glass transition temperatures for common polymer types range between 100 and -100 °C. Freezing at -25 °C should not have a detrimental effect of the preservation of microplastics (Zeus Industrial Products, Inc., 2005)

### 4.1.2 Tributary sediments

Tributary sediment from Red Hill Creek, Etobicoke Creek, Humber River and Don River (Fig. 4.1) were sampled with a hand-held stainless steel Petite Ponar sediment grab, 16 x 14.5 cm in dimension (Wildco, Yulee, FL) in summer 2015 by wading or lowering the instrument from a bridge. Caution was taken to avoid sediment disturbance during wading, by approaching sample sites from the downstream direction. Sample location was constrained foremost by accessibility and second by the presence of a sediment depositional environment. At each of seven sample locations, two grab replicates were homogenized in a metal tray and spooned into 0.5 L PET collection bottles.

The Don River sediment sample (DR-1) was taken on a straight section of the river along the wooded Lower Don River Trail in the Toronto Region. This section of the river was directly downstream from a rocky section and water flow was rapid. The sample was collected from the subsurface sediments adjacent to a sandy bar along the riverbank where the flow was slow and pooling. The Humber River was sampled in two locations; sample HR-1 just upstream from the Old Mill Bridge, and sample HR-2 near Kings Mill Park, about one kilometer downstream from the Old Mill Bridge. Sample HR-1 was taken from along the outer bank on a wide curve in the river course where boulders surrounded an accumulation of sandy sediment. Along this stretch of the Humber River, flat cobbles dominated the sediment of the river bed, which were exposed in many regions in the low flow conditions. In the region immediately adjacent to the sample, a coffee cup lid, a large plastic sheet, an aluminum can and a plastic bag were observed. A heavy 30-minute rain storm occurred between sampling of HR-1 and HR-2. Sample HR-2 was taken along a straight section of the river which was also noticeably narrower and deeper than where sample HR-2 was taken. Sediments were collected adjacent to the riverbank, where thick sediment deposition had accumulated. Etobicoke Creek was sampled along a straight section of the river inside of Marie Curtis Park. Sample EC-1 was taken from a thin sediment bar exposed slightly at the crest located within about 500 m of the creek mouth on Lake Ontario. The river bed was rocky with predominantly flat angular cobbles. Sample EC-2 was collected from the concrete jetty extending the river mouth into the lake. The sample comprised a large cobble covered in algal growth. The Red Hill Creek samples were collected along a gently curved section of the tributary adjacent to Globe Park and about 3 km from the creek mouth at Hamilton Harbour. Flow was low enough to allow for wading across the creek. Sample RC-1 was collected from the inner bank along a bar of coarse grained sand and pebbles. Sample RC-2 was taken 50 meters downstream from the outer bank where sediment had accumulated over the hard substrate. All samples were kept cool until return to the laboratory where they were stored at -25°C until analysis.

Quadrat surveys were conducted at each tributary (Fig. 4.2 and 4.3 f-j) in summer 2015, for which plastics debris visible with the naked eye, including microplastics < 5 mm and macroplastics > 5 mm were collected by hand from the top 3 cm of sediment. Two quadrats of dimension 2 x 2 m were staked out at random on each tributary bank in the vicinity of the sediment grab sites and sampled once. All samples were kept cool until return to the laboratory where they were stored at -25°C until analysis.

### 4.1.3 Beach sediments

Beach sediments were collected from five beaches located on the northwestern shore of Lake Ontario between Burlington and the eastern extent of Toronto; Beachway Park, Bronte Beach, Marie Curtis Park, Sunnyside Beach and Woodbine Beach (Fig. 4.2) in summer 2015. Much of the Canadian shoreline of Lake Ontario is built-up with large boulders or is inaccessible due to privatization of lands, which limited sampling to public sandy beaches.

Using a stainless-steel split-spoon corer with a maximum depth of 30 cm, cores were collected from each beach (Fig. 4.1) along a transect perpendicular from the shoreline. Two cores were taken on each transect at approximately 2 m and 6 m from the water's edge to represent the proximal and distal foreshore. The foreshore sediments were observed to be periodically submerged with changes in water level due to storm surges. The core was equipped with an inner segmented PVC core, each segment measuring 10 cm thick and having a ~ 5 cm inner diameter. Upon opening the core, each segment was capped with a PE cap. All proximal foreshore sites, except at Marie Curtis Beach, were limited to a sampling depth of 20 cm due to the high water content below that depth.

Beach transect and quadrat surveys were conducted at each beach (Fig. 4.2) in summer 2014, for which plastics debris visible with the naked eye, including microplastics < 5 mm and macroplastics > 5 mm were collected by hand from the top 3 cm of sediment. Along a 50 m transect parallel to the water's edge, six 1 m wide swaths were marked at 0, 10, 20, 30, 40 and 50 m. The sediment was searched for visible plastic debris from the water's edge to the upper extent of the beach as constrained by the presence of vegetation or a structure, such as a boardwalk. Transects were positioned such that the midpoint of the transect line (25 m) coincided with the axis of the core samples.  Two quadrats of dimension 2 x 2 m were staked out at random on each beach, except at Beachway Park where four quadrats were staked out. Quadrats were either proximal (at or below the strandline) or distal (above the strandline) from the summer fair-weather waterline. Each quadrat was sampled for visible plastics debris daily over a period of 8 days. All samples were kept cool until return to the laboratory where they were stored at -25°C until analysis.

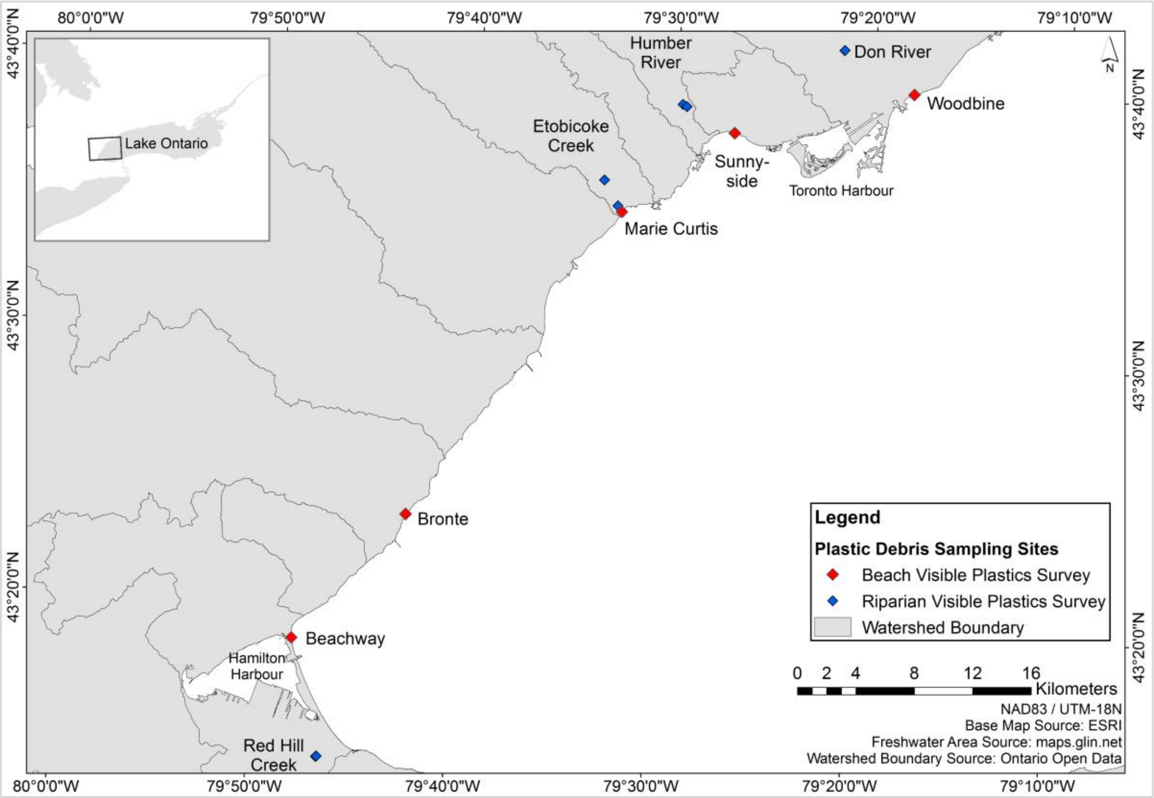

**Figure 4.2** Locations of beach transect and quadrat surveys and tributary quadrat surveys for visible plastic debris on the northwestern shore of Lake Ontario.

Beachway Park is a 2 km long sandy beach located at the western extent of the north shore of Lake Ontario adjacent to Hamilton Harbour. It is located within the city of Burlington and is highly attended during summer weekends and holidays. Bronte Beach is located in Oakville at the mouth of Bronte Creek where a boating harbor is located. The bayed, 100 m long beach faces mainly to the east, with the northern extent facing south and bordered by a seawall. The sand was notably shelly. Marie Curtis Beach is located in Mississauga between the mouth of Etobicoke Creek to the northeast and the mouth of a smaller coastal runoff creek to the southwest. The beach is about 400 m long and the sediment is medium grained sand with dispersed pebbles and small cobbles. There was visible debris accumulation along the northeast concrete jetty wall. Sunnyside Beach is located in Toronto along the midsection of Humber Bay, just east of the Humber River mouth. The beach is sandy and protected by a sectioned seawall ~ 100 m offshore. The beach is heavily attended in the summer months. Woodbine Beach, located on the eastern extent of Toronto is a popular spot for beach-goers in the city. The beach is south-east facing and embayed. Samples were taken along the narrow north-eastern section of the beach. Sediment was medium grained to cobble-sized. Woodbine Beach, located on the eastern extent of Toronto is a popular spot for beach-goers in the city. The beach is south-east facing and embayed. Samples were taken along the narrow north-eastern section of the beach. Sediment was medium grained to cobble-sized.

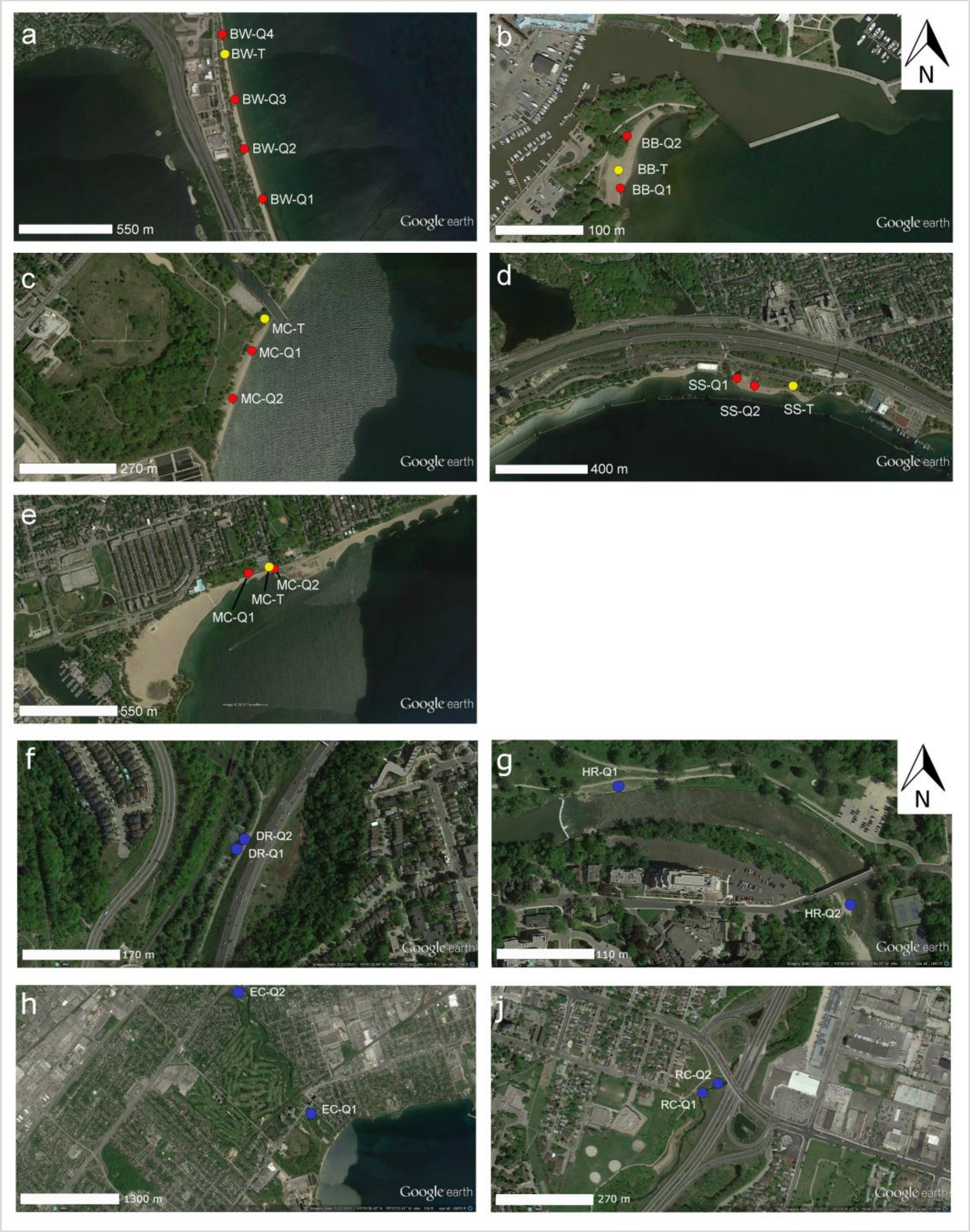

**Figure 4.3** Locations of beach transect midpoints (yellow), beach quadrat (red), and tributary quadrat (blue) surveys for visible plastic debris on the northwestern shore of Lake Ontario: (a) Beachway Beach, (b) Bronte Beach, (c) Marie Curtis Beach, (d) Sunnyside Beach, (e) Woodbine Beach, (f) Don River, (g) Humber River, (h) Etobicoke Creek and (j) Red Hill Creek.

## 4.2 Microplastics quantification

Two procedures were used to separate microplastics from the sediment. The original method, used on the nearshore gravity core samples, was modified to increase sample preservation, efficiency, and reduce potential contamination. Remaining samples, including nearshore grab and core sediments, tributary grab sediments and beach core sediments, were processed following the modified methods. Beach transect and quadrat survey samples, in which plastics were already separated from sediment, were processed separately from the sediment samples.

### 4.2.1 Nearshore gravity core and select grab samples

Nearshore sediments sampled using the gravity corer, and three grab samples, S3031-3 were analyzed following the original procedure outlined in this section. The samples were thawed then transferred to aluminum pie trays and dried at 70 °C. The sediment was transferred to a glass beaker containing 250 mL deionized water and magnetically stirred for 2 minutes. Once settled for a minimum of 5 minutes (longer for samples with a high clay content), the supernatant was decanted and filtered through VWR® Grade 114 qualitative fast flow 25 $\mu$m filter paper and washed into a clean beaker to dry at 70 °C. Dried contents were then transferred to a glass beaker containing a 1.5 g cm$^{-3}$ solution of sodium polytungstate (SPT), and the stirring and decanting procedure was repeated. Samples were covered tightly with aluminum foil until visual processing. Following density separation, sediments were wet sieved through a 0.063 mm mesh then dried and weighed to determine the silt and clay content of the samples.

### 4.2.2 Nearshore grab and trap samples, tributary grab samples and beach core samples

The remaining sediment samples were processed using the following revised method. Samples were thawed, transferred to aluminum pie trays, dried at 70°C, and weighed. Each sediment sample was then analyzed for grain size using a Taylor sieve shaking apparatus with sieve mesh sizes of 5.6 mm, 2.0 mm, 0.063 mm for 5 minutes 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 clay fraction.

Following shaking, each fraction was weighed, the >2 mm and >5 mm fractions were visually examined for microplastic, and the >0.063 mm fraction was transferred through a sample splitter. Half of the >0.063 fraction was then transferred to a beaker containing a 250 mL of 1.5 g $cm^{-3}$ solution of SPT in order to separate microplastics and other organics from inorganic sediments. The sample was stirred for 2 minutes then transferred to a glass separation funnel, using more SPT solution to rinse entire contents of beaker into the funnel. Once sediment had settled, non-buoyant material was allowed to pass through the funnel spout. Buoyant material was subsequently drained through a polycarbonate/polyester 0.053 $\mu$m sieve, rinsed thoroughly then transferred to a second separation funnel containing 500 mL of filtered deionized water in order to separate microplastics with a density of > 1 g $cm^{-3}$ from those with a density < 1 g $cm^{-3}$. After samples had settled, the non-buoyant and buoyant fractions were consecutively drained through a polycarbonate/polyester 0.053 $\mu$m sieve and transferred to glass vials. Samples were dried at 70°C, then covered until visual processing.

### 4.2.3 Visual Identification of microplastics isolated from sediments

Potential microplastics were visually identified using a Nikon SMZ1500 stereo microscope at a magnification of between 15× and 225×. Material that was buoyant in the SPT solution, but not in the filtered deionized water, was marked as high-density (HD) and was visually processed separately from the low-density (LD) material (expected to be low density plastics that were deposited though increases in density) that was buoyant in water. Particles which were visually identified as microplastics were counted and sorted by type into three categories: fibres, fragments, and spherical beads. All counted particles were photographed using a Nikon digital camera DXM1200F connected to the microscope, then stored in vials.

### 4.2.4 Beach quadrat and transect samples

Plastics debris collected through the quadrat and transect surveys were dried at 70°C, then transferred to a sieve shaker with mesh sizes 1 mm and 5.6 mm to separate macroplastics from microplastics. Particles smaller than 1 mm were not included in analysis. Plastics were visually categorized as pellets, fragments, foams (any intact or fragmented pieces of expanded or porous plastic) and intact objects, then quantified and weighed using a mass balance.

## 4.3 Polymer identification

Randomly chosen microplastics found in the sediment samples and a subgroup of microplastics > 5.6 mm collected during the transect surveys were identified using Raman spectroscopy, and in select cases X-ray fluorescence spectroscopy (XRF). Analysis was conducted at the Museum Conservation Institute at the Smithsonian Institution.

### 4.3.1 Spectroscopic analysis of microplastics in nearshore gravity core and tributary grab samples

Spectroscopic analysis of 90 particles identified in the sediment samples was conducted with a NXR Fourier-transform Raman module coupled to a 6700 Fourier transform infrared spectrometer (Thermo Electron Corporation, Madison, WI, USA). 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. The FT-Raman module was equipped with a continuous wave near infrared ND : $YVO_4$ excitation laser (1064 nm), a $CaF_2$ beam splitter, and a germanium detector cooled with liquid nitrogen. 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 micron 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 libraries[1] and custom libraries

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[1] HR FT-Raman Polymer Library (copyright 1997-2001, 2004 Thermo Electron Corporation for 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)

prepared by the Smithsonian’s Museum Conservation Institute. All spectra were analyzed using the automated search function of the software and also visually before identification was finalized. 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.

Microplastics analyzed with Raman spectroscopy were from the gravity cores taken in Humber Bay and in Toronto Harbour. A small subset of microplastics from the Humber River, Don River and Etobicoke Creek sediments were also analyzed.

### 4.3.2 Spectroscopic analysis of microplastics in beach transect samples

Spectroscopic analysis of 45 microplastic pellets, fragments and foams < 5.6 mm collected at Bronte Beach was conducted using a Nicolet Almega XR dispersive Raman spectrometer (Thermo Electron Corporation, Madison, WI, USA). The spectrometer was equipped with a 780 nm, 100 mW diode excitation laser focused through a 10× M-plan apochromatic objective lens of a BX51 confocal microscope (Olympus, Melville, NY, USA). The spectrometer was fitted with a low resolution diffraction grating (360 lines/mm), a 100-micron pinhole aperture, and an electronically cooled CCD detector. Laser power was chosen empirically to maximize the SNR without damaging the sample, and ranged from 0.025-0.1 W across a 100 micron round laser spot. Spectra were a co-addition of 16 scans collected at a spectral resolution of ~3.9 $cm^{-1}$ across 94-3469 $cm^{-1}$ 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 libraries (see footnote 1) and custom libraries prepared by the Smithsonian’s Museum Conservation Institute. All spectra were analyzed using the automated search function of the software and also visually before identification was finalized.

### 4.3.3 Spectroscopic analysis of microplastics using X-ray fluorescence spectroscopy

Three samples were also analyzed by X-ray fluorescence spectroscopy (XRF) to confirm the presence of chlorides in suspected polyvinyl chloride plastics as well as to look for inorganic fillers in pellets. The instrument used was a Bruker Artax 400 $\mu$XRF spectrometer equipped with a Rhodium tube, a poly-capillary lens with a ~100 $\mu$m focal spot and a Peltier cooled silicon drift detector. The excitation voltage ranged between 25-50 kV and the current ranged between 490 and 492 $\mu$A.

## 4.4 Contamination controls

Precautions were taken throughout the sampling and laboratory analysis procedure to minimize contamination of the samples from airborne microplastics. Containers 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 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 laboratory room and the drying oven for 2 hours, immediately followed by visual inspection with the same stereo microscope used for sediment sample analysis. Two replicate tests were conducted for each space.

## 4.5 Spatial trends analysis

Esri® geographic information software ArcGIS version 10.3.1 was used to explore trends and relationships between observed microplastic abundance in nearshore sediments and geographic variables including human population and the plastic industry. Population and industry facilities are used as proxies for consumer and supplier activity, respectively. Human population and plastics-related industry facilities 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.

### 4.5.1 Data model

Datasets were projected within ArcGIS from their original geographic coordinate system (e.g. North American Datum 1983) to a common projected coordinate system used for this project: North American Datum 1983, Universal Transverse Mercator, Zone 18 North (NAD83/UTM-18N). Secondary-level and quaternary-level watershed polygon shapefile datasets were retrieved from the Government of Ontario Open Source Data Catalogue and Land Information Ontario and the watersheds draining directly to Lake Ontario and the St. Lawrence River were extracted to define the study area. Quaternary-level watersheds are defined as small scale tributary and coastal stream systems. Watersheds which drained to a common output point on the lake/river boundary were combined. Multiple drainage points to the lake/river per watershed were permitted where small coastal creeks exist and for which separate quaternary watersheds were not delineated.

The 2011 Census data for southern Ontario was sourced from Statistics Canada at the dissemination block level (highest resolution) and was used to generate population density within each watershed using raster analysis. Wastewater treatment plants proximal to the Ontario shoreline of Lake Ontario and the 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 to the Don River (City of Toronto, 2006). Storm drain outlets are therefore not individually mapped in this study.

Plastic-related industry contact addresses were collected from ThomasNet, a free online supplier discovery and product sourcing directory. Through the search engine, businesses with descriptions or names containing the words ‘plastic’ or ‘polymer’ were selected and verified to be in the plastics industry by qualitative analysis of the description. The search was conducted for the top 30 categorical returns associated with the searches for ‘plastic’ and ‘polymer’. 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 located in Ontario were included.

Microplastic sample locations ($N$ = 50, excluding quadrat and transect samples) were recorded using a handheld Geographic Positioning Device (GPS) using the World Geodetic System 1984 (WGS84) spatial reference system at the time of sample collection. Spatial analysis of watershed area, population and industry count was conducted according to the model outlined in Appendix B.

### 4.5.2 Regression analysis of microplastics and watershed parameters

Bivariate correlations were used to test for correlations between the factors watershed area ($F_a$), population ($F_{pop}$) and industrial levels ($F_{ind}$).

In an effort to investigate the presence of any relationships between the watershed factors and microplastic abundance in proximal sediments, sediment samples were paired with watersheds by distance from the closest tributary mouth associated with watersheds in the study area. A coordinate was assigned to the mouth of the main tributary of each watershed in the study area, using the junction of the watercourse (shapefile provided by Ontario Open Data) and the lake boundary of the watershed. Each tributary mouth coordinate was assigned the properties of the associated watershed, $F_a$, $F_{pop}$, and $F_{ind}$. Using an inverse distance weighted (IDW) function, up to four watersheds within a distance of 10 km, were assigned to each sediment sample location. For each sediment sample the inverse distance weighted function was calculated independently for the three watershed factors using Eq. 4.2:

Eq. 4.2 $$X = \sum_{i=1}^{4} \frac{F_i}{d^2}$$

Where $X$ is the sum IDW value for a given sediment sample, calculated for factor, $F$, using the geographic distance, $d$, of the sediment sample from nearby tributary mouths, $i$.

## 4.6 Statistical analysis

Components of the plastics abundance and geospatial data were explored using statistical analyses conducted with GNU PSPP 0.10.1 software. In cases where statistically significant differences between means were examined, either an independent samples *t*-test or an Analysis of variance (ANOVA) test was used, depending on the number of groups being compared; a *t*-test was used to compare two groups and an ANOVA was used for comparisons between more than two groups. For ANOVA tests, a post hoc test was employed to determine which groups had statistically different means. In cases where three groups were compared, a Fisher's least significant difference (LSD) post hoc test was used. For comparisons of more than three groups, a stricter post hoc test is required. In these cases, a Scheffé's post hoc test was used. A significance level of $P \leq 0.05$ was used for all comparisons. Correlation and regression analyses were used to explore relationships between watershed properties ($F$), IDW calculated factors ($X$) and microplastic abundance ($N$ kg$^{-1}$).

Transformations were made to the data to meet the basic assumptions of the *t*-test, ANOVA, correlation and regression analyses that values are normally distributed around a mean and that variances are homogenous. For measures (e.g. microplastic abundance normalized to sediment volume or area sampled) a natural log transformation was used, specifically: $x = \ln(x_i + 1)$, where $x$ is the transformed value and $x_i$ is the initial value. Where proportional values were being compared an arcsin square root transformation of $x = \arcsin(\sqrt{x_i})$ was used. Most comparisons required data transformations to meet the assumptions of a normal distribution as data distributions were generally heavily skewed to low values.

To test for equal variances between groups the Levene's test of homogeneity was applied before each analysis. Variances were assumed not equal among groups when the Levene's test revealed a significant *p*-value, $p < 0.05$. When this occurred for groups being compared by a *t*-test, the *t*-test results assuming unequal variances were used. When the Levene's test resulted in a significant *p*-value for groups compared with an ANOVA, the test results were not reported as significant unless sample group sizes were equal or if variance and sample size were positively correlated.

# Chapter 5

# 5 Results

This section is divided into three parts: 1) results pertaining to microplastics < 5.6 mm in size found in nearshore, tributary and beach sediment samples, 2) results pertaining to visible plastics debris (particles 1-5.6 mm and items >5.6 mm) collected through the transect and quadrat surveys of beach and riparian sediments, and 3) results pertaining to the geographic analysis of population and industry in watersheds in the study area.

## 5.1 Microplastics in Lake Ontario and St. Lawrence River sediments

A total of 6,331 particles were visually identified as microplastics in nearshore, tributary and beach sediment samples. Microplastics abundance for each sample site was normalized to particles per kg of dry sediment ($N$ kg$^{-1}$, dw) using the initial mass of the dried sediment sample. Microplastics were identified in every sediment sample, and abundances varied between 20 and 27,830 kg$^{-1}$ (Fig. 5.1, Appendix A).

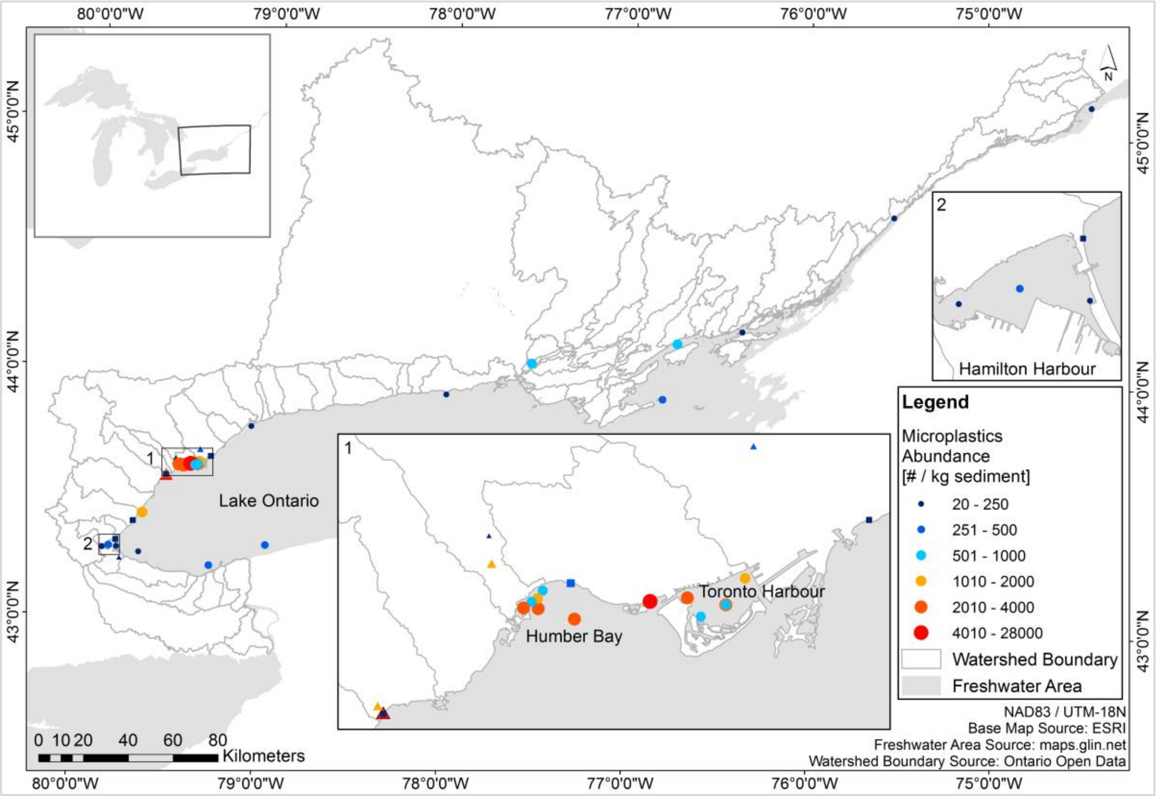


**Figure 5.1** Microplastics abundance normalized to particles N $kg^{-1}$ sediment (dry weight, dw) for 50 nearshore (circle), tributary (triangle) and beach (square) sites in Lake Ontario. The inset shows the Greater Toronto Area in detail.

Maximum microplastics abundance was found at site P-EC2, at the mouth of Etobicoke Creek. The sample was primarily composed of algae detached from a rocky substrate.

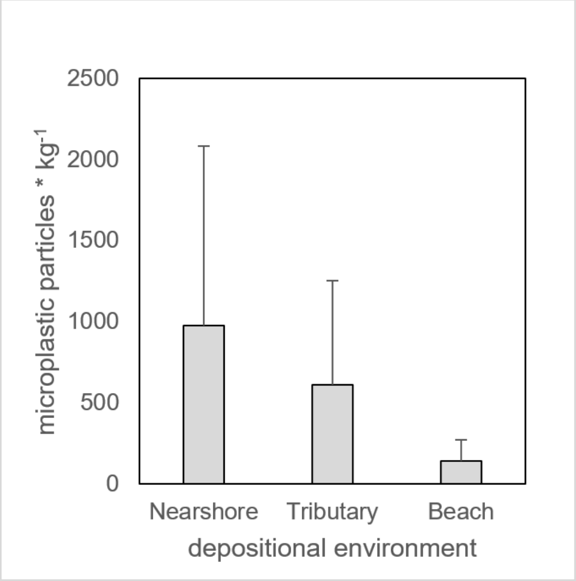


**Figure 5.2** Average abundance of microplastic particles, < 2 mm, in nearshore, tributary and beach depositional environments. Error bars show the standard deviation from the mean.

This sample contained the greatest number of microplastics (*N*=800) compared to all other grabs of similar volume. The extrapolated total 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 $kg^{-1}$. Nearshore sediments contained on average the greatest abundance of microplastics with 980 $kg^{-1}$, followed by tributary sediments with 610 $kg^{-1}$ and beach sediments with 140 $kg^{-1}$ (Fig. 5.2).

### 5.1.1 Airborne contamination levels

In the sample processing laboratory, the drying oven and microscopy laboratory airborne contamination levels were 2, 3 and 1.5 fibres $h^{-1}$ of exposure, respectively, on the scale of a standard 9 cm diameter glass Petri dish (area: $A = 64\ cm^2$). Only during oven drying were samples exposed for prolonged periods, up to 24 h with vial openings of $A \sim 2\ cm^2$. Samples exposed in larger rimmed containers ($A \leq 315\ cm^2$) inside the oven were exposed for a maximum of 12 h. Thus, contamination of the sediment samples with fibres may have occurred primarily during the drying stages of sample preparation.

### 5.1.2 Particle abundance in nearshore environments

Microplastics in nearshore sediments were most concentrated in Humber Bay and Toronto Harbour. Microplastic loads of > 1,000 $kg^{-1}$ were found only at sites in the Greater Toronto Area (GTA) and offshore of Oakville (sample S-7541), west of Toronto. Nearshore gravity core sediments contained relatively high microplastic concentrations compared to the trap and grab samples; average lake-wide microplastic abundance for gravity core, trap and grab samples were 2,130 $kg^{-1}$, 1,070 $kg^{-1}$ and 730 $kg^{-1}$, respectively.

Microplastics abundance, as recorded in the sediments sampled with the gravity corer, is plotted against cumulative sediment mass, which is the mass of sediment accumulated above a certain depth within the core (Fig. 5.3). 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*): $CMS = \sum_{i=1}^{d} \left(\frac{m_d}{\pi r^2}\right)$. Intervals were each 1 cm; *d* is given the value of the deeper end of each interval. For example for an interval spanning depths of 2-3 cm below the sediment surface, *d* is assigned a value of 3. Microplastics abundance 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. 5.3, Fig. 5.4a). As shown in Fig. 5.4b, there was no significant difference between the average microplastic abundance ($N$ $kg^{-1}$) in the Humber Bay cores (M=1,898, SD=1,363) and the Toronto Harbour cores (M=2,472, SD=2,545) as tested with an independent samples *t*-test ($t$ (3)=0.34, $p$=0.75). Approximately 65-95% of the total number of particles found in each core were separated in the second separation phase, with SPT (Fig. 5.4c). These particles are assumed to have a density > 1.5 g $cm^{-3}$.

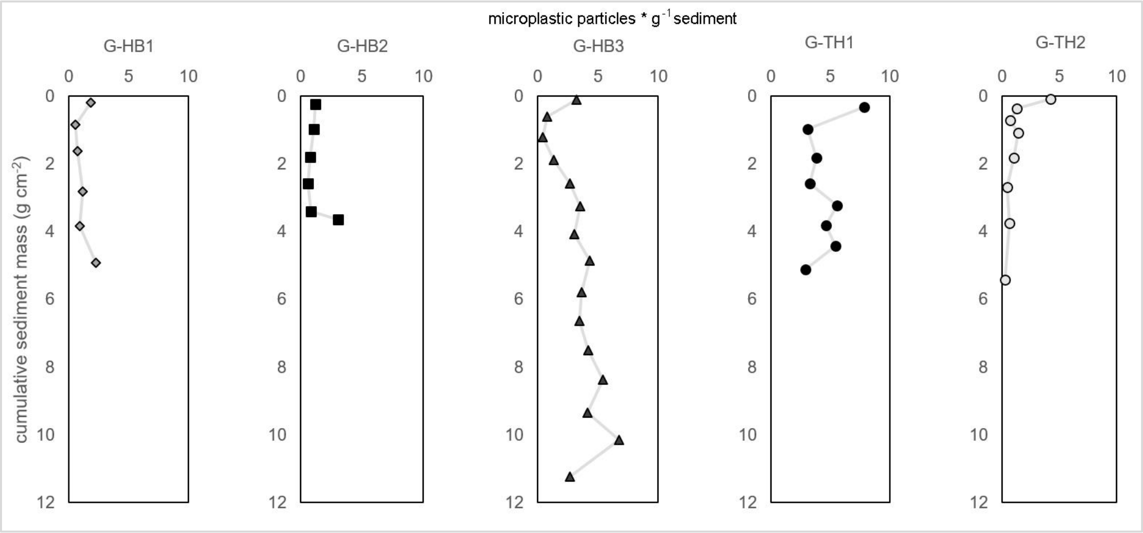


**Figure 5.3** Microplastics (< 2 mm) abundance, $N$ $g^{-1}$ sediment (dw), plotted against cumulative sediment mass (g $cm^{-2}$), dw, for nearshore sediments of Humber Bay and Toronto Harbour as sampled by gravity core.

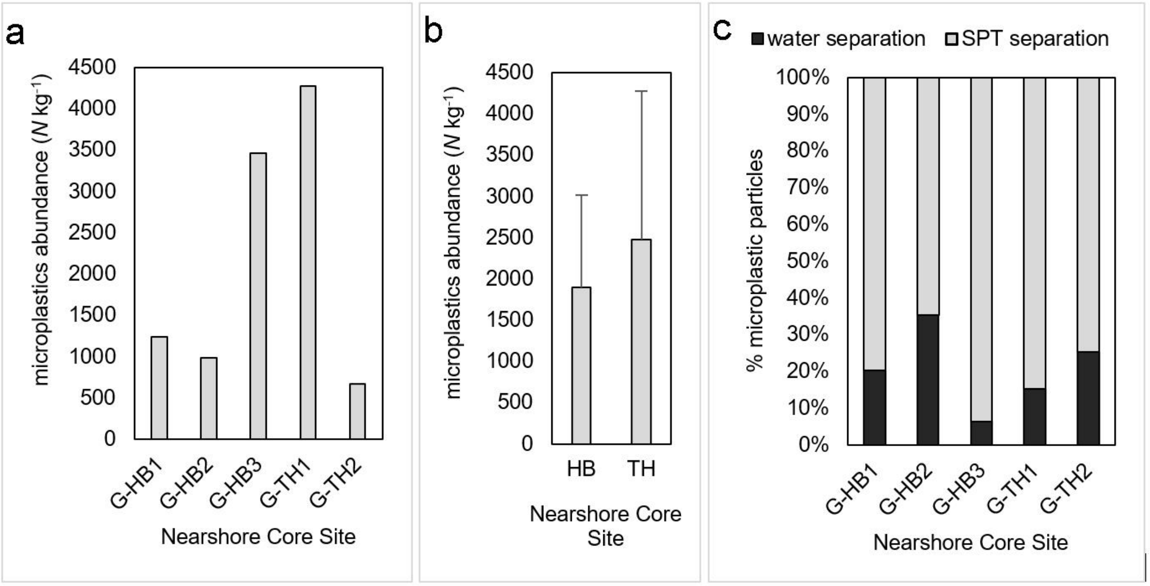


**Figure 5.4** (a) Microplastics abundance, $N$ kg$^{-1}$ sediment (dw), integrated over depth for each gravity core nearshore sediment sample and (b) averaged across sites in Humber Bay (HB) and Toronto Harbour (TH); error bars show standard deviation from the mean. (c) The percentage of microplastic particles isolated from sediments using density separation technique with solution of sodium polytungstate (SPT), density = 1.5 g cm$^{-3}$, versus deionized water, density = 1.0 g cm$^{-3}$.

Among trap samples, microplastics abundance was averaged across the three replicate samples at each site (mean + SD, shown in Fig. 5.5). Highest abundances were found in the traps placed in Humber Bay (T-2047) and lowest abundances were found in the traps placed in Hamilton Harbour (T-258, Fig. 5.5). In Toronto Harbour (T-1364) microplastics abundance was ~750 kg$^{-1}$. A one-way ANOVA revealed significantly different means ($F$ (2, 6) = 19.71, $p$ = 0.002). Using an LSD post hoc test, it was determined that microplastic abundance was significantly higher at T-2047 than at T-258 ($p$=0.001) and T-1364 ($p$=0.017), and abundance at T-1364 was significantly greater than at T-258 ($p$=0.024).

The nearshore grab samples were collected during the summer months of 2012 and 2014 (Appendix A). Abundances ($N$ kg$^{-1}$) averaged across all sediments from each year showed no significant difference between collection years (independent samples $t$-test, $t$ (26) = 1.28, $p$ = 0.2), although 2014 samples had on average 200 kg$^{-1}$ more than 2012 samples, with similar standard deviation (Fig. 5.6a). Comparison between years may be confounded due to inconsistent sampling between years, with a larger number of samples collected in 2014 than in 2012 and samples representing each year from different locations.

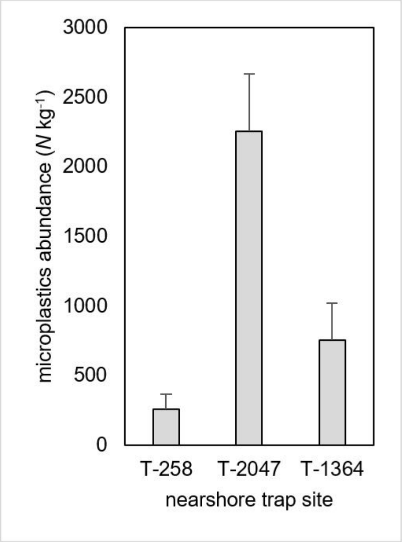


**Figure 5.5** Microplastics abundance, $N$ kg$^{-1}$ sediment (dw), among nearshore trap sediment samples, averaged across replicates ($N$ = 3). Error bars show standard deviation from the mean.

There was no significant correlation between microplastics abundance and the depth below the water surface (Pearson's correlation: $r$ (28) = 0.24, $p$ = 0.2). Low microplastic particle abundances of < 1000 kg$^{-1}$ were quantified across the range of depths sampled, and half of the nearshore samples where abundances > 1000 kg$^{-1}$ were quantified had depths in a narrow range of between 5 and 10 m. Maximum microplastics abundance decreases with depth; deeper sediments had consistently lower maximum microplastics abundance.

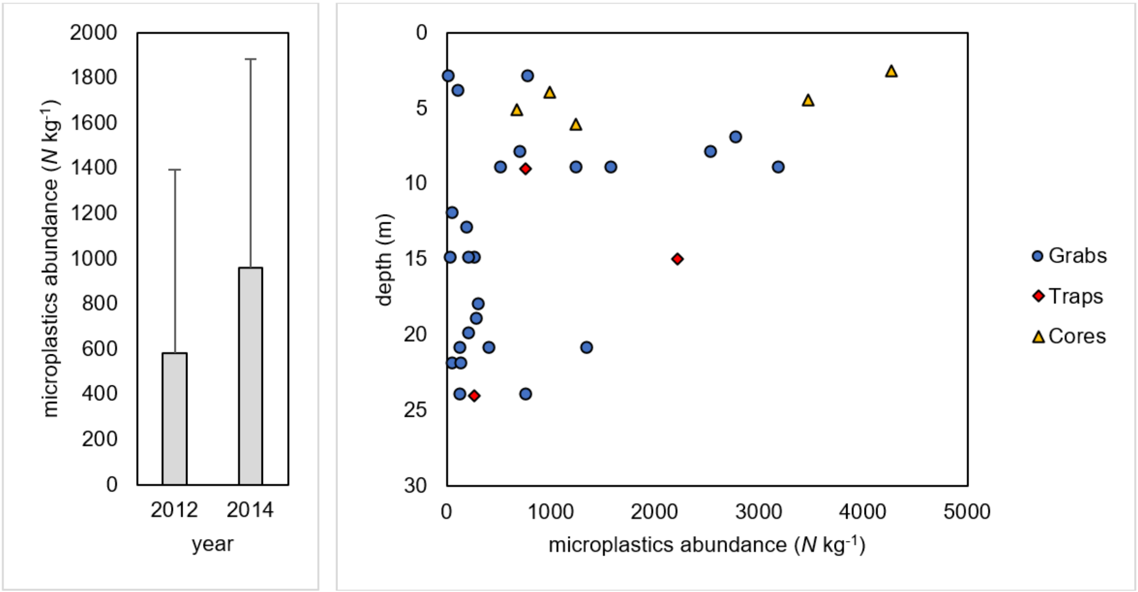


**Figure 5.6** (a) Mean microplastics abundance, $N$ kg$^{-1}$ sediment (dw), for samples collected in 2012 and 2014. Error bars show standard deviation. (b) Microplastics abundance, $N$ kg$^{-1}$ sediment (dw), in nearshore samples plotted against water depth.

### 5.1.3 Particle abundance in riverine environments

Statistically significant differences in the abundance of microplastics could not be determined due to the absence of a replicate sample for the Don River. Microplastic abundance, however, varied over three orders of magnitude (2 orders of magnitude not including sample P-EC2) with lowest levels (~30 kg$^{-1}$) in Red Hill Creek and highest levels (~28,000 kg$^{-1}$) in Etobicoke Creek (Fig. 5.7). Sediments collected from the Don and Humber rivers had average microplastics concentrations of ~500 kg$^{-1}$ and ~900 kg$^{-1}$.

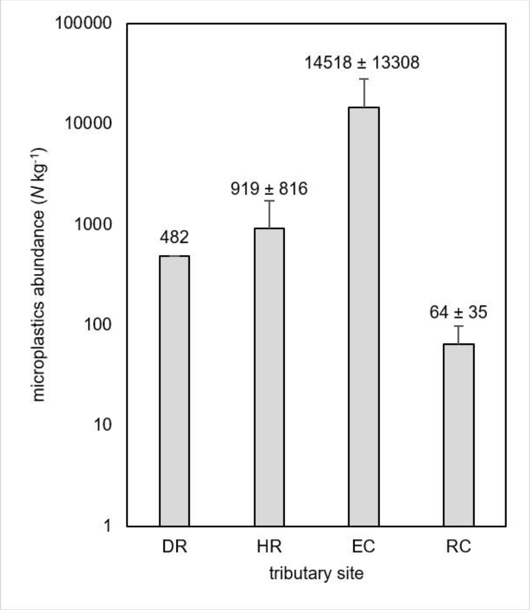


**Figure 5.7** Microplastics (< 2 mm) abundance, $N$ kg$^{-1}$ sediment (dw), averaged (error bars indicate standard deviation) for tributaries draining into Lake Ontario including Don River (DR), Humber River (HR), Etobicoke Creek (EC) and Red Hill Creek (RC). In each tributary (except DR), two proximal sites were sampled.

Microplastics abundance in tributary sediments displayed variability on short spatial scales (Fig. 5.1). For example, in Humber River and Etobicoke Creek, downstream sites (P-HR1 and P-EC2) contained microplastic counts one to two orders of magnitude greater than sites within 1 km upstream (P-HR2 and P-EC1).

### 5.1.4 Particle abundance in beach environments

Among beach sediments, microplastics were most abundant (500 and 700 kg$^{-1}$) in the top 10 cm at both locations at Sunnyside Beach. On a regional scale, fewer microplastics were found at beaches at greater distance from Toronto (Fig. 5.8a).

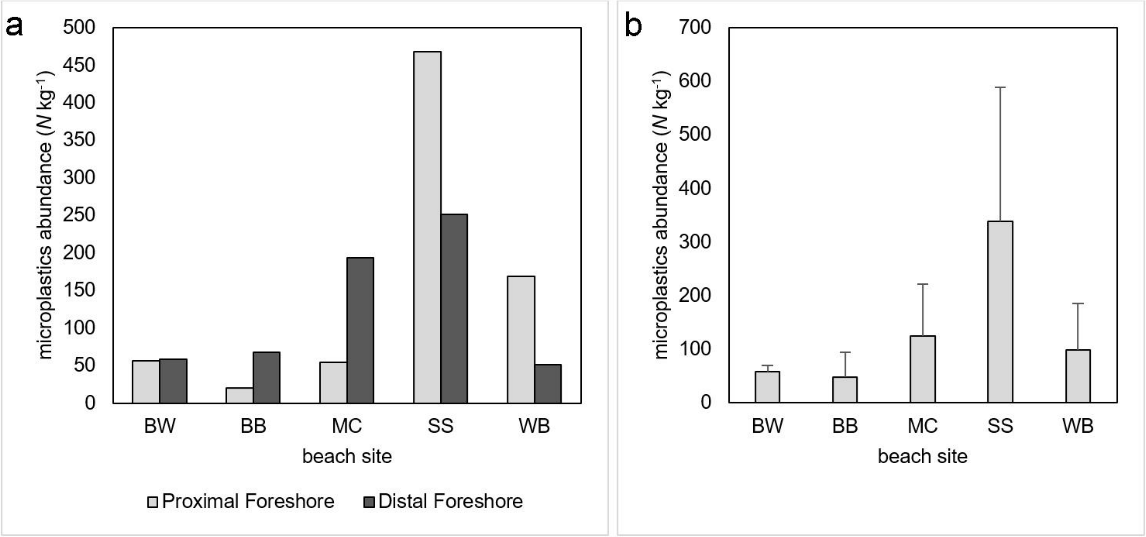


**Figure 5.8** (a) Microplastics (< 2 mm) abundance, *N* kg$^{-1}$ sediment (dw), integrated over core depth for beach sediments, proximal foreshore vs. distal foreshore and (b) averaged between proximal and distal foreshore (error bars indicate standard deviation) at Beachway (BW), Bronte (BB), Marie Curtis Park (MC), Sunnyside (SS) and Woodbine (WB) beaches. Error bars show standard deviation.

Mean microplastic particle abundance (*N* kg$^{-1}$) was calculated for each beach site by averaging the proximal and distal foreshore samples, each calculated as total microplastic abundance over total sediment weight of all intervals (Fig. 5.8b). A one-way ANOVA revealed significantly different means between Bronte Beach and Sunnyside beach sites ($F$ (4, 21) = 3.74, $p = 0.019$, Scheffé's post hoc: $p = 0.027$). Microplastics abundance was not significantly different between proximal and distal foreshore sites when averaged across all beaches (Fig. 5.9a) as tested with an independent samples *t*-test ($t$ (24) = 0.29, $p = 0.5$).

Microplastics abundance was averaged across all samples for each depth interval separately analyzed: 0-10 cm, 10-20 cm and 20-30 cm below the sediment surface (Fig. 5.9b). A negative trend between microplastics abundance and depth below the sediment is apparent, however, no significant difference between means was detected with one-way ANOVA (*F* (2, 23) = 0.1, *p* = ns). Assumption of equal variances among groups, was not met (Levene's test: *p* = 0.02), however, because the smaller sample group (depth 20-30 cm) had smaller variance, the *F*-value is likely a conservative estimate, and the ANOVA may still hold.

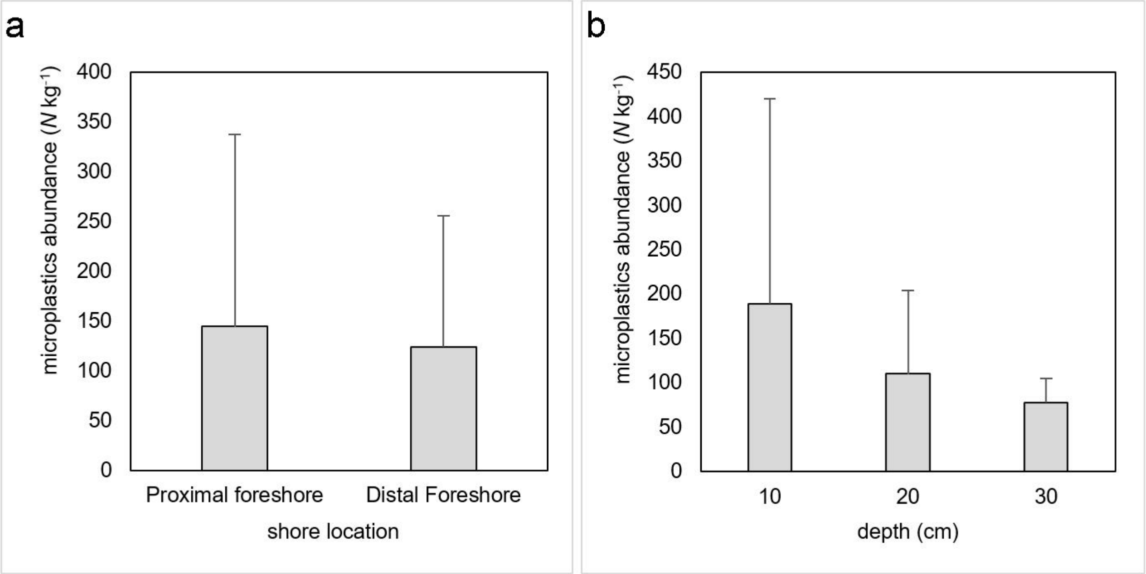


**Figure 5.9** (a) Mean microplastics (< 2 mm) abundance, $N$ kg$^{-1}$ sediment (dw), for proximal and distal foreshore beach sediments, and (b) averaged across sites for each depth interval (0-10 cm, 10-20 cm and 20-30 cm). Error bars show standard deviation.

### 5.1.5 Particle morphology

Microplastics in nearshore depositional zones were almost exclusively < 2 mm in size. Microplastics 2 – 5.6 mm in size were found only in one nearshore sediment sample in Toronto Harbour (site S-3030) and accounted for ~ 0.02% of the particles across all nearshore sites. Plastic particles 2 – 5.6 mm were slightly more common in tributary sediments with 84 particles at site P-EC2 and one particle at site P-RC2; overall 4% of the microplastics found in tributaries were in this size range. Approximately 8% of plastics in beach sediments were 2 – 5.6 mm, the majority of which were found at Marie Curtis and Sunnyside (example particles shown in Fig. 5.10a) beach sites and at the mouth of Etobicoke Creek, sample P-EC2. For microplastics 2 – 5.6 mm, fragments (including films and foams) and beads (industrial pellets) were most common. These results are similar to those reported by Alomar et al. (2016) who found a more homogenous distribution of < 2 mm microplastics as compared to those > 2 mm.

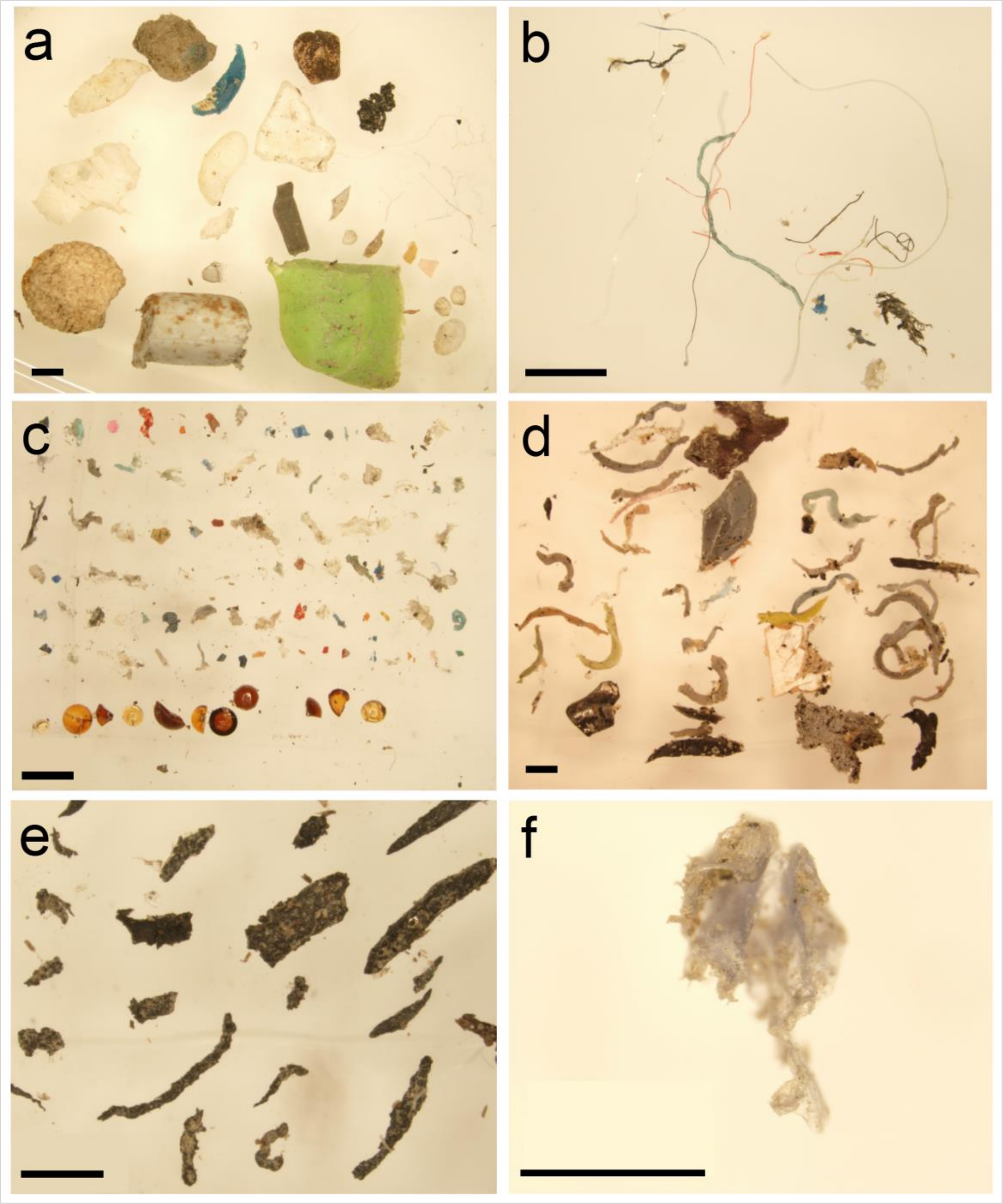


**Figure 5.10** Examples of microplastics identified in sediment samples from tributaries, beaches and the nearshore lake bottom of Lake Ontario. All scale bars are 1 mm. (a) Macro- and microplastic fragments, fibres, foams and pellet isolated from the upper 10 cm of proximal foreshore sediments at Sunnyside

Beach. (b) Microplastic fragments and fibres isolated from nearshore sediment in Toronto Harbour as collected in a sediment trap. (c) Microplastics found in grab sediments (sample S-3027) in Humber Bay. Fragments include hexagonal glitter (pink, first row, *N*=1) and whole and fragmented PSS beads (bottom row, *N*=11) 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.

Fragments and fibres were the dominant morphologies for microplastics < 2 mm in all depositional zones. Fibres were most abundant in nearshore (trap) sediments and least abundant in tributary sediments (Fig. 5.11a). Statistically different mean abundances of each morphology as compared using one-way ANOVA ($F$ (2, 12) = 30.94, $p < 0.001$) are shown in Fig. 5.11b. The underlying assumption of homoscedasticity was not met (Levene's test: $p = 0.04$) however, sample sizes were equal across groups alleviating the negative effect of unequal variances on the validity of the ANOVA. As determined with an LSD post hoc test, beads were significantly less abundant than fragments ($p < 0.001$) and fibres ($p < 0.001$), and fibres were less abundant than fragments ($p = 0.011$). Beads were found in all depositional environments, but were not found in the sediment traps (Fig. 5.11a).

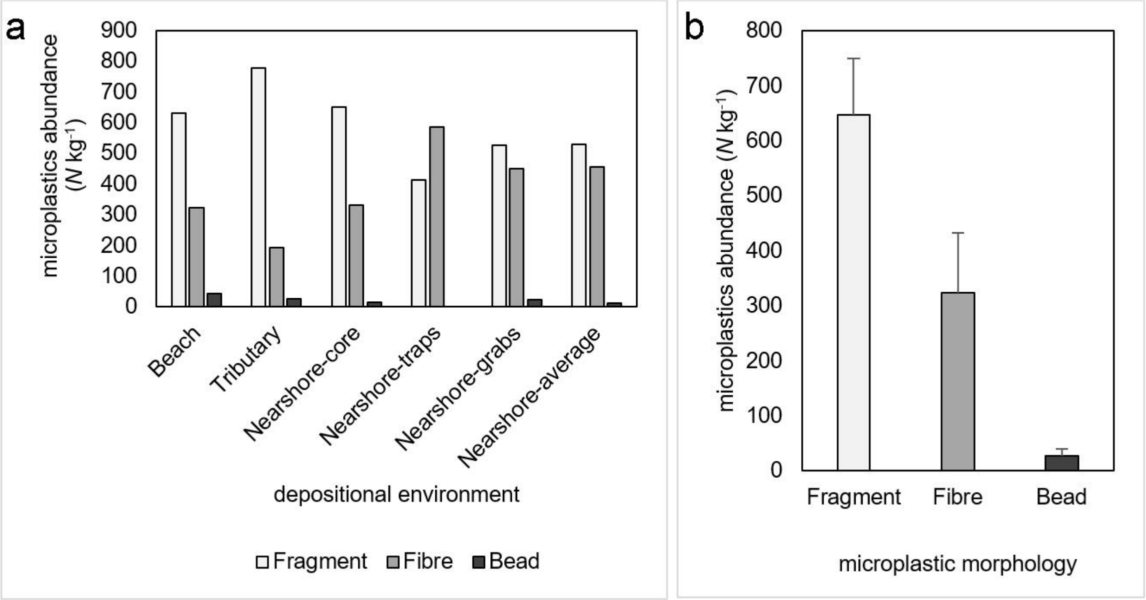


**Figure 5.11** Microplastics (< 2 mm) abundance, $N$ kg$^{-1}$ sediment (dw), by particle morphology for (a) each sediment sample type and (b) averaged across all samples (error bars show standard deviation from the mean).

The relative abundances of fragments, fibres and beads in the nearshore cores are shown in Fig. 5.12. Fragments and fibres were most abundant and beads were a minor component, but were more abundant in the Toronto Harbour cores than in the Humber Bay cores.

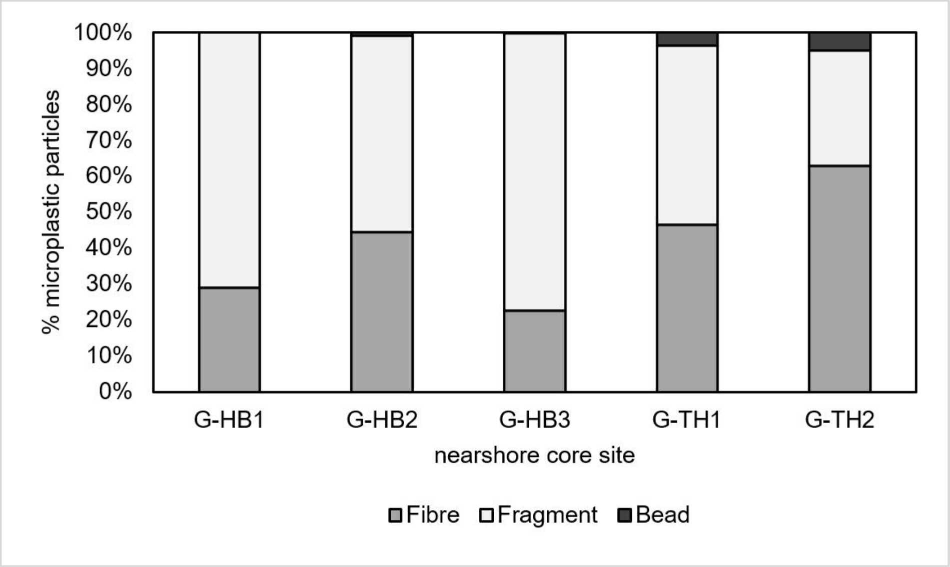


**Figure 5.12** Proportion of fragments, fibres and beads in nearshore sediment core samples.

In general, microplastics were of variable colour, texture, grade of degradation, size and shape; however, specific types of microplastics were common across depositional zones. Fibres were highly regular in diameter along their entire length, varied in colour and ranged in length from tens of microns to several millimeters (Fig. 5.10b). Irregularly shaped, bulbous to wispy fragments with smooth surfaces and translucent diaphaneity were common (e.g. Fig. 5.10c, f). Beads were most commonly perfectly spherical, translucent, amber or black coloured material appearing in a variety of sizes and sometimes cracked or fragmented (Fig. 5.10c, far right column). Oblong, helical forms composed of rigid, opaque material were common in the tributary and nearshore sediments, particularly at Etobicoke Creek (Fig. 5.10d). These particles had smooth clean surfaces and did not appear fragmented. In a conservative classification, it is estimated 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 in size. Non-rigid, black, opaque particles appearing as amorphous chunks or long thin helical twists accounted for ~7% of microplastics collected in the study (Fig. 5.10e).

### 5.1.6 Particle composition

Of the 4,364 suspected plastic particles identified within the nearshore gravity core and tributary sediments, 90 fragments and beads (2.1% of fragments and beads) were analyzed using Raman spectroscopy. Of the analyzed particles, 60 (67%) were positively identified as synthetic polymers (Fig. 5.13). An additional five particles could not be identified as containing a specific synthetic polymer but were found to contain plastic-associated compounds, including phthalates, i.e. plasticizers, and toluidine red, a colourant. Three (3.3%) 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 which may have been transferred to the buoyant fraction during the decanting procedure.

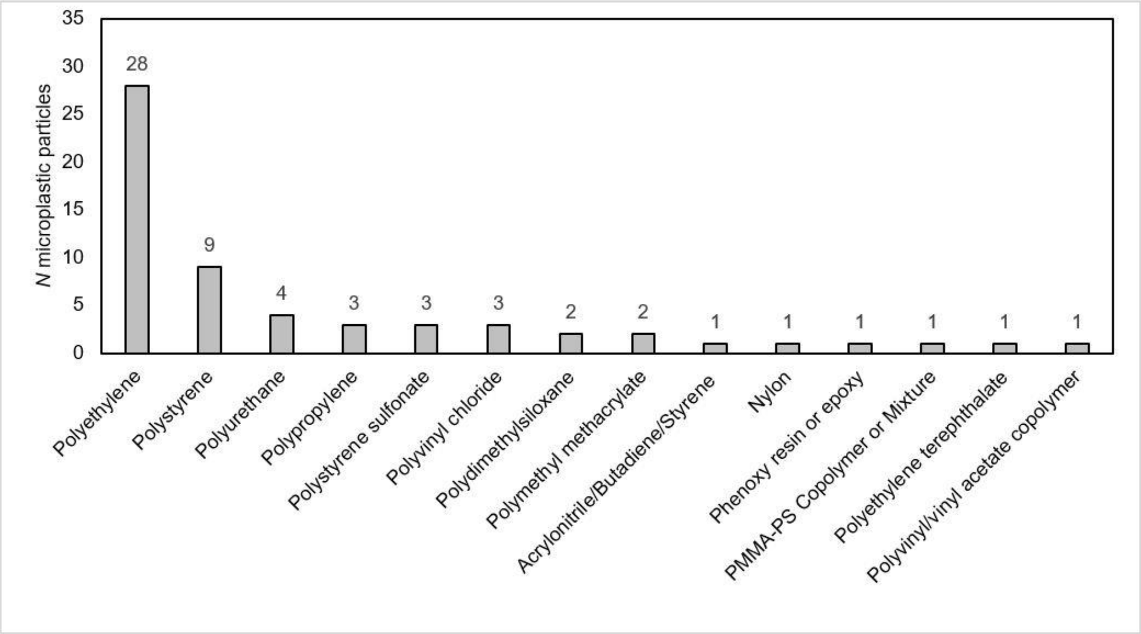
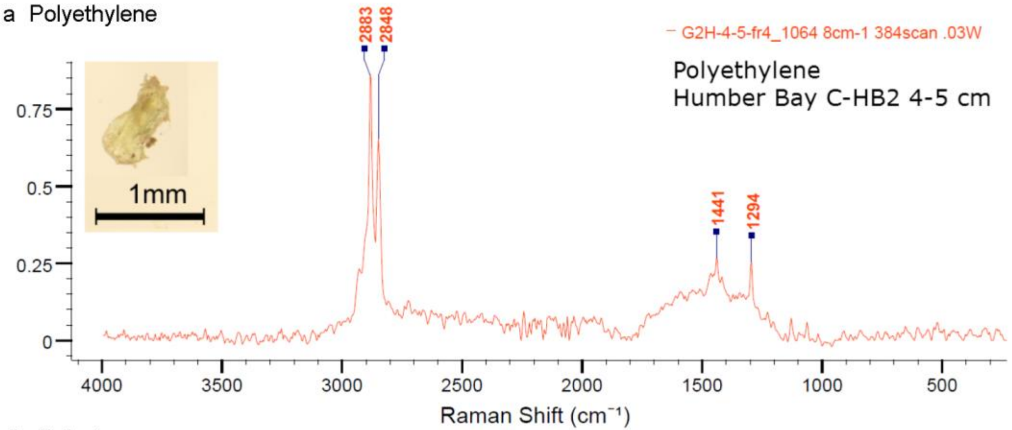


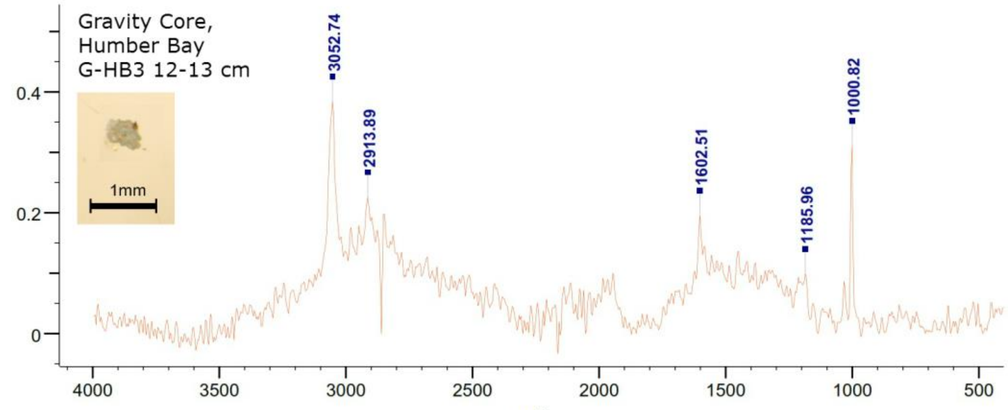
**Figure 5.13** Synthetic polymers and compounds identified in the FT-Raman spectroscopic analysis of particles isolated from Lake Ontario nearshore and tributary sediments. Of ninety particles analyzed, 60 were plastic in composition, 3 were non-plastics (e.g. quartz, calcium carbonate), 5 were plastic-associated compounds (e.g. phthalates, toluidine colourant), and 22 could not be identified.

Thirty-one percent of the analyzed particles were identified as PE, 10% as PS and 4% as polyurethane (PU). Polypropylene, PVC, and polystyrene sulfonate (PSS) each made up 3% of the analyzed particles. Other polymers including PET, PMMA, polyvinyl/vinyl acetate copolymer, PMMA-PS copolymer or mixture, ABS, nylon, phenoxy/epoxy resin, and polymethylsiloxane (silicone) were identified in smaller percentages. The Raman spectra of select microplastic particles of various composition are shown in Fig. 5.14. Twenty-two (24%) 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 all particles including fragments, fibres and beads) of particles analyzed. A more thorough analysis of polymer composition is required to determine the appropriate count adjustment for the particles collected in this study.

a Polyethylene



b Polystyrene



c Polyurethane

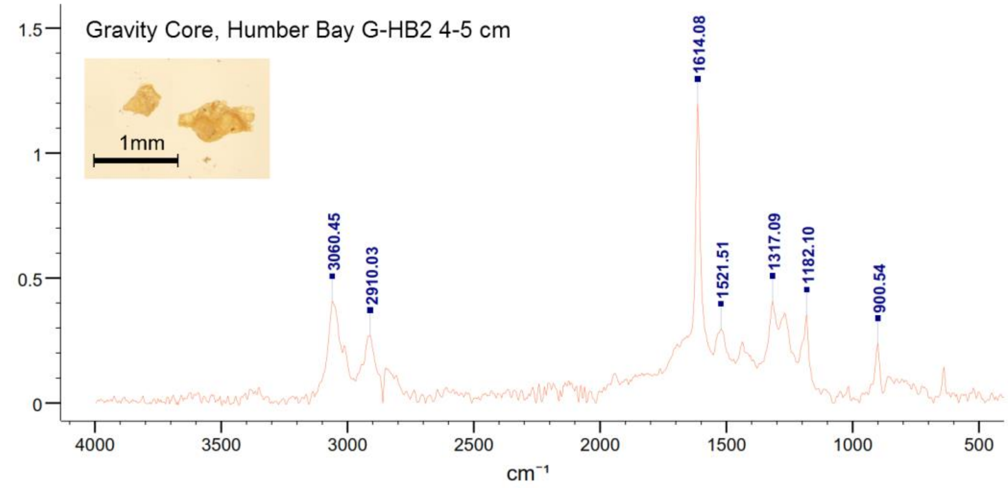
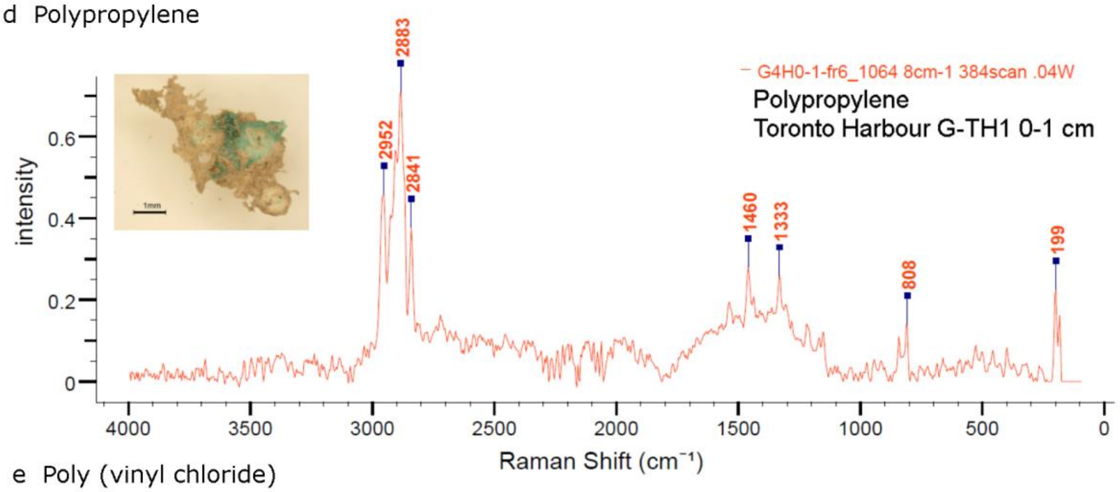
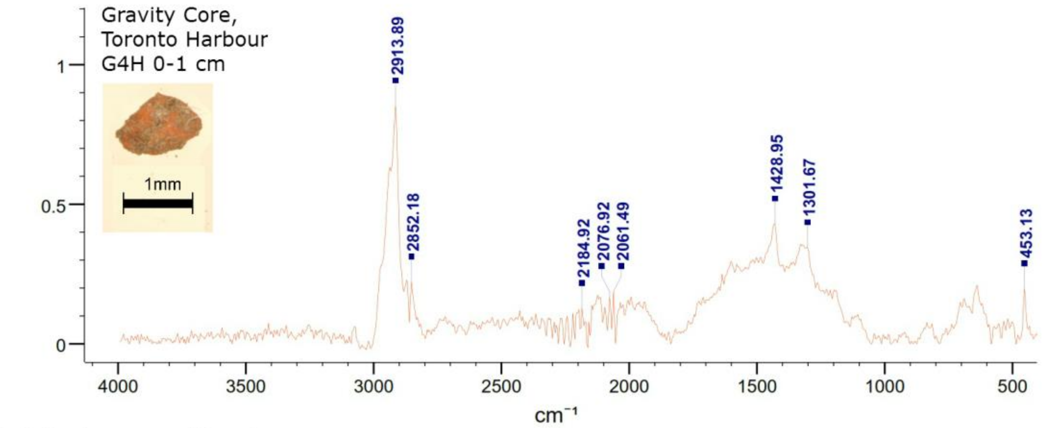


**Figure 5.14 a – c** Raman spectra of select microplastic particles found in the Toronto Harbour and Humber Bay sediments sampled by gravity core.

d Polypropylene



e Poly (vinyl chloride)



f Polystyrene sulfonate

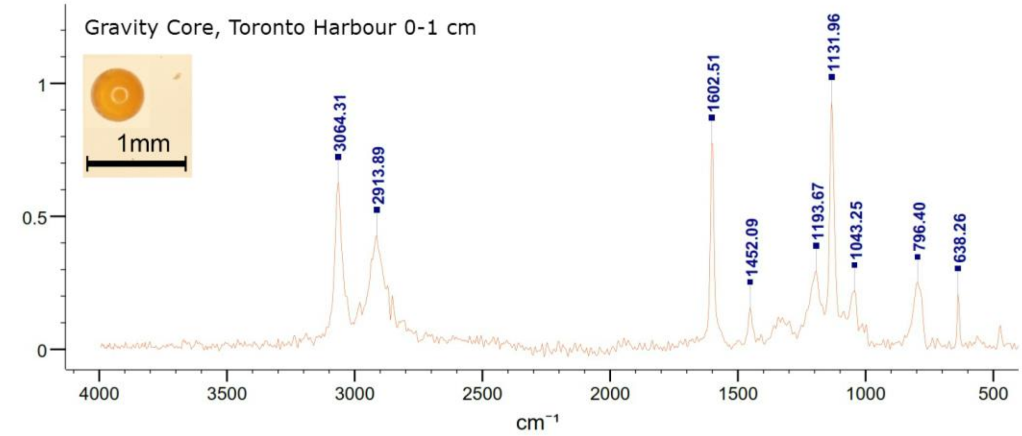


**Figure 5.14 d – f** Raman spectra of select microplastic particles found in the Toronto Harbour and Humber Bay sediments sampled by gravity core.

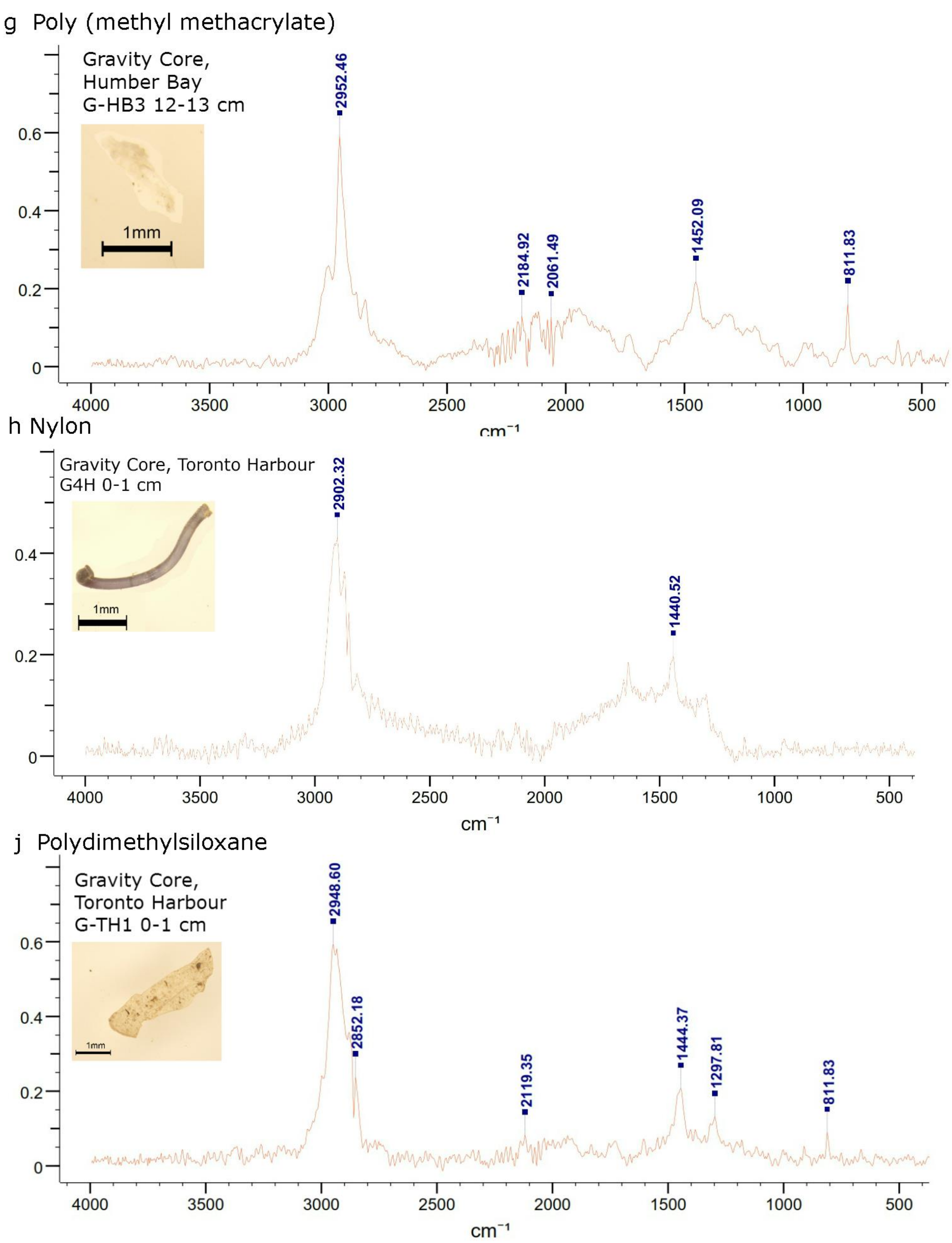


**Figure 5.14 g - j** Raman spectra of select microplastic particles found in the Toronto Harbour and Humber Bay sediments sampled by gravity core.

Six of the microplastic particles analyzed with Raman spectroscopy were pellets and fragments 2 - 5.6 mm in size from sample P-EC2, Etobicoke Creek. Of four fragments, 3 were identified as PS and one as PP. Of two pellets, one was identified as ABS and one as PS.

One fragment from C-HB2, in depth interval 2-3 cm, which was suspected to be PVC based on the characteristic peaks in the Raman spectra, was analyzed using $\mu$XRF confirming the presence of chlorine. Other elements detected in the sample were silicon, potassium, calcium, iron and tungstate.

Several patterns relating plastic morphology and composition were recognised. Fragments identified as PE were consistently characterised 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 lower laser power. This problem was also noted by Lenz et al. (2015); however, their analyses provided identification of similarly described particles as black tire rubber. Yellow, translucent, rigid fragments were commonly identified as PU (Fig. 5.14c). Several of the smooth, spherical, transparent, amber-red beads (Fig. 5.10c, Fig. 5.14f) were identified as polystyrene sulfonate (PSS). Most fibres, having a diameter of $< 50\ \mu$m, did not return spectra of sufficient quality and were therefore not compositionally identified.

Particles that were positively identified as plastic were categorized based on the relative density of the polymer. Low-density plastics included PE and PP polymers. High-density plastics included all other plastics identified, excluding plastics-associated compounds: toluidine and phthalates. In Fig. 5.15a, the ratio of LD to HD plastics found in each analyzed nearshore core interval and tributary sample is plotted against water depth where sample was taken, revealing a positive trend ($R^2 = 0.76$) with increasing depth. A significant correlation was found (Pearson’s correlation: $r$ (10) = 0.87, $p < 0.001$).

Among nearshore core samples, there was no correlation between the ratio of LD to HD plastics and the depth within the sediment (Pearson’s correlation: $r$ (10) = 0.01, $p = 0.97$) as shown in Fig. 5.15b.

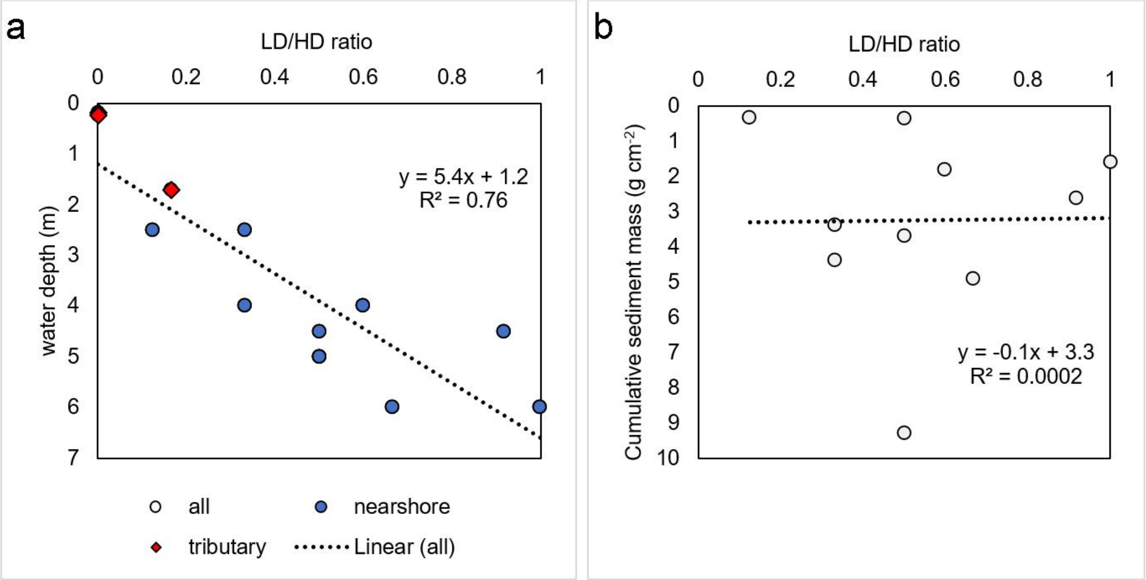


**Figure 5.15** (a) The ratio of low-density (LD) plastics to high-density (HD) plastics among particles identified with Raman spectroscopy in nearshore gravity core and tributary sediments (a) plotted against water depth of sample, and (b) plotted against cumulative sediment mass (i.e. depth below the sediment surface) for nearshore gravity core sediments only.

### 5.1.7 Sediment grain size analysis

Sediments were characterized by grain size variation, with fractions defining the fine component (clay and silt grains < 0.063 mm), sand grains (0.063 – 2 mm), pebbles (2-5.6) and large pebbles and cobbles (> 5.6 mm). Beach sediments were predominantly sandy and pebbly, with a very minor fine fraction. Tributary sediments were predominantly sandy, with on average 18% of the sediment comprising silt and clay sized particles. Nearshore sediments exhibited a large range of sediment grain sizes, from predominantly sand to predominantly clay and silt. Figure 5.16 shows the mean proportion of grains < 0.063 mm in sediments collected from each depositional environment.

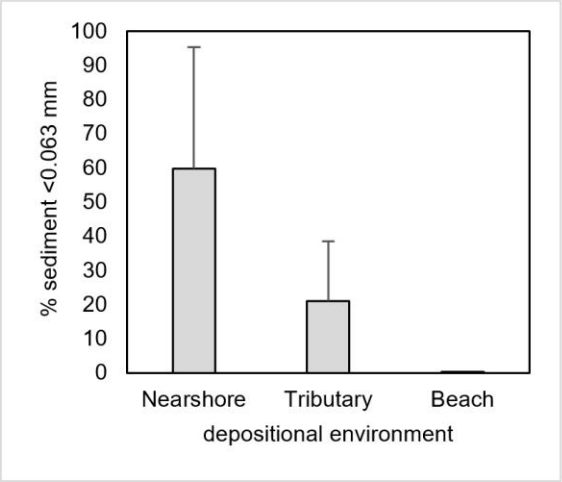


**Figure 5.16** Fine fraction (clay and silt, < 0.063 mm) in sediments averaged across depositional environment. Error bars show standard deviation from the mean.

Microplastic abundance was plotted against the percentage of silt and clay sized grains to test for a correlation between microplastic abundance and sediment grain size, as has been done in the literature (Lenz et al., 2015). No correlation was found between microplastics abundance and proportion of clay and silt in the sediment (Fig. 5.17, Pearson correlation: $r$ (47) = 0.02, $p$ = 0.90).

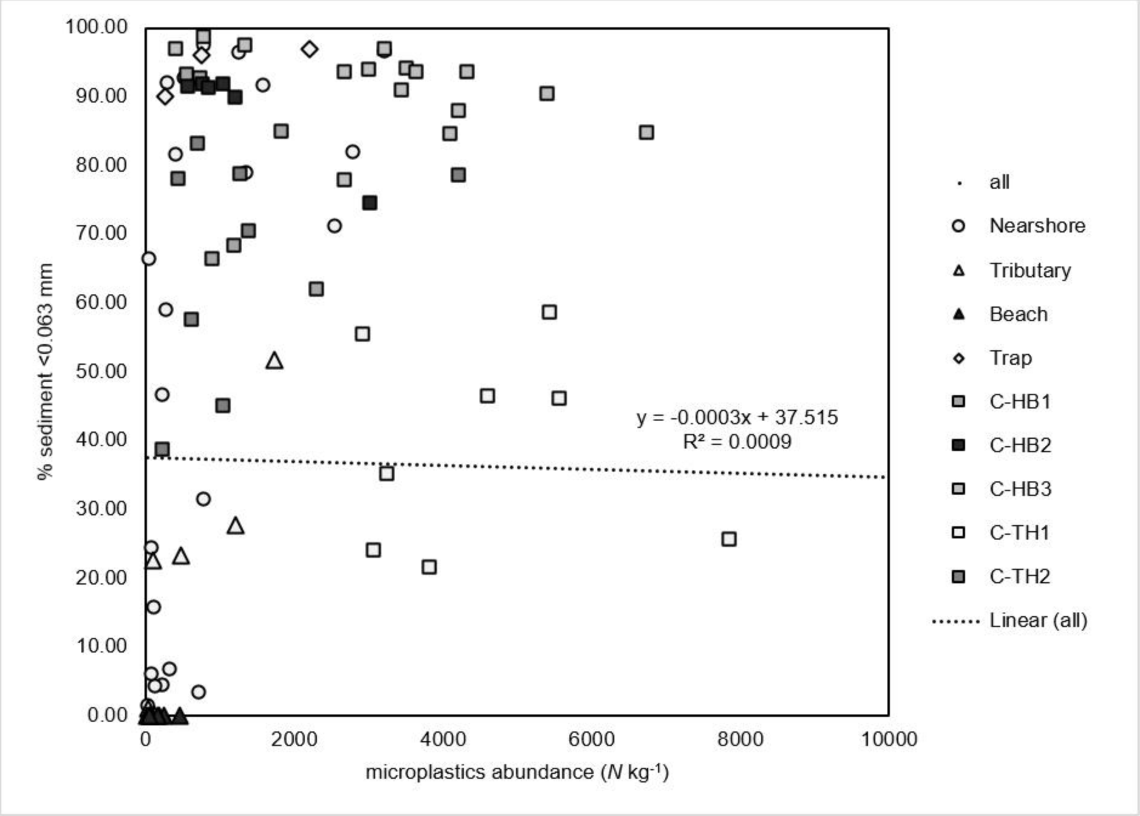


**Figure 5.17** Microplastics (< 2 mm) abundance, *N* kg$^{-1}$ sediment (dw), against the percent of sediment < 0.063 mm.

Sediment grain size variation for the nearshore core samples is plotted in Fig. 5.18 with respect to CSM (g cm$^{-2}$). The sediment in TH-1 is noticeably coarser-grained than the other four cores, and exhibits highest microplastics abundance. Browne et al. (2010); Mathalon & Hill (2014) and Alomar et al. (2016) also report the absence of a correlation between sediment grain size and microplastic abundance in estuary, beach intertidal and nearshore sediments, respectively. Vianello et al. (2013), however, do report a positive relationship between the mud fraction and abundance of microplastics in the Venice Harbour sediments.

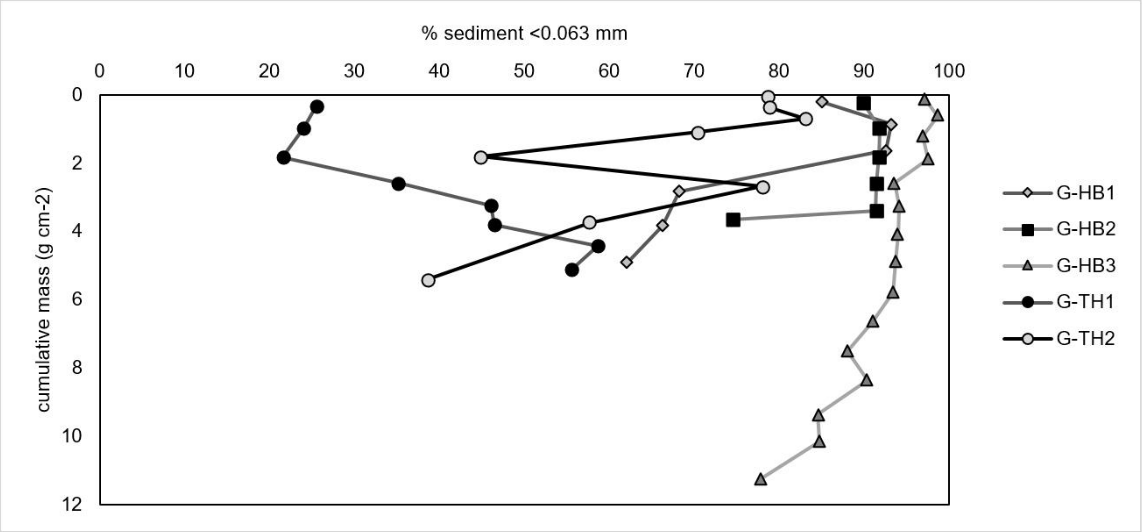


**Figure 5.18** Percent fine fraction (silt and clay, < 0.063 mm) plotted against cumulative sediment mass (g cm$^{-2}$), dw, for nearshore sediments of Humber Bay and Toronto Harbour as sampled by gravity core.

One factor that may have affected microplastics abundance analysis was the inconsistency in sample preparation. Samples that caked when dried were first wet sieved through a 0.063 mm mesh sieve then dried again, whereas samples that were not caked were dry sieved immediately. Figure 5.19 shows the mean microplastics abundance and the mean proportion of the fine fraction for each sieving condition: dry sieved only, wet then dry sieved, and not sieved (nearshore cores).

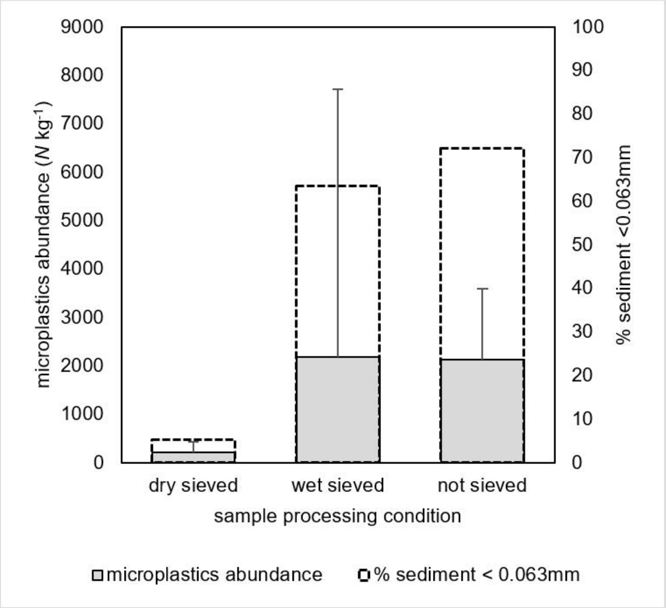


**Figure 5.19** Mean microplastics (< 2 mm) abundance, $N$ kg$^{-1}$ sediment (dw), and mean proportion of the fine fraction (silt and clay, < 0.063 mm) for each sample processing condition. Error bars show the standard deviation from the mean for microplastics abundance.

A comparison of means between groups is not valid because variation between the groups could be a function of either processing condition or sediment type (sand or clay), and these two explanatory variables cannot be isolated due to the sampling and methodology design.

## 5.2 Spatial survey of visible macroplastics and microplastics in Lake Ontario beach and tributary sediments

Visible microplastics (1-5.6 mm) and macroplastics (> 5.6 mm) were collected from 5 beaches and from the banks of 4 tributaries at the western end of Lake Ontario. Samples were collected using quadrat surveys and transect surveys; the latter were conducted at beaches only. Plastic debris abundance, morphology and composition are discussed.

### 5.2.1 Transect surveys of mean plastic debris abundance on the western Lake Ontario shoreline

The transect survey plastic debris abundance results are reported as plastic items per m$^2$ ($N$ m$^{-2}$) and are referred to as ‘cross-shore’ because microplastics abundance is averaged across the width of the beach (Appendix C,D). Average plastic debris abundance was calculated by averaging across the six transect lines. Transect lengths were measured from the waterline to the vegetation line and averaged across the six transect lines.

Average microplastic debris (1-5.6 mm) abundance at each beach ranged from 4 – 16 $m^{-2}$ Fig. 5.20, with highest abundances at Marie Curtis Beach and lowest abundances at Bronte Beach, however, means were not significantly different between sites as tested with one-way ANOVA ($F$ (4, 25) = 2.21, $p$ = 0.097). When grouped by beach oriention based on where each transect was conducted, beaches that were generally east-facing (Beachway, Bronte; ME = 1.83, SD = 0.75) did not have significantly lower plastic debris abundance than beaches that were generally south-facing (Marie Curtis, Sunnyside and Woodbine; ME = 2.12, SD = 0.85) as tested with an independent samples $t$-test ($t$ (28) = 0.94, $p$ = 0.36).

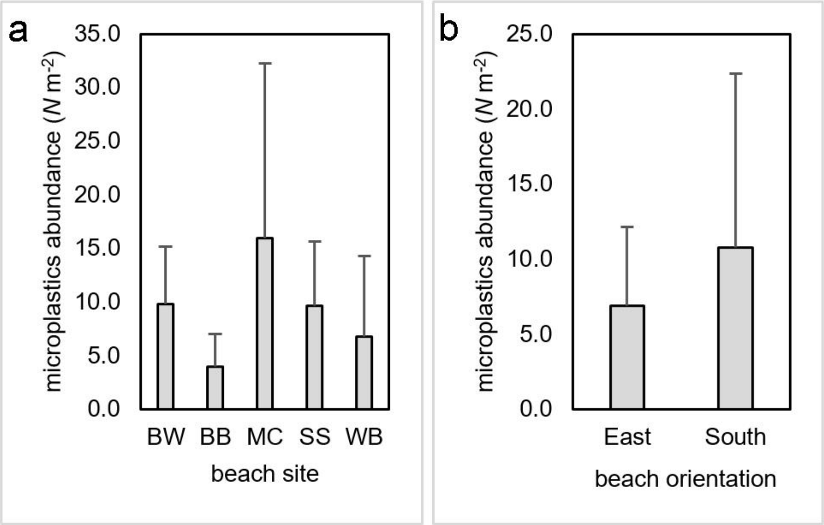


**Figure 5.20** Microplastics (1 – 5.6 mm) abundance, $N$ $m^{-2}$, on beaches of the northwestern shore of Lake Ontario as determined through a transect survey, by (a) site: Beachway (BW), Bronte (BB), Marie Curtis Park (MC), Sunnyside (SS) and Woodbine (WB) and (b) general beach orientation as measured at the mid-point of each transect.

### 5.2.2 Quadrat surveys of summer daily accumulation rate of plastic debris on the western Lake Ontario shoreline

Whereas transect surveys were used to assess the background plastic debris contamination levels on the northwestern beaches of Lake Ontario, the quadrat surveys, which were conducted over 8 consecutive days, were used to asses the daily accumulation rates of plastic debris (Appendix C, E). Quadrats were grouped into proximal and distal foreshore categories based on whether or not they were affected by daily changes in water level due to wind forcing. Accumulation rates were calculated separately for proximal foreshore quadrats and distal foreshore quadrats.

Plastic debris abundance (all plastics > 1 mm) averaged across all beach quadrats was 20 $m^{-2}$ $d^{-1}$, over a period of 8 days. Weekly accumulation rates of plastic debris (micro- and macro-plastics), calculated by summing accumulation of plastic debris over seven days (excluding Day 1), were ~90 $m^{-2}$ at the proximal foreshore and ~150 $m^{-2}$ at the distal foreshore, as averaged across all beaches. Accumulation at the distal foreshore quadrats at Bronte was not observed to be affected by storm high-water levels during the sampling period; however, large amounts of pellets were collected at the quadrat over the period of 8 days, suggesting sampling error due to not finding all plastics in the quadrat on the first day. The Woodbine distal foreshore quadrat was, in contrast, occasionally affected by high-water events during the sampling period, making the high accumulation rates at this site acceptable. Low accumulation rates were recorded at BW distal foreshore quadrat. High abundances of microplastics at the distal foreshore quadrats may be attributed to wind and high water wave action before the sampling period commenced. Distal foreshore quadrats were not sampled at Marie Curtis and Sunnyside.

Average daily accumulation rates of microplastics (1 – 5.6 mm) ranged from 20 – 80 $m^{-2}$ across all quadrats (Fig. 5.21a), and from ~5 – 80 $m^{-2}$ across proximal foreshore quadrats (Fig. 5.21b). There were significant differences in average microplastics accumulation rates between beach locations for all quadrats as tested with one-way ANOVA ($F$ (4, 89) = 3.45, $p$ = 0.01), however, a Scheffé's post hoc test revealed that the null hypothesis of equal means could not be rejected. When comparing only proximal foreshore accumulation rates, significant differences among mean accumulation rates of microplastics was again suggested with one-way ANOVA (*F* (4, 65) = 5.30, $p = 0.01$). Lower mean accumulation rates of microplastics at Bronte compared to Marie Curtis were confirmed with a Scheffé's post hoc test ($p = 0.002$). For both comparisons, the underlying assumption of homoscedasticity was not met (Levene's test: $p < 0.001$); however, variance and sample size were positively correlated, suggesting that the F-value is likely a conservative estimate and that the ANOVA may still hold.

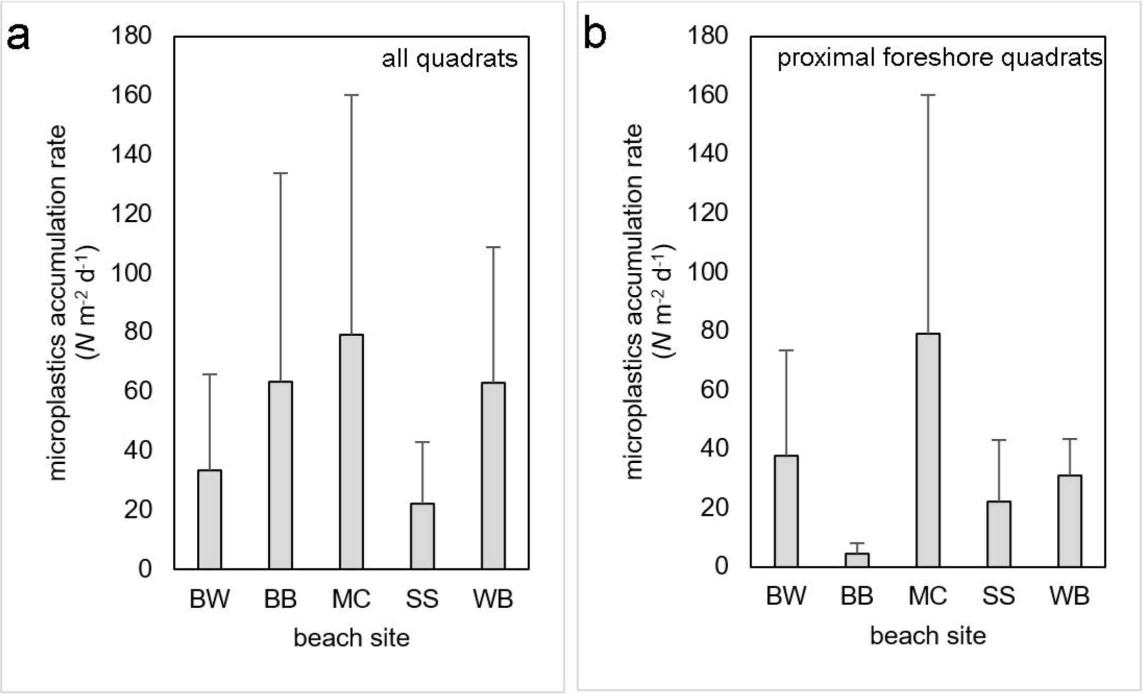


**Figure 5.21** Microplastics (1 – 5.6 mm) accumulation rates, $N$ m$^{-2}$ d$^{-1}$, averaged for (a) all quadrats and (b) proximal foreshore quadrats at Beachway (BW), Bronte (BB), Marie Curtis Park (MC), Sunnyside (SS) and Woodbine (WB) beaches on the northwestern shore of Lake Ontario.

Across all quadrats, those sampled when the sediment was wet (either from rain, dew, or wave action) had significantly lower microplastic (1 - 5.6 mm) daily accumulation rates than quadrats sampled when the sediment was dry (independent samples *t*-test, *t* (92) = 3.43, $p = 0.001$) as shown in Fig. 5.22a.

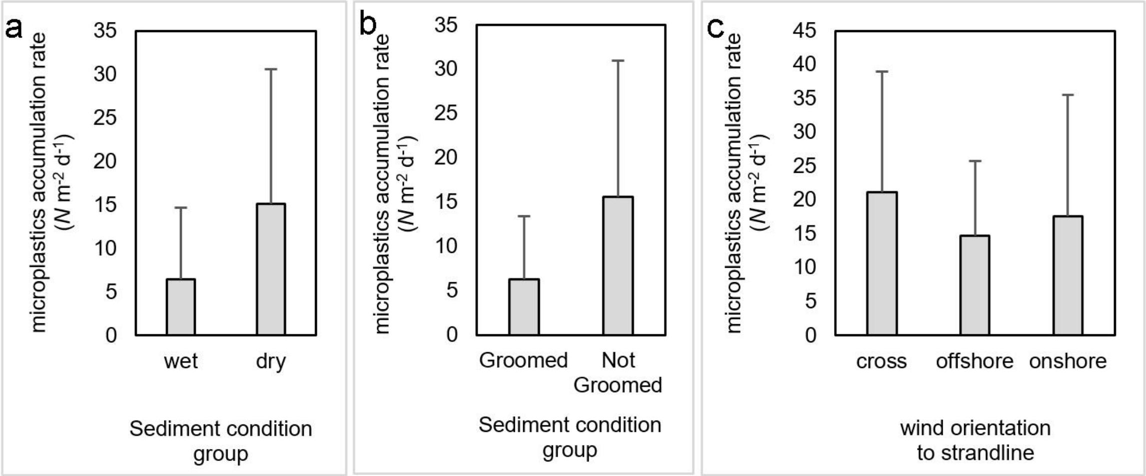


**Figure 5.22** Microplastics (1 – 5.6 mm) accumulation rates, *N* $m^{-2}$ $d^{-1}$, averaged for (a) wet vs. dry sampling conditions, (b) groomed vs. not groomed sampling conditions and (c) cross-wind, offshore wind and onshore wind sampling conditions for all proximal quadrats on beaches on the northwestern shore of Lake Ontario.

Beachway and Sunnyside beaches were observed to have been groomed periodically during the 8-day study period by a combing tractor. Quadrats in which the sediment had been groomed in the 24-hour period before the daily sample was taken had significantly lower microplastic daily accumulation rates than quadrats where sediment had not been groomed (Fig. 5.22b, independent samples *t*-test: $t\ (86) = 3.72$, $p < 0.001$).

At the start of each quadrat sampling process, wind direction and speed was measured. Comparing wind direction to the shoreline orientation, proximal foreshore quadrats could be categorized into three groups – cross-shore wind, offshore wind and onshore wind – each for which mean plastic debris abundance could be calculated (Fig. 5.22c). There was no significant difference between measured wind direction on proximal foreshore daily total (macro and microplastics) accumulation as tested with one-way ANOVA ($F\ (4, 25) = 2.21$, $p = 0.097$).

In order to assess whether there was a difference in mean daily plastic debris accumulation in the proximal foreshore quadrats (*N* $m^{-2}$) and background levels of plastic debris (*N* $m^{-2}$), as investigated through the transect survey, an independent samples *t*-test was applied to across site means (Fig. 5.23). Means were not significantly different (*t* (71.5) = 0.24, *p* = 0.81).

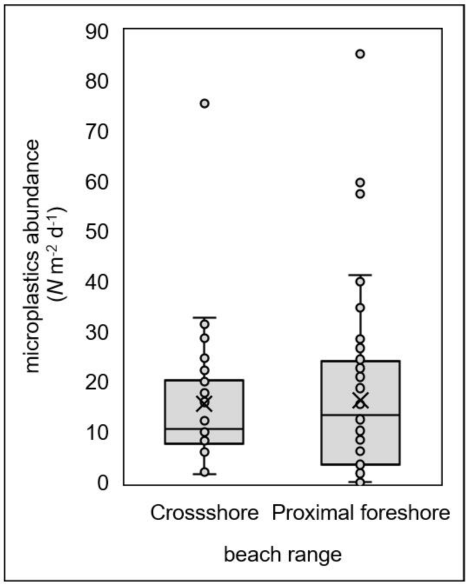


**Figure 5.23** Box-plot showing the distribution of microplastics (1 – 5.6 mm) abundance comparing the cross-shore (transect survey) and proximal foreshore (quadrat survey).

### 5.2.3 Quadrat surveys of summer daily accumulation rate of plastic debris in the riparian zone of western Lake Ontario tributaries

Visible plastic debris was sampled using a quadrat survey at four tributaries draining into western Lake Ontario (Appendix F, G). Abundance of plastic debris was normalized to pieces per square meter ($N$ m$^{-2}$) by dividing debris counts by the quadrat area and averaging both quadrats. Mean plastics abundance varied from 14 – 60 m$^{-2}$ (Fig. 5.24) There was no significant difference in mean plastic debris abundance across sites as tested with one-way ANOVA (*F* (3, 12) = 1.74, *p* = 0.21). Plastic debris abundances per square meter were greatest at Etobicoke Creek, for both macro and microplastics combined and for microplastics alone. The abundance of macroplastics was similar across all sites.

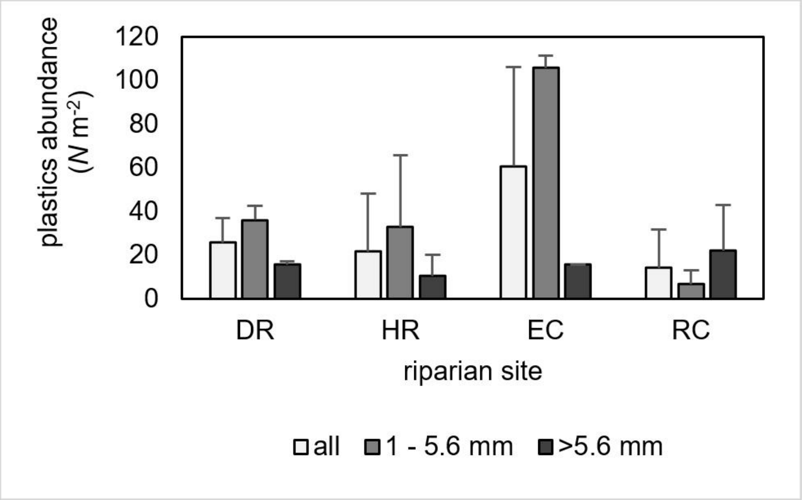


**Figure 5.24** Plastic debris abundance, $N$ m$^{-2}$, by size category for four riparian sites: Don River (DR), Humber River (HR), Etobicoke Creek (EC) and Red Hill Creek (RC) along the northwestern shore of Lake Ontario.

### 5.2.4 Particle morphology

Between beach transects, the fraction of plastic items collected that were 1 - 5.6 mm in size was about 20% lower at beaches in the GTA, compared to eastern sites Bronte and Beachway (Fig. 5.25a). A one-way ANOVA revealed statistically different means between the proportions of microplastics across sites ($F$ (4, 25) = 5.32, $p = 0.003$); however, only the mean levels at Marie Curtis and Beachway were significantly different (Scheffé's post hoc test, $p = 0.015$).

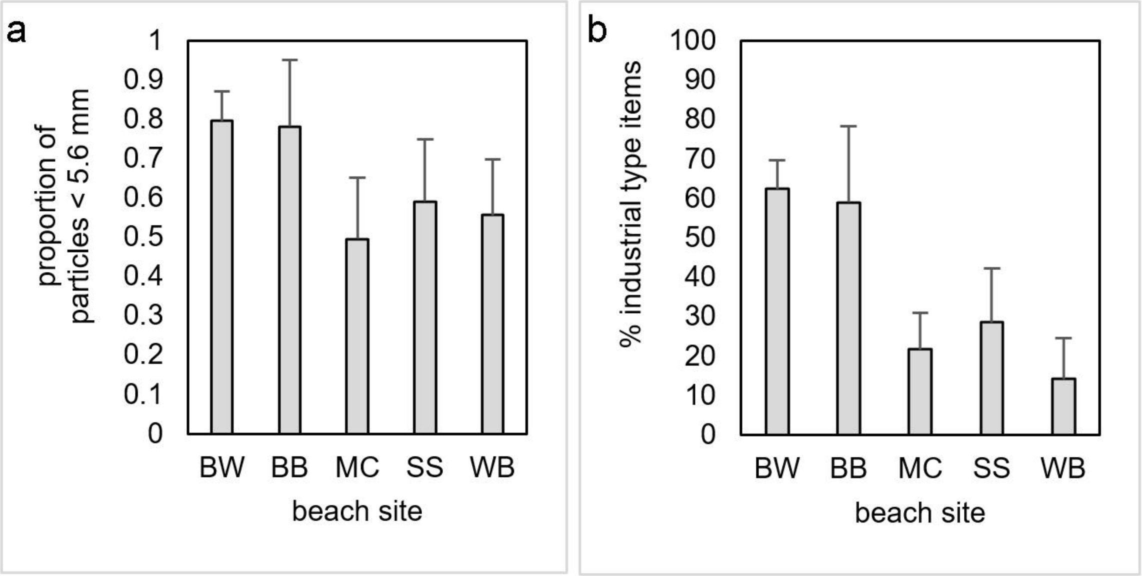


**Figure 5.25** (a) Relative proportions of microplastics (particles 1 – 5.6 mm) compared to macroplastics (particles > 5.6 mm) for cross-shore plastics debris transect survey. (b) Relative proportions of industrial type items (pellets) for cross-shore plastics debris transect survey.

Between transects, the fraction of plastic items collected that were certainly industrially sourced (pellets) was ~40% lower at beaches in the GTA, compared to Bronte and Beachway beaches on the eastern extent of the northern shore (Fig. 5.25b). Using a one-way ANOVA, mean proportions of pellets to other types of debris were different across beaches (F (4,25) = 5.97, p = 0.002). The levels at Woodbine were significantly lower than at Beachway (Scheffé's post hoc test: p = 0.008) and at Bronte beaches (Scheffé's post hoc test: p = 0.013).

The morphological characteristics of the plastic debris were compared between the proximal foreshore (daily accumulation) and the cross-shore for each beach site. The ratio of microplastic to macroplastic was about 0.58 and 0.63 at proximal foreshore and cross-shore, respectively, and was notably consistent across sites with standard deviations of 0.08 and 0.13 respectively. Mean proportions of industrial- to consumer-type plastics were 0.22 and 0.44 for the proximal foreshore and cross-shore, respectively.

A more detailed representation of the proportion of each morphology (fragments, beads, foam, intact object) is given for the proximal foreshore (Fig. 5.26a) and cross-shore (Fig.

5.26b) for each of the five surveyed beaches. Plastic debris deposited on the banks of four streams entering western Lake Ontario was collected from two quadrats at each tributary, and were sorted using the same size categories as the beach quadrats: 1-5.6 mm and > 5.6 mm. When averaged across all riparian quadrats (Fig. 5.26c), microplastics were more abundant, however, no significant difference between mean abundance ($N$ m$^{-2}$) of macroplastic and microplastic debris was found using an independent samples $t$-test ($t$ (14) = 0.66, $p$ = 0.52).

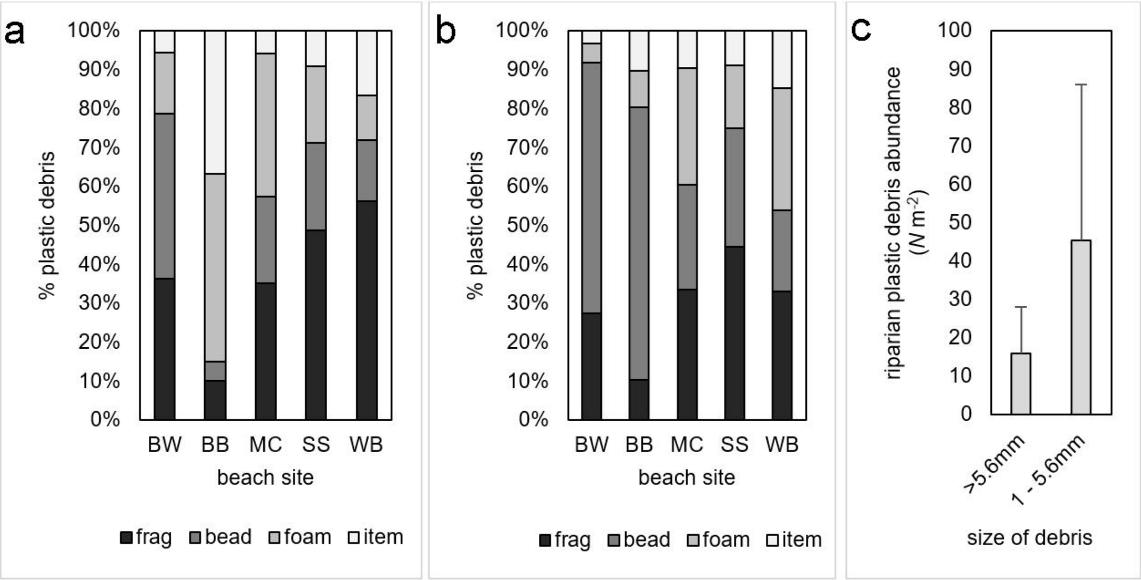


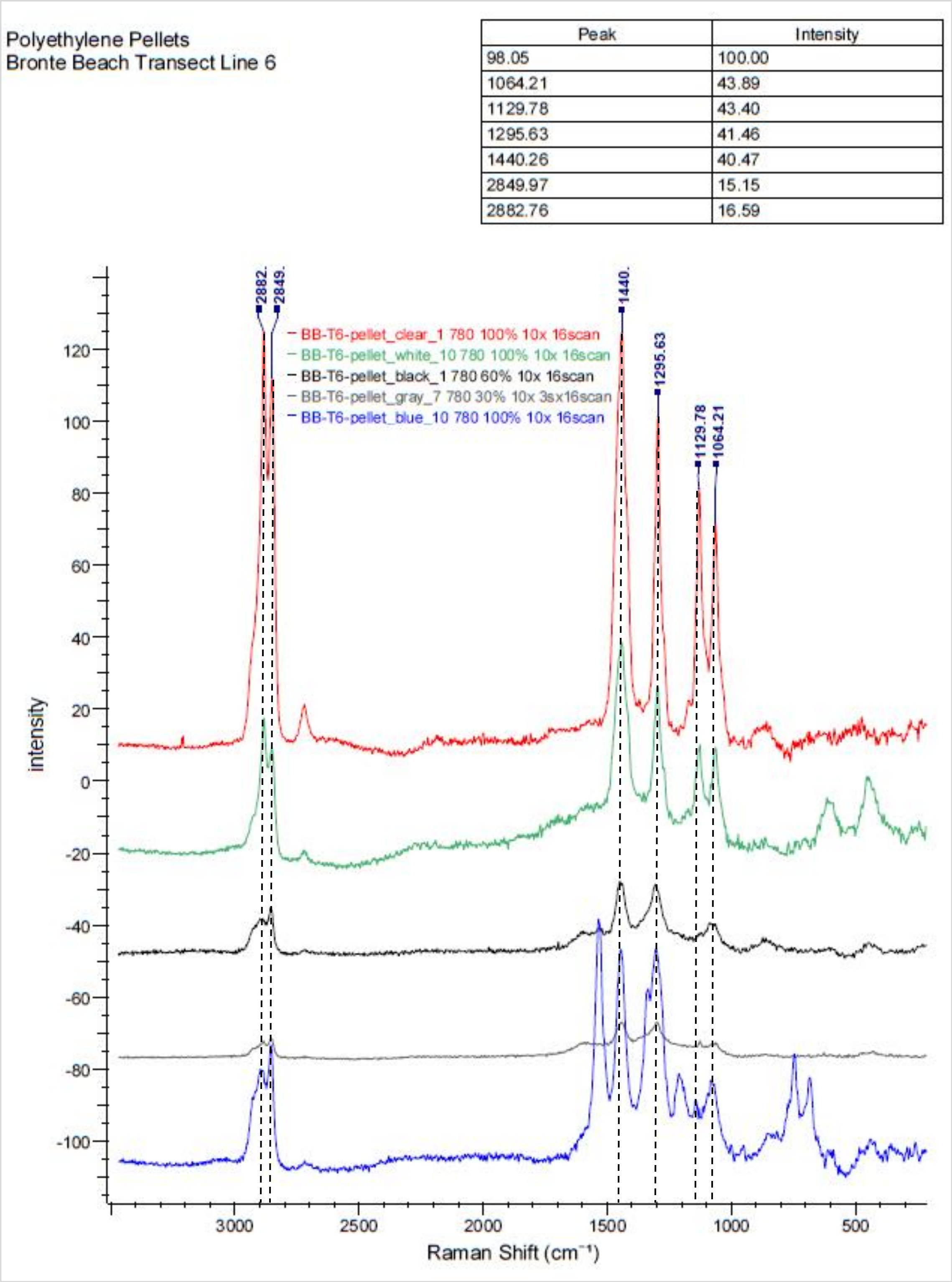
**Figure 5.26** Relative proportions of fragments (frag), pellets (bead), foam plastics (foam) and intact objects (item) averaged for (a) the proximal foreshore quadrats and (b) the cross-shore transects. (c) The average plastic debris abundance, for macroplastics (> 5.6 mm) and microplastics (1 – 5.6 mm), across the four riparian sites. Error bars show standard deviation from the mean.

### 5.2.5 Particle composition

Of the 45 beads, fragments and foam particles (1 - 5.6 mm) sampled at Bronte (BB-T6), all were positively identified as synthetic polymers. Three particles of white foam were identified as PS. Two fragments of similar appearance were identified as PP and PS (non-expanded), separately. Of the remaining 40 pellets, 36 (90%) were identified as PE, and 4 (10%) were identified as PP. Spectra produced by clear pellets had easily identifiable peaks, however, the spectra of many colored pellets were distorted. Blue ($N$=9), gray ($N$=10), opaque white ($N$=9) and black ($N$=1) pellets were all identified as PE, except for

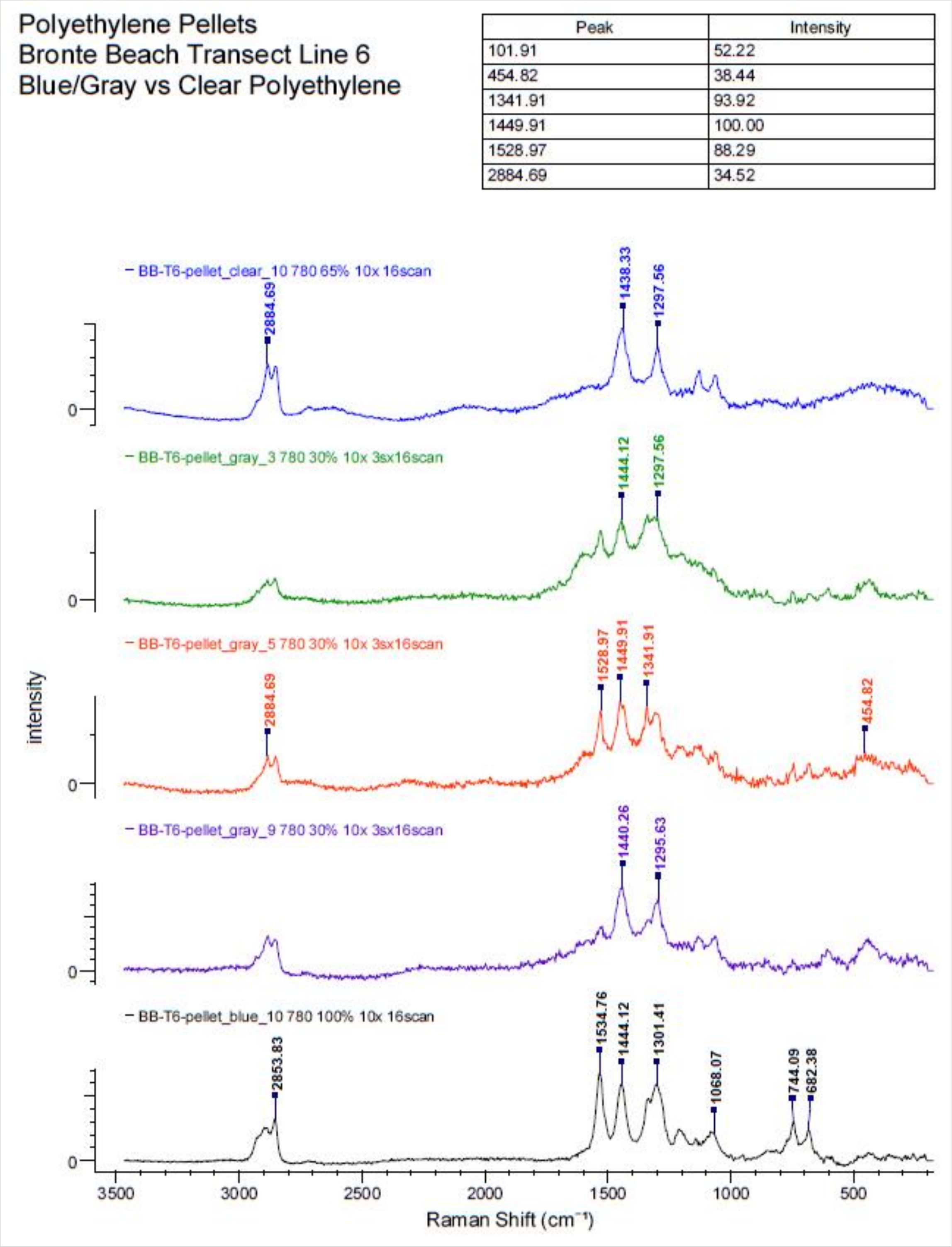
4 white pellets, which were identified as PP. In Fig. 5.27, spectra of clear, white, black, gray and blue PE pellets are stacked for peak comparison. Variations may be attributed to the presence of additives, dyes, or fillers. For example, spectra of blue pellets and several gray pellets (Fig. 5.28) show characteristic peaks for PE, but also additional peaks suggesting the presence of additives and/or fillers, potentially phthalate blue and talc. In Fig. 5.29, the spectra for two white pellets identified as PP are displayed together with the spectra for a PP fragment found in Etobicoke Creek. Pellet_white_5 likely contains rutile and pellet_white_6 has a peak at 1085 which is characteristic of calcium carbonate. This may suggest a calcite filler, as is commonly used in pellet manufacturing (Byrdson, 1999; Lenz, 2015). The spectra of the four items identified as PS are shown in Fig. 5.30, 3 corresponding to expanded PS foam pieces and 1 to an unexpanded PS fragment.

Two pellets were also analyzed with $\mu$XRF to test for suspected fillers. One light blue pellet (PEBl3) which was identified as PE with Raman spectroscopy, was analyzed at 40 kV (60 seconds live time). The elements titanium, calcium, iron, copper, zinc, potassium and silicon were detected, with the largest peaks being titanium, calcium and iron. The second pellet (PEG6), which was gray, was analyzed at 25 kV (60 seconds live time) and 50 kV (240 seconds live time). The spectra revealed the presence of calcium, titanium, iron, copper and zinc as well as smaller amounts of silicon, aluminum, sulfur, phosphorous, potassium, chromium, lead and zirconium.



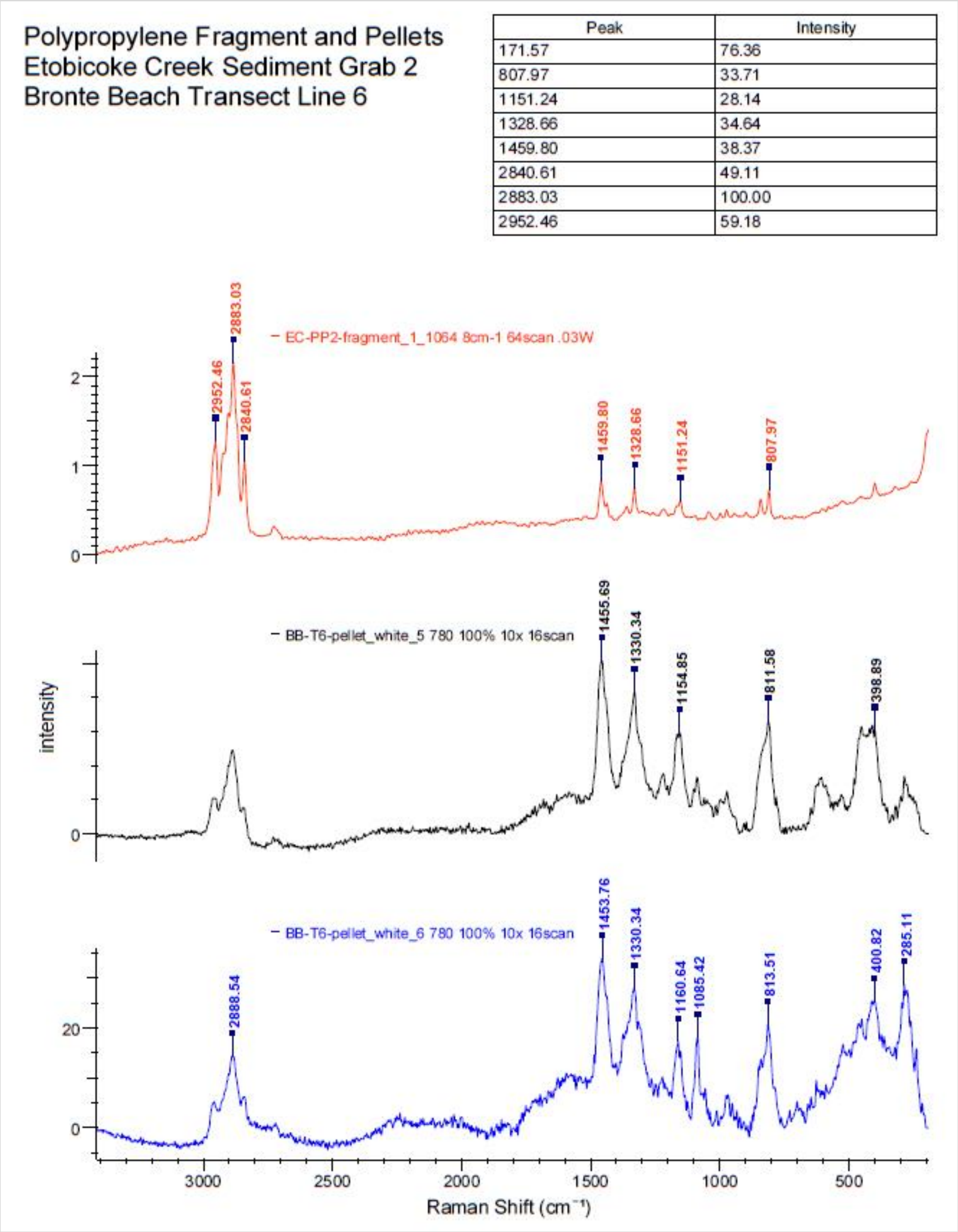
| Peak | Intensity |
|---|---|
| 98.05 | 100.00 |
| 1064.21 | 43.89 |
| 1129.78 | 43.40 |
| 1295.63 | 41.46 |
| 1440.26 | 40.47 |
| 2849.97 | 15.15 |
| 2882.76 | 16.59 |

**Figure 5.27** Raman spectra of select polyethylene pellets of various colour. Dashed lines indicate characteristics peaks for pure polyethylene



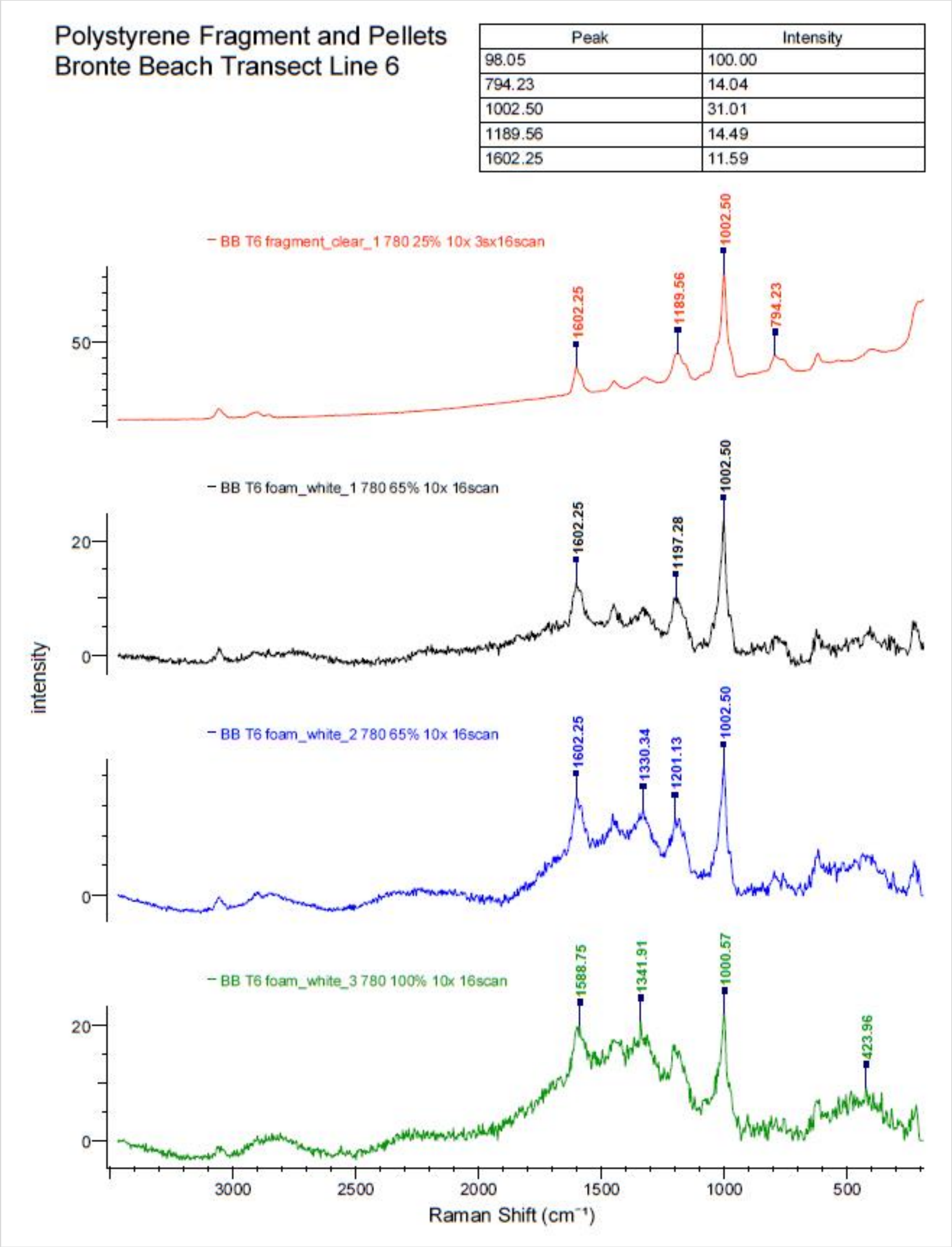
| Peak | Intensity |
|---|---|
| 101.91 | 52.22 |
| 454.82 | 38.44 |
| 1341.91 | 93.92 |
| 1449.91 | 100.00 |
| 1528.97 | 88.29 |
| 2884.69 | 34.52 |

**Figure 5.28** Raman spectra of blue and gray polyethylene pellets with reference to a transparent (clear) polyethylene pellet. Blue and gray pellets display extra peak at ~1528 $cm^{-1}$ and blue pellet displays extra peak at ~744 $cm^{-1}$ and ~682 $cm^{-1}$.



| Peak | Intensity |
|---|---|
| 171.57 | 76.36 |
| 807.97 | 33.71 |
| 1151.24 | 28.14 |
| 1328.66 | 34.64 |
| 1459.80 | 38.37 |
| 2840.61 | 49.11 |
| 2883.03 | 100.00 |
| 2952.46 | 59.18 |

**Figure 5.29** Raman spectra of polypropylene fragment and opaque white coloured pellets.



| Peak | Intensity |
|---|---|
| 98.05 | 100.00 |
| 794.23 | 14.04 |
| 1002.50 | 31.01 |
| 1189.56 | 14.49 |
| 1602.25 | 11.59 |

**Figure 5.30** Raman spectra of select polystyrene plastics including a rigid transparent (clear) fragment and expanded foam fragments.

## 5.3 Watershed analysis of Lake Ontario

A total of 66 watersheds were analyzed for their population and abundance of plastics-related industries. Watershed area ranged from 34 to 14,300 km$^2$, with the Trent River watershed being the largest. Watershed population ranged from 441 to 1,580,000 people. The Don River watershed had the greatest population, whereas the Toronto Urban Catchment watershed had the highest population density with ~7,380 people km$^{-2}$ (Fig. 5.31). Both of these watersheds empty into the Toronto Harbour.

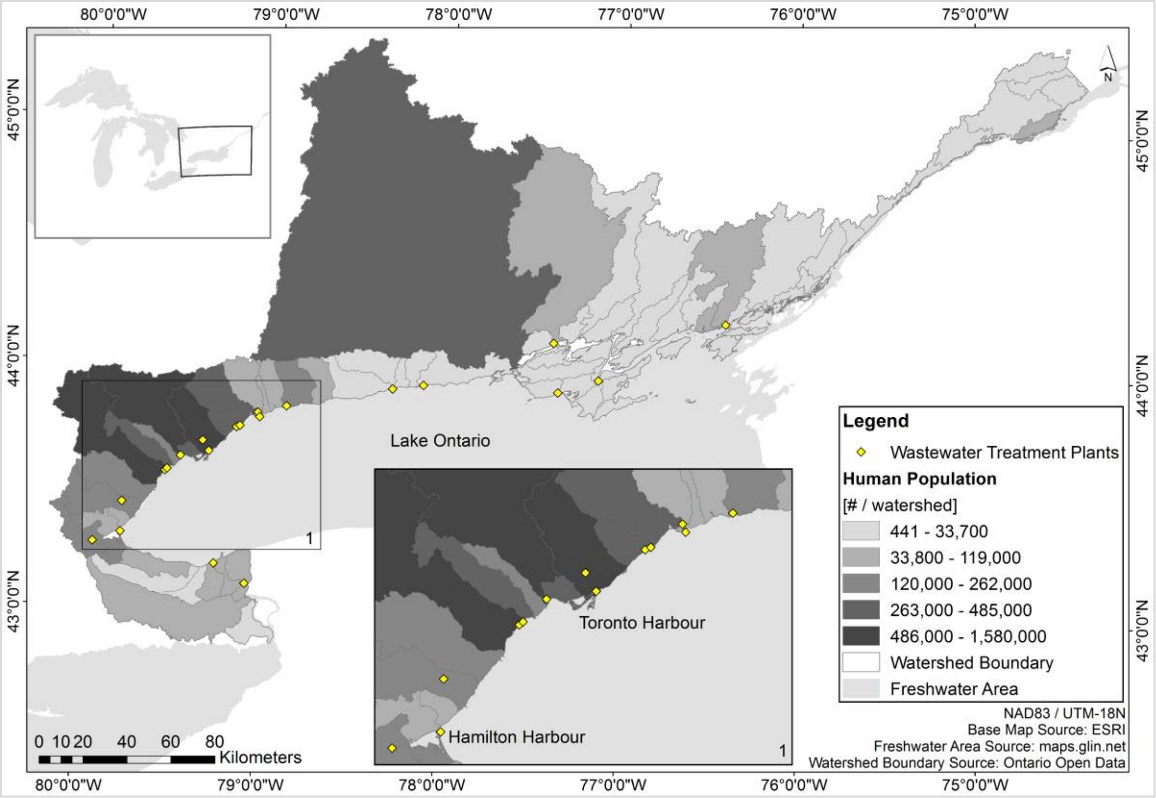


**Figure 5.31** Human population map for watersheds draining into Lake Ontario and the St. Lawrence River. Locations of wastewater treatment plants on the shoreline of the study are included.

With regards to industry intensity, Etobicoke Creek contains the largest number of plastic product manufacturers, distributors and service businesses combined, at 62 business facilities (0.3 facilities km$^{-2}$). There is a clear clustering of the plastic industry in the Greater Toronto Area extending towards the Hamilton Region (Fig. 5.32). Several watersheds did not include any plastic industry facilities, as identified through the ThomasNet directory. Figure 5.33 shows a detailed view of population levels, wastewater treatment plant facilities, plastics-industry facilities and microplastic abundance in the GTA.

The calculated area, population and industry count for each watershed are given in Appendix J and were used to generate the IDW calculated values ($X_a$, $X_{pop}$, and $X_{ind}$) for each sediment sample. Of the 50 sediment samples, 47 were within 10 km of at least one major tributary mouth and were included in the IDW correlation analyses.

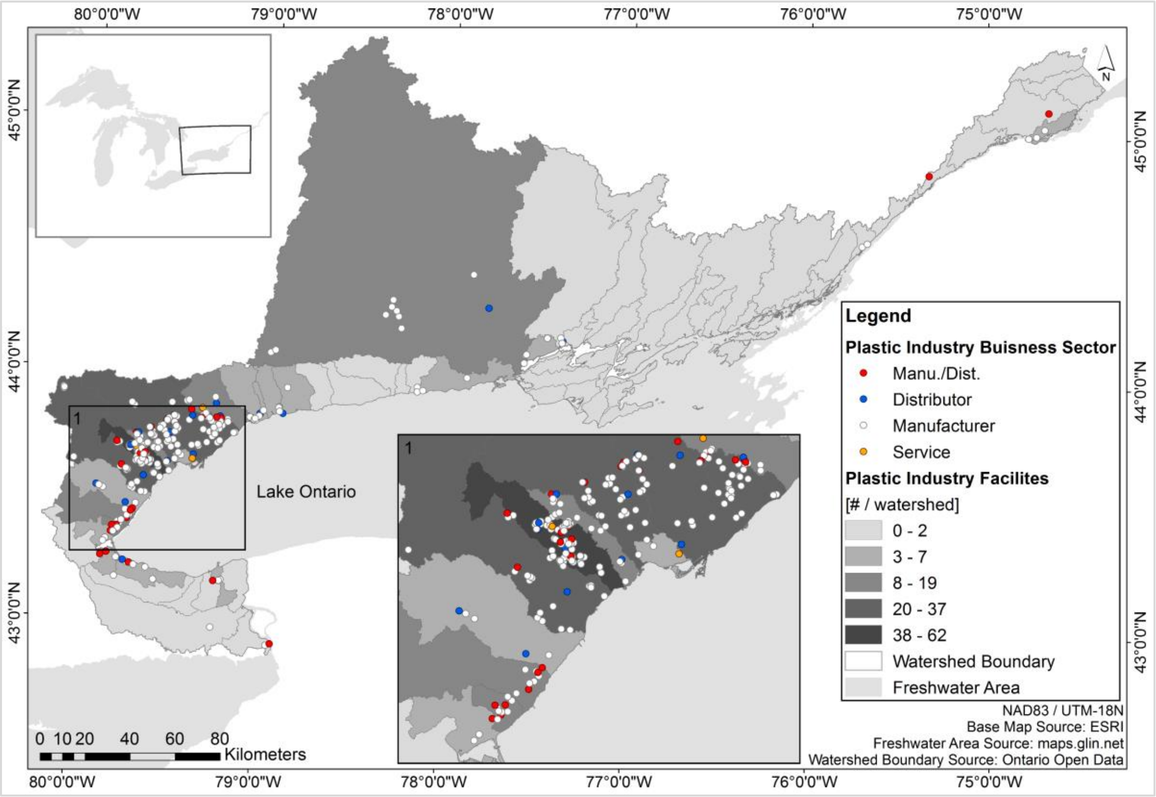


**Figure 5.32** Locations of plastics-related manufacturing, distributing and service facilities within the watersheds draining into Lake Ontario and the St. Lawrence River.

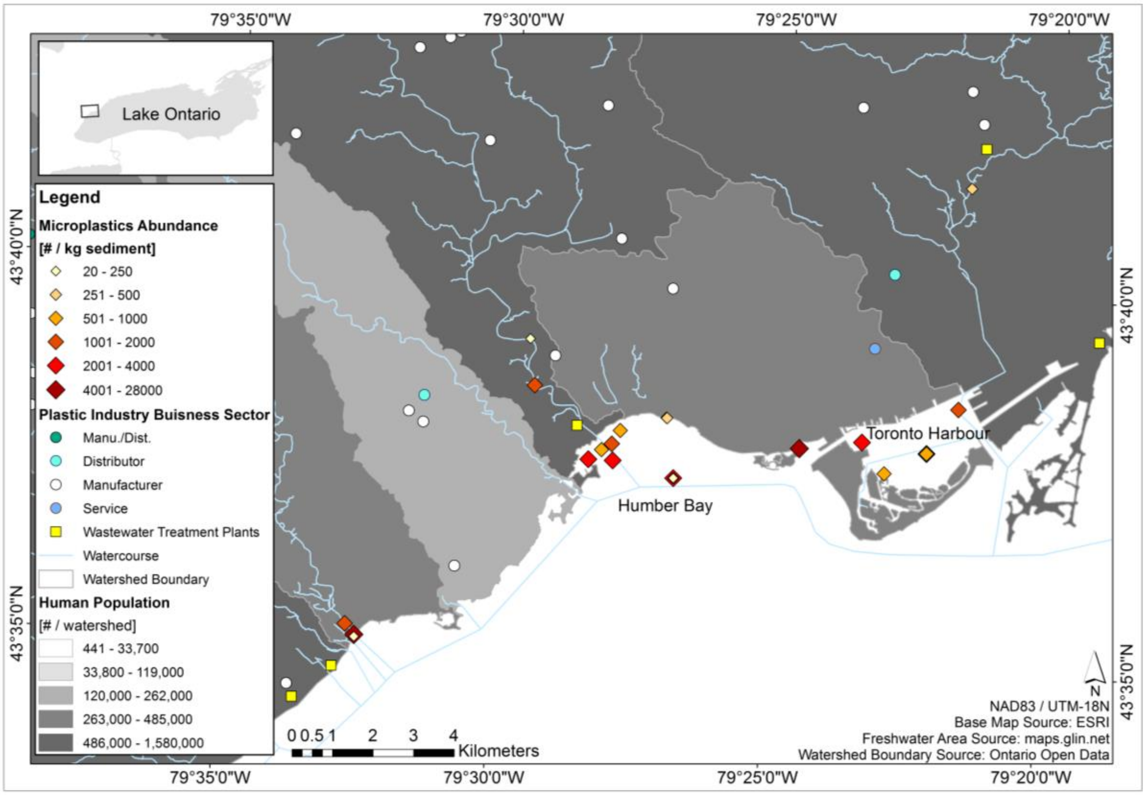


**Figure 5.33** Microplastics abundance, *N* kg$^{-1}$, in nearshore, tributary and beach sediments of the Greater Toronto Area. Plastics-related industry facilities and wastewater treatment plants show potential point sources of microplastics. Human population of watersheds draining into the Toronto Harbour and Humber Bay is indicated by the gray shading and represents an estimate of the relative intensity of non-point sources of microplastics to this urban coastal region of Lake Ontario.

In order to test for correlations between the watershed properties, a bivariate (Pearson) correlation test was used to compare area ($F_a$), population ($F_{pop}$) and industrial levels ($F_{ind}$) across the 66 watersheds in the study area. Data were first transformed using a $\log_{10}$ function to meet underlying normality and equal variance assumptions. All three variables were significantly correlated; area and population ($r$ (73) = 0.46, $p < 0.001$, Fig. 5.34a), area and industry ($r$ (73) = 0.26, $p = 0.029$, Fig. 5.34b) and population and industry ($r$ (73) = 0.78, $p < 0.001$, Fig. 5.34c).

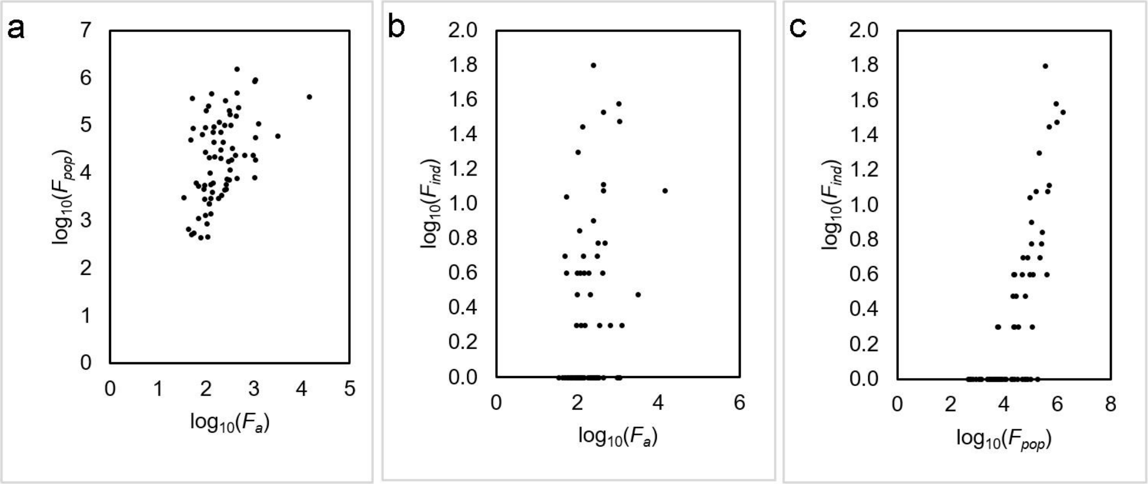


**Figure 5.34** Correlation of watershed characteristics pertaining to potential microplastics sources: area ($F_a$), population ($F_{pop}$) and abundance of plastics-related industry ($F_{ind}$) across 66 watersheds draining directly into Lake Ontario.

Due to significant correlation between the watershed properties and the likelihood of not including important variables (such as hydrologic effects), a multivariate regression analysis regarding the relative contribution of each factor to microplastic contamination levels could not be conducted. However, the IDW values ($X_a$, $X_{pop}$, and $X_{ind}$) were plotted against microplastics abundance, after being $\log_{10}$ transformed data, to meet underlying normality and equal variance assumptions, and correlated to investigate which factor best explained variation in microplastics abundance (Fig. 5.35).

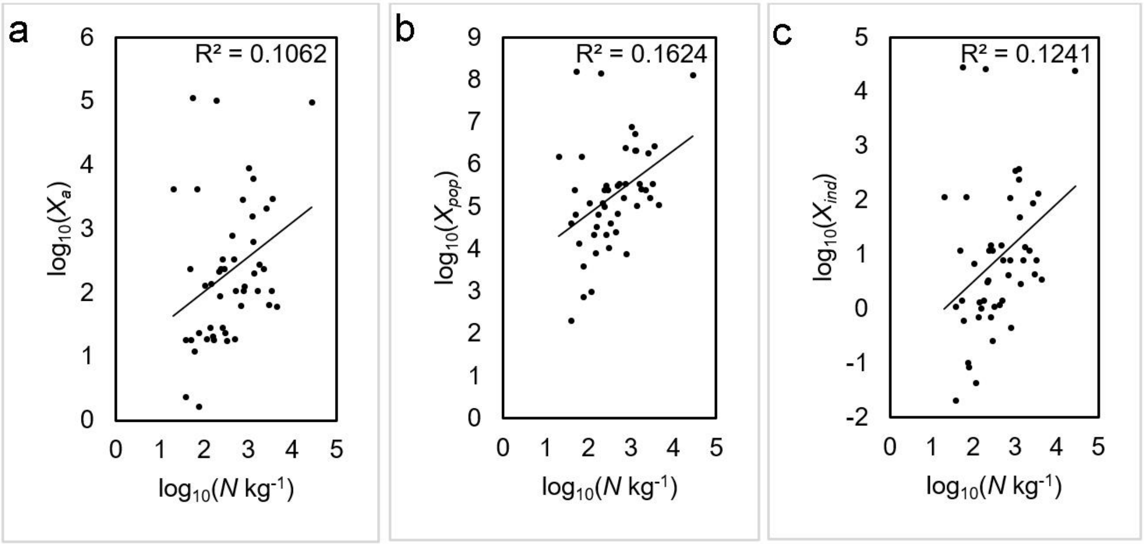


**Figure 5.35** Microplastics abundance, *N* kg$^{-1}$ and inverse distance weighted factors of watershed area ($X_a$), population ($X_{pop}$), and plastics-related industry intensity ($X_{ind}$) for watersheds draining to points within 10 km of the sediment sample.

A bivariate (Pearson) correlation test was performed on the $\log_{10}$ transformed data (*N* kg$^{-1}$ and $X_a$, $X_{pop}$, and $X_{ind}$), to meet underlying normality assumptions. It revealed statistically significant correlations between microplastics abundance and each of the three factors. Approximately 10% of the variation in microplastics abundance was explained by watershed area ($r$ (47) = 0.32, $p$ = 0.031), ~16% by population ($r$ (47) = 0.39, p = 0.007) and ~12% by the number of plastics-related industries ($r$ (47) = 0.35, p = 0.016). The watershed population factor had the highest Pearson correlation factor as well as the most significant linear correlation.

# Chapter 6

# 6 Discussion

The distributions and compositions of plastic debris in the coastal sediments of Lake Ontario and the St. Lawrence River are examined in reference to the possible factors determining microplastics transport, sources of plastics to the lake and the human geography of the region. The discussion is subdivided into: 1) microplastics collected via instrumental sampling and processed with density separation techniques, 2) plastic debris sampled by visual survey, 3) proposed sources of plastic debris, drawing from the literature as well as from provincial, municipal and industrial data sources, and 4) the scope of the methods and research design with suggestions for future studies.

## 6.1 Microplastics in Lake Ontario and St. Lawrence River sediments

Microplastics, ~0.25 - 2 mm in size, are ubiquitous in nearshore, tributary and beach sediments along the Canadian shoreline of Lake Ontario and the St. Lawrence River. The distribution of microplastics, as described in Sections 5.1 and 5.2, is not spatially homogenous, either laterally across the study area or vertically within the sediment core samples. This may be a function of geomorphology, external environmental processes and intrinsic characteristics of the microplastic particles affecting transport behavior. The origins and sources of the microplastic debris can be suggested based on category and composition of the particles.

### 6.1.1 Lateral trends in microplastics abundance

The markedly intense microplastics contamination in the coastal sediments of 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. The concentration of the plastics industry is also high in these 5 watersheds, which encompass approximately half of the plastics production facilities that were identified in the study region. Determining how many microplastics are derived from consumer activities versus industrial activities, however, is complicated by the apparent spatial autocorrelation of watersheds with large populations and abundant plastics-related industry facilities (watersheds with large populations also have an abundance of plastics-related industry facilities). The statistically highly significant correlation between population and industry facility count among the watersheds in this study, suggest that a higher resolution study (for example on a sub-watershed scale) would be necessary in order to disentangle the relationship between population, industry and microplastics abundance. The low correlation $R^2$ values in Fig. 5.35 reveal that there are other variables affecting microplastics abundance besides watershed area, population and industry. Examples include the distance of industrial sites from the lake, local variations in hydrologic conditions, and spatial variability of unidentified sources and outfalls.

The watershed with the greatest population density in the study area is the Toronto Urban Catchment Basin, with a mean of 7,380 people km$^{-2}$. This watershed is coastal, extending at most 10 km inland. The drainage systems in this watershed comprise a network of storm-water and sewage drains, rather than natural tributaries. Although wastewater treatment plants are used to treat sewage and sometimes storm water, in combined sewer systems, heavy precipitation events often result in flows that are greater than the maximum capacity of the system. Bypasses and combined sewer overflow (CSO) events have been investigated by the environmental law company, Ecojustice, who report that in Lake Ontario, at least 11.5 billion L of untreated sewage was released into Lake Ontario during bypass events in 2006-2007 alone, not including CSO events (MacDonald and Podolsky, 2009). These events may be an important source of microplastics to the lake and river, as wastewater treatment plants have been shown to remove microplastics from sewage (Carr et al., 2016). In addition to wastewater treatment plants, storm-water outfalls draining urban areas may be notable sources of microplastics. Storm-water is generally not treated, and may contain plastic street litter, especially where nets or grates are not installed. Even where grates are installed, microplastics are able to pass through the grate openings.

The correlation analysis in Section 5.3, Watershed Analysis of Lake Ontario, suggests that the watershed factors of population, industry and drainage area account for only 10 - 16% of the variation in microplastics abundance. The high concentrations of microplastics in Toronto Harbour and Humber Bay may also be influenced by the morphology of the shoreline. The sample with the second greatest abundance of microplastics (4,270 $kg^{-1}$) was the nearshore core, G-TH1, taken from a small mooring harbour on the Outer Toronto Harbour.  It has been shown that subsurface 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) and Hall (2008) show that in both summer and winter, currents in the vicinity of Toronto Harbour move along the shore from southwest to northeast. The peninsula located just west of Humber Bay may protect the southeast shore of Humber Bay and the Inner Toronto Harbour from severe waves and winds during the dominant anticyclonic surface water circulation during summer and winter seasons in the northwestern basin of Lake Ontario (Beletsky et al., 1999). Similarly, the Toronto Islands may reduce water flow velocity, and associated resuspension and transport events, in the Inner Toronto Harbour and Humber Bay during easterly long-fetch storm events (Rukavina, 1976), increasing the relative abundance of microplastics in this region, compared to exposed coastline regions. 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 is completely enclosed with only one major outflow into the lake, but contains relatively low microplastic contamination levels in comparison to what would be expected given the coastal morphology of the harbour. This indicates that the distribution of microplastics in sediments is foremost dependent on source loads.

The decrease of maximum microplastics abundance with depth in nearshore sediments agrees with modelling and field studies of nearshore debris in marine environments (Ballent et al., 2013; Claessens et al., 2011). A decrease in abundance with depth is consistent with a decrease in abundance away from the shore, suggesting that microplastics are sourced mainly from the shoreline (at tributary mouths or other point sources).

Spatial variability, on scales of meters to hundreds of meters, was exhibited in the near shore sediments of Toronto Harbour and Humber Bay where sample sites were proximal and where multiple samples were collected from the same site. The four separate grab and trap samples collected from the Humber Bay Index station (S-7546 and S-HB14, S-3025, T-2047) along the Toronto waterfront had microplastic counts between 4 and 221 $hg^{-1}$, 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). The variability observed on small spatial scales in Toronto Harbour and Humber Bay implies that the microplastics abundances observed along the remainder of the lake coastline, where sampling was conducted sparsely, may be underestimating the amount of microplastics in those regions. Quantifying the various environmental factors such as near-bottom flow velocity, turbulence and degree of harbouring in similar future investigations may allow for further clarification of how these factors affect microplastics distribution in near shore environments.

Extreme variability of microplastics abundance was also exhibited in tributaries (Fig. 5.1) on small spatial scales of tens to several hundreds of meters, and reflects the variable hydrodynamic environments in tributaries. Tributary site P-EC2, for example, had two orders of magnitude more microplastic particles than beach sediments within 100 m at Marie Curtis Park, and one order of magnitude more microplastics than sediments 350 m upstream. Variations may also be affected by the regularity and spacing of storm-water and/or industrial outfalls, the presence of obstructing structures and the areal extent of the watershed. Densely spaced outfalls, as well as reduced flow rates due to obstructing structures may be associated with increased microplastic emplacement.

The dense concentration of microplastics at the tributary mouth of Etobicoke Creek compared to upstream sediments is consistent with reduced bottom boundary shear stresses, the driving force of particle motion in a transport fluid, as tributaries widen and flatten into the lake. In a marine model study, 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 (Halfman et al., 2006). In terms of ecological implications, the apparent accumulation of microplastics at tributary mouths suggests that bottom-feeding fish dwelling in these regions may be most prone to microplastics ingestion. Fish species found near the mouths of tributaries in the Toronto region are various species of carp, the Northern Hog Sucker, Redhorses, and catfish (pers. comm., L. Erdle of Ontario Streams). The sample with greatest microplastics abundance was one comprising mainly algae, taken from the mouth of Etobicoke Creek. This finding suggests that plastics are trapped in the algal growth on the stream bed. As discussed by Gutow et al. (2015) seaweeds may be an important factor in the transfer of microplastics to benthic herbivores, particularly in the case of microplastics that are in the submillimeter size range.

Microplastics abundance on beaches did not vary significantly between the proximal and distal foreshore, however, this could be attributed to the low sample size. The greatest abundances were found in samples from the beaches closest to Toronto, with abundances decreasing with distance from Sunnyside Beach, in both directions. In comparison with nearshore and tributary samples, the beach samples had the lowest abundance of microplastics, which may be attributed to periodic high wave action. Buoyant plastics are expected to accumulate along the high water line. Non-buoyant plastics, which are still less dense than sand grains, are thus expected to be winnowed out of the sediment during wave action and either carried to the high water line or washed back out to the lake, leaving the sediments relatively free of microplastics contamination.

Microplastic contamination loads in Lake Ontario sediments are comparable to those reported in similar studies from around the world, as summarized in Table 6.1. In comparison with a similar investigation of microplastics in the sediments of Lake Erie (Dean, 2016), microplastic abundance was overall greater in Lake Ontario. In the nearshore lake bottom sediments of Lake Erie average microplastics abundance was 89 $kg^{-1}$, compared to 980 $kg^{-1}$ in Lake Ontario bottom sediments. In tributaries of Lake Erie, microplastics abundance was on average 140 $kg^{-1}$, compared to 610 $kg^{-1}$ for tributaries of Lake Ontario. Average microplastics abundance on Lake Erie beaches, as sampled with a corer, was ~112 $kg^{-1}$, compared to 140 $kg^{-1}$ on Lake Ontario beaches. The greater abundance of microplastics in Lake Ontario may be attributed to greater population and industrial activity in the regions surrounding the lake associated with a larger source of plastics to the lake, or to different hydrological conditions.

**Table 6.1** A summary of average microplastics contamination in various marine and freshwater sediments. Microplastics contamination is reported as average particle abundance per kg dry sediment, $N$ $kg^{-1}$ (dw).

| **Study** | **Study Area** | **Depositional Environment** | **Avg. $N$ $kg^{-1}$ (dw)** |
|---|---|---|---|
| Turra et al., 2014 | Sao Paulo, Brazil | Marine Beach | 0.1[a] |
| Dekiff et al., 2014 | Germany | Marine Beach | 2[b] |
| VanCauwenberghe 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.

### 6.1.2 Vertical trends in microplastics abundance

The nearshore gravity core samples provide insight into the vertical variability of microplastics in sediments in a region of the lake where plastic concentrations are possibly the highest in Lake Ontario (Fig. 5.1). In four of the five nearshore cores, the abundance of microplastics decreased from the first interval to the second, across ~1 g $cm^{-2}$ of accumulated sediment (Fig. 5.3). Microplastics abundance was normalized to sediment weight, meaning that this decrease may be attributed to the greater content of water and natural organics (i.e. plant and animal detritus) in the upper unconsolidated layer. The relative buoyancy of microplastics compared to the lithic sediments may also affect the increase in abundance in the upper centimeters of the nearshore gravity cores. Below the first core interval, microplastic abundance is fairly constant with depth, suggesting constant levels of input and hydrologic conditions, except at site G-HB3 where microplastics abundance increases gradually with increasing depth over the full sediment profile.

Considering the calculated sediment accumulation rate of ~1.7 mm $yr^{-1}$ for the nearshore environment of the western basin of Lake Ontario (Rukavina, 1976), the deepest gravity core, which penetrated to a depth of 15 cm (11.2 g $cm^{-2}$), may represent the last ~90 years. Sediment accumulation rates calculated using the sediment trap samples, give accumulation rates of 0.22 g $cm^{-2}$ $yr^{-1}$ in Toronto Harbour, 0.28 g $cm^{-2}$ $yr^{-1}$ in Hamilton Harbour, and 0.55 g $cm^{-2}$ $yr^{-1}$ in Humber Bay. Using these nearshore sediment accumulation rates, the deepest gravity core may represent between 20 and 50 years of accumulated sediment. Considering the increase in water content in the unconsolidated sediment of the upper layer, however, a much shorter time period may actually be represented. Frequent resuspension of surface sediments in the nearshore zone by storm events (Klump et al., 2000) can equal annual deposit volumes, as has been shown for Lake Michigan (Eadie et al., 1996; Schwab et al., 2000). Following large-scale resuspension events, particles with higher settling velocities would be expected to settle first, with more buoyant particles, such as plastics and plant detritus, settling more slowly.

Plastics resuspended by storm events may be confined to the nearshore in the presence of a coastal plume in the summer months (Mortimer, 1988; Hall, 2008) but during winter, when lake stratification breaks down, offshore transport of plastics would be expected to increase in intensity. 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.

Beach microplastics were identified throughout the upper 20-30 cm of sediment in all proximal and distal foreshore beach locations. Average abundances decreased from the top 10 cm interval to the bottom 10 cm interval, with the greatest decrease, of about 100 $kg^{-1}$, between 0-10 and 10-20 cm (Fig. 5.9b). This trend, however, is not statistically significant and was possibly skewed by low sample size. Although this study only investigated to a maximum depth of 30 cm, a 3-dimensional study of beach plastics showed that < 10% of plastics were found within the top 5 cm of sediment on a marine beach and that microplastics could be distributed throughout the sediment profile to at least 2 m below the sediment surface (Turra et al., 2014).

### 6.1.3 Physical characteristics and transport behavior of microplastics

The transport behaviors of microplastics, which are in part governed by their physical properties, such as density (polymer composition) and shape, may impact the distribution patterns of microplastics in Lake Ontario and the St. Lawrence River. A small percentage of the microplastic particles visually identified were analyzed with Raman spectroscopy, however, the results suggest that visual identification had a ~60% success rate, and a 3% rate of false identification, with the remaining percentage being particles that could not be identified.

Thirty-four percent of the spectroscopically analyzed particles were low-density polymers, PE and PP (Fig. 5.13). Such a high percentage of low-density plastics was not expected in the sediments because such particles should float. 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 & Andrady, 1991; Andrady, 2011; Zettler et al., 2013; McCormick et al., 2014), adsorption of natural substances to the surfaces of particles (Corcoran et al., 2015; 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., 2016). Many microplastics in the present study, particularly those with irregularly shaped, textured or degraded surfaces, appeared to have clay-like particles adhered to their surfaces. Inorganic fillers were not identified in any of the Raman spectra of the particles identified as PE and PP, however, in two pellets analyzed with $\mu$XRF, the elements titanium and calcium were detected in relative abundance, suggesting the presence of titanium oxide and calcite fillers.

The positive trend between the fraction of low-density (PE and PP) to high-density plastics and water depth (Fig. 5.15a) suggests that buoyancy plays a role in determining how plastics are transported; i.e. how far away from shore or from their source they are transported. Low-density plastics are expected to have lower critical shear stress values (required flow energy needed to resuspend a particle) and lower settling velocities than particles made of higher density. This could translate to lower density particles traveling further from their source. This trend also suggests that more dense plastics are constrained to nearshore areas. Our results are consistent with the identification of primarily low-density polymers, PE and PP, in the offshore sediments of Lake Ontario (Corcoran et al., 2015). In tributaries, which are generally characterized by increased shear stresses and consistent unidirectional flows, low-density plastics would be expected to be transported through the system.

In comparing morphology of microplastics found among depositional environments, fragments were more abundant than fibres, and beads were less abundant than fibres. The lower quantity of fibres compared to fragments may be explained by the difference in morphology. Fibres generally have a large surface area to volume ratio, and may therefore have lower settling velocities and likewise be more susceptible to turbulence and shear stress than fragments. This would suggest that fibres are transported further in suspension than fragments. This is further supported by the observation of a greater proportion of fibres to fragments in the nearshore trap samples compared to the grab and core samples. Fibres may stay in suspension for long enough periods to be transported through the lake system without being deposited in the sediment compartment. An alternative explanation could be that the abundance of fibres being introduced to tributaries and the lake is less than that of fragments. Similarly, the spherical, smooth PSS beads were found in nearshore grabs and gravity cores, and in tributary and beach sediments, but were absent in the trap sediments, which suggests that these beads remain in the benthic zone and are transported exclusively by bedload modes. Beads were overall least abundant, which could possibly be attributed to low source levels.

## 6.2 Visible plastics debris in Lake Ontario beach and riparian sediments

The distribution of visible plastics on the beaches and on the riverbanks of western Lake Ontario provides complementary information to that of the distribution of microplastics. The lateral trends in overall abundance observed for visible plastic debris on the five beaches were similar to the lateral trends observed for microplastics. Visible debris was most abundant at Marie Curtis Beach (Fig. 5.20a), whereas microplastics in beach cores were greatest at Sunnyside Beach in downtown Toronto (Fig. 5.8b). The average (± SD) abundances of microplastics in the beach cores versus beach transects are compared in Fig. 6.1; visible plastics abundance underestimates small (< 2 mm) microplastics abundance by three orders of magnitude.

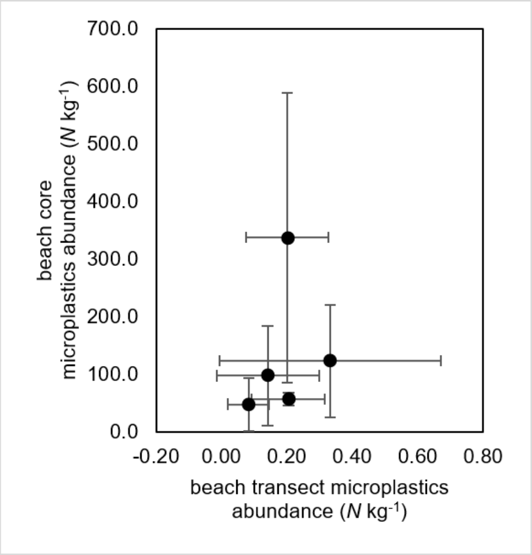


**Figure 6.1** Comparison of microplastics abundance on five beaches of the northwestern shore of Lake Ontario as quantified through a transect survey (particles 1 – 5.6 mm) and through sediment coring (particles ~ 0.25 – 2 mm). Error bars show standard deviation from the mean.

The transect surveys were conducted to determine a background level for plastic debris abundance. When comparing only microplastic debris (1-5.6 mm), abundance did not vary significantly between beaches, nor between generally south- and east-facing beaches. 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. As modelled by Hall (2008), depth averaged summer circulation runs along the northwest coastline from west to east, suggesting that the summer nearshore currents would push stranded debris to the north-east extent of the beaches. The transect at Marie Curtis was conducted on the north-east end of the beach against a jetty wall (Fig. 4.3c), which may explain the relatively high areal density of plastics. However, the transect at Woodbine Beach was also conducted on the north-east end but did not contain much plastic debris. Wind direction also does not explain variability in proximal foreshore microplastics accumulation rates (Fig. 5.23c). Proximal foreshore quadrats sampled during cross-shore winds had slightly higher microplastics accumulation rates compared to onshore wind quadrats, whereas quadrats sampled during offshore winds had lower accumulation rates. This may be attributed to sampling procedure; wind data was collected at the time of sampling, and not averaged over the 24-hour period leading up to the sampling time.

Other factors that may have affected plastics abundance and calculated accumulation rates are sediment wetness and beach grooming. Quadrats sampled when wet had significantly lower abundances of microplastics compared to quadrats sampled when sediment was dry. This difference may be attributed to the compaction and clumping nature of wet sand, which may have reduced microplastic visibility during manual collection. Beach grooming was also correlated with reduced levels of microplastics, suggesting that beach grooming is effective at reducing plastic debris on beaches, including microplastics, however plastics may simply be moved to a different part of the beach during the process.

The percentage of debris items 1-5.6 mm in size was less (~55%) at beaches in the GTA – Marie Curtis, Sunnyside and Woodbine – compared to beaches on the western extent of the northern shore (~80%). This observation may be attributed to a relatively greater input from beach-goer waste and proximity to the urban center of Toronto. Micro- to macro-plastics ratios for foreshore and cross-shore were similar (58 and 63% microplastics), suggesting continuity in the proportions of microplastics and macroplastics washing ashore over time.

A smaller proportion of industrial pellets was observed at the GTA beaches compared to at Beachway and Bronte when considering cross-shore levels. This may be attributed to a relatively greater input from beach-goer waste and proximity to the urban center of Toronto, or it could be attributed to a relatively smaller input from industrial sources. From the analysis of plastics-related industry in the study area, it seems that the former scenario is more likely, as the plastics industry is prevalent along the entire region where beaches where sampled, and may be even more prevalent in the GTA compared to further west along the coast. Alternatively, this trend, and that of lower microplastics abundance at the same beaches, could be attributed to other variables, such as beach combing (observed at Beachway and Sunnyside) and beach attendance. Beach combing would increase the relative abundance of microplastics, and beach attendance and associated littering would decrease the relative abundance. The relative proportions of fragments, pellets, foams and intact objects were similar at the proximal foreshore compared to the cross-shore, except at Bronte. Pellets were the primary type of plastic debris cross-shore, and only made up 5% of the particles washing up on the foreshore. This could reflect variability in source over time, with fewer pellets being deposited over the study period compared to previously, or could just be that pellets are accumulating slowly on the distal foreshore.

Visible debris abundance on the beaches of Lake Ontario are consistent with the abundances reported for the shorelines of the other Great Lakes, and with previous studies of Lake Ontario. Maximum spatial densities of plastics debris were 34 $m^{-2}$, 8.4 $m^{-2}$ and 3.7 $m^{-2}$, for shorelines of Lakes Huron, St. Clair, and Erie, respectively (Zbyszewski et al., 2014). At Humber Bay West in Lake Ontario, an average triweekly accumulation rate of 19 $m^{-2}$ was recorded (Corcoran et al., 2015). In this study, maximum plastic debris accumulation was 32 $m^{-2}$ and averaged at ~16 $m^{-2}$, cross-shore.

Pellet accumulation on the shoreline of the Humber River was 5.25 $m^{-2}$ averaged across two sampling days (Corcoran et al., 2015). Accumulations of microplastics on the banks of Red Hill Creek were on a similar level compared those measured for the Humber River, however, all plastics were included in this study, whereas only pellets were included in the Humber River study. Accumulations on the banks of the Humber River as measured in this study were within the same order of magnitude, but were approximately 33 $m^{-2}$. At the Don River, similar average accumulations were observed, but at Etobicoke Creek, accumulations were an order of magnitude larger.

Subsurface (tributary) microplastics abundances plotted against river bank (riparian) abundances for all four tributaries show a linear correlation on a log scale (Fig. 6.2). This relationship suggests that small microplastics < 2 mm may be exponentially more abundant than visible macro debris. Assuming this is true, visible surveys may greatly underestimate microplastics contamination levels.

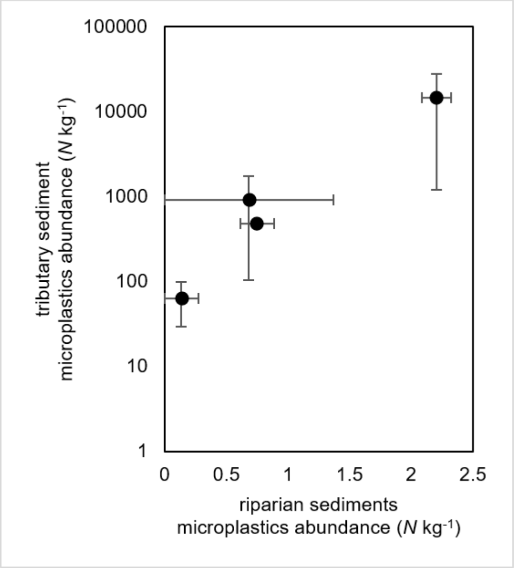


**Figure 6.2** Comparison of microplastics abundance in four tributaries draining to the northwestern shore of Lake Ontario as quantified through a riparian quadrat survey (particles 1 – 5.6 mm) and through sediment grab sampling of submerged tributary sediments (particles ~ 0.25 – 2 mm), log scale. Error bars show standard deviation from the mean.

Plastics manufacturing reports for Canada reveal that PE is the resin type produced at the greatest volume (CIAC, 2014; CIAC, 2015) which agrees with the predominantly PE composition of pellets collected on Bronte Beach. The presence of Pb in one of the pellets analyzed with $\mu$XRF, could be explained by adsorption from the lake water or sediment, which has been shown to have elevated concentrations of Pb in parts of Lake Ontario (Forsythe & Marvin, 2005), or by trace contamination during manufacturing (Rochman, Hentschel, et al., 2014). This finding has ecological implications because the ingestion of pellets by organisms may occur.

## 6.3 Potential sources of plastics debris along the Canadian coastline of Lake Ontario and the St. Lawrence River

The results indicate that microplastics in coastal sediments of Lake Ontario likely originate in proximal watersheds and are transported to the site of deposition through tributaries. Microplastics may also be transported to the lake through storm drains, but we did not study this aspect in detail. Assigning particular origins to the microplastics isolated from the nearshore, tributary and beach sediments is, however, extremely challenging due to the small size and fragmented nature of microplastics and the unknown range of possible sources.

### 6.3.1 Possible sources of microplastics

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. 5.10e) may originate from vehicle tires as suggested by Lenz et al. (2015). The natural wear down process of tires over driving time may contribute small particles to the environment. 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 particles < 2 mm in size. Fibrous microplastics are thought to originate from the production, washing and natural aging of textiles, such as synthetic clothing and carpets (e.g. Browne et al., 2011).

The amber-colored beads (Fig. 5.10c, bottom row) identified to contain PSS may be compared to beads composed of a crosslinked polystyrene resin 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. It is possible, however, that many of the irregularly shaped particles that were categorized as fragments originate from cosmetic products. Leslie (2014) reports that microplastics used in personal care products range in shape from spherical to amorphous, suggesting that ‘microbeads’ are not limited to bead morphologies.

Seven of the 12 plastic types that are manufactured in Canada, according to the CIAC, are present in the sampled sediment. High-density ($>1$ g cm$^{-3}$) plastics comprised 48% and PE comprised 46% of the particles identified as plastics with Raman spectroscopy. In comparison, high-density resins comprise 16% and PE comprised 80% of Canadian synthetic resin/rubber exports by weight in 2013 (CIAC, 2014, p. 35). In addition to the chemical clues, the distinct morphology of many plastics hints to industrial source.

The oblong, helical fragments (Fig. 5.10d) abundant in the Etobicoke Creek samples 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). Common deflashing techniques include manual or automated cutting and trimming, abrasion by media blasting, tumbling, and cryogenics (SME, 2016). The shaving-like particles identified in the samples could potentially be the waste flash particles resulting from this process. These particles would be difficult to contain in a factory environment because of their small size. This speculation is consistent with Etobicoke Creek being the tributary draining a relatively small watershed with the greatest abundance of plastics-related industry facilities in the study area.

Turra et al. (2014) also reported a correlation between the proximity of industrial plants and microplastic pellet abundance on a beach in San Paulo, Brazil. Free et al. 2014 made a similar conclusion, attributing the absence of pellets and microspheres in the water samples of Lake Hovsgol, Mongolia to the lack of industry in the area. These two studies indicate that local industry and waste management are significant factors in regulating microplastics pollution in freshwater and marine environments.

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 much greater loads are being released by the manufacturing and moulding facilities and draining directly into the lake. In the United States, EPA regulations of plastics in effluent are 18 mg $l^{-1}$ for fibers, 24 mg $l^{-1}$ for thermoplastic resins and 64 mg $l^{-}$

[1] for thermosetting resins, however, industrial activity on the US side was not analyzed. In addition, non-buoyant plastics from the southern coastline of the lake are not expected to be transported to the northern coastline due to the strong easterly current running from the Niagara River mouth east along the southern shoreline.

### 6.3.2 Possible solutions for reducing microplastic contamination

Microplastics abundance in Lake Ontario sediments may be greatly reduced, and further degradation of the nearshore ecosystem quality could be prevented, with the implementation and improvement of basic management tools in the plastics industry. Operation Clean Sweep (OCS) is an international program with the goal of reducing the loss of plastic pellets, dust and powders during their transport and production, however, only four of the companies on their partners list are located in Ontario: Ropak Packaging, D-M-E Company, Gorski Bulk Transport, and PDI. OCS provides a thorough implementation kit including pledges, a best practices manual, and practical materials such as checklists and audit worksheets, free of cost, to participating companies. The abundance of pellets and other industrially sourced debris found along the northwestern shore of the lake warrants further investigation into the effectiveness of programs such as OCS and further development of such programs to include, and focus on, particles < 2 mm.

The adoption of best practice programs is likely the most cost efficient solution to address microplastic contamination originating from industry, but a sustainable and complete solution requires participation from all sectors of the community. The dominance of fragment and fibre morphologies in this study indicate a large proportion of microplastics come from consumer activity. Outside of the plastics industry, an accelerated transition to a circular plastics economy should be attempted. Businesses and product developers could develop closed loop life-cycle products, incorporate innovative packaging designs and decrease packaging in general. Extended producer responsibility, which requires companies to account for and cover costs of material recovery for their plastic products, should be adopted by manufacturers, distributers and service businesses in Ontario. On a broader scale, an immense economic opportunity for the plastics industry is a transition to a circular economy as discussed and outlined in The New Plastics Economy proposed by the World Economic Forum (Neufeld et al., 2016). This transition would increase the end-of-life value of plastic products, thereby simultaneously improving recycling and recovery rates, reducing plastic waste entering landfills and the environment, and reducing the input of microplastics created through fragmentation of litter.

Increasing awareness of the issue of plastics pollution among consumers of plastic products, and providing simple and economically rewarding means by which consumers can reduce the amount of plastic waste produced and littered is a third aspect needed to address microplastic contamination of the environment. Municipal programs that provide communities with a strengthened connection to and understanding of the natural environment is a first step in reducing waste. Programs could additionally provide information on the issue of plastic pollution and its environmental and economic consequences. On a second tier, municipalities could improve and continually monitor their waste collection programs, to reduce waste volumes and spillage during collection. Improvements to the recycling programs, particularly in large municipalities, to increase the range of accepted plastics, would likely reduce plastic waste going to landfill and would help in the transition to a circular plastics economy.

Several examples of improvements in the waste collection systems in the study area have already shown promise in reducing waste volumes and spillage. For example, in Toronto, Hamilton and the Region of Peel, residents are required to pay for the collection of their garbage, providing residents with an economic incentive to reduce the amount of waste produced. In Ontario, several major retailers and the non-profit, Stewardship Ontario, have teamed together to demand consistency in the type of plastic (PET) used for clear rigid packaging of produce and fresh food products. This was done for the purpose of increasing the volume of PET in the recycling stream and reducing contamination in the feedstock of recycled materials sold to Ontario based recycling companies and companies buying recycled plastics.

There are many ways to increase the effectiveness of recycling programs. Closed recycling carts, which are used in three largest municipalities, reduce wind-blown litter. Easily navigable and detailed lists of accepted and unaccepted recycled items are key in ensuring maximal and correct participation of residents. In addition, the simpler and more all-inclusive the list of accepted items the more likely participation will increase. In Toronto and the Region of Peel, for example, films and polystyrene are accepted in the recycling program. In places where these items are not accepted, it is likely that they contaminate the recycling waste streams. Regular and frequent pick up times, may improve recycling rates by simplifying the schedule to which participants must adhere.

Aspects that may be detrimental to the effectiveness of a recycling program are complicated, item specific lists, such as those with special instructions (e.g. remove the zippers on plastic sandwich bags, clean them, make sure all films are in a separate bag, tied off, no black plastics). Such instructions are difficult to follow and require participants to spend extra time to recycle properly, which reduces participation levels. In addition, variations between municipalities cause confusion and make it difficult for visitors and travellers to adhere to the recycling codes properly. Municipalities in Ontario could benefit from a standardized recycling program.

Future monitoring of microplastics in coastal sediments may help determine whether and how changes in management of plastics in industry and by consumers are affecting abundance and distribution patterns of this widespread contaminant. Monitoring specific aspects of plastics debris may provide more valuable information regarding the effectiveness of policy changes. For example, trends in abundance of fibres could be monitored specifically during the widespread implementation of fibre filters in washing machines and waste water treatment plants, and trends in the abundance of various targeted polymers, such as PET, PVC or PS, could be monitored with respect to policy changes affecting the use of specific polymers.

## 6.4 Discussion of methods, limitations and suggestions for future research

In this section, difficulties encountered through the development of the study and the apparent limitations of the study are discussed. In light of these realizations, suggestions for future research are given.

### 6.4.1 Overall study design

This study design establishes of a baseline of contamination levels of microplastics in this region. On a regional scale, the study provides a clear view of the distribution of microplastics in the coastal sediments of Lake Ontario, but on a local scale, variations in microplastics abundance are not well explained. A series of locally focused, high resolution sediment sampling schemes are suggested for certain regions where microplastics pollution is exceptionally high and for where important information is missing. For example, establishing a regular sampling pattern and increasing the sample resolution along tributaries would allow for a better understanding of the role that tributaries play in transporting microplastics to the lake. Similarly, a higher resolution of sampling along the northwest shore of Lake Ontario may reveal a clearer trend between microplastics abundance and watershed population and industry-density. It is recommended that future studies investigate the role of storm drain outfalls in the inflow of microplastics debris, for example by sampling consistently adjacent to storm water outfalls along the lake shore and along tributaries.

The sampling design for visible beach and riparian plastics could be improved to better deal with small scale spatial and temporal variability. Moreira et al. (2015) start a discussion regarding beach microplastic sampling design and artefacts of sampling, such as overlapping strandlines and tidal effects. Although tide effects are not present in the Great Lakes (Rao & Murthy, 2001), changes in water level due to wind-forcing are observed. The beach quadrats, although randomly chosen, did not allow for a clear understanding of accumulation rates as they were located differently with respect to the waterline and were not consistently placed with reference to the ends and backs of the beach. An improvement in sampling design for determining accumulation rates of microplastics would be to sample a regular stretch of the strandline (high-water debris line) at regular periods of time.

### 6.4.2 Sample processing: density separation

An improvement in the density separation procedure was made after one set of samples had already been processed. This may reduce the comparability of samples, however, microplastics abundances were all standardized in the same way, using the initial sediment sample dry weight. The change in methods, as outlined in Section 4.2, was made to decrease the potential loss of plastics and potential contamination from air-borne plastics during transfer between containers. It would therefore be expected that plastics abundance in the first set of samples (nearshore cores) would be lower than in the second set, assuming a decrease in sample loss during transfer. The inverse trend, however, was observed. The lower abundance of plastics in the second set of samples cannot be conclusively attributed to the change in methods as the methods were not compared using a control sample.

The improved separation technique using separatory funnels, was not without flaws. First, insufficient solution volume or mixing within the separation funnels may have resulted in some pieces to be pulled against their individual natural tendency if caught in an aggregate of other material. Initially, microplastics separated from the sediment samples were categorized by the density separation stage at which they were attained, i.e. plastics that float in SPT and those float in water were analyzed as separate samples, under the assumption that low density plastics such as PE and PP would all be in the water fraction, and all high-density plastics such as PS and PMMA would be in the SPT fraction. This assumption was not met, and low-density plastics were frequently found in the SPT fraction. It is suggested that a single density separation stage of SPT be used to reduce processing time and improve processing efficiency. It is also suggested that sediments are first digested to remove biological detritus and non-plastic organics before density separation to reduce clumping effects. Processing efficiency would be improved by reducing the volume of material to visually sort and to increase the visibility of plastics. This would also negate buoyancy effects of adhered organic solids on microplastic particles.

### 6.4.3 Sample processing: visual identification

Fibre counts are least reliable due to potential contamination from the air during sampling and processing. The longest period of time the samples were exposed to air was during drying time in the oven. Samples needed to be uncovered to allow the evaporation of water. It could be beneficial to construct some sort of covering that would prevent fallout of microplastics from air and still allow for evaporation. A water permeable membrane foil or a funneling system may be cost effective solutions.

Fibres were most problematic during visual processing with the stereo microscope. White and translucent fibres could have been undercounted because they could not be easily distinguished from the white background. This could have been remedied by using both a black and white background, however this would have doubled sampling time, which was not feasible in the time allotted for the completion of this study. A more general issue of visual identification of microplastics is the effect of magnification. Visual processing time and accuracy are inversely related to the magnification at which samples are viewed. High magnification may allow for smaller particles to be identified however, it drastically decreases the rate at which samples can be processed. It may be important to define the magnification to a limited and optimal range to increase comparability between samples.

Microplastic counts may have been lowered by loss during transfer of the dried sample to the glass Petri dish for visual analysis. Generally, a small portion of the adhered to the vial walls due to static electricity and the extremely small size of particles. In order to compensate, vial walls were scraped and the vial tapped over the dish to transfer as much of the sample as possible. Digesting samples before density separation would likely mitigate the problem of sticky organic material, however, it would not help with the static electricity problem. Digested samples would probably be best contained on a vacuum filter.

### 6.4.4 Sample processing: grain size distribution

Analysis of grain size distribution was included in this study because it was hypothysized that microplastic distribution is governed by the same forces determining sediment deposition. A similar study (Vianello et al., 2013) had reported a relationship between the fine fraction (clays and silt) and microplastics abundance, but others had reported no relationship (i.e. Alomar et al., 2016). In this study no simple relationship was found, suggesting that plastic with lower densities and lower critical shear stresses, is more easily transported than sediment grains. The reason for this is not easily explained. It may be because microplastic abundance depends more strongly on another variable, or because, only the upper limit of microplastic abundance can be correlated to the grain size distribution. Perhaps the comparison is flawed because the targeted plastic particles were larger than the fine fraction, and instead microplastic abundance should be compared to the fine-medium sand fraction.

### 6.4.5 Sample processing overall

Future research could investigate optimal separation techniques. Although several publications already address this topic (Claessens et al., 2013; Imhof et al., 2012; Woodall et al., 2015; Zhu, 2015), standardizing techniques across the globe is extremely challenging due to variations in available instrumentation and funding. Standardization in reporting concentrations seems to be a more straight-forward approach to increasing comparability between studies.

Overall, a procedure as follows could overcome many of the issues encountered in this study: dry and weigh sediment, digest organics, wash in density separation solution, rinse floating fraction to remove residual SPT, transfer to vacuum filtration system, simultaneous visual and spectroscopic analysis.

### 6.4.6 Spectroscopic analysis

Spectroscopic analysis has been deemed essential for correct identification of microplastics, as visual identification is a less accurate method and is more vulnerable to false identification (e.g. Song et al., 2015). Plastics of different composition can often appear similar due to the presence of dyes and similar physical properties among types, and the range of mixtures and types of plastics is extensive. In this study, Raman spectroscopy was used to analyze suspected microplastics to confirm correct identification and investigate the range of polymers present. A major limitation to this analysis was the time available for running samples as constrained by cost and instrument availability.

Raman spectroscopy is an analytical technique that describes the structure of organic molecules and minerals by measuring the energy distribution of inelastic light scattered by a sample. Raman analysis is well suited for the analysis of micron to millimeter sized synthetic polymers due to it being a potentially non-destructive technique requiring no direct physical contact with the samples, no special sample preparation and a resolution of 50 $\mu$m. These qualities allowed for a quick analysis, of between 16 seconds and 5 minutes per sample. Nonetheless, several obstacles were met during analysis. Particles that were dark in color, for example the black rubber, would combust even at the lowest laser power of 0.01 Watts. In other cases, fluorescence, often exhibited by dyes associated with plastics, masked the peaks of the Raman spectra of the polymer, preventing identification of the plastic (Lenz et al., 2015). Some particles exhibited identifiable peaks, but could not be matched to a particular plastic, potentially because the spectra were composites of a mixture of multiple resin types, additives, dyes, and foreign adhered substances, which could not be resolved due to lack of mixture analysis capabilities of the software (Lenz et al., 2015).

### 6.4.7 Watershed modeling

A major weakness in the model is related to the amalgamation of certain watersheds that drain to a common point in Lake Ontario/St. Lawrence River. Several of the watersheds in the study (e.g. Humber, Don, Credit, Trent) are amalgamated river systems, many of which have control structures such as dams, weirs, reservoirs and lakes. In comparison to the Humber River watershed, which was combined with four up-stream river and creek systems, the Trent River was combined with over 20 up-stream river systems that all eventually collect to the Trent River and throughout which are many large lakes. The presence of large lakes implies that plastics flowing into them may not be transported downstream. This suggests that any region draining through a lake before reaching the tributary flowing directly into Lake Ontario should not be included in the watershed system, in the case where non-buoyant plastics are being studied. 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 is pollution transported? What are the minimum flow velocities and shear stresses found in each tributary and how much do these values vary over the length of the tributary? Are these values sufficient to support plastic bedload and suspended load transport? What percentage of the plastics found in the sediments are originally positively buoyant?

# Chapter 7

## 7 Summary and conclusions

This study was conducted with the objective to reveal the current state of plastics contamination in the nearshore, tributary and beach sediments of Lake Ontario and St. Lawrence River, along the Canadian coastline. Microplastics, < 5.6 mm, were quantified in submerged and exposed nearshore, tributary and beach sediments and visible plastic debris comprising microplastics, 1 – 5.6 mm, and macroplastics > 5.6 mm were quantified in the beach and riparian zones of tributaries along the northwestern shore of Lake Ontario. Plastics were characterized by size and morphology using visual identification and a subset of the visually identified particles were compositionally analyzed with Raman spectroscopy. Two geographic parameters, population and plastics related industry facilities, were mapped on a watershed basis and analyzed with reference to the spatial distribution of microplastics using an inverse distance weighted function.

This study reveals that microplastics, ~0.25 – 5.6 mm, were most concentrated in the nearshore sediments of Toronto Harbour and Humber Bay and in tributary sediments at the mouth of Etobicoke Creek. Abundances of > 100 $kg^{-1}$ were found almost exclusively in the Greater Toronto Region, the most populated and industry intensive region in the study area, which strongly suggests that negatively buoyant microplastics are not transported to great distances. Overall, sinks for microplastics are the nearshore zone, tributary depositional zones and beach margins.

Microplastics are ubiquitous in submerged sediments along the Canadian coastline of Lake Ontario and the upper St. Lawrence River, however, factors affecting their distribution remain difficult to determine. The density and morphology of plastic particles appears to influence how far they are transported from their source, with particles of lower density and irregular morphology being transported further. External factors, including natural forces such as water flow, and anthropogenic forces such as beach combing, strongly influence the abundance and distribution of microplastics.

Sources of microplastics are primarily urban litter, textile and potential industrial waste, as indicated by the abundance of fragments and fibres. Fragments are derived from both the breakdown of larger fragments, i.e. litter, and primary sources including newly suggested sources: ion-exchange PSS beads and deflashing waste. Compositionally, polyethylene was most abundant, reflecting the common usage and production of this type of polymer and its buoyancy compared to other polymers.

Watershed area, human population and plastics-related industry counts individually account for approximately 10 – 20 % of the variation in microplastics abundance in the coastal sediments of Lake Ontario, based on an inverse distance weighted model.

The ubiquitous presence of microplastics in the nearshore sediments makes them a potential hazard for the lake ecosystem on the whole, as they are available to benthic communities. Although the impacts of microplastics contamination on ecosystem health and functioning is uncertain, it is crucial to improve and continue efforts towards understanding, monitoring and preventing further microplastics contamination in Lake Ontario and the other Great Lakes for the conservation of an important ecosystem in the Great Lakes.

This study addresses several of the knowledge gaps identified in the Great Lakes Land Based Marine Debris Workshops held by the National Oceanic and Atmospheric Administration in 2011 and 2013, including the spatial distribution and extent of contamination and the level of subsurface sediment contamination.

This thesis provides a baseline for future monitoring of microplastics contamination in the coastal sediments of Lake Ontario and starts a discussion of the general trends relating microplastics contamination to potential sources. The observed distribution of microplastics in the coastal sediment gives a general understanding of the transport and fate of microplastic debris in aquatic environments but also brings up new questions. Some suggestions for future research follow. How does microplastics abundance vary over time in the nearshore zone? Are microplastics continually resuspended in the nearshore zone? Which sources contribute the most microplastics contamination? Which sources are most easily addressed with policy developments? What other factors influence the distribution of negatively buoyant microplastics? The effect of future changes in policy regarding microplastics may be determined by future monitoring of microplastics contamination, particularly in the coastal sediments near Toronto where greatest microplastics contamination was found.

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# Appendices

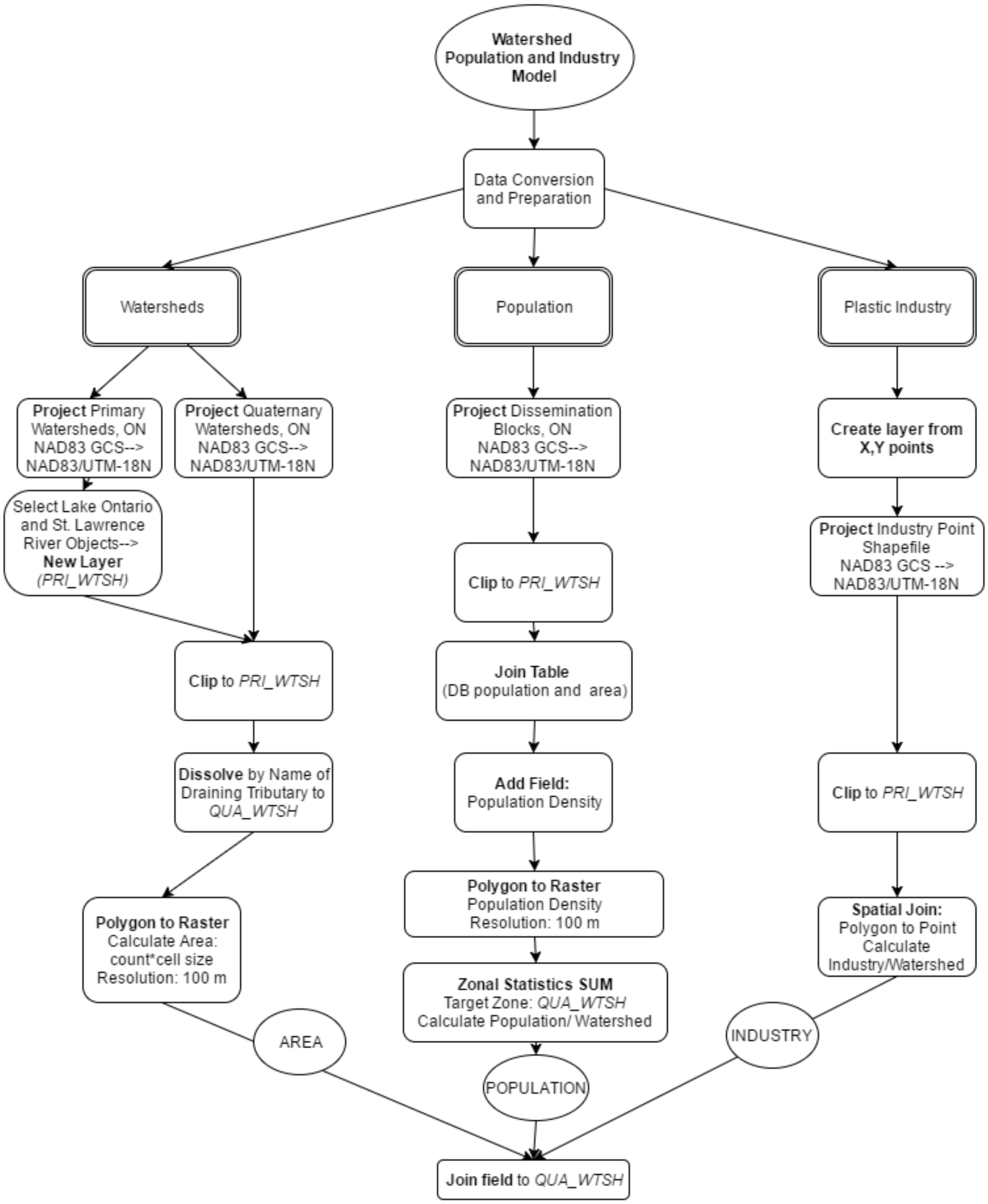
**Appendix A. Summary of sediment samples by name, site location description, depositional environment, sampling instrument type, date, geographic coordinates and underwater depth. A depth of zero is assigned to beach samples taken above the lake water level. Microplastic abundance is reported as particles kg of dry sediment; $N$ kg$^{-1}$. The fine fraction (clay and silt sized particles) is reported as the percent of sediment < 63 $\mu$m (% S < 63 $\mu$m).**

| Sample | Site* | Env. | Type | Year | Month | Lat. (°) | Long. (°) | Depth (m) | $N$ kg$^{-1}$ | % S <63 $\mu$m |
|---|---|---|---|---|---|---|---|---|---|---|
| S-7481 | Six Mile Cr | N | Grab | 2012 | Aug | 43.320 | -78.979 | 18 | 320 | 6.79 |
| S-7486 | Port Dalhousie | N | Grab | 2012 | Aug | 43.228 | -79.283 | 19 | 290 | 92.0 |
| S-7491 | Stoney Cr | N | Grab | 2012 | Aug | 43.268 | -79.671 | 22 | 70 | 24.4 |
| S-7541 | Oakville | N | Grab | 2012 | Aug | 43.426 | -79.661 | 21 | 1360 | 78.9 |
| S-7546 | Humber Bay, index | N | Grab | 2012 | Aug | 43.623 | -79.447 | 15 | 280 | 59.0 |
| S-7553 | Toronto Hb, index | N | Grab | 2012 | Aug | 43.632 | -79.370 | 9 | 3210 | 96.7 |
| S-7501 | Pickering | N | Grab | 2012 | Aug | 43.794 | -79.085 | 20 | 230 | 4.40 |
| S-7506 | Chub Point | N | Grab | 2012 | Aug | 43.953 | -78.012 | 21 | 140 | 4.23 |
| S-7514 | Trenton | N | Grab | 2012 | Aug | 44.088 | -77.544 | 3 | 800 | 31.4 |
| S-7509 | Prince Edward | N | Grab | 2012 | Aug | 43.958 | -76.812 | 21 | 430 | 81.7 |
| S-7521 | North Channel | N | Grab | 2012 | Aug | 44.181 | -76.735 | 24 | 780 | 97.4 |
| S-7526 | McDonnell Bay | N | Grab | 2012 | Aug | 44.234 | -76.375 | 4 | 120 | 15.8 |
| S-7531 | Prescott | N | Grab | 2012 | Aug | 44.698 | -75.532 | 3 | 40 | 1.41 |
| S-7536 | Lake St. Francis | N | Grab | 2012 | Aug | 45.137 | -74.416 | 12 | 80 | 5.84 |
| S-3025 | Humber Bay, index | N | Grab | 2014 | Jul | 43.623 | -79.447 | 15 | 230 | 46.6 |
| S-3026 | Humber Rv, mouth | N | Grab | 2014 | Jul | 43.633 | -79.464 | 8 | 730 | 3.47 |
| S-3027 | Humber Bay, STP | N | Grab | 2014 | Jul | 43.626 | -79.466 | 8 | 2550 | 71.2 |
| S-3028 | Toronto Hb, index | N | Grab | 2014 | Jul | 43.632 | -79.370 | 9 | 1590 | 91.6 |
| S-3029 | Don Rv, mouth | N | Grab | 2014 | Jul | 43.642 | -79.361 | 9 | 1250 | 96.2 |
| S-3030 | Toronto Hb, west | N | Grab | 2014 | Jul | 43.633 | -79.390 | 7 | 2790 | 82.0 |
| S-HB14 | Humber Bay, index | N | Grab | 2014 | Jul | 43.623 | -79.447 | 15 | 50 | 66.4 |
| S-TH14 | Toronto Hb, index | N | Grab | 2014 | Jul | 43.632 | -79.370 | 9 | 530 | 92.6 |
| S-3031 | Hamilton Hb, index | N | Grab | 2014 | Jul | 43.289 | -79.836 | 24 | 130 | N/A |
| S-3032 | Hamilton Hb, west | N | Grab | 2014 | Jul | 43.281 | -79.872 | 13 | 210 | N/A |
| S-3033 | Hamilton Hb, SE | N | Grab | 2014 | Jul | 43.285 | -79.794 | 22 | 160 | N/A |
| T-258 | Hamilton Hb, index | N | Trap | 2014 | Nov | 43.289 | -79.836 | 24 | 260 | 90.0 |
| T-2047 | Humber Bay, index | N | Trap | 2014 | Nov | 43.623 | -79.447 | 15 | 2210 | 97.0 |
| T-1364 | Toronto Hb, index | N | Trap | 2014 | Nov | 43.632 | -79.370 | 9 | 750 | 96.0 |
| G-HB1 | Humber Bay | N | Core | 2014 | Aug | 43.630 | -79.466 | 6 | 1240 | 77.9 |
| G-HB2 | Humber Bay | N | Core | 2014 | Aug | 43.629 | -79.469 | 4 | 990 | 88.4 |
| G-HB3 | Humber Bay | N | Core | 2014 | Aug | 43.626 | -79.473 | 4.5 | 3470 | 91.7 |
| G-TH1 | Toronto Harbour | N | Core | 2014 | Aug | 43.631 | -79.409 | 2.5 | 4270 | 36.7 |
| G-TH2 | Toronto Harbour | N | Core | 2014 | Aug | 43.627 | -79.383 | 5 | 670 | 66.2 |
| P-DR1 | Don Rv | T | Grab | 2015 | Jun | 43.691 | -79.360 | 0.18 | 480 | 23.3 |
| P-HR1 | Humber Rv | T | Grab | 2015 | Jun | 43.652 | -79.493 | 0.23 | 100 | 0.28 |
| P-HR2 | Humber Rv | T | Grab | 2015 | Jun | 43.642 | -79.491 | 0.26 | 1740 | 51.8 |
| P-EC1 | Etobicoke Cr | T | Grab | 2015 | Jun | 43.587 | -79.545 | 0.09 | 1210 | 27.7 |
| P-EC2 | Etobicoke Cr | T | Grab | 2015 | Jun | 43.585 | -79.542 | 2.5 | 27830 | 0.00 |
| P-RC1 | Red Hill Cr | T | Grab | 2015 | Jun | 43.240 | -79.774 | 0.35 | 100 | 22.7 |

| | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| P-RC2 | Red Hill Cr | T | Grab | 2015 | Jun | 43.240 | -79.774 | 0.11 | 40 | 1.01 |
| C-BW1 | Beachway Park | B | Core | 2015 | Jun | 43.312 | -79.800 | 0 | 60 | 0.09 |
| C-BW2 | Beachway Park | B | Core | 2015 | Jun | 43.312 | -79.800 | 0 | 60 | 0.09 |
| C-BB1 | Bronte Beach | B | Core | 2015 | Jun | 43.392 | -79.710 | 0 | 20 | 0.04 |
| C-BB2 | Bronte Beach | B | Core | 2015 | Jun | 43.392 | -79.710 | 0 | 70 | 0.03 |
| C-MC1 | Marie Curtis Park | B | Core | 2015 | Jun | 43.584 | -79.542 | 0 | 50 | 0.06 |
| C-MC2 | Marie Curtis Park | B | Core | 2015 | Jun | 43.584 | -79.542 | 0 | 190 | 0.09 |
| C-SS1 | Sunnyside Beach | B | Core | 2015 | Jun | 43.637 | -79.450 | 0 | 470 | 0.05 |
| C-SS2 | Sunnyside Beach | B | Core | 2015 | Jun | 43.637 | -79.450 | 0 | 250 | 0.09 |
| C-WB1 | Woodbine Beach | B | Core | 2015 | Jun | 43.666 | -79.299 | 0 | 170 | 0.03 |
| C-WB2 | Woodbine Beach | B | Core | 2015 | Jun | 43.666 | -79.299 | 0 | 50 | 0.05 |

*Abbreviations: Hb: harbour; Rv: river; Cr: creek; STP: sewage treatment plant outfall; Env.: depositional environment; N: nearshore; T: tributary; B: beach.

# Appendix B. Geographic model outline for mapping population, industry and microplastic abundance in the watersheds draining directly into Lake Ontario, using Esri® geographic information software ArcGIS version 10.3.1.



# Appendix C. Metadata for beach surveys of visible plastic debris (> 1 mm)

| **Location** | **Beach Way Park** | **Bronte Beach Park** | **Marie Curtis Park** | **Sunnyside Park** | **Woodbine Beach Park** |
|---|---|---|---|---|---|
| Site Reference | BW (LO-1) | BB (LO-2) | MC (LO-3) | SS (LO-6) | WB (LO-5) |
| Beach Texture | Fine Sand | Fine sand to cobbles, fine shell component | Fine sand to cobbles, woody debris | Medium sand to pebbles, inside breakwater | medium sand (silt-cobble) |
| Beach Slope | 8° | 5° | 20° | 10° | 16° |
| Beach orientation (transect midpoint) | ENE | ESE | SE | S | SSE |
| Standline width (m) | Not observed | 0.5 | 2 | 0.9 | 1.5 |
| Transect width (m) | 12.8 | 20 | 9 | 20 | 9 |
| Transect area ($m^2$) | 76.8 | 120 | 54 | 120 | 54 |
| Transect direction | east to west | south to north | north to south | west to east | east to west |
| Transect midpoint | 43.3123, -79.8004 | 43.3920, -79.7101 | 43.5844, -79.5417 | 43.6366, -79.4497 | 43.6660, -79.2988 |
| Quadrat 1 coord. | 43.307, -79.797 | 43.3917, -79.7099 | 43.5835, -79.5422 | 43.6369, -79.4529 | 43.6654, -79.3010 |
| Quadrat 2 coord. | 43.307, -79.799 | 43.3924, -79.7099 | 43.5822, -79.5429 | 43.6366, -79.4519 | 43.6660, -79.2988 |
| Quadrat 3 coord. | 43.314, -79.800 | | | | |
| Quadrat 4 coord. | 43.3123, -79.8004 | | | | |
| Q1 foreshore location | proximal | proximal | proximal | proximal | distal |
| Q2 foreshore location | distal | distal | proximal | proximal | proximal |
| Q3 foreshore location | proximal | | | | |
| Q4 foreshore location | proximal | | | | |

# Appendix D. Beach transect surveys of visible plastic debris (> 1 mm)

| **Location** | **Sample** | **Date** | **Time** | **Wind** | **Beach groomed** | **Wet sand** | **Total (*N*)** | ***N* m$^2$** | **Total (g)** | ***N* > 5.6 mm** | ***N* < 5.6 mm** | ***N* m$^2$ < 5.6 mm** |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BW | T1 | 27-Aug 2014 | 12:00 | NW | y | n | 78 | 6.09 | 7.91 | 23 | 55 | 4.30 |
| BW | T2 | 27-Aug 2014 | 12:00 | NW | y | n | 113 | 8.83 | 8.56 | 27 | 86 | 6.72 |
| BW | T3 | 27-Aug 2014 | 12:00 | NW | y | n | 286 | 22.34 | 15.15 | 47 | 239 | 18.67 |
| BW | T4 | 27-Aug 2014 | 12:00 | NW | y | n | 108 | 8.44 | 8.68 | 37 | 71 | 5.55 |
| BW | T5 | 27-Aug 2014 | 12:00 | NW | y | n | 228 | 17.81 | 9.59 | 28 | 200 | 15.63 |
| BW | T6 | 27-Aug 2014 | 12:00 | NW | y | n | 132 | 10.31 | 8.71 | 30 | 102 | 7.97 |
| BB | T1 | 26-Aug 2014 | 16:00 | SW | n | n | 52 | 2.60 | 10.29 | 28 | 24 | 1.20 |
| BB | T2 | 26-Aug 2014 | 16:00 | SW | n | n | 200 | 10.00 | 10.83 | 32 | 168 | 8.40 |
| BB | T3 | 26-Aug 2014 | 16:00 | SW | n | n | 39 | 1.95 | 4.98 | 20 | 19 | 0.95 |
| BB | T4 | 26-Aug 2014 | 16:00 | SW | n | n | 119 | 5.95 | 6.05 | 19 | 100 | 5.00 |
| BB | T5 | 26-Aug 2014 | 16:00 | SW | n | n | 40 | 2.00 | 3.18 | 14 | 26 | 1.30 |
| BB | T6 | 26-Aug 2014 | 16:00 | SW | n | n | 164 | 8.20 | 7.04 | 21 | 143 | 7.15 |
| MC | T1 | 28-Aug 2014 | 12:00 | NW | n | n | 223 | 24.78 | 56.25 | 150 | 73 | 8.11 |
| MC | T2 | 28-Aug 2014 | 12:00 | NW | n | n | 680 | 75.56 | 93.82 | 220 | 460 | 51.11 |
| MC | T3 | 28-Aug 2014 | 12:00 | NW | n | n | 180 | 20.00 | 48.11 | 118 | 62 | 6.89 |
| MC | T4 | 28-Aug 2014 | 12:00 | NW | n | n | 171 | 19.00 | 61.19 | 139 | 32 | 3.56 |
| MC | T5 | 28-Aug 2014 | 12:00 | NW | n | n | 296 | 32.89 | 36.77 | 139 | 157 | 17.44 |
| MC | T6 | 28-Aug 2014 | 12:00 | NW | n | n | 191 | 21.22 | 38.69 | 113 | 78 | 8.67 |
| SS | T1 | 30-Aug 2014 | 10:15 | SW | y | y | 245 | 12.25 | 48.34 | 158 | 87 | 4.35 |
| SS | T2 | 30-Aug 2014 | 10:15 | SW | y | y | 574 | 28.70 | 40.04 | 166 | 408 | 20.40 |
| SS | T3 | 30-Aug 2014 | 10:15 | SW | y | y | 201 | 10.05 | 28.87 | 116 | 85 | 4.25 |
| SS | T4 | 30-Aug 2014 | 10:15 | SW | y | y | 320 | 16.00 | 29.18 | 79 | 241 | 12.05 |
| SS | T5 | 30-Aug 2014 | 10:15 | SW | y | y | 220 | 11.00 | 37.69 | 134 | 86 | 4.30 |
| SS | T6 | 30-Aug 2014 | 10:15 | SW | y | y | 402 | 20.10 | 42.53 | 150 | 252 | 12.60 |
| WB | T1 | 29-Aug 2014 | 11:30 | E | n | n | 29 | 3.22 | 11.91 | 21 | 8 | 0.89 |
| WB | T2 | 29-Aug 2014 | 11:30 | E | n | n | 15 | 1.67 | 0.95 | 7 | 8 | 0.89 |
| WB | T3 | 29-Aug 2014 | 11:30 | E | n | n | 93 | 10.33 | 29.31 | 58 | 35 | 3.89 |
| WB | T4 | 29-Aug 2014 | 11:30 | E | n | n | 145 | 16.11 | 42.28 | 83 | 62 | 6.89 |
| WB | T5 | 29-Aug 2014 | 11:30 | E | n | n | 283 | 31.44 | 33.47 | 77 | 206 | 22.89 |
| WB | T6 | 29-Aug 2014 | 11:30 | E | n | n | 93 | 10.33 | 22.01 | 46 | 47 | 5.22 |

## Appendix E. Beach quadrat surveys of visible plastic debris (> 1 mm) conducted in summer 2014. X = not determined.

| Location | Sample | Foreshore location | Date | Time | Wind | Wind orientation to strandline | Beach groomed | Wet sand | Total (*N*) | *N* m$^{-2}$ | Total (g) | *N* >5.6 mm | *N* <5.6 mm |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| BW | Q1 | Proximal | 27-Aug | 8:30 | NW | offshore | y | n | 84 | 21 | 7.667 | 21 | 63 |
| BW | Q1 | Proximal | 28-Aug | 8:00 | W | offshore | n | n | 75 | 18.75 | 9.036 | 25 | 50 |
| BW | Q1 | Proximal | 29-Aug | 8:00 | NW | offshore | n | n | 120 | 30 | 6.264 | 25 | 95 |
| BW | Q1 | Proximal | 30-Aug | 8:15 | SE | onshore | y | n | 92 | 23 | 6.776 | 35 | 57 |
| BW | Q1 | Proximal | 31-Aug | 14:00 | W | offshore | y | n | 67 | 16.75 | 5.409 | 27 | 40 |
| BW | Q1 | Proximal | 1-Sep | 13:30 | S | cross | y | y | 56 | 14 | 4.313 | 22 | 34 |
| BW | Q1 | Proximal | 2-Sep | 8:45 | NW | offshore | n | y | 41 | 10.25 | 8.482 | 19 | 22 |
| BW | Q1 | Proximal | 3-Sep | 8:30 | W | offshore | n | y | 38 | 9.5 | 6.852 | 24 | 14 |
| BW | Q2 | Distal | 26-Aug | 8:30 | NW | offshore | y | n | 53 | 13.25 | 2.221 | 14 | 39 |
| BW | Q2 | Distal | 28-Aug | 8:00 | W | offshore | y | n | 39 | 9.75 | 2.672 | 16 | 23 |
| BW | Q2 | Distal | 29-Aug | 8:00 | NW | offshore | n | n | 49 | 12.25 | 4.011 | 18 | 31 |
| BW | Q2 | Distal | 30-Aug | 8:15 | SE | onshore | y | n | 44 | 11 | 1.347 | 17 | 27 |
| BW | Q2 | Distal | 31-Aug | 14:00 | W | offshore | y | n | 28 | 7 | 1.554 | 10 | 18 |
| BW | Q2 | Distal | 1-Sep | 13:30 | S | cross | y | n | 37 | 9.25 | 3.677 | 15 | 22 |
| BW | Q2 | Distal | 2-Sep | 8:45 | NW | offshore | y | y | 1 | 0.25 | 0.339 | 1 | 0 |
| BW | Q2 | Distal | 3-Sep | 8:30 | W | offshore | n | y | 12 | 3 | 0.958 | 9 | 3 |
| BW | Q3 | Proximal | 27-Aug | 8:30 | NW | offshore | y | n | 5 | 1.25 | 12.24 | 5 | 0 |
| BW | Q3 | Proximal | 28-Aug | 8:00 | W | offshore | y | n | 2 | 0.5 | 0.056 | 2 | 0 |
| BW | Q3 | Proximal | 29-Aug | 8:00 | NW | offshore | y | n | 8 | 2 | 1.119 | 8 | 0 |
| BW | Q3 | Proximal | 30-Aug | 8:15 | SE | onshore | y | y | 4 | 1 | 1.527 | 2 | 2 |
| BW | Q3 | Proximal | 31-Aug | 14:00 | W | offshore | y | y | 2 | 0.5 | 0.163 | 2 | 0 |
| BW | Q3 | Proximal | 1-Sep | 13:30 | S | cross | y | y | 3 | 0.75 | 2.706 | 3 | 0 |
| BW | Q3 | Proximal | 2-Sep | 8:45 | NW | offshore | y | y | 11 | 2.75 | 4.38 | 11 | 0 |
| BW | Q3 | Proximal | 3-Sep | 8:30 | W | offshore | y | y | 6 | 1.5 | 1.329 | 6 | 0 |
| BW | Q4 | Proximal | 27-Aug | 8:30 | NW | offshore | y | n | 165 | 41.25 | 23.241 | 56 | 109 |
| BW | Q4 | Proximal | 28-Aug | 8:00 | W | offshore | n | n | 50 | 12.5 | 17.318 | 22 | 28 |
| BW | Q4 | Proximal | 29-Aug | 8:00 | NW | offshore | n | n | 101 | 25.25 | 5.372 | 23 | 78 |
| BW | Q4 | Proximal | 30-Aug | 8:15 | SE | onshore | y | n | 116 | 29 | 10.41 | 36 | 80 |
| BW | Q4 | Proximal | 31-Aug | 14:00 | W | offshore | n | y | 118 | 29.5 | 5.929 | 20 | 98 |
| BW | Q4 | Proximal | 1-Sep | 13:30 | S | cross | n | y | 107 | 26.75 | 7.268 | 31 | 76 |
| BW | Q4 | Proximal | 2-Sep | 8:45 | NW | offshore | n | y | 47 | 11.75 | 5.041 | 12 | 35 |
| BW | Q4 | Proximal | 3-Sep | 8:30 | W | offshore | n | y | 34 | 8.5 | 1.034 | 6 | 28 |
| BB | Q1 | Proximal | 26-Aug | 16:00 | SW | offshore | n | n | 14 | 3.5 | 6.8148 | 12 | 2 |
| BB | Q1 | Proximal | 28-Aug | 10:00 | W | cross | n | n | 19 | 4.75 | 10.3522 | 11 | 8 |
| BB | Q1 | Proximal | 29-Aug | 16:30 | NE | cross | n | n | 8 | 2 | 0.1683 | 6 | 2 |
| BB | Q1 | Proximal | 30-Aug | 17:30 | S | onshore | n | y | 7 | 1.75 | 2.2715 | 2 | 5 |
| BB | Q1 | Proximal | 31-Aug | 13:00 | SE | onshore | n | y | 2 | 0.5 | 0.0098 | 1 | 1 |
| BB | Q1 | Proximal | 1-Sep | 12:00 | S | onshore | n | y | 12 | 3 | 0.1412 | 1 | 11 |
| BB | Q1 | Proximal | 2-Sep | 14:15 | S | onshore | n | y | 11 | 2.75 | 0.428 | 4 | 7 |
| BB | Q1 | Proximal | 3-Sep | 13:30 | NW | offshore | n | y | 1 | 0.25 | 0.0188 | 0 | 1 |
| BB | Q2 | Distal | 26-Aug | 16:00 | SW | offshore | n | n | 159 | 39.75 | 12.4679 | 19 | 140 |
| BB | Q2 | Distal | 28-Aug | 10:00 | W | cross | n | n | 242 | 60.5 | 10.1151 | 17 | 225 |
| BB | Q2 | Distal | 29-Aug | 16:30 | NE | cross | n | n | 182 | 45.5 | 9.0843 | 26 | 156 |
| BB | Q2 | Distal | 30-Aug | 17:30 | S | onshore | n | n | 131 | 32.75 | 8.1037 | 13 | 118 |
| BB | Q2 | Distal | 31-Aug | 13:00 | SE | onshore | n | n | 149 | 37.25 | 5.4766 | 10 | 139 |
| BB | Q2 | Distal | 1-Sep | 12:00 | S | onshore | n | n | 110 | 27.5 | 7.5999 | 12 | 98 |
| BB | Q2 | Distal | 2-Sep | 14:15 | S | onshore | n | y | 48 | 12 | 2.9136 | 11 | 37 |
| BB | Q2 | Distal | 3-Sep | 13:30 | NW | offshore | n | n | 74 | 18.5 | 3.3405 | 9 | 65 |
| MC | Q1 | Proximal | 27-Aug | 15:30 | NW | offshore | n | n | 139 | 34.75 | 12.1988 | 67 | 72 |
| MC | Q1 | Proximal | 28-Aug | 11:30 | NW | offshore | n | n | 91 | 22.75 | 5.3584 | 40 | 51 |
| MC | Q1 | Proximal | 29-Aug | 15:15 | E | onshore | n | n | 120 | 30 | 8.291 | 44 | 76 |
| MC | Q1 | Proximal | 30-Aug | 16:30 | SE | onshore | n | n | 342 | 85.5 | 10.0025 | 57 | 285 |
| MC | Q1 | Proximal | 31-Aug | 11:15 | SW | cross | n | n | 239 | 59.75 | 10.7762 | 28 | 211 |
| MC | Q1 | Proximal | 1-Sep | 11:00 | S | cross | n | n | 230 | 57.5 | 10.5143 | 30 | 200 |
| MC | Q1 | Proximal | 2-Sep | 13:15 | SW | cross | n | y | 160 | 40 | 3.8014 | 28 | 132 |
| MC | Q1 | Proximal | 3-Sep | 12:45 | W | offshore | n | n | 67 | 16.75 | 4.0629 | 7 | 60 |
| MC | Q2 | Proximal | 26-Aug | 15:30 | NW | offshore | n | n | 108 | 27 | 35.4801 | 96 | 12 |
| MC | Q2 | Proximal | 28-Aug | 11:30 | NW | offshore | n | n | 85 | 21.25 | 37.3959 | 73 | 12 |
| MC | Q2 | Proximal | 29-Aug | 15:15 | E | onshore | n | n | 87 | 21.75 | 34.9782 | 69 | 18 |
| MC | Q2 | Proximal | 30-Aug | 16:30 | SE | onshore | n | n | 144 | 36 | 32.6257 | 98 | 46 |
| MC | Q2 | Proximal | 31-Aug | 11:15 | SW | cross | n | n | 81 | 20.25 | 41.2502 | 55 | 26 |

| | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| MC | Q2 | Proximal | 1-Sep | 11:00 | S | cross | n | n | 114 | 28.5 | 18.1544 | 78 | 36 |
| MC | Q2 | Proximal | 2-Sep | 13:15 | SW | cross | n | y | 85 | 21.25 | 26.0202 | 65 | 20 |
| MC | Q2 | Proximal | 3-Sep | 12:45 | W | offshore | n | n | 64 | 16 | 26.7693 | 55 | 9 |
| SS | Q1 | Proximal | 27-Aug | 19:30 | NA | NA | X | n | 17 | 4.25 | 4.7234 | 13 | 4 |
| SS | Q1 | Proximal | 28-Aug | 18:00 | NW | offshore | X | n | 56 | 14 | 2.7421 | 18 | 38 |
| SS | Q1 | Proximal | 29-Aug | 10:15 | SE | onshore | y | n | 51 | 12.75 | 4.0283 | 23 | 28 |
| SS | Q1 | Proximal | 30-Aug | 10:15 | SW | onshore | y | y | 63 | 15.75 | 2.3924 | 18 | 45 |
| SS | Q1 | Proximal | 31-Aug | 10:15 | W | cross | X | n | 14 | 3.5 | 0.4164 | 3 | 11 |
| SS | Q1 | Proximal | 1-Sep | 10:00 | SE | onshore | n | y | 62 | 15.5 | 1.9402 | 18 | 44 |
| SS | Q1 | Proximal | 2-Sep | 10:15 | SW | onshore | n | y | 99 | 24.75 | 5.3093 | 22 | 77 |
| SS | Q1 | Proximal | 3-Sep | 10:00 | W | cross | X | y | | | | | |
| SS | Q2 | Proximal | 27-Aug | 19:30 | NA | NA | X | n | 47 | 11.75 | 5.6488 | 28 | 19 |
| SS | Q2 | Proximal | 28-Aug | 18:00 | NW | offshore | X | n | 19 | 4.75 | 3.7415 | 15 | 4 |
| SS | Q2 | Proximal | 29-Aug | 10:15 | SE | onshore | y | n | 28 | 7 | 30.0051 | 21 | 7 |
| SS | Q2 | Proximal | 30-Aug | 10:15 | SW | onshore | y | y | 25 | 6.25 | 2.9305 | 17 | 8 |
| SS | Q2 | Proximal | 31-Aug | 10:15 | W | cross | X | y | 14 | 3.5 | 1.8086 | 9 | 5 |
| SS | Q2 | Proximal | 1-Sep | 10:00 | SE | onshore | n | y | 17 | 4.25 | 0.8974 | 10 | 7 |
| SS | Q2 | Proximal | 2-Sep | 10:15 | SW | onshore | n | y | 38 | 9.5 | 3.2779 | 25 | 13 |
| SS | Q2 | Proximal | 3-Sep | 10:00 | W | cross | X | y | | | | | |
| WB | Q1 | Distal | 27-Aug | 18:00 | NE | offshore | n | n | 195 | 48.75 | 18.8071 | 117 | 78 |
| WB | Q1 | Distal | 28-Aug | 16:00 | NW | cross | n | n | 84 | 21 | 10.5793 | 27 | 57 |
| WB | Q1 | Distal | 29-Aug | 11:30 | E | offshore | n | n | 109 | 27.25 | 7.6225 | 40 | 69 |
| WB | Q1 | Distal | 30-Aug | 14:30 | SE | cross | n | n | 166 | 41.5 | 9.2299 | 45 | 121 |
| WB | Q1 | Distal | 31-Aug | 9:00 | SW | onshore | n | n | 85 | 21.25 | 1.7414 | 13 | 72 |
| WB | Q1 | Distal | 1-Sep | 9:00 | SE | cross | n | n | 102 | 25.5 | 19.3139 | 19 | 83 |
| WB | Q1 | Distal | 2-Sep | 11:30 | W | onshore | n | y | 100 | 25 | 2.8888 | 21 | 79 |
| WB | Q1 | Distal | 3-Sep | 11:15 | SW | onshore | n | n | 236 | 59 | 8.3282 | 33 | 203 |
| WB | Q2 | Proximal | 26-Aug | 18:00 | NE | offshore | n | n | 51 | 12.75 | 30.6799 | 45 | 6 |
| WB | Q2 | Proximal | 28-Aug | 16:00 | NW | cross | n | n | 87 | 21.75 | 34.9857 | 66 | 21 |
| WB | Q2 | Proximal | 29-Aug | 11:30 | E | offshore | n | n | 98 | 24.5 | 18.3794 | 60 | 38 |
| WB | Q2 | Proximal | 30-Aug | 14:30 | SE | cross | n | n | 84 | 21 | 10.5899 | 50 | 34 |
| WB | Q2 | Proximal | 31-Aug | 9:00 | SW | onshore | n | n | 76 | 19 | 13.4293 | 41 | 35 |
| WB | Q2 | Proximal | 1-Sep | 9:00 | SE | cross | n | n | 56 | 14 | 7.1882 | 30 | 26 |
| WB | Q2 | Proximal | 2-Sep | 11:30 | W | onshore | n | y | 78 | 19.5 | 17.9303 | 29 | 49 |
| WB | Q2 | Proximal | 3-Sep | 11:15 | SW | onshore | n | n | 75 | 18.75 | 18.123 | 36 | 39 |

## Appendix F. Metadata for riparian quadrat survey of visible plastic debris (> 1 mm).

| Quadrat Number | Location | Don River | Humber River | Etobicoke Creek | Red Hill Creek |
|---|---|---|---|---|---|
| 1 | Coordinates | 43.6908056°, -79.3602222° | 43.6524722°, -079.4947778° | 43.5880833°, -079.5452222° | 43.2400833°, -079.7742222° |
| | Slope | 20 | 1 | 5 | 7 |
| | Distance from water (cm) | 70 | 0 | 80 | 0 |
| | sediment grain size and description | fine-med sand/ woody debris strandline, half wet/half dry some vegetation | grassy, med grain sand, concrete | med grained sand, logs, sticks, grassy corner with woody debris | silty to very coarse grained/pebbles/cobbles |
| 2 | Coordinates | 43.6909167°, -079.3600556° | 43.6511667°, -079.4912778° | 43.6035278°, -079.5578611° | 43.2403333°, -079.7736389° |
| | Slope | 10 | 2 | 8 | 8 |
| | Distance from water (cm) | 140 | 200 | 1000 | 20 |
| | Sediment grain size and description | med-fine sand, woody strandline ~10 cm wide | flat cobbles, fine silt/clay layer, shells | clay/ slaty pebbles to slaty/sandstone cobbles/boulders, vegetated sparsely, woody strandline through quadrat | no sediment, reedy/woody debris in densely vegetated river bank |

## Appendix G. Riparian quadrat survey of visible plastic debris (> 1 mm).

| Sample | Sample Date | Size (mm) | Fragments (*N*) | Pellet (*N*) | Foam (*N*) | Intact Object (*N*) | Total (*N*) | Total (g) |
|---|---|---|---|---|---|---|---|---|
| DR-Q1 | June 6 2015 | >5.00 | 14 | 0 | 49 | 5 | 68 | 6.5517 |
| | | ≤5.00 | 16 | 6 | 148 | 0 | 170 | 0.6428 |
| DR-Q2 | June 6 2015 | >5.00 | 15 | 0 | 31 | 10 | 56 | 11.7835 |
| | | ≤5.00 | 31 | 21 | 66 | 0 | 118 | 1.4116 |
| HR-Q1 | June 5 2015 | >5.00 | 17 | 0 | 60 | 3 | 80 | 7.3543 |
| | | ≤5.00 | 13 | 118 | 132 | 0 | 263 | 3.8948 |
| HR-Q2 | June 5 2015 | >5.00 | 0 | 0 | 0 | 2 | 2 | 4.8194 |
| | | ≤5.00 | 0 | 0 | 0 | 0 | 0 | 0 |
| EC-Q1 | June 6 2015 | >5.00 | 7 | 0 | 51 | 4 | 62 | 7.1303 |
| | | ≤5.00 | 23 | 219 | 204 | 0 | 446 | 5.575 |
| EC-Q2 | June 6 2015 | >5.00 | 30 | 2 | 9 | 22 | 63 | 10.9397 |
| | | ≤5.00 | 72 | 313 | 16 | 0 | 401 | 9.291 |
| RC-Q1 | June 7 2015 | >5.00 | 2 | 0 | 0 | 2 | 4 | 5.2467 |
| | | ≤5.00 | 0 | 0 | 0 | 0 | 0 | 0 |
| RC-Q2 | June 7 2015 | >5.00 | 74 | 0 | 50 | 48 | 172 | 222.3946 |
| | | ≤5.00 | 27 | 0 | 25 | 0 | 52 | 0.9756 |

## Appendix H. Raman spectroscopic analysis of select nearshore (core) and tributary microplastics (~0.25 – 2 mm).

| Sample/filename | Identification by OMNIC Search Algorithm | Identification based on visual examination of peaks, O. Madden, Smithsonian Institute | Final Identification based on automated spectral matching, visual exam of spectrum & specimen, and other analysis to date |
|---|---|---|---|
| **P-DR1** | | | |
| DR1(1)H-fr1_1064 8cm-1 512scan .05W! | 90% Vinyl Chloride, 10% Vinyl Acetate, 41% match | Vinyl chloride/vinyl acetate copolymer | Vinyl chloride/vinyl acetate copolymer |
| **G-HB1** | | | |
| **G1H-2-3** | | | |
| G1H-2-3fr5_1064 8cm-1 384scan .03W | Polyethylene 53% match | Polyethylene | Polyethylene |
| G1H-2-3fr7_1064 8cm-1 128scan .03W | Polyethylene, Oxidized 89% match | Polyethylene | Polyethylene |
| G1H-2-3fr8_1064 8cm-1 64scan .04W | Polyethylene 72% match | Polyethylene | Polyethylene |
| G1H-2-3-fr1_1064 8cm-1 192scan .03W | Polyethylene, Oxidized 74% match | Polyethylene | Polyethylene |
| G1H-2-3-fr4_1064 8cm-1 832scan .03W | | | Unidentified |
| G1H-2-3-fr6_1064 8cm-1 128scan .03W | Polyethylene 83% match | Polyethylene | Polyethylene |
| **G1H-5-6** | | | |
| G1H-5-6-fr-11_1064 8cm-1 512scan .02W! | | | Unidentified |
| G1H-5-6-fr14_1064 8cm-1 1664scan .04W! | | | Unidentified |
| G1H-5-6-fr32_1064 8cm-1 384scan .03W | Polyethylene 72% match | Polyethylene | Polyethylene |
| G1H-5-6-fr33_1064 8cm-1 1152scan .03W | DOW Great Stuff Window and Door Insulating foam (a spray polyurethane foam) 33% match | Polyurethane | Polyurethane |
| G1H5-6-fr40_1064 8cm-1 384scan .03W! | | Possibly polyolefin (polypropylene or polymethylpentene, but not polyethylene) | Unidentified, polyolefin possible |
| **G1L-2-3** | | | |
| G1L-2-3-fr4_1064 8cm-1 512scan .05W! | | | Unidentified |
| G1L-2-3-fr5_1064 8cm-1 192scan .03W | Polyethylene, oxidized 81% match | Polyethylene | Polyethylene |
| **G1L-5-6** | | | |
| G1L-5-6-fr2_1064 8cm-1 64scan .04W! | | Maybe polyethylene | Unidentified |
| G1L-5-6-fr3_1064 8cm-1 320scan .035W | Polyethylene, oxidized 74% match | Polyethylene | Polyethylene |
| G1L-5-6-fr4_1064 8cm-1 512scan .024W! | | PET plus a red colorant? | Unidentified |
| **G-HB2** | | | |
| **G2H-2-3** | | | |

| | | | |
|---|---|---|---|
| G2H-2-3-fr1_1064 8cm-1 320scan .03W! | | Polyvinyl chloride | Polyvinyl chloride |
| G2H-2-3-fr2_1064 8cm-1 320scan .04W | Polyethylene, oxidized 54% match | Polyethylene | Polyethylene |
| G2H-2-3-fr3_1064 8cm-1 488scan .05W! | | PET plus a red colorant? | Unidentified |
| G2H-2-3-fr5_1064 8cm-1 192scan .03W | Polyethylene, oxidized 90%match | Polyethylene | Polyethylene |
| G2H-2-3-fr8_1064 8cm-1 320scan .05W | Polystyrene, 75% match | Polystyrene | Polystyrene |
| **G2H-4-5** | | | |
| G2H-4-5-fr2_1064 8cm-1 512scan .04W! | Polyurethane 48-54% match to various commercial polyurethane products | Polyurethane | Polyurethane |
| G2H-4-5-fr3_1064 8cm-1 512scan .04W! | DAP 3.0 Window, Door, Trim & Siding, crystal clear, cured, 22% match | Phthalate, polymer unknown. Possibly diisoheptyl phthalate. Not butyl benzyl phthalate. | Phthalate, polymer unknown. Possibly diisoheptyl phthalate. Not butyl benzyl phthalate. |
| G2H-4-5-fr4_1064 8cm-1 384scan .03W | Polyethylene, oxidized 84% match | Polyethylene | Polyethylene |
| G2H-4-5-fr7_1064 8cm-1 512scan .04W! | DAP 3.0 Window, Door, Trim & Siding, crystal clear, cured, 29% match | Phthalate, polymer unknown. Possibly diisoheptyl phthalate. Not butyl benzyl phthalate. | Phthalate, polymer unknown. Possibly diisoheptyl phthalate. Not butyl benzyl phthalate. |
| G2H-4-5-fr10_1064 8cm-1 256scan .04W! | Polyurethane 81-76% match to various commercial polyurethane insulating foam products | Polyurethane | Polyurethane |
| **G2L-2-3** | | | |
| G2L-2-3-fr1_1064 8cm-1 256scan .035W | Polyethylene, oxidized 64% match | Polyethylene | Polyethylene |
| **G2L-4-5** | | | |
| G2L-4-5-f3_1064 8cm-1 256scan .05W! | | | Unidentified |
| **G-HB3** | | | |
| **G3H-4-5** | | | |
| G3H-4-5 fr2_1064 8cm-1 512 scan .05W | Polyethylene, oxidized 90% match | Polyethylene | Polyethylene |
| G3H 4-5 fr3_1064 8cm-1 64scan .045W | Polyethylene, oxidized 40% match | Polyethylene | Polyethylene |
| G3H-4-5 fr4_1064 8cm-1 128 scan .034W | Polyethylene, oxidized 66% match | Polyethylene | Polyethylene |
| G3H-4-5 fr8_1064 8cm-1 320 scan .05W | Polyethylene, oxidized 67% match | Polyethylene | Polyethylene |
| G3H-4-5 fr9_1064 8cm-1 128 scan .048W | Polyethylene, oxidized 76% match | Polyethylene | Polyethylene |
| G3H-4-5 fr11_1064 8cm-1 64 scan .023W | Polyethylene 87% match | Polyethylene | Polyethylene |
| G3H 4-5 fr6_1064 8cm-1 128 scan .038W | Polyethylene, oxidized 85% match | Polyethylene | Polyethylene |
| G3H 4-5 fr10_1064 8cm-1 512 scan .048W | Phenoxy resin or various commercial epoxy products 47-44% match | Phenoxy resin or epoxy | Phenoxy resin or epoxy |
| G3H 4-5 fr-7_1064 8cm-1 512 scan .029W | | Polypropylene, isotactic, quite certain | Polypropylene |
| **G3H-12-13** | | | |
| G3H-12-13fr1_1064 8cm-1 512scan .038W | Polyethylene, 42% match | Polyethylene | Polyethylene |
| G3H-12-13-fr2_1064 8cm-1 512scan .029W! | Vinyl chloride/vinyl acetate copolymer 90/10, 14% match | Vinyl chloride/vinyl acetate copolymer, possible match | Vinyl chloride/vinyl acetate copolymer possible |
| G3H-12-13fr3_1064 8cm-1 512scan .038W | Vinyl chloride/vinyl acetate copolymer 88/12, 17% match | Vinyl chloride/vinyl acetate copolymer, possible match | Vinyl chloride/vinyl acetate copolymer possible |
| G3H-12-13fr4(2)_1064 8cm-1 2048scan .05W | Polymethyl methacrylate 56% match | Polymethyl methacrylate | Polymethyl methacrylate |
| G3H-12-13fr4_1064 8cm-1 512scan .04W | Polymethyl methacrylate 38% match | Polymethyl methacrylate | Polymethyl methacrylate |
| G3H-12-13fr5_1064 8cm-1 512scan .03W | Polystyrene 64% match | Polystyrene | Polystyrene |
| **G3L-4-5** | | | |
| G3L-4-5 fr1 FT 8cm-1 50um .069W | Polyethylene, oxidized, 52% match | Polyethylene | Polyethylene |
| G3L-4-5 fr2 FT 8cm-1 50um .37W | Polyethylene, 69% match | Polyethylene | Polyethylene |

| | | | |
|---|---|---|---|
| G3L-4-5fr3_1064 8cm-1 320scan .037W | Polyethylene, oxidized, 72% match | Polyethylene | Polyethylene |
| **<u>G3L-12-13</u>** | | | |
| G3L-12-13f_1(2)_1064 8cm-1 512 scan .027W | | | Unidentified |
| G3L-12-13fl_1(1)1064 8cm-1 256scan .079W | | | Unidentified |
| G3L-12-13fr1_1064 8cm-1 128scan .05W | Polyethylene, 80% match | Polyethylene | Polyethylene |
| G3L-12-13fr2_1064 8cm-1 192scan .03W | Polyethylene, 92% match | Polyethylene | Polyethylene |
| G3L-12-13fr3_1064 8cm-1 512scan .039W | Elmers Glue All Max and other commercial polyurethane adhesives and foam sealants 42-38% match. | Polyurethane | Polyurethane |
| **G-TH1** | | | |
| **<u>G4H-0-1</u>** | | | |
| G4H-0-1-fr1_1064 8cm-1 448scan .05W! | Elmer's China + Glass Cement 32% match; DEVCON Home Plastic Welder 29% match | Polymethyl methacrylate and polystyrene | Polymethyl methacrylate polystyrene mixture or copolymer |
| G4H-0-1-fr3_1064 8cm-1 320scan .04W! | Benzyl butyl phthate 64% match; other phthalates (dipropyl, dibutyl, diethyl) 68-71% match | Benzyl butyl phthalate | Benzyl butyl phthalate |
| G4H0-1-fr6_1064 8cm-1 384scan .04W | Polypropylene, isotactic 76% match | Polypropylene plus something else unidentified | Polypropylene |
| G4H-0-1-fr7_1064 8cm-1 384scan .02W! | | Toluidine red (colorant) with unidentified polymer | Toluidine red, unidentified polymer |
| G4H-0-1-fr10_1064 8cm-1 512scan .03W! | Nylon 6/6 40% match (Nylon 6, 6/9, 6/12, and 6/10 matches from 32-33%) | Nylon | Nylon |
| G4H-0-1-fr15_1064 8cm-1 320scan .08W | Polyethylene terephthalate, 74% match | Polyethylene terephthalate | Polyethylene terephthalate |
| G4H-0-1-fr17_1064 8cm-1 384scan .04W! | Polyvinyl chloride, 37% match | | Polyvinyl chloride |
| G4H-0-1-pe-5_1064 8cm-1 448scan .04W! | Poly(sodium 4-styrenesulfonate) 90% match | Poly(sodium 4-styrenesulfonate) 88% match | Poly(sodium 4-styrenesulfonate) |
| **<u>G4H-1-2</u>** | | | |
| G4H-1-2>2mm-fr1_1064 8cm-1 512scan .025W | | | Unidentified |
| **<u>G4H-6-7</u>** | | | |
| G4H-6-7-fr6_1064 8cm-1 128scan .04W | Polyethylene, 88% match | Polyethylene | Polyethylene |
| G4H-6-7-fr13_1064 8cm-1 256scan .03W! | | | Unidentified |
| G4H-6-7-fr28_1064 8cm-1 256scan .03W! | | Polyvinyl chloride likely | Polyvinyl chloride |
| G4H-6-7-fr37_1064 8cm-1 256scan .03W | Polystyrene, 49% match | Polystyrene | Polystyrene |
| G4H-6-7-fr43_1064 8cm-1 320scan .04W | | | Unidentified |
| **<u>G4L-0-1</u>** | | | |
| G4L-0-1-fr1_1064 8cm-1 256scan .02W! | White Lightning Silicone Ultra Low Odor Gutter & Flashing clear, DAP Silicone products, and other commercial silicone sealants, 48-50% match | Polydimethylsiloxane | Polydimethylsiloxane |
| G4L-0-1-fr2_1064 8cm-1 320scan .024W | White Lightning Silicone Ultra Low Odor Gutter & Flashing clear, DAP Silicone products, and other commercial silicone sealants, 48-50% match | Polydimethylsiloxane | Polydimethylsiloxane |
| G4L-0-1-fr4_1064 8cm-1 384scan .05W! | | | Unidentified |
| G4L-0-1-fr6_1064 8cm-1 128scan .03W! | | | Unidentified |
| **<u>G4L-6-7</u>** | | | |
| G4L-6-7-fr-1(2)_1064 8cm-1 2048scan .05W! | DAP 3.0 Window, Door, Trim & Siding, | Phthalate, polymer unknown. Possibly diisoheptyl phthalate. Not butyl benzyl phthalate. | Phthalate, polymer unknown. Possibly diisoheptyl phthalate. Not butyl benzyl phthalate. |

| | | | |
|---|---|---|---|
| | crystal clear, cured, 22% match | | |
| **GTH-2** | | | |
| **G5H-1-2** | | | |
| G5H-1-2-fr1_1064 8cm-1 192scan .02W | Polyethylene, oxidized, 69% match | Polyethylene | Polyethylene |
| G5H-1-2-fr2_1064 8cm-1 576scan .0247W! | | | Unidentified |
| G5H-1-2-fr5! | | | Unidentified |
| G5H-1-2-fr5_1064 8cm-1 1182scan .03W! | | | Unidentified |
| **G5H-6-7** | | | |
| G5H-6-7-fr3_1064 8cm-1 576scan .05W! | | | Unidentified |
| G5H-6-7-pe1_1064 8cm-1 512scan .05W! | | | Unidentified |
| G5H-6-7-pe2_1064 8cm-1 640scan .05W! | | | Unidentified |
| G5H-6-7-pe3_1064 8cm-1 512scan .05W | Polystyrene, 92% match | Polystyrene | Polystyrene |
| **G5L-1-2** | | | |
| G5L 1-2 fr1_1064 8cm-1 512scan .05W | Polystyrene 81% match | Polystyrene | Polystyrene |
| G5L-1-2-fr2_1064 8cm-1 512scan .04W! | Calcium carbonate, 49% match | Calcium carbonate, but unclear if there is also a polymer | Calcium carbonate, possibly from an organism, or present as filler in a polymer |
| G5L-1-2-fr3_1064 8cm-1 512scan .04W-quartz | Quartz, 77 % match | Quartz | Quartz |
| G5L-1-2-fr4_1064 8cm-1 512scan .05W! | Quartz, 71% match | Quartz | Quarz |
| **G5L-6-7** | | | |
| G5L-6-7-fr2_1064 8cm-1 192scan .03W | Polyethylene, oxidized, 56% match | Polyethylene | Polyethylene |
| **P-HR1** | | | |
| HR1(2)H-fr1_1064 8cm-1 512scan .05W! | Poly(Methyl methacrylate, 35% match | Poly(methyl methacrylate) | Poly(methylmethacrylate) |
| HR1(2)H-fr2_1064 8cm-1 256scan .02W! | | | |
| HR1(2)H-pe1_1064 8cm-1 512scan .03W | | | |
| HR1(2)H-pe2_1064 8cm-1 512scan .014W! | | | |
| **P-EC2** | | | |
| EC-PP2H-fr1_1064 8cm-1 64scan .03W | Polypropylene, isotactic, 93% match | Polypropylene | Polypropylene |
| EC-PP2H-fr2_1064 8cm-1 128scan .03W | Polystyrene, 93% match | Polystyrene | Polystyrene |
| EC-PP2H-fr3_1064 8cm-1 128scan .03W | Polystyrene, 94% match | Polystyrene | Polystyrene |
| EC-PP2H-fr4_1064 8cm-1 64scan .03W | Polystyrene, 93% match | Polystyrene | Polystyrene |
| EC-PP2H-pe1_1064 8cm-1 64scan .03W | Styrene/Acrylonitrile Copolymer, 68/32, 90% match | Acrylonitrile/Butadiene/Styrene resin (ABS) | Acrylonitrile/Butadiene/Styrene resin (ABS) |
| EC-PP2H-pe2_1064 8cm-1 192scan .03W | Polystyrene, 94% match | Polystyrene | Polystyrene |

## Appendix I. Raman spectroscopic analysis of beach (transect survey) microplastics (1 – 5.6 mm).

| | | | TALLY OF COMPOUNDS FOUND | | | | |
|---|---|---|---|---|---|---|---|
| **Sample / filename** | **Identification by OMNIC search algorithm and O. Madden (Smithsonian Institute)** | **2nd component** | **PE** | **PP** | **PS** | **Rutile** | **$CaCO_3$** |
| LO-2 8-26 T6 1-5.6mm fow1 780 100% 10x 16scan | Polystyrene foam | | | | 1 | | |
| LO-2 8-26 T6 1-5.6mm fow2 780 100% 10x 16scan | Polystyrene foam | | | | 1 | | |
| LO-2 8-26 T6 1-5.6mm fow3 780 100% 10x 16scan | Polystyrene foam | | | | 1 | | |
| LO-2 8-26 T6 1-5.6mm frc1 780 25% 10x 3sx16scan | Polystyrene | | | | 1 | | |
| LO-2 8-26 T6 1-5.6mm frc2 780 25% 10x 3sx16scan | Polypropylene | | | 1 | | | |
| LO-2 8-26 T6 1-5.6mm peb1 780 60% 10x 16scan | Polyethylene, likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl1 780 100% 10x 16scan | Polyethylene likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl2 780 100% 10x 16scan | Polyethylene likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl3 780 100% 10x 16scan | Polyethylene likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl4 780 100% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl5 780 100% 10x 16scan | Polyethylene likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl7 780 100% 10x 16scan | Polyethylene likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl8 780 100% 10x 16scan | Polyethylene likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl9 780 100% 10x 16scan | Polyethylene likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pebl10 780 100% 10x 16scan | Polyethylene likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec1 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec1 780 100% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec2 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec3 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec4 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec5 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec6 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec7 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec8 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec9 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pec10 780 65% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg1 780 30% 10x 16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg2 780 30% 10x 3sx16scan | Polyethylene, likely | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg3 780 30% 10x 3sx16scan | Polyethylene | Rutile, likely; unidentified additive (also in peg5 and peg9, and most pebl (blue) nurdles) | 1 | | | 1 | |
| LO-2 8-26 T6 1-5.6mm peg4 780 30% 10x 3sx16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg5 780 30% 10x 3sx16scan | Polyethylene | Unidentified additive (also in peg3 and peg9, and most pebl (blue) nurdles) | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg6 780 25% 10x 3sx16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg7 780 30% 10x 3sx16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg8 780 30% 10x 3sx16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg9 780 30% 10x 3sx16scan | Polyethylene | Unidentified additive (also in peg3 and peg5, and most pebl (blue) nurdles) | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm peg10 780 30% 10x 3sx16scan | Polyethylene | | 1 | | | | |
| LO-2 8-26 T6 1-5.6mm pew1 780 65% 10x 16scan | Polypropylene | Rutile, likely | | 1 | | 1 | |
| LO-2 8-26 T6 1-5.6mm pew2 780 65% 10x 16scan | Polyethylene | Rutile, likely | 1 | | | 1 | |
| LO-2 8-26 T6 1-5.6mm pew3 780 100% 10x 16scan | Polyethylene | Rutile | 1 | | | 1 | |
| LO-2 8-26 T6 1-5.6mm pew5 780 100% 10x 16scan | Polypropylene | Rutile, likely | | 1 | | 1 | |
| LO-2 8-26 T6 1-5.6mm pew6 780 100% 10x 16scan | Polypropylene | Calcium carbonate | | 1 | | | 1 |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| LO-2 8-26 T6 1-5.6mm pew7 780 100% 10x 16scan | Polypropylene | | | 1 | | | |
| LO-2 8-26 T6 1-5.6mm pew8 780 100% 10x 16scan | Polyethylene | Rutile | 1 | | | 1 | |
| LO-2 8-26 T6 1-5.6mm pew9 780 100% 10x 16scan | Polyethylene | Rutile | 1 | | | 1 | |
| LO-2 8-26 T6 1-5.6mm pew10 780 100% 10x 16scan | Polyethylene | Rutile | 1 | | | 1 | |
| | | | **36** | **5** | **4** | **8** | **1** |

## Appendix J. Area (km$^2$), population ($N$) and number of plastics-related industry facilities in the 66 watersheds draining directly to Lake Ontario and the upper St. Lawrence River, in the province of Ontario.

| Watershed Name | Area ($F_a$) | Population ($F_{pop}$) | Industry ($F_{ind}$) |
|---|---:|---:|---:|
| Amherst Island | 75.2 | 441 | 0 |
| Bay of Quinte | 428.3 | 7854 | 0 |
| Beaudette River | 178.8 | 2992 | 0 |
| Blessington Creek | 122.1 | 5891 | 1 |
| Bowmanville Wilmot Graham Creeks | 227.7 | 45244 | 0 |
| Bronte Creek | 426.4 | 159058 | 11 |
| Burlington Urban | 53.7 | 89483 | 10 |
| Butlers Buells Creeks | 97.1 | 28262 | 2 |
| Carruthers Creek | 47.6 | 50966 | 4 |
| Cataraqui River | 1069.8 | 56815 | 0 |
| Cobourg Brook | 150.9 | 22573 | 1 |
| Collins Creek | 200.9 | 30725 | 0 |
| Credit River | 1052.5 | 911010 | 29 |
| Delisle River | 267.3 | 7479 | 0 |
| Don River | 437.8 | 1580067 | 33 |
| Duffins Creek | 319.1 | 101355 | 5 |
| Etobicoke Creek | 245.9 | 340869 | 62 |
| Fifteen Sixteen Mile Creeks | 139.3 | 6307 | 0 |
| Forty Mile Beamsville Bartlett Prudhomme Creeks | 243.7 | 104464 | 7 |
| Frenchman Black Usshers Creeks | 204.0 | 20773 | 2 |
| Gage Creek | 68.0 | 5434 | 0 |
| Gananoque River | 1058.3 | 19210 | 0 |
| Ganaraska River | 316.4 | 11681 | 0 |
| Graham Creek | 334.3 | 19514 | 0 |
| Hamilton Harbour North | 138.4 | 74223 | 4 |
| Hamilton Harbour South | 112.8 | 262232 | 6 |
| Hamilton Harbour West | 315.0 | 171518 | 0 |
| Highland Creek | 129.7 | 480341 | 27 |
| Howe Island | 42.0 | 669 | 0 |
| Humber River | 1005.9 | 867202 | 37 |
| Jones Lyn Golden Creeks | 263.7 | 5838 | 0 |
| Larue Mills Creek | 69.7 | 1128 | 0 |
| Little Cataraqui Creek | 82.6 | 65154 | 0 |
| Lynde Creek | 187.7 | 118755 | 3 |
| Millhaven and Parrot Creeks | 285.9 | 17863 | 0 |
| Mimico Creek | 100.3 | 205298 | 19 |
| Moira River | 3113.5 | 61518 | 2 |
| Napanee River | 959.2 | 24388 | 0 |
| Napanee Urban | 238.8 | 4521 | 0 |
| One Two Four Eight Mile Creeks | 202.5 | 74759 | 0 |
| Oshawa Farewell Creeks | 300.1 | 208496 | 4 |
| Potters Creek | 115.5 | 21825 | 3 |
| Prince Edward County 1 | 106.0 | 468 | 0 |
| Prince Edward County 10 | 96.1 | 1302 | 0 |
| Prince Edward County 11 | 49.2 | 518 | 0 |
| Prince Edward County 2 | 122.4 | 2942 | 0 |
| Prince Edward County 3 | 133.3 | 4043 | 0 |
| Prince Edward County 4 | 116.7 | 2331 | 0 |
| Prince Edward County 5 | 259.6 | 4691 | 0 |
| Prince Edward County 6 | 115.2 | 2264 | 0 |
| Prince Edward County 7 | 34.2 | 3068 | 0 |
| Prince Edward County 8 | 124.1 | 1395 | 0 |
| Prince Edward County 9 | 61.2 | 6368 | 0 |
| Raisin River | 641.4 | 24127 | 1 |
| Rouge River | 434.8 | 484557 | 12 |
| Saint Laurence Direct | 88.6 | 4737 | 0 |
| Salmon River | 1037.1 | 8049 | 0 |
| Shelter Valley Creek | 402.0 | 23930 | 3 |
| Sixteen Mile Creek | 466.6 | 245199 | 5 |
| St Lawrence Direct 1 | 93.5 | 2909 | 0 |
| St Lawrence Direct 2 | 117.6 | 10167 | 0 |
| St Lawrence Direct 3 | 93.1 | 5669 | 1 |

| | | | |
|---|---|---|---|
| St Lawrence Direct 4 | 210.8 | 3524 | 0 |
| St Lawrence Direct 5 | 143.0 | 45541 | 3 |
| St Lawrence Direct 6 | 298.3 | 7425 | 0 |
| Toronto Urban Catchment Basin | 51.8 | 382225 | 3 |
| Trent River | 14297.4 | 405142 | 11 |
| Twelve Mile Creek | 145.6 | 96573 | 0 |
| Twenty Mile Creek | 344.4 | 33705 | 1 |
| Welland Canal | 95.9 | 91895 | 3 |
| Welland River | 1220.3 | 112532 | 1 |
| Wolfe Island East | 53.9 | 550 | 0 |
| Wolfe Island West | 104.0 | 880 | 0 |

# Curriculum Vitae

| | |
|---|---|
| **Name:** | Anika Ballent |
| **Post-secondary Education and Degrees:** | Jacobs University Bremen<br>Bremen, Germany<br>2009-2012 B.Sc. Earth and Space Sciences |
| **Honours and Awards:** | Arcangelo Rea Family Foundation Scholarship<br>2015 |
| **Related Work Experience** | Teaching Assistant<br>The University of Western Ontario<br>2014-2016 |

**Publications:**

Ballent, A. Corcoran, P., Madden, O., Helm, P., Longstaffe, F. (2016). Sources and sinks of microplastics in Canadian Lake Ontario nearshore, tributary and beach sediments. *Marine Pollution Bulletin*, http://dx.doi.org/10.1016/j.marpolbul.2016.06.037, in press.

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