

ANALYSIS OF MICROPLASTIC SOURCES IN THE SOUTH SASKATCHEWAN RIVER
AND SELECTED SASKATOON STORM PONDS

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By

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ABSTRACT

Due to their widespread presence in all ecosystems, microplastics have been classified as significant persistent environmental contaminants. Aquatic organisms' reproductive cycles, access to energy, and growth may all be adversely affected by microplastics in water bodies. As a result, it is important to identify the origins and quantities of microplastic in significant Saskatchewan waterways, particularly the South Saskatchewan River, which supplies water to more than 50% of the province's residents for a variety of uses. In this study, we used Raman microspectroscopy to examine the compositions and loadings of microplastics in samples taken from three storm ponds in the City of Saskatoon and seven sites along the South Saskatchewan River. Microplastics were identified in all river and storm pond samples with the mean concentrations of $4.43 \pm 2.88 \text{ m}^{-3}$ and $6.44 \pm 3.62 \text{ m}^{-3}$ respectively. Although the small sample size and large variability in the mean microplastics concentrations between samples limits meaningful statistical analysis, our results suggest that the mean microplastics load at Miry creek ($12.00 \pm 9.12 \text{ m}^{-3}$) is higher compared to $3.18 \pm 3.00 \text{ m}^{-3}$ for all other river samples, indicating Diefenbaker dam may be acting as a sink for microplastics along the waterways. Fibers dominate the morphology class of microplastics recovered, while polymers from polyethylene terephthalate (PET), polypropylene (PP), and polystyrene (PS) were the major microplastics chemically identified among the samples. Particle contributions from both dyed and undyed natural fibers were also analyzed. This study represents the first exploration of microplastic levels in the South Saskatchewan River and selected Saskatoon' storm ponds, thereby improving our understanding of this pervasive environmental contamination on the Canadian prairies.

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LIST OF ABBREVIATIONS

ATR.....	Attenuated total reflection
BC.....	Brown Cotton
CCD.....	Charged coupled device
CP.....	Copper pthalocyanine
2-D.....	2-dimensional
DY.....	Diarylide yellow
FPA.....	Focal plane array
FTIR.....	Fourier transform infrared
μ -FTIR.....	Micro-Fourier transform infrared
GES.....	Good Environmental Status
GESAMP.....	The Group of Experts on the Scientific Aspects of Marine Environmental Protection
GFF.....	Glass microfiber filter
HDPE.....	High density polyethylene
He-Ne.....	Helium-Neon
JAMSTEC.....	Japan Agency for Marine-Earth Science and Technology
JAMSS.....	JAMSTEC microplastic-sediment separator
k.....	Reaction rate constant
LDPE.....	Low density polyethylene
MCT.....	Mercury/cadmium/telluride
MDPE.....	Medium density polyethylene

MFSD..... Marine Strategy Framework Directive

MPs..... Microplastics

N. A..... Numeric aperture

Nd:YAG..... Neodymium-Yttrium Aluminum Garnet

Nd: YVO4..... Neodymium-Yttrium ortho-Vanadate

NIR.....Near infrared

PAHs.....Polycyclic aromatic hydrocarbons

PC.....Poly-cotton

PCBs.....Polychlorinated biphenyls

PCD.....Photo-conductive device

PCRFS.....Polymer-coated fertilizers

PE.....Polyethylene

PET.....Polyethylene terephthalate

PMMA.....Poly (methyl methacrylate)

POOH.....Hydroperoxide

PP.....Polypropylene

PS.....Polystyrene

PSF.....Polysulfone

PTFE.....Polytetrafluoroethylene

PVC.....Polyvinyl chloride

Pyr-GC-MS.....Pyrolysis-gas chromatography-mass spectroscopy

RB5.....Reactive black 5

SAP.....Super absorbent polymer

SEM.....Scanning electron microscope

SEM-EDS.....Scanning electron microscope coupled with energy-dispersive X-ray spectroscopy

TDS-GC/MS.....Thermal desorption-gas chromatography/mass spectroscopy

TGA.....Thermogravimetric analysis

TGA-DSC.....Thermogravimetric analysis coupled with differential scanning calorimetry

TGA-MS.....Thermogravimetric analysis coupled with mass spectroscopy

Unc.....Uncharacterized

Uv.....Ultraviolet

VIG.....Vat indigo

LIST OF SYMBOLS AND MATHEMATICAL TERMS

\approxApproximately

ΔChange

μmicro

λWavelength

$\bar{\nu}$Wavenumber

CHAPTER ONE: INTRODUCTION

Plastics have found applications in homes and industries all over the world.¹ The world plastics market value was estimated to be worth about USD 457.73 billion in 2022 and might increase to about USD 645.37 billion by 2029 due to extensive plastics demand worldwide.² However due to increased plastics production, slow biodegradability of plastics, poor waste disposal systems, and unavailability of cheap recycling technologies, plastics waste has become a menace to our environment. For example, only 9% of the 353 million tons of plastic waste generated globally in 2019 was recycled. It was reported that out of the remaining 91%, only 50% was collected by waste management agencies and placed in landfills, about 22% was indiscriminately released into the terrestrial and the aquatic environments, while the remaining 19% were incinerated.³ This large plastic (macroplastics) waste particles are recalcitrant in the environment and present hazards to both aquatic and terrestrial ecosystems. Recently, much attention has been given to the degradation products of macroplastics into microplastics and nanoplastics which exist not only on land or in waterways, but in the atmosphere, in human respiratory and alimentary systems, in land animal organs, and in the skin, respiratory organs, and digestive organs of aquatic species owing to their small size which aids ingestion by animals, and their ease of being mobilized in the air, water, and on land. Investigating the sources, transportation, concentrations, and implications of microplastics and their chemical additives on land, waterways, sediments, and atmospheres are new frontiers in plastics research.

1.1. Microplastics Sources

Microplastics in the environment are classified as primary and secondary microplastics. Primary microplastics are plastics manufactured for specific applications based on their sizes, or as plastic

residue released directly into the environment. There are seven major primary sources of microplastics: plastic pellets, personal care products, synthetic textiles, road markings, tire wear, marine coatings, and city dust.⁴ Plastic pellets which are usually about 2 – 5 mm in size are employed as raw materials for molding other plastic products of different shapes. These particles may be lost due to spillage during manufacturing processes and eventually find their way into the environment.⁵ Microbeads used as ingredients in personal care, cosmetics, and cleaning products such as skin care, toothpaste, detergents, and face scrubs contribute about 2% of the total primary microplastics released into the waterways globally.⁶ Fibers and microfibers detached from synthetic textiles during laundry processes are a major source of microplastic pollution in freshwater bodies, and a great percentage of that is recovered in wastewater treatment plants (WWTPs). They contribute about 35% - the largest contribution to the primary source of microplastics all over the world.^{4,7} Tire wear in the form of tire dust and brake pad dust which are mobilized by wind and rainfall contributes about 28% of global primary microplastic pollution.⁴ Moreover, about 7% of primary microplastics are from polymer products such as polymer tapes, epoxy, and paints used for road markings that get abraded over time.⁸ Emissions from marine coating materials such as anti-corrosive paints, anti-fouling paints, and solid coatings during shipbuilding and maintenance, as well as city dust from abrasion of artificial turfs, synthetic footwear, and other anthropogenic sources contribute about 4% and 24% to global primary microplastics pollution respectively.^{4,9}

Secondary microplastics are formed from the degradation of larger pieces of plastics in the environment. The sources of these large plastics on land and in the aquatic environments may include plastic bottles, fishing nets, shipbuilding, laundering of synthetic fabrics, and agricultural plastic mulch.^{8,10,11} More so, about 74% of the microplastics reported in oceans around the world

could be attributed to the degradation products of plastics produced in the 1990s, indicating secondary microplastics as a major source of microplastic pollution in the aquatic ecosystem.¹²

The degradation of macroplastics to smaller microplastics or nanoplastics can occur via mechanical degradation, photodegradation, chemical degradation, or biodegradation¹³ as illustrated in figure 1.1

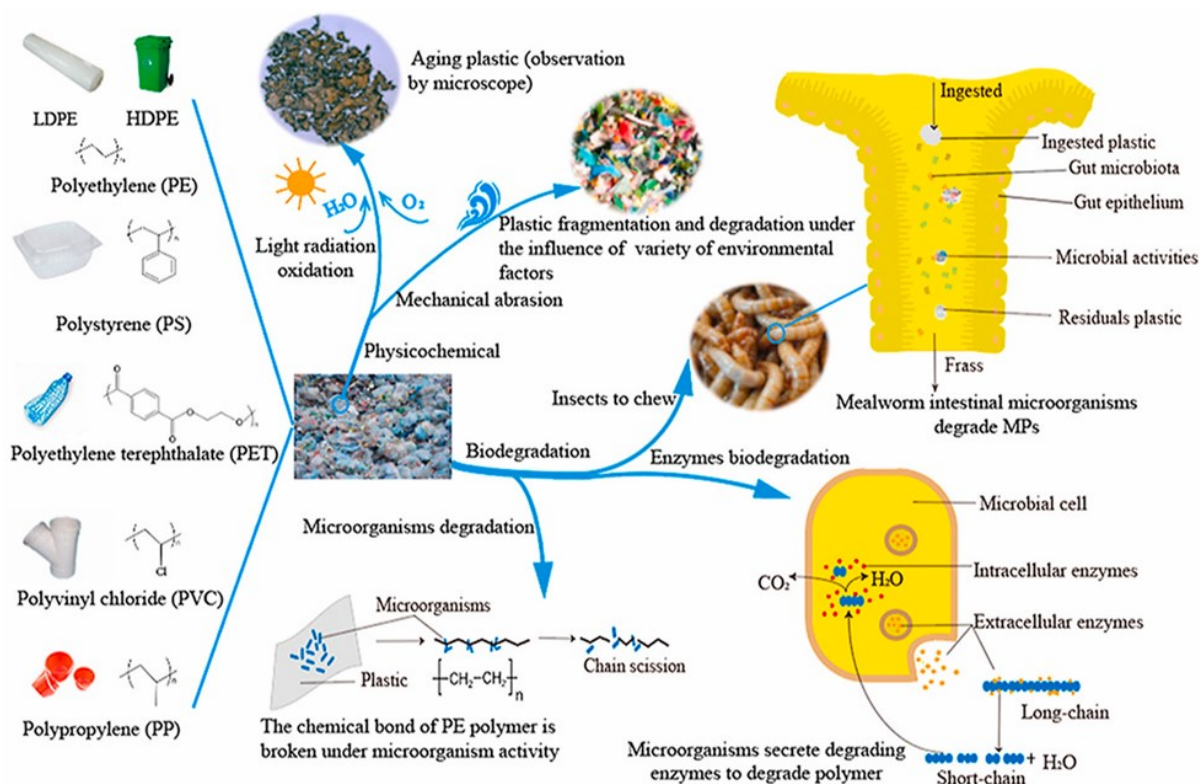


Figure 1.1: The common processes of macroplastics and microplastics in the environment.¹³

Mechanical degradation is an important step in the initial macroplastic degradation. It involves the fragmentation of large plastic materials by abrasive forces and forces such as heating and cooling, freezing, thawing, wetting and drying as the plastics move through different environments.

Mechanical degradation of polymers facilitates other processes of degradation by helping to increase the surface area for reactions and action of microorganisms.^{14,15}

Photodegradation or photooxidation of large plastic materials, especially dyed (pigmented) plastics can occur on exposure to UV (295 nm – 400 nm) sunlight, or sometimes visible light.¹⁶ Upon irradiation with light in the presence of oxygen, degradation of plastics may proceed through the direct reaction of singlet oxygen ($^1\text{O}_2$) with the substrate or production of radicals and subsequent reaction with molecular oxygen ($^3\text{O}_2$).^{16–18} The reaction of UV light and oxygen leads to the formation of more O-functional groups such as hydroperoxides (POOH) and carbonyl (C=O) on the plastic surface which may increase the fragility of the plastic.^{19,20} Some photosensitive groups known as promoters, such as carbonyl groups and metal complexes are sometimes deliberately incorporated into some polymer chains to enhance their degradation rates in the environment as present in polyethylene and polystyrene mulch films used for post-plant operations.^{14,21} Photodegradation rates are also influenced by the environment of plastics. For example, it has been suggested that photodegradation is faster in air and on land compared to in aquatic environments, while it is also faster with plastics found on the water surface than those that are partially or totally submerged in water due to decreasing light intensity and oxygen content with increasing depth.^{18,22–24}

Biodegradation, also known as the biotic degradation of plastics, can be classified into two types depending on the environment: aerobic and anaerobic. Aerobic degradation is the chemical degradation of plastics by actions of micro-organisms (bacteria, fungi, algae) in the presence of oxygen to yield CO_2 , H_2O , and in some cases N_2 , H_2 , and CH_4 inclusive. Anaerobic biodegradation occurs when micro-organisms breakdown plastic particles in the absence of oxygen by making use of some enzymes and other terminal electron acceptors such as nitrate (NO_3), sulphate (SO_4^{2-}),

ferric iron (Fe^{3+}), manganese (Mn^{3+} , Mn^{4+}), and bicarbonate (HCO_3^-) to yield methane (CH_4) gas and water. Biodegradation is majorly initiated by hydrolysis and oxidation of amides, esters, or urethane bonds at the side chains or in the polymer backbone as catalyzed by microbes' enzymes. Optimum temperature, appropriate pH, presence of oxygen, presence of suitable microbes, and presence of other terminal electron acceptors are some of the factors that enhance the biodegradation of plastics. Polymers from polyvinyl alcohol, polyacrylamides, polyethylene glycol, starch, and cellulose are easily biodegraded in the environment.^{13,24-27}

1.2. Microplastics Definitions

Microplastics have emerged over years from different applications of plastic polymers for different users based on size specificity, and from the degradation of macroplastics in the environment. Microplastics have been broadly defined as plastic particles that are less than 5mm in diameter.²⁸ Although 5 mm is generally accepted as the upper limit of microplastic size, some researchers are advocating the use of additional designations to account for the different health and chemical effects posed by different sizes of microplastics. For example, a few scientists define additional size categories of plastics such as mesoplastics and nanoplastics. However, the size ranges for these categories are not standardized, as shown in Table 1.1; sometimes the same term is used by different groups to mean very different size ranges.^{10,29}

Table 1.1: Classification of Plastics Debris in the Environment, Based on The Group of Experts on the Scientific Aspects of Marine Environmental Protection, GESAMP (2015)^{10,29} and other authors.

Class	Size Ranges	Size Ranges	Size Ranges
	Lambert et al	GESAMP	(MSFD GES)
Macroplastics	>5 mm	2.5 - 100 cm	> 2.5 cm
Mesoplastics	1 – 5 mm	0.1 – 2.5 cm	0.5 cm – 2.5 cm
Microplastics	0.1 µm – 1 mm	1 - 100 µm	1 - 500 µm
Nanoplastics	≤ 0.1 µm	< 1 µm	< 1 µm

Nanoplastics, the smallest category of plastic particles, are an emerging concern. It is believed that nanoplastics might display different physical and chemical properties to their parent materials.³⁰ Recently, concerns are being raised about their prevalence in the environment and possible health hazards they might cause since their extremely small particle size could facilitate their transport and toxicological impacts on humans and on the environment.³⁰

1.3. Morphology of Microplastics

The shape of microplastics may affect their mobility, settling, buoyancy, and persistence in the environment.³¹ Microplastics identified in the environment are generally classified as fibers, pellets or nurdles, spheres, fragments, and films based on the common quantitative rubrics for characterizing particle morphology of length, width, height, roundness, and irregularity.³²

Fibers are characterized as being flexible with a uniform thickness and color. Fibers in wastewater, freshwater, and seawater may also exist as interwoven or knitted fibers known as bundles and are majorly from natural textile fibers such as cotton, wool, silk, and linen; and synthetic textile fibers such as polyesters, rayon, spandex, acrylics, and microfibers.³²

Pellets and spheres are similar in their spherical shapes, but pellets can also come in cylindrical shapes and are usually larger than spheres (about 3 - 5 mm).³² Pellets in the environment may originate from industrial thermoplastic manufacturing, while spheres or micro-beads (2 – 100 mm) are normally released from cosmetic products or spill from plastic manufacturing.³³ Fragments in the form of virgin polymers, or from aging or environmental degradation of larger plastics have a characteristic rigid structure and irregular shapes. Fragments may exist in different colors due to their varying origins such as plastic packaging materials, coating materials, fishing gear, and food service items.^{31,34}

Films are flat, malleable, and generally two-dimensional in shape, and are made from the extrusion of the polymer melt. Polymer films are made from natural polymers such as cellophane or from synthetic polymers such as polyvinyl chloride (PVC), polyamides (Nylon), polyethylene terephthalate (PET), and polystyrene (PS). Due to their great tensile strength and stability, they are usually applied as packaging and lining materials.^{31,32,35}

1.4. Microplastics Transport on Land and its Implications

The land is the first point of microplastic pollution in our ecosystem due to human activities and land use. Plastics used in the packaging of consumer products may be lost along the recycling chain and further degraded into microplastics or nanoplastics over time by mechanical abrasion, UV irradiation, or biodegradation and then buried in the soil.³⁶ Road dust particles, which include paints for road markings, tire wear, brake pads, abrasion from artificial turf, and fragmented

polymers from building construction sites, are major contributors to microplastic pollutions on land.³⁶⁻³⁸ Industrial spillage and landfills are also important potential point sources of microplastic contamination on land since about 79% of the world's plastic waste resides in landfills.³⁹⁻⁴¹ Further, agricultural activities have been reported to add to microplastic concentrations in soil. Materials such as mulching films, greenhouse covers, irrigation systems, silage films, and harvesting nets applicable in various agricultural practices are made from plastic polymers that may accumulate in the soil during ploughing.⁴²⁻⁴⁴ Polyethylene, polypropylene, and polyvinyl chloride, are among the polymers that have been identified in mulched soils and agricultural lands.^{45,46}

Another important potential source of microplastic contamination on land is sewage sludge. Sludge from wastewater treatment plants and sewage treatment plants has high microplastic concentrations due to sedimentation.⁴⁷ These sludges are applied as a source of inexpensive organic fertilizers on farmlands to improve crop yield. Microplastics in the form of synthetic polyesters and fragments have been identified in soil samples after the application of sewage sludge to farmlands.^{47,48} Compost materials for fertilizing applications, seed coatings made of super absorbent polymer, and polymer-coated fertilizers used for regulating the delivery of fertilizers and pesticides into the soil are other important pathways of microplastic emissions into soil.^{49,50} Recent studies have revealed that the annual microplastic emissions on farmlands in North America is between 44 to 330 thousand tons, while in Europe it ranges from 63 to 430 thousand tons annually.^{36,44}

Microplastics on land can be transported either horizontally or vertically within the soil profile. Surface runoff, wind, ploughing, and harvesting activities are the means of horizontal transportation of microplastics on land, while small animals in the soil (the decomposers) may be responsible for vertical microplastic transport within the soil profile. For example, microplastics

can also adhere to the moist body of earthworms as they burrow within the soil and are transported further down the soil table.^{45,51} Soil cracking and digging by burrowing animals such as rodents and moles also enhance the distribution and dispersal of microplastics within the soil. Microplastics can also be transported via downward elongation of plant roots already trapping microplastics within the soil. Infiltration of surface water through the soil profile can also promote the transfer of microplastics from the soil surface to the deeper part of the soil voids, even reaching the groundwater.^{52,53} Further, studies have reported that factors such as flushing, length of interconnected pore space of the soil, the dry-wet cycle of sand, homogenous and heterogeneous aggregation of microplastics, and the characteristics of the microplastics (e.g., size, shape, and aging) affect the vertical transportation and transportation distance of microplastics in the soil.^{45,46,51} For example, it has been reported that small size microplastics have greater mobility in the soil because of their smaller water resistance.⁵¹ Also, microplastics in the form of fibers and microfibers are less efficiently transported within the soil than fragments and spheres due to their ease of entangling with soil particles as a result of their elongated structures.^{45,54}

The presence of microplastics in soil may influence both the structural and physicochemical properties of the soil. For example, polymer films found in soil have been reported to decrease the rate at which water percolate through the soil, while polyester fibers in soil increased the water-holding capacity of the soil but decreased the bulk density and water-stable aggregation of the soil fertility.^{6,55-57} Further studies show that increasing microplastic concentration caused a linear increase in the water evaporation and desiccation properties in two clay soils, indicating microplastics could interfere with the permeability and water retention capacity of soil.⁵⁶⁻⁵⁹ Microplastics also have been reported to have a significant effect on the actions of soil enzymes such as urease, catalase, phenol oxidase, and fluorescein diacetate hydrolase, indicating an impact

on soil fertility.^{60,61} Further, microplastics can be ingested by soil animals and garden chickens which could negatively impact their metabolic processes. For example, a concentration of ~130 microplastics g⁻¹ in the feces of chicken within a garden soil has been reported, and considerable microplastics contamination was reported in about 50% of 425 land-based snail specimens analyzed for microplastic contamination.^{39,62,63} Although the trophic transfer of microplastics within the terrestrial ecosystem has not been fully studied, there are concerns that humans may be exposed to microplastic pollution on land through inhalation of polymer dust and consumption of contaminated food and drinks.⁶⁴⁻⁶⁷

1.5. Microplastics in Aquatic Ecosystems and Implications

The aquatic ecosystem, which comprises fresh water and marine water bodies, is an important reservoir for microplastics and a medium for microplastics transport. The freshwater waterway consists of rivers, lakes, ponds, streams, and wetlands while the oceans and estuaries constitute the marine water bodies mostly studied for microplastic contaminations. While much attention has been given to the investigation of microplastic abundance in marine water bodies, with an estimate of about 24.4 trillion microplastics present in the world's ocean surface water, freshwater bodies are emerging areas for microplastic research.⁶⁸ Discharges from industrial wastewater treatment systems into rivers, and contaminations due to tourism activities and municipalities are some of the major contributors to microplastic contaminations of the marine water bodies reported.⁶⁹ Freshwater is considered one of the most complicated systems for microplastic transport and retention.³⁷ Microplastic contamination of the freshwater systems comes majorly from wastewater discharges and microplastics present in the surface runoff from urban areas and farmlands.⁷⁰ Synthetic fibers and fragments from polyesters, polyethylene (PE), polypropylene (PP), PVC, and PS are among the most frequently detected microplastics in surface freshwater, indicating

microplastic emission from laundry processes in homes, industrial processes, and degradation of plastic packaging materials.⁷⁰ Many researchers have reported that microplastic abundance in rivers and lakes is influenced by population density and proximity to urban centers,^{45,71} although results from other researchers do not show correlations.⁷² Another important factor that may influence microplastic loads in freshwater is rainfall patterns. Studies have shown that microplastic concentrations in rivers and stormwater, especially close to urban areas, increase with rainfall volume.⁷³ Besides urban surface runoff and runoff from farmlands, the increased microplastic concentration recorded after rainfall might be due to the strengthening of the water current velocity during the rainfall, causing resuspension of the microplastics in the river sediments into the upper water surfaces and enhancing horizontal transportation of microplastics.^{74,75}

Aquatic sediments present another sink for microplastics; high microplastic loads have been detected in both freshwater and marine sediments around the world. It was widely reported that microplastic concentrations in sediment samples are higher than those of their surface water samples.^{74,76,77} This may be attributed to microplastics discharged into water bodies sinking to the bottom of the water by the combined actions of gravity and biofouling.⁷⁸ It is believed that dense microplastics such as PET (1.40 g cm³), PVC (1.20 – 1.44 g cm³), polycarbonates (1.20 g cm³), and fiber-reinforced plastics (1.74 – 1.94 g cm³) are more likely to be deposited in the sediments while less dense and thin polymers such as fibers are suspended in the upper water surface.⁴⁵ Ageing, biofouling, and aggregation of microplastics are other processes that enhance the sinking of microplastics to the riverbed. Microplastic loads in marine sediments have been suggested to have a direct correlation with water flow rate, sediment depth, and closeness to shoreline.^{45,72,77,79} Microplastics are also present in frozen water (snow and ice).⁸⁰ Frozen freshwater and sea ice entrain several pollutants, including microplastics, which can be transported away from where the

ice is formed. Their accumulation in ice is affected by wind currents and changes in seasonal weather patterns.^{81,82} Although investigating microplastic pollution of sea ice is still a growing area of interest, significant concentrations of microplastics including PP, PE, PVC, and polytetrafluoroethylene (PTFE), have been detected in the subsurface Arctic water samples in Norway, subsurface water off Northeast Greenland, and in the surface water around the Antarctic Peninsula.^{83,84}

Since microplastics have been identified in different aquatic species including fishes, zooplankton, turtles, bivalves, shrimps, and whales, the presence of microplastics in freshwater and marine water bodies may pose both direct and indirect negative impacts on the aquatic species and on their trophic levels.^{85,86} The bioavailability and toxicity of microplastics in the aquatic environment have been linked to both the physical and chemical properties of the microplastics.⁸⁷ Physical properties such as size, color, density, and shape of the microplastics may have a great influence on their bioavailability, toxicity, and distribution in aquatic environments as aquatic species, especially selective forager organisms may ingest microplastics with the same physical features of their natural prey.^{87,88} For example, microplastics smaller than 100 μm are within daphnids' favorable food size and are frequently detected in the guts of daphnids,^{87,89} while blue polyethylene fragments which have the same color and morphology as copepod prey are often recovered in the guts of amber stripe scads (*Decapterus muroadsi*).⁹⁰ Further, the connection between color and pollutant adsorption on microplastics is not yet known in microplastic toxicological studies.⁸⁷ Findings have indicated that black microplastics are more prone to adsorbing chemical pollutants such as polychlorinated biphenyls (PCBs) and polycyclic aromatic hydrocarbons (PAH), than white plastic particles.⁹¹ The underlying reason for the variation in the adsorption capacity of microplastics with color is an interesting area of investigation for future studies. Chemical

properties of microplastics such as functional groups, crystallinity, and the stability of the polymer chemicals and additives, as well as the surface charge of microplastics affect microplastic toxicity in the aquatic ecosystem.^{79,87} For example, it has been reported that microplastics' inherent characteristics such as hydrogen bonding, van der Waals forces, electronic interactions, and hydrophobic interactions determine the adsorption of antibiotic residues on microplastic surfaces.⁹² Likewise, no appreciable difference was observed in the adsorption of Ni on PS, and Ni on PS-COOH. However, higher toxicity to the aquatic environment was reported when Ni was adsorbed on PS-COOH, than Ni adsorbed on PS, indicating functional groups influence on accumulation and toxicity of microplastics in water.^{87,93}

Generally, studies have suggested that ingestion of microplastics by aquatic species and the consequent breakdown of microplastics into their monomers and the release of their chemical additives such as plasticizers, reinforcements, and pigments are highly toxic to aquatic life and ecological stability.³⁷ Physical damages that have been reported in organisms due to microplastic ingestion include gut/intestinal blockage, inflammation of villi, and cleavage of enterocytes.⁹⁴ Translocation of microplastics and assimilation of their chemical residues from the digestive system through the circulatory system to other target organs also causes physiological damage to the aquatic organisms such as disruption of the endocrine and immune systems, gene alteration, oxidative stress, retarded growth, and infertility.⁹⁵ These microplastic particles may also act as vectors for binding and transmission of pollutants in the water such as PAHs, dyes, heavy metals, and drug residues, leading to their bioaccumulation in the aquatic environments and in aquatic organisms.⁹⁶ Microplastics may also have direct negative impacts on the aquatic ecosystem by causing energy deficiency in individual organisms which eventually affects the energy balance along the food web.⁷² Microplastics have also been detected in human blood, fetuses, alimentary

tracts, and feces, likely due to inhalation or ingestion via the drinking of contaminated water, consumption of contaminated sea foods, or consumption of contaminated table salts from the sea.⁹⁷⁻¹⁰⁰ Although the effects of microplastics on humans are not fully understood yet, there are indications from current studies that microplastics could impact negatively the respiratory, digestive, and nervous systems of humans.⁸⁷

1.6. Characterization Techniques for Microplastics Analyses

Analysis of microplastics involves several steps which includes sample collection, sample pre-treatment or digestion, extraction of microplastics, microplastics quantification, physical characterization, and chemical characterization. Since there are no standardized methods for each step of the microplastics analysis, the best methods applicable for microplastics analysis in water, sediments, and soil samples are debatable. For example, the common sampling methods employed in estimating microplastic abundance in water samples include the use of a neuston net (333 mm mesh size) and plankton net (~100 mm mesh size) with an attached flow meter, pumps, and sieves.¹⁰¹ The type of sampling method utilized by researchers may influence the outcome of the microplastic analysis. Similarly, researchers' characterization techniques employed in the microplastic analysis are mainly based on the objectives of the study, and on the characterization instrument available.

This section will focus on some techniques applicable to the quantification and physical/chemical characterization of microplastics. Microplastic quantification and physical and chemical characteristics are essential parameters in understanding the microplastic load and its sources in a sample.

1.6.1. Quantification and Physical Characterization

Quantification and physical characteristics such as size, morphology, structure, color, and texture of microplastics are determined using several techniques such as visual identification, optical microscopy, and scanning electron microscopy (SEM). Visual identification involves sorting and differentiating large microplastic particles (1 – 5 mm) from debris by the use of the naked eye, while optical microscopy combines optical lenses/objectives with visible light to identify the shape, color, and size of smaller microplastics.^{102,103} Although the visual identification technique is easy and less expensive compared to other sophisticated techniques, it is time-consuming and regarded as an error-prone technique due to biases in the counting and magnification factor that may result from the operator, especially as the size of the microplastics decreases.¹⁰⁴ This technique may also generate some false-positive results due to interference from plastic-like particles such as cellulose, rayon, paint, coal/fly ash, and keratin as it is difficult to differentiate them from microplastics with the naked eye.¹⁰⁵

Scanning electron microscopy (SEM) helps address the limitations encountered with visual identification and optical microscopy in differentiating small-size microplastics from plastic-like particles.¹⁰³ Scanning electron microscopy coupled with energy-dispersive X-ray spectroscopy (SEM-EDS) produces an electron beam that scans the surface of a sample, and also generates element-specific X-ray radiation, to produce spatially resolved topographical and elemental composition of the sample. Information regarding the weathering process of the microplastics in their natural environment can be determined from the high magnification SEM-EDS image.^{106,107} Although SEM-EDS provides a distinct image and composition of the MP that further helps to distinguish it from organic and inorganic plastic-like particles, it has inherent limitations in its inability to chemically identify polymer types and it is time-consuming due to special sample

preparation processes such as applying on conductive coating and mounting of sample on a pin stub using conductive tape.^{105,108}

1.6.2. Chemical Characterization Techniques

Chemical characterization techniques may involve the application of both destructive and non-destructive techniques to gain information on the chemical makeup and structure of the microplastics extracted in a sample. Destructive analytical techniques commonly employed in the analysis of microplastics include but are not limited to pyrolysis-gas chromatography-mass spectrometry (Pyr-GC-MS), thermal desorption-gas chromatography/mass spectrometry (TDS-GC/MS), and thermogravimetric analyses (TGA) coupled with a solid-phase adsorber. The most used non-destructive techniques for chemical characterization of microplastics are Fourier transformed infrared (FTIR) and Raman spectroscopy.

1.6.2.1. Pyrolysis-Gas Chromatography-Mass spectrometry (Pyr-GC-MS)

This technique enables the simultaneous detection of polymer types and additives by thermal decomposition of the sample usually under an inert atmosphere and the detection of thermal degradation fragments/products of the polymer. The resulting pyrolysis fragments of the polymer structure are then separated by gas chromatography and further characterized by their mass-to-charge ratios in the mass spectrometer.^{109–111} The characteristic degradation products and their charged ions can be used for qualitative identification of both the parent polymers and chemical additives. One advantage of Pyr-GC-MS is that it is fast since the samples do not need pretreatment analysis. In addition, the technique is not limited by organic or inorganic contaminants in the polymer sample, nor limited by the size or shape of the polymer.¹¹¹ However, the Pyr-GC-MS technique has some limitations associated with its applications. For example, it is not possible to

quantify the number of microplastics present in a sample since the polymer is destroyed thermally, and the degradation fragments are usually presented as the mass fraction or mass concentration of plastics. Another limitation of the technique is its inability to determine the particle size of the polymer, which is an important parameter in understanding the sources or the origin of the microplastics. However, the technique can be used to complement the results from the FTIR and Raman techniques that are excellent for characterizing microplastics.¹¹²

1.6.2.2. Thermogravimetric (TGA)- hyphenated Techniques

The Thermogravimetric technique is based on heating up a sample at a controlled rate in a controlled atmosphere (inert or air), then observing the mass loss by the sample during this process over time from which the temperature at which the pyrolysis of the sample occurs can be determined. This technique is a destructive technique that brings about pyrolysis of the sample, and the polymer type can be identified and quantified by coupling other analytical instruments such as mass spectrometer (TGA-MS), differential scanning calorimetry (TGA-DSC), and thermal extraction-desorption gas chromatography-mass spectrometry (TGA-TD-GC-MS) with the thermogravimetric instrument forming TGA-hyphenated techniques.¹⁰⁶

The TGA-MS method allows the evolving gas from the sample being heated in the TGA set-up to be analyzed directly by passing through the mass spectrometer detector, and the mass-to-charge ratio or the characteristic ion corresponding to the mass loss in the degraded sample recorded can be used to qualitatively determine the composition of the evolving gas from the sample. TGA-MS is fast with minimal sample preparation required and it is suitable for analyzing microplastics in sediment samples. However, the application of TGA-MS for microplastics analysis might be

challenging especially when varieties of contaminants are present on the plastic samples which makes data interpretation more difficult.¹¹³

Changes in the thermodynamics parameters of microplastics such as enthalpies, heat capacities, and temperatures of phase transition can be used to determine the polymer type and the quantity of the polymer present using the TGS-DSC technique. This is done by monitoring changes corresponding to either endothermic or exothermic conditions in a sample. A change in the temperature results in the appearance of the peak in the DSC system, and the area under the peak can be analyzed for quantification of concentration.¹¹¹ Particle size, the degree of polymer branching, and the presence of impurities and additives influence the characteristics of transition temperatures obtained by DSC.¹¹⁴ The TGA-DSC technique has the advantage over TGA-MS in that it is easy to operate and inexpensive. In addition, it provides a piece of comprehensive information on any presence of impurities or chemical additives in the microplastics.¹¹⁵

The TGA-TD-GC-MS technique also offers higher sensitivity and selectivity to the microplastics analysis since the evolving gases are separated by the gas chromatography before being detected by the MS detector. It also has the added advantage in that it is fully automated and higher amounts of the representative samples and organic plastic additives present in the samples can be analyzed in one run. Limitations associated with the TGA-TD-GC-MS technique are its lower sensitivity to inorganic additives, and a complex data interpretation is required.¹¹¹

1.6.2.3. Fourier-Transform Infrared (FTIR) Spectroscopy

Fourier-transform Infrared spectroscopy remains one of the most versatile and reliable non-destructive spectroscopy techniques for microplastic analyses. FTIR is based on the principle of molecules absorbing a specific wavelength of light, causing the excitation of vibrational modes that are specific to the chemical bonds. The strength of absorbance of molecular vibrations in FTIR

is proportional to the number of specific bond types present in the sample. In FTIR, a collimated radiation beam from the source is split into two beams of nearly equal power by a beam splitter. One of these beams is reflected from a stationary mirror, while the other is reflected from a moveable mirror (with constant velocity). The two reflected beams then recombine such that the intensity variation of the combined beam can be measured as a function of differences in the path lengths of the two beams on reaching the detector. The resulting signal (interferogram) is Fourier transformed by the computer into a full spectrum as a function of wavenumber (cm^{-1}).¹¹⁶ Since no two unique molecular structures produce the same Infrared spectrum, this makes FTIR spectroscopy applicable in many analyses, including characterizing the microplastic composition and deducing the physiochemical weathering of microplastics.^{117,118} FTIR operation for microplastic analyses can be optimized in three different modes depending on the sample and the information required. There is micro-FTIR (μ -FTIR), attenuated total reflection (ATR-FTIR), and the Focal-plane array (FPA-FTIR). Micro-FTIR combines microscopy with FTIR spectroscopy which makes it best suited for analyzing samples considered too small for the conventional FTIR techniques to analyze, in that it can collect IR signals at a high spatial resolution down to $5\ \mu\text{m}$.¹¹⁹ Micro-FTIR principally consists of an optical microscope and an infrared microscope. The optical microscope helps to visually focus on the sample while the infrared microscope with reflection optics focuses the infrared beam and adjusts the beam spot size to be focused on the specific area of interest in the sample.¹¹⁶ μ -FTIR in transmittance mode is mostly applied in the identification of natural fibers and semi-synthetic fibers.¹²⁰ These fibers are considered thin enough to transmit light. In addition to the fact that it can be used to characterize a single microplastic sample due to its high spatial resolution, μ -FTIR has the added advantage in that a loss of specimen and

modification of specimens are prevented since the technique does not require an extensive sample preparation, compared with the conventional FTIR techniques.¹¹⁹

ATR-FTIR is another important technique widely accepted for fast microplastic characterization since it provides chemical information about the functional groups distributed on the surface of the samples.¹¹⁹ In this technique, a beam of infrared incident light is passed through an ATR crystal and undergoes total internal reflection at the interface between the crystal and the less dense sample medium. The penetrating radiation known as the evanescent wave interacts with the sample at the surface and the bulk and then exits at the opposite end of the crystal where it is analyzed in the FTIR spectrometer.¹²¹ The penetrating depth of the evanescent radiation (about 0.5 μm to 2 μm) depends on the refractive index of the two media, the wavelength of the incident radiation, and the angle of the incident beam with respect to the interface.¹¹⁶ The signal-to-noise ratio is affected by the number of reflections and the total length of the optical light path.¹²¹ The ATR-FTIR technique requires that the sample must be large enough (about 10 μm) to cover a sufficient area of the crystal probe. The μ -ATR-FTIR technique, which combines particle identification by microscopy and chemical characterization by spectroscopy, is most appropriate for analyzing microplastic particles majorly from water and biological samples since it allows for easy visualization of tiny fibers and mapping of the functional groups present in the dry samples and even in animal tissues.^{117,120,122}

Focal plane array (FPA)-FTIR is another fast technique for microplastics analysis because multiple spectra and imaging of the microplastics can be acquired within a minute with the aid of the grid of detectors. In this technique, a sample is irradiated in either transmission or reflectance mode or with an ATR objective. The plane perpendicular to the optical axis (focal plane) is imaged on the array of detectors, which concurrently record the distribution of the chemical species within the focal plane as characterized by FTIR. Each element on the array pixel of the sample, microplastics

for instance, corresponds to an independent infrared spectrum on the membrane filter. Therefore, this technique is fast and suitable for characterizing microplastics with small particle sizes with high spatial resolution and promptness.¹²³

1.6.2.4. Raman Spectroscopy

Raman spectroscopy is one of the most reliable analytical techniques currently being used for both quantitative and qualitative analysis of microplastics. The application of Raman microscopy in microplastics analysis produces imaging with a very high spatial resolution down to 1 μm and provides a unique spectrum for each polymer present.^{120,122} The versatility of Raman spectroscopy in the chemical characterization of microplastics is because the technique is non-contact and non-destructive. In addition, when operated in the chemical imaging mode, it provides improved information on the characteristics of the polymer such as chemical composition, particle size, individual particle shape, and the amount of each type of polymer present in the analyzed sample.¹⁰⁶

Principle:

Raman spectroscopy is a vibrational spectroscopy based on the principle of inelastic scattering of light by molecules. When a sample is irradiated with a monochromatic light, the molecule may scatter the incident photons elastically (Rayleigh scattering) and a small fraction of it is scattered inelastically (Raman scattering). In the Rayleigh Scattering process, the incident photon causes the molecule to be promoted to a higher virtual energy state. The molecule then relaxes back to its initial ground vibrational energy state ($v = 0$) causing no net change in energy or frequency, ($\nu_s = \nu_i$). The Raman scattering (inelastic) process may occur in two ways. If the molecule in a ground vibrational state ($v = 0$) is excited to a virtual energy state but then relaxes back to a higher

vibrational energy state such as $v = 1$, the scattered photon has less energy compared to the incident photon energy ($\nu_s < \nu_i$). This kind of Raman scattering is known as a Stokes shift. Moreover, when a molecule originally in the first vibrational energy state ($v=1$) is excited to a virtual energy state and then relaxes to the ground vibrational energy state ($v=0$), the scattered photon energy will be higher than the incident energy photon ($\nu_s > \nu_i$) giving rise to an anti-Stokes Shift. For analytical purposes, application of the Stokes radiation intensity (lines) predominates since very few molecules reside in the first excited vibrational state at room temperature according to Boltzmann distribution. Therefore, the anti-Stokes line is less intense, while the more intense Stokes line is usually measured for analysis purposes. The Raman scattering provides information about the energy levels of the normal modes of the molecule from which the chemical composition of the molecule such as the orientation of its atoms, bond strength, geometry, intermolecular interactions, etc. can be deduced.¹²⁴

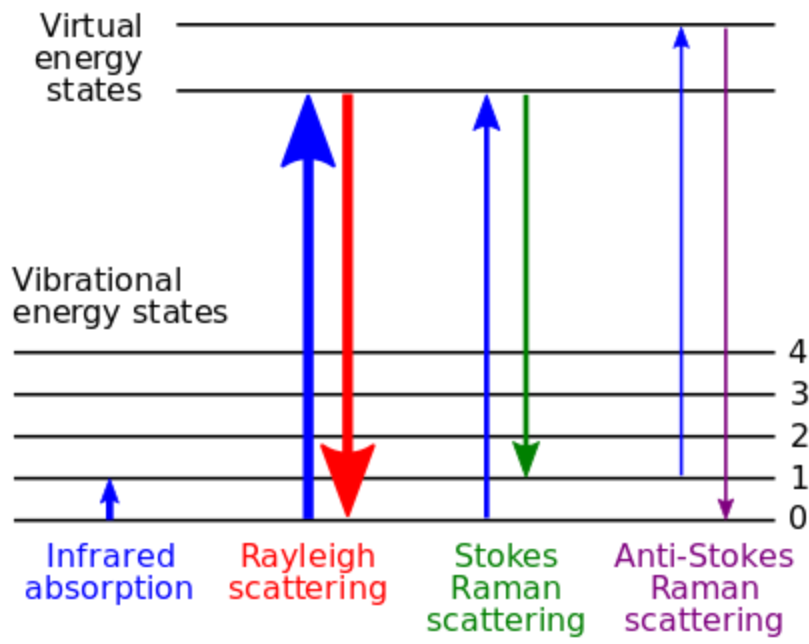


Figure 1.2: Energy-level diagram showing the states involved in Raman spectra¹²⁵. (Adapted from reference 128)

A Raman signal is expressed as a plot of intensity vs Raman Shift (wavenumber, cm^{-1}). A typical Raman spectrum may cover a wavenumber range between 4000 and $5 \Delta\text{cm}^{-1}$. The magnitude of the Raman shift, $\bar{\nu}$ is described by equation 1 as:

$$\bar{\nu} = 1/\lambda_0 - 1/\lambda_1 \dots\dots\dots (\text{eqn. 1})$$

Where the wavelength of the excitation laser is λ_0 in nm and λ_1 is the Raman scattered wavelength in nm. Although the extent of Raman a shift is not dependent on the wavelength of the incident light, Raman scattering intensity is dependent on the change in polarizability of the molecule, wavelength, and intensity of the excitation laser, and the number of scattering molecules. Polarizability of the molecule defines the looseness, or proneness to distortion of the electron cloud around a molecule when in contact with an external electric field. Molecules that undergo

symmetric vibrational modes (stretching and bending) are polarizable and are Raman active. Generally, linear homonuclear and non-polar molecules are strongly Raman active, while asymmetrical molecules and polar molecules are strongly IR active. Therefore, both IR and Raman spectroscopy are complementary in their applications.¹²⁴

The frequency of the incident light can affect not only the scattered light intensity but the beam focus and sample depth penetration as well. Lasers are the predominant excitation source used in Raman spectrophotometry; lasers provide a nondivergent stable and intense beam of radiation. Some of the lasers used in the Raman technique include the argon ion laser (488 nm and 514.5 nm), krypton ion laser (530.9 and 647.1 nm), frequency-doubled neodymium – yttrium aluminum garnet (Nd: YAG) and neodymium -yttrium ortho-vanadate (Nd: YVO4) diode lasers (532 nm), helium–neon (He-Ne) (632.8 nm), near infrared (IR) diode lasers (785 and 830 nm), and Nd: YAG and Nd: YVO4 lasers (1064 nm). Using a short wavelength laser may produce a high energy incident light that could cause high molecular excitation to a virtual state that coincides with one of the electronic states of the sample, giving rise to fluorescence, or may cause photodegradation of the sample. This can be overcome by using a long-wavelength laser source close to the near-infrared (NIR) region. For example, Nd: YAG lasers (1064 nm) can be used at high power to suppress fluorescence without causing photodecomposition of the sample^{126,127}. A disadvantage of using longer wavelength excitation is a reduction in sensitivity since Raman scattering intensity is inversely proportional to the fourth power of excitation wavelength, hence, a shorter wavelength laser has greatly increased sensitivity. Instrument settings and parameters such as laser power, exposure time, and the number of acquisitions or accumulations can be manipulated to reduce or eliminate fluorescence and photobleaching/photodegradation while maintaining good signal strength.^{128–130}

The Raman spectrophotometer uses a combination of monochromators gratings, notch filters, and holographic notch/edge filters to separate the weak Raman line from the strong Rayleigh scattering, while detectors such as photomultiplier tubes (single channel detectors), charge-coupled devices (CCD), and multi-channel detectors may be used to convert the incoming optical signal into a charge which is integrated and transferred to computer readout devices.¹²⁶

1.7. Motivation for the Study and Objectives

The South Saskatchewan River is the 10th largest river in Canada about 1392 km (865 miles) in length and an average flow volume of 280 m³s⁻¹.¹³¹ It serves as one of the major bedrocks for the socio-economic activities in the province of Saskatchewan. About 50% of the population rely on the river for the supply of potable water, recreation, irrigation, and industrial uses.¹³² The sustainable use of the river for these socio-economic activities depends on the water quality and water quantity. Since microplastics are ubiquitous, their presence in the South Saskatchewan River and storm ponds may impact negatively on the water quality and the survival of its aquatic species. There are concerns that the recreational, industrial, agricultural, municipal and land use activities around these waterways may be point sources of microplastics contamination of the river and stormwater. However, no previous studies have been carried out on the microplastics concentrations in the South Saskatchewan River and storm ponds in Saskatoon, and the significance of seasonal changes to microplastics loads in the waterways is not known.

In this study, we characterized microplastics sampled from several locations along the South Saskatchewan River and some selected storm ponds in Saskatoon based on the following objectives:

1. To quantify microplastics loads of the South Saskatchewan River and Saskatoon storm ponds

2. To investigate seasonal changes in microplastics concentration of the river and storm ponds
3. To characterize microplastics composition
4. To determine microplastics sources

The results from this research will help the research community to understand the sources and the level of microplastics loads in Saskatchewan waterways.

CHAPTER TWO: EXPERIMENTAL

2.1. Sampling Sites

Water samples were collected by the collaborator (M. Brinkmann) at seven sites along the South Saskatchewan River and at three selected storm ponds in Saskatoon between May and September 2020 (**Fig.2.1**). The South Saskatchewan River flows primarily in a North-Easterly direction. It passes through one major city (Saskatoon, which has one waste-water treatment plant (WWTP)) and one dam (Diefenbaker Dam, on Lake Diefenbaker). The Miry Creek location is upstream of the dam, while all other sites are downstream of it. Miry Creek and Outlook locations are upstream of Saskatoon, and Clarkboro and St. Louis sites are downstream. All other sampling locations are within Saskatoon city limits. Fred Heal and Beaver creek sites are directly upstream of the Saskatoon WWTP while Clarkboro and St. Louis sites are directly downstream. The town of Outlook has a wastewater lagoon that is discharged each late spring between May 18 – 23, 2020. Samples were collected upstream and downstream of the lagoon including during flushing in May, and after flushing in June/July and August/September 2020.

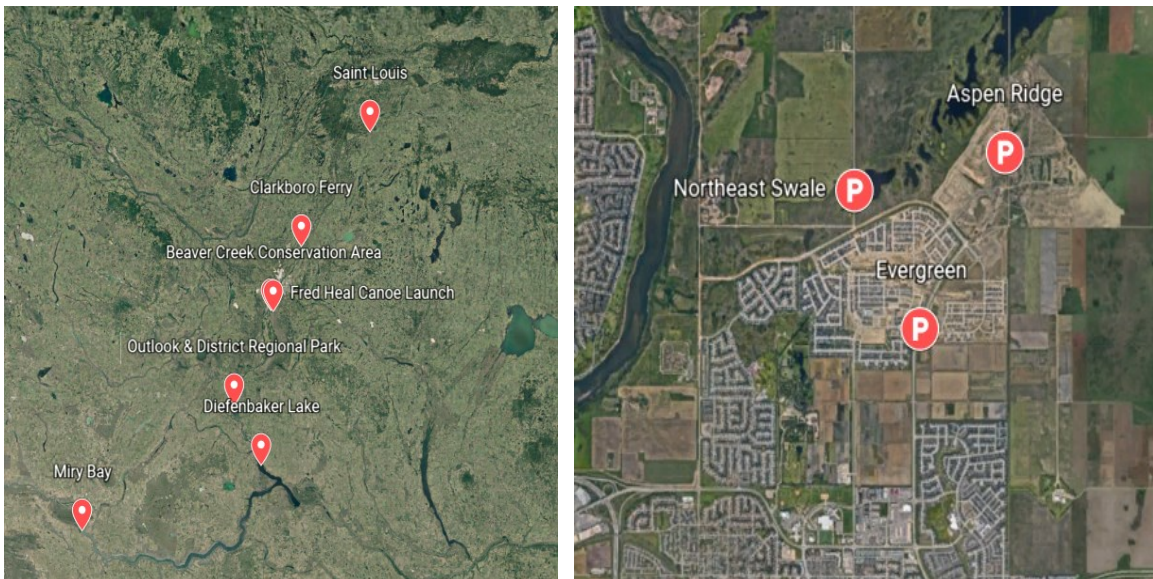


Figure 2.1: Showing the map image of sample sites on the South Saskatchewan River (left image) and Storm ponds (right image) as obtained from Google Earth. The pin icon indicates river sample locations while the P icon indicates the storm pond sample location

The storm ponds sites which include Evergreen, Aspen ridge and Northeast Swale are all located within Saskatoon urban areas. Ponds at Evergreen and Aspen ridge collect surface runoff water majorly from residential settlements, while NE Swale is located in a nature and wildlife conservation area of the city.

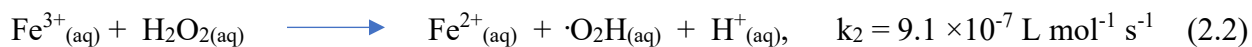
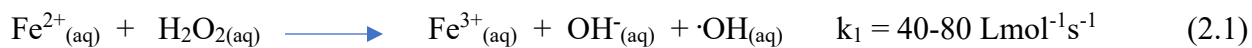
2.2. Sampling

The water samples collected were grouped into three sampling seasons, namely May, June/July, and August/September to reflect the seasonal changes in microplastic concentrations. For each sampling period, two or three replicate or triplicate water samples were collected by pumping 500 liters of water just below the surface near the shore, through a 10 μm plankton net using a metered pump, with the net terminal connected to 125 - mL pre-screened collection bottles.¹³³ This ensured microplastics were concentrated to about 400- fold prior to further treatments. The water samples were then stored in a refrigerator at 4 °C to maintain their original compositions prior to digestion processes.

2.3. Digestion

The water samples collected contained some trace organic matters (plant fibers and roots) which might interfere with the microplastics analysis since some plant fibers are similar in shape and texture to textile fibers. To prevent a false positive result, our collaborators digested the water samples by Fenton's oxidation process to get rid of this non-plastic organic matter. This was done by first acidifying each of the samples with concentrated sulfuric acid to a pH less than three, followed by a stepwise addition of Fenton's reagent (0.25 g of ferrous sulfate ($\text{FeSO}_{4(\text{aq})}$) and 12.5 mL of 30% by volume hydrogen peroxide ($\text{H}_2\text{O}_{2(\text{aq})}$)).¹³³ In this reaction, $\text{Fe}^{2+}_{(\text{aq})}$ is oxidized to $\text{Fe}^{3+}_{(\text{aq})}$ by degrading the $\text{H}_2\text{O}_{2(\text{aq})}$ into hydroxyl radicals ($\cdot\text{OH}$) (**Eqn. 2.1**). The $\text{Fe}^{3+}_{(\text{aq})}$ further reacts

with the excess $\text{H}_2\text{O}_{2(\text{aq})}$ to produce $\text{Fe}^{2+}_{(\text{aq})}$ and hydroperoxyl radical ($\cdot\text{O}_2\text{H}$) in a cyclic process (Eqn. 2.2).



The $\text{Fe}^{2+}_{(\text{aq})}$ acts as a catalyst, and the $\text{H}_2\text{O}_{2(\text{aq})}$ is continuously consumed to generate $\cdot\text{OH}_{(\text{aq})}$ that completely mineralizes the organic matter into $\text{CO}_{2(\text{g})}$, water, and inorganic salts. The hydroperoxyl radicals generated also contribute to the degradation process of the organic plant materials.^{134,135} The water samples were kept at room temperature for about 2-3 days for the oxidation process to complete.

2.4. Extraction

Microplastics were extracted in a solution of sodium iodide (NaI , 1.6 g cm^{-3}) by density difference using a small glass separator unit as described by Nakajima *et al.*¹³⁶ The extraction process is visually described in **Fig. 2.2**. To describe briefly, a known volume of the digested water sample was carefully transferred into the single unit of the small glass separator device with the upper plate and lower plates joined and clipped together to prevent any loss of sample (**Fig. 2.2a**). The glass jar was rinsed several times with ultrapure Milli-Q water ($18.2 \text{ M}\Omega \text{ cm}^{-1}$) to ensure all particles were transferred into the glass separator unit. About 160 g of NaI (99+%, Alfa-Aesar Thermo Fisher) was added to the water sample in the glass unit and then made up to 150 mL by adding ultrapure deionized water to achieve a solution density of 1.6 g cm^{-3} and the solution reaching half volume of the upper plate. The glass unit was then covered with aluminum foil to prevent exposure to light and other external contaminants before the solution was being stirred

gently for about 30 minutes using a glass covered VWR stir bar (25.4 x 9.5 mm) (**Fig. 2.2b**). In **figures 2.2c and 2.2d**, the solution in the glass unit was allowed to settle for about 4 hours, after which the upper half of the device which is expected to contain the microplastics and other less dense particles was separated from the lower half containing other settled denser materials or sediments, by simply sliding the upper plate over the lower plate in opposite direction such that the extended lower plate acts as a base for the liquid in the upper plate, hence the liquids were separated without any loss of materials or disturbing the system.

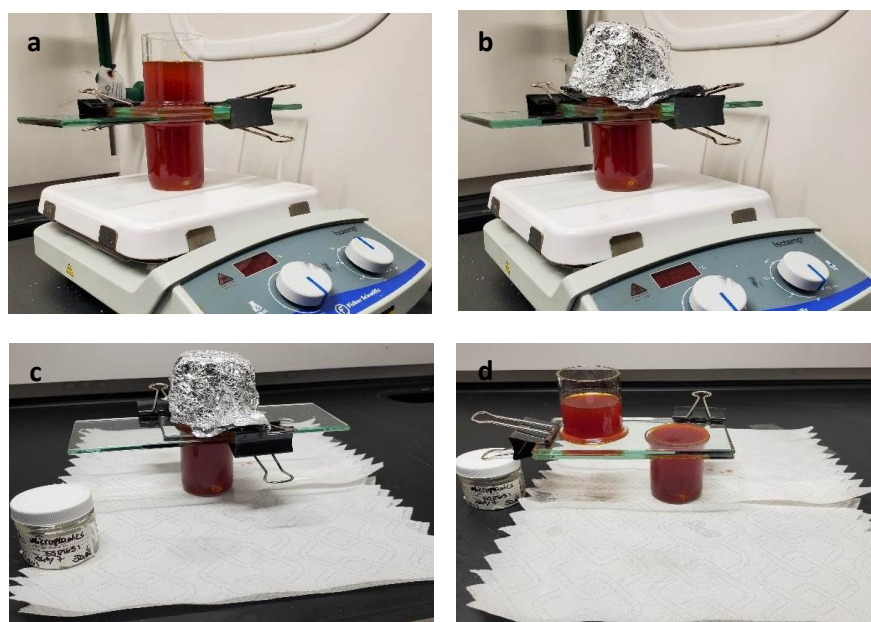


Figure 2.2: Showing the stages of microplastics extraction using the glass unit. (a) Sample in NaI solution in the unit. (b) Solution being stirred for 30 minutes with VWR stir bar. (c) Settled sample. (d) Separation of the top and bottom half of the sample.

The solution in the upper half was extracted by carefully transferring it to a glass funnels containing a damp 0.7- μm pore size Whatman glass microfiber filter paper (GFF) and then filtered. The internal wall of the upper plate of the glass separator device was thereafter rinsed several times with deionized water to ensure no particle is adhered to the glass wall. The microplastics collected on the GFF were rinsed several times with deionized water to ensure all NaI solution was washed

off. The GFF containing the expected microplastics particles was then allowed to air-dry while covered with aluminum foil in a laminar flow hood to ensure all particles collected remained in their original physical and chemical states and prevent any loss or contamination from airborne plastics. To prevent contamination, all extraction processes were carried out in a laminar flow hood and ensuring only glass materials were employed in the processes and a cotton made laboratory coat was worn throughout the process.

2.5. Microplastics Quantification and Characterization

The extracted microplastics on the GFF were quantified visually under white light using a Renishaw confocal microscope. The samples were brought to a sharp focus with a 10x/0.25 numerical aperture (N.A.) Leica objective. A montage of 500 μm by 500 μm pictures of each particle identified was created while scanning through the entire area of the filter. The number of particles were then counted manually. Utmost care was taken such that any recalcitrant plant fibers or animal larva – characterized by inconsistent colour and texture or showing segmented surfaces – were not counted. An additional (separate) image of each identified particle was acquired using a 40x/0.60 N.A. Olympus objective. These magnified images were used to better determine particle physical structures and colours.

Chemical characterization of each identified particle was done by obtaining their spectra using a Renishaw confocal Raman spectroscopy instrument equipped with a CCD detector, an 1800 l/mm (vis) grating and a 50 mW, 532 nm continuous wave diode-pumped solid state (DPSS) excitation laser. Instrument parameters such as acquisition time, laser power, and number of accumulations were adjusted for each particle to optimize signal intensity and signal-to-noise ratio while preventing saturation of the CCD detector and photochemical damage of the sample. Acquisition

times of 5 – 10 s and laser powers of 5 – 10% were generally used for pellet and fragment samples, while acquisition times of 1 – 5 s and laser powers of 1 – 5% were generally used for fiber and film particles, which are prone to photo-damage. Static scans centered around 1400 cm^{-1} (400 – 1500 cm^{-1}), and extended scans between 100 to 4000 cm^{-1} were collected for each identified particle using the 40x objective. The collected spectra were further processed by normalizing the peak intensities and removing fluorescence contributions to the Raman spectra using the baseline subtraction tool in the Wire5.2 software of the instrument. The spectra were then matched with an in-house Raman polymer library to identify the specific polymer make-up of the microplastics using the component analysis tool of the software as illustrated in **Figure 2.3**.

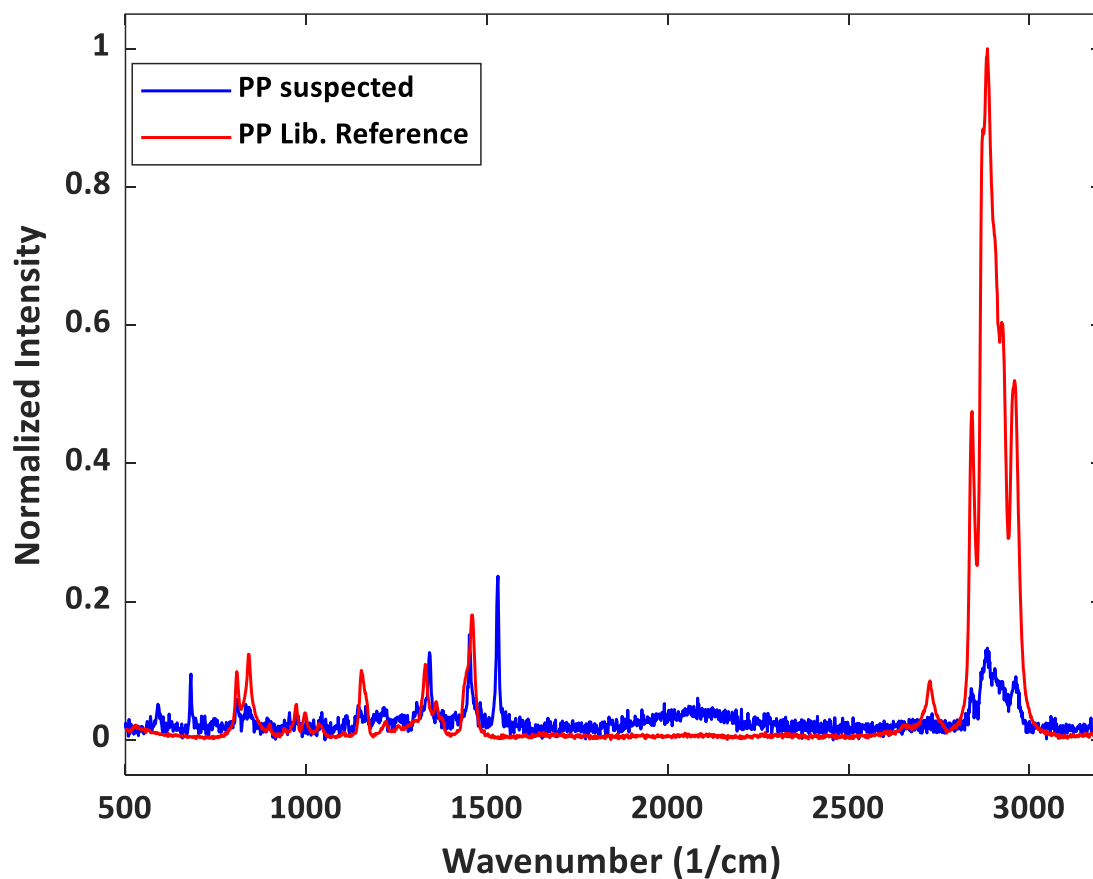


Figure 2.3: Showing a suspected polypropylene spectrum (blue) matched with the polypropylene reference library (red)

2.6. Polymer Library

The in-house Raman polymer library was developed by collecting Raman spectra of common plastics used for different applications. Low-, medium-, and high-density polyethylene (LDPE, MDPE, HDPE), PET, PP, polysulfone (PSF), poly (methyl methacrylate (PMMA), low and high molecular weight PVC and nylon 6 were obtained from Sigma Aldrich (St. Louis, Missouri, USA) and were used without any further pre-treatment. Polystyrene reference spectra were acquired from

commercially available polystyrene foil. **Figure 2.4** shows the representative spectral of the reference polymers acquired for the polymer library. Raman spectra of other particles identified, mostly from natural textile fibers and microfibers which are not within the scope of the in-house polymer library were characterized by subjecting them to other open-source polymer databases such as Openspecy¹³⁷ and Public spectra¹³⁸ to further ascertain their chemical makeup.

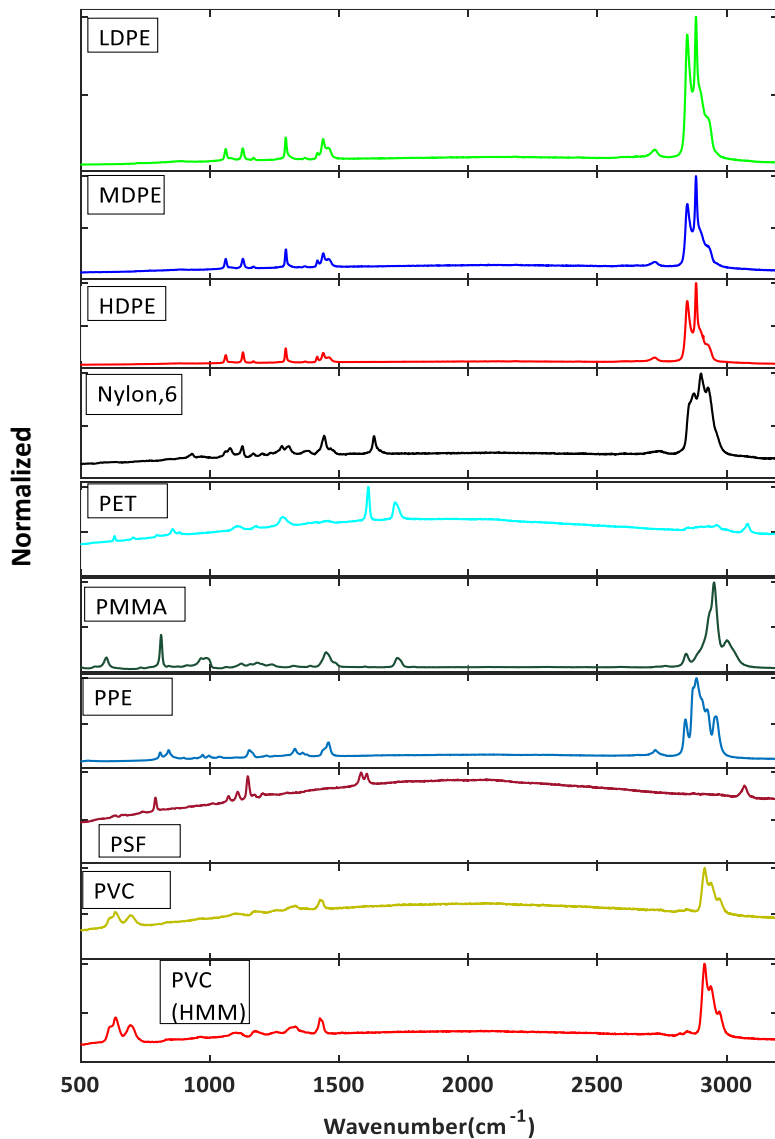


Figure 2.4: Reference Raman spectra of some selected polymers obtained for the spectral library

2.7. Method Validation

The percent recovery of the glass separator device based on the density of the polymer samples was validated by extracting six virgin polymer samples (500 – 1000 μm) in 1.6 g.cm^{-3} NaI using the small glass separator device. All virgin polymer samples were obtained from Sigma Aldrich and were used without further purification. Some polymers were categorized into polymers with densities less than or similar to the density of distilled water (1.00 g cm^{-3}) namely nylon 6 (1.08 g cm^{-3}), PE (0.925 g cm^{-3}) and PP (0.900 g cm^{-3}). The remaining polymers had densities greater than the density of distilled water: PET (1.68 g cm^{-3}), PSF (1.24 g cm^{-3}) and PVC (1.40 g cm^{-3}).

The results (**Fig. 2.5**) indicate that the separator unit shows 100% recovery for polymers with densities less than or close to 1.00 g.cm^{-3} , while the recovery of polymers with densities greater than 1.00 g.cm^{-3} ranges from $98.3\% \pm 0.6\%$ to $100\% \pm 0.0\%$ (overall mean recovery $99.1\% \pm 0.8\%$). Analysis of their overall mean recovery rate using t-test, with $P > \alpha$ (p-value = 0.2248, $\alpha = 0.05$) suggests there is no significant difference between the overall mean recovery rate of less dense polymer samples and the dense polymer samples when extracted in a dense solution of NaI using the small glass density separator device. Hence, the method is highly efficient for recovering both dense and less dense microplastics from water samples.

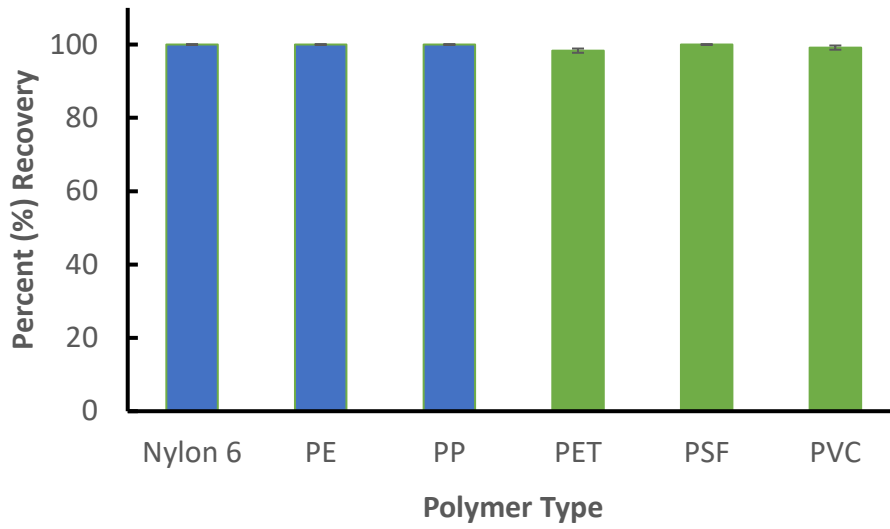


Figure 2.5: Percent recovery of the small glass separator unit. Blue bars indicate polymers with densities less than or similar to the density of distilled water, while green bars indicate polymers which have densities greater than the density of distilled water.

CHAPTER THREE: RESULTS AND DISCUSSION

3.1. Particle Concentrations and Classification

Total particle concentrations, including microplastics and natural textile fibers, are shown in **Figure 3.1**. The mean particle concentration averaged across all sampling sites and sampling times was 63.2 ± 27.2 particles m^{-3} . The majority of the particles ($\sim 77\%$) were from natural fibers, while microplastics accounted for $\sim 23\%$ of particles. Among the river samples, the total microplastic concentrations were much higher at Miry Creek (12.00 ± 9.12 m^{-3}) than at all other sampling locations (mean of 3.18 ± 3.00 m^{-3}); however, there is no statistical difference between these samples at 95% confidence interval. The higher microplastic loadings are likely due to Miry Creek being upstream of Lake Diefenbaker, while all other sites are downstream. We suspect that the Gardiner dam located on Lake Diefenbaker may be acting as a reservoir for sediments, and likely for microplastics before the water discharges into the South Saskatchewan River just before the Outlook municipality. Previous studies have suggested that sediments collected behind dams could be possible sinks for microplastics.^{139,140} This may also explain the lower total mean microplastic concentration of 4.43 ± 2.88 m^{-3} recorded in the South Saskatchewan River compared to the mean concentration of 26.2 ± 18.4 m^{-3} reported for the North Saskatchewan River where no dam is directly constructed on the river.¹³⁹ In addition, the mean microplastics concentration of the South Saskatchewan River is many times lower than the 20 - 410 particles m^{-3} reported for the Ottawa River and its tributaries but appears to be similar to those in the Red, Assiniboine, and Nelson Rivers near Winnipeg, Manitoba with a mean concentration of approximately 5.3 microplastics m^{-3} .¹³⁹⁻¹⁴¹ Particle concentrations in the Saskatoon storm ponds were similar to those in the river samples (48.7 ± 13.3 particles m^{-3}). The Northeast Swale had the largest relative contribution from microplastics (60%).

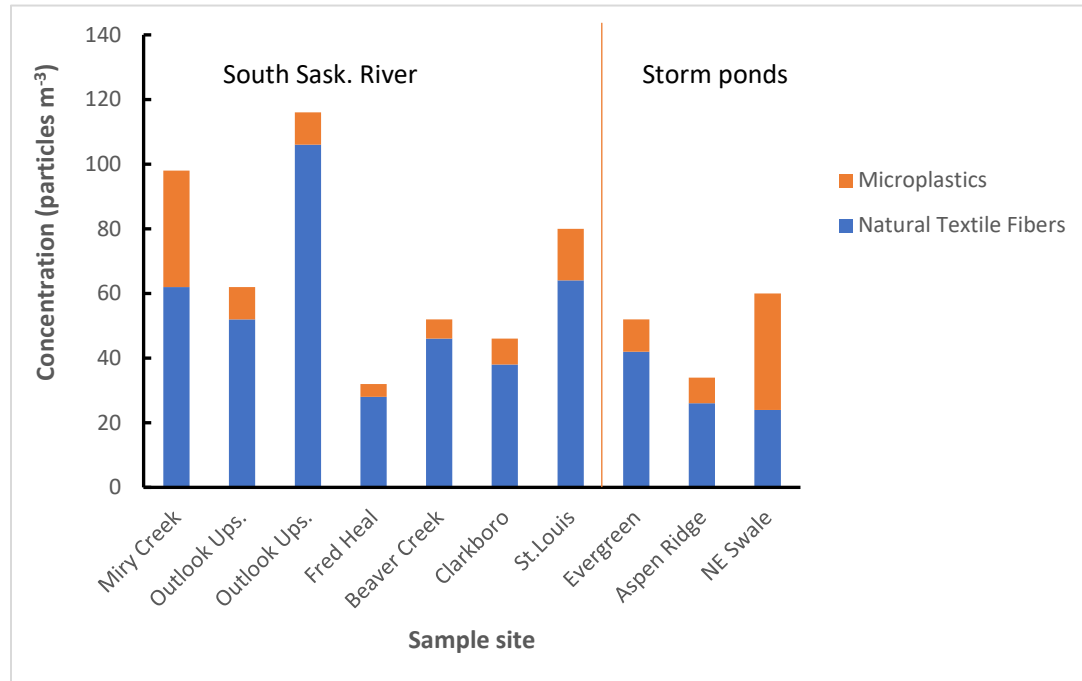


Figure 3.1: Composite total particle concentrations in river and storm pond samples showing contributions from natural textile fibers and microplastics. Sample sites are ordered from upstream to downstream

We classified the microplastics in all samples under four (4) main morphological categories, which include polymer fibers, which are flexible with a uniform thickness and colour; fragments, with characteristic rigid structure and irregular shapes; spheres, which are spherical in shape and are about 3 – 5 mm in size; and polymer films, which are flat (2-D shape) and of different colours^{31,32}. The images of some microplastics collected are shown in Fig. A.2.1 of the appendix. **Figure 3.2** shows the morphology distribution of microplastics in all the samples. Synthetic fibers were the dominant microplastics accounting for about 51% of all microplastics detected. Microplastics in

the form of fragments contributed about 42%, while films and spheres contributed about 4% and 3% respectively to the total microplastics detected in all samples.

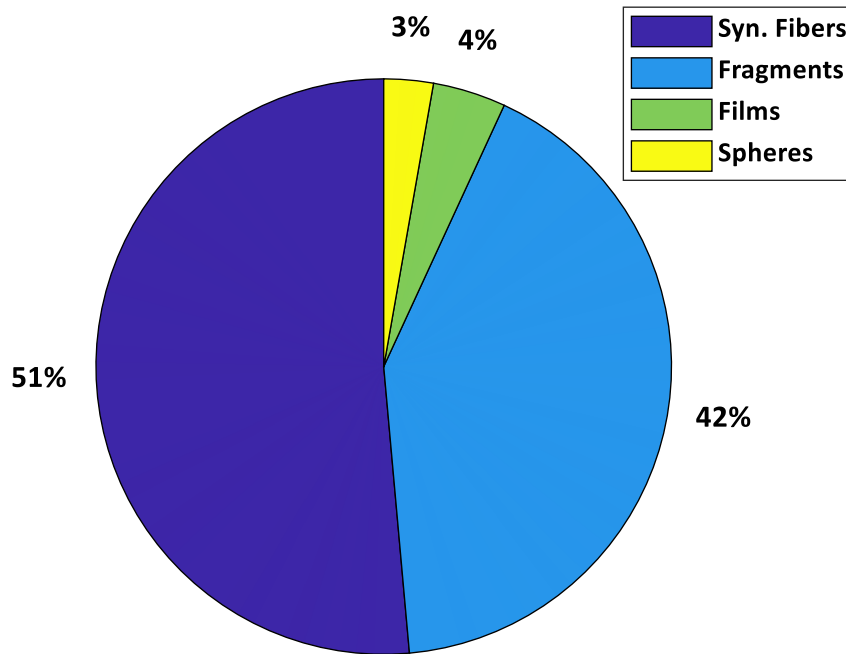


Figure 3.2: Fractional contributions of microplastics type identified in all samples.

The total microplastic concentrations of different samples were examined in relation to their sampling seasons as shown in **Figure 3.3**. While the large variability and a small number of replicates preclude detailed statistical analysis, a few observations are worth discussing. “Outlook upstream” and “Outlook downstream” are respectively upstream and downstream of the town of Outlook, SK. In the late period of Spring, 2020 (May 18th –23rd), the contents (or effluent) of the wastewater lagoon were discharged into the South Saskatchewan River. While no microplastics were detected in either April/May or August/September, a relatively high concentration of 10 microplastics m⁻³ was observed in the June/July sampling season at Outlook downstream. It could

be suggested that the wastewater, including its sediments, was fully mobilized, and accumulated downstream of the river during that period, hence, a high microplastics concentration was detected, with a correspondingly high concentration of natural fiber detected in the sample as illustrated and discussed in **Figure 3.1**.

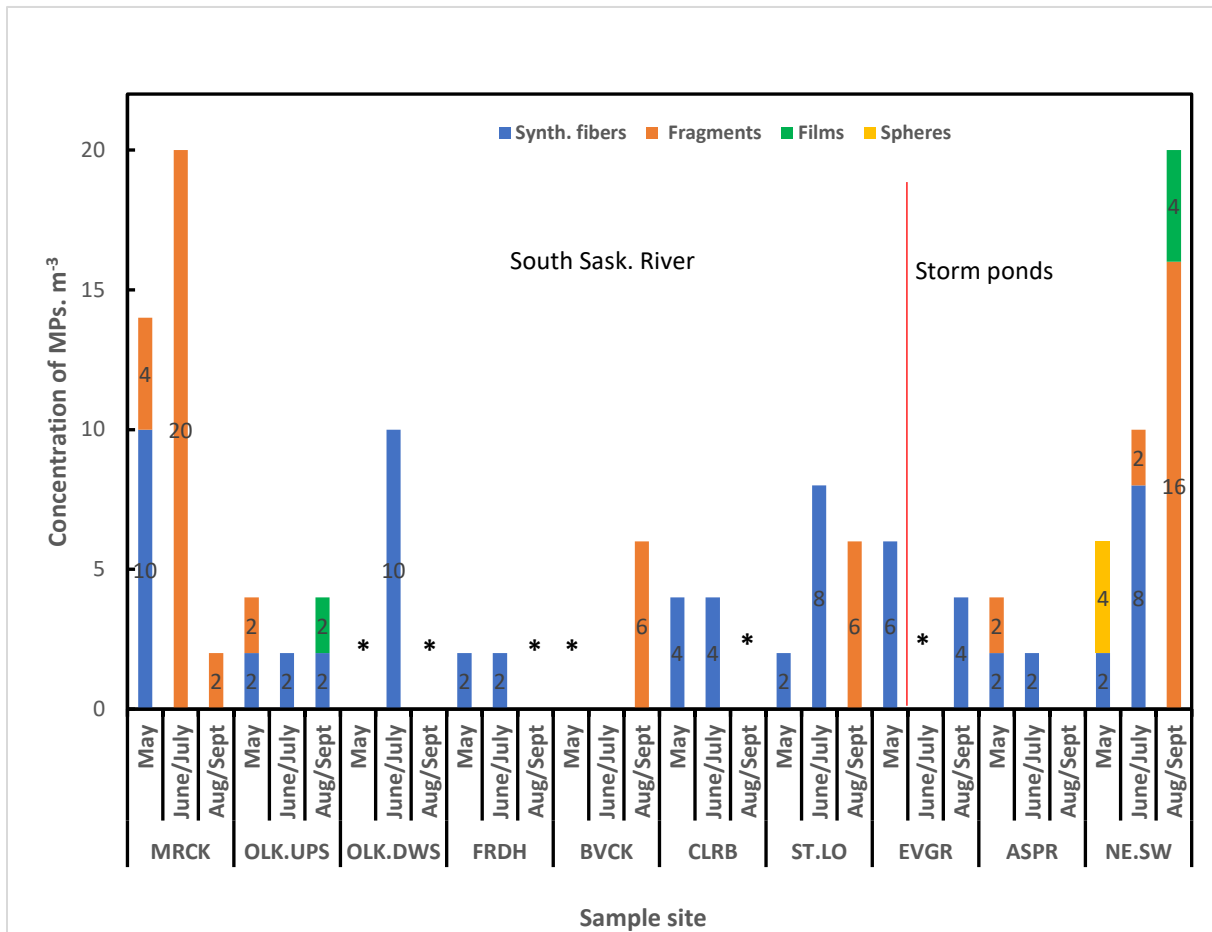


Figure 3.3: Morphological properties of microplastics in each sample for all the three sampling seasons. “*” Indicates no detectable MP in the sample. No sample was acquired during June/July sampling period for Beaver creek site, or in August/September sampling period for Aspen ridge. Sample sites are abbreviated as Miry creek (MRCK), Outlook upstream (OLK.UPS), Outlook downstream (OLK.DWS), Fred heal (FRDH), Beaver creek (BVCK), Clarkboro (CLRB), St.Louis (ST.LO), Evergreen (EVGR), Aspen ridge (ASPR), and Northeast swale (NE.SW). Sample sites are ordered from upstream to downstream.

Samples collected at Clarkboro and St. Louis, which are downstream of Saskatoon's WWTP, did not show elevated microplastic levels compared to other sampling locations, either within or upstream of Saskatoon. This suggests that the WWTP in Saskatoon are likely not acting as significant point sources of microplastic pollution to the river, but that the wastewater Lagoon in Outlook is during discharge and maintenance. The importance of WWTPs as point sources depends on factors including population density, different treatment processes employed at various WWTPs, water flow rates, and the recovery efficiencies of these WWTPs.¹³⁹⁻¹⁴² For example, WWTPs in Edmonton have been reported to not have a direct influence on the microplastic concentrations on the North Saskatchewan River,¹³⁹ while WWTPs have been reported to be direct point sources of microplastics to Lake Winnipeg and the Ottawa River.^{139,142-144}

The mean microplastic concentrations in Saskatoon's storm ponds were 6.44 ± 3.6 microplastics m^{-3} . Concentrations in Evergreen and Aspen Ridge were similar to those in the river. However, concentrations in the Northeast Swale, a conservation site within Saskatoon, were much higher, with a mean of $12 \pm 7.7 m^{-3}$, similar to the concentration in Miry Creek. The composition of the microplastics in the Northeast Swale was also distinct from that of other locations (both river and storm ponds), with less than 30% of microplastics consisting of synthetic fibers. For comparison, synthetic fibers accounted for 53% of microplastics from river samples, and 88% in the Evergreen and Aspen Ridge storm ponds. Polymer fragments accounted for 50% of particles in the Northeast Swale, with spheres and films each accounting for 11% of particles. Spheres were not detected at any other sampling site, and only one other sampling site (Outlook upstream, during the August/September sampling period) contained films. The reason for the anomalous microplastic concentration and type is not known.

There are few reports of microplastics concentrations in storm ponds. A mean microplastics concentration of 15,400 particles m^{-3} was reported in stormwater runoff released into Lake Ontario, suggesting that urban stormwaters contribute significantly to the microplastics pollution of Lake Ontario.^{85,145} It is likely that microplastics concentrations in storm ponds depend on numerous factors, likely including local population density and land use.

3.2. Chemical Characterization

Raman spectra were acquired for each particle, and composition was determined by comparison with polymer spectra from the in-house spectral library or open-source spectral libraries. **Figure 3.4** shows the fractional composition of all samples excluding natural fibers. Polyethylene terephthalate (PET) was the dominant polymer, accounting for nearly half of all polymers. Polypropylene (PP) accounted for 36%, and polystyrene (PS) accounted for 3%. We were unable to definitively characterize the remaining 12% of particles due to Raman signals too low to be differentiated from the background, or to scattering or fluorescence from chemical additives overshadowing the Raman signal. Likely sources of PET and PP are textiles, packaging, and various consumer products.¹⁴⁶ Polystyrene (often referred to as Styrofoam) is commonly used for manufacturing numerous consumer products ranging from disposable dishes to medical appliances.

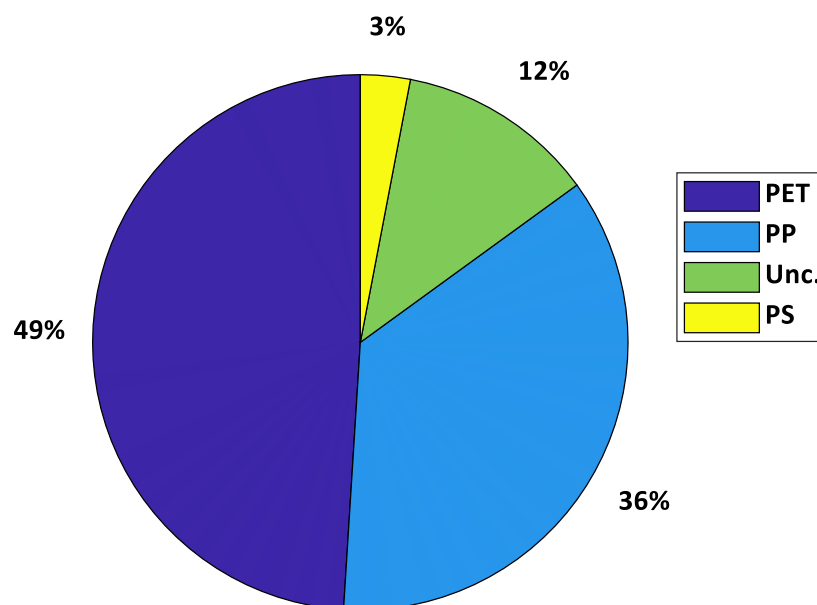


Figure 3.4: Fractional composition of the major polymer types identified in the microplastics. PET = polyethylene terephthalate, PP = polypropylene, PS = polystyrene, and Unc. = uncharacterized.

We note that the fractional composition shown in **Fig. 3.4** is not necessarily representative of microparticles within the South Saskatchewan River as a whole. For example, PET is denser than water (1.38 g cm^{-3}) and is expected to reside primarily near or within the sediment layer.¹⁴⁷ Since sampling in this campaign was performed near the surface, we do not expect to collect it, even though it is a significant component of microplastics usually recovered in freshwater samples since it is applicable in manufacturing of most synthetic textile fibers, fishing nets, and lines.¹⁴⁸ However, high flow velocity and strong hydrodynamics of the river especially due to rainfall may cause resuspension of dense microplastics at the subsurface.¹⁴⁹ Similarly, while polystyrene particles were present in our samples, they accounted for only 3% of all the polymers found in the

samples. Polystyrene is very buoyant, and partitions readily to the air-water interface. Sampling this interface (e.g., via skimming techniques) might yield a far greater contribution from polystyrene. Natural textile fibers accounted for ~77% of all particles analyzed. Most (77%) of fibers were dyed; signal from the dyes dwarfed the Raman spectra of the underlying fibers.

Figure 3.5 shows the distribution of dyed and undyed natural fibers. Undyed brown cotton and polycotton—a blend of cotton and polyethylene terephthalate materials—accounted for 3 and 17% of natural fibers respectively. The majority of fibers (51%) were dyed with Reactive Black 5 dye (RB5), and an additional 26% were dyed with Vat Indigo Dye (VIG). Diarylide Yellow (PY 83) and Copper phthalocyanine (Pigment Blue 15:0) contributed about 1% each to the total natural textile fibers. An additional 1% of natural fibers were uncharacterized. The Raman spectra of these microplastics and natural fibers, including their band assignments are summarized in fig. A.3.1 – A.4.5 and table A.3.1 – A.3.3 in the appendix.

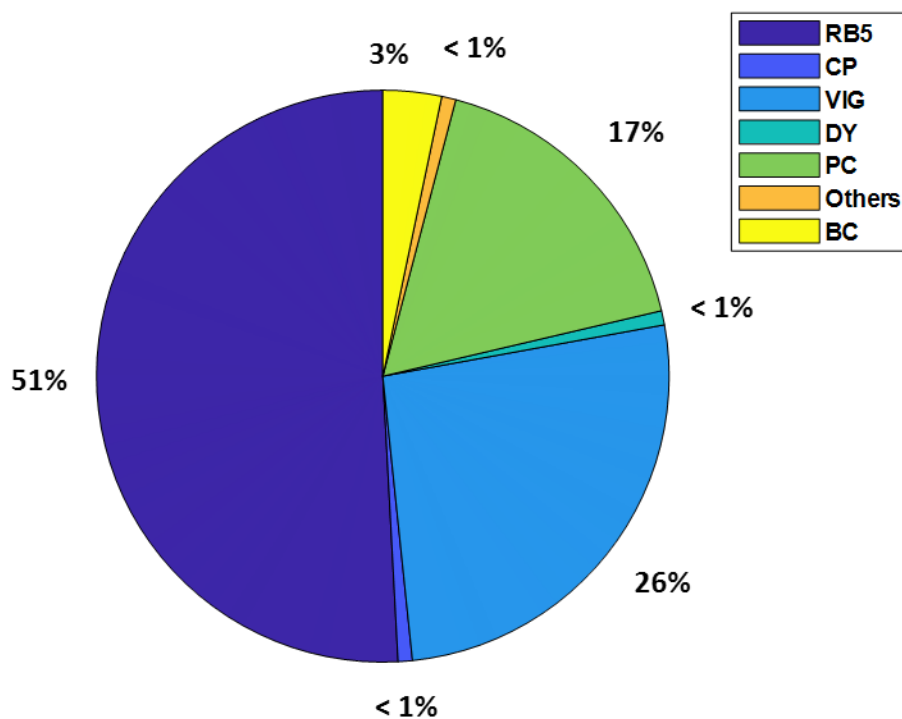


Figure 3.5: Fractional composition of natural textile fiber types, with some identified by the specific standard dyes. RB5 = Reactive Black 5 dye, VIG = vat indigo dye, PC = polycotton (PC), and BC = brown cotton fibers (BC). Others includes diarylide yellow dye (DY), copper phthalocyanine (CP) and other dyes.

Figure 3.6, which summarizes microplastic composition and concentration at each sampling site, highlights the variability in composition across sites. While natural textile fibers accounted for the majority of particles at most locations, they accounted for only 63% and 40% for Miry Creek and Northeast Swale, the two locations with the highest synthetic particle loadings. The relative concentrations of individual polymers were also different at these two sites. At most sites, PET was the dominant polymer, whereas it accounted for less than 11% and 18% of polymers in Miry Creek and Northeast Swale. Beaver Creek was also an outlier in this regard. Although this site had low polymer loadings and microplastics were only detected in the August/September sampling season, all microplastics detected at this location consisted of polypropylene polymer fragments.

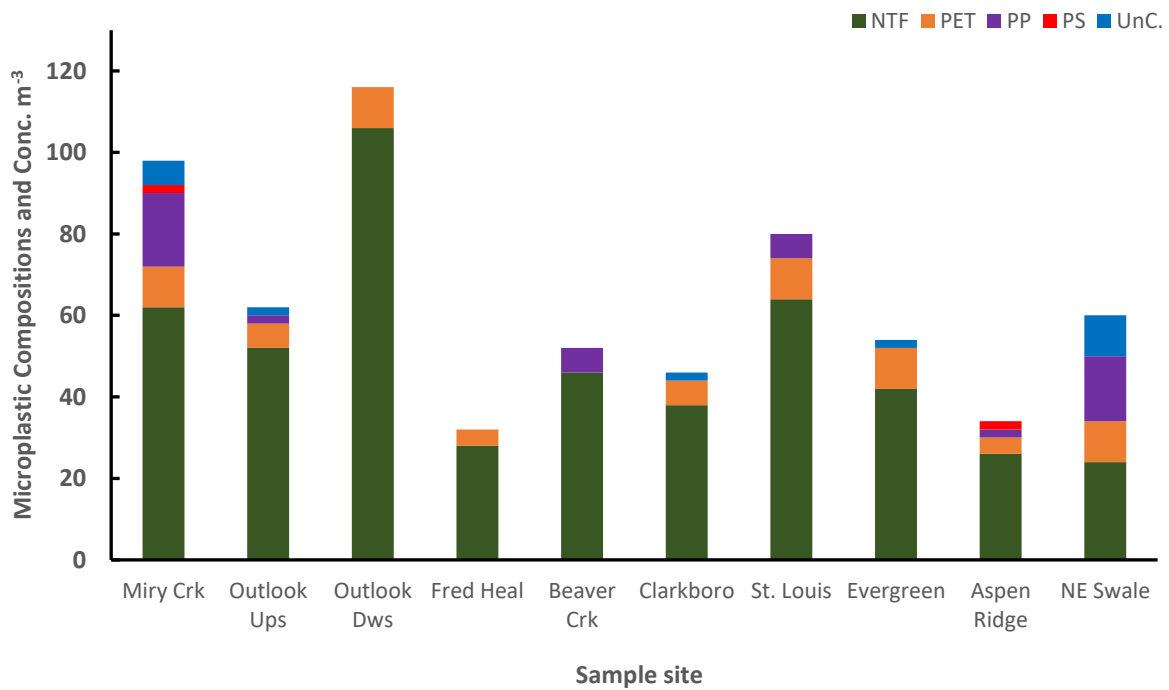


Figure 3.6: Distribution of microplastics polymer types (PET = polyethylene terephthalate, PP = polypropylene, and PS = polystyrene) identified in each sample site, including uncharacterized microplastics (Unc.), and natural textile fibers (NTF).

CHAPTER FOUR: CONCLUSION

While microplastic concentrations and composition have been studied in numerous Canadian waterways, this is, to our knowledge, the first study focused on the South Saskatchewan River. Our results suggest that microparticle concentrations in this river are very low, especially downstream of the Diefenbaker dam. Purging of the Outlook wastewater lagoon during the spring increased downstream particle loadings, resulting in concentrations five times greater than the mean of all samples. Conversely, the WWTP in Saskatoon did not noticeably affect downstream particle levels.

The majority of particles in the river are natural textiles, likely from weathering of fibers and microfibers detached from the textiles during the laundry processes. Although it may be difficult to eliminate these textile fiber pollutants from the waterways, the use of washing machines with attached in-line filters could help capture most of these fibers at the source, thereby reducing their concentrations in the wastewater. Most of the microplastics identified are suggested to be from degraded plastics commonly applicable to the packaging and manufacturing of consumer products. Discharges of surface runoff water into the waterways and land use may have contributed to the varying microplastic concentrations recorded at different sampling sites.

This study also adds to the sparse literature describing microplastic concentrations in storm ponds. Our results suggest that microplastic concentrations and compositions in Saskatoon storm ponds are generally similar to those in the river, although the relatively high levels of polymers in the Northeast Swale – a conservation area – suggests a local, currently unknown source.

Overall, both total particle levels and microplastic levels were low in the South Saskatchewan River and in Saskatoon storm ponds. However, consistent release and accumulation of these

microplastics and natural textile fibers in our fresh waterways could negatively impact the socio-economic values of the waterway and the aquatic species in these waterways if the necessary mitigation measures are not taken.

4.1. Limitations of the Study

The results of this research work have provided detailed information about microplastic contamination levels in the South Saskatchewan River and storm ponds. However, the result of this research is subject to some constraints that might have impacted on the results reported by the researcher. One among these constraints is the low number of replicate samples analyzed for each site causing high uncertainties in the measurements and difficult statistical comparison.

Another limitation of the study is the scope of the research which did not cover the estimation of the particle size of the microplastics recovered due to the size of the filters employed during sampling. Determination of the microplastics' particle size would have helped to further understand the distribution of the particle size of the particles analyzed. In addition to this, although we identified tire wear from vehicles in almost all the samples analyzed, especially at sample sites within urban areas and storm ponds, the scope of this study did not involve quantification of these tire wear in the samples. Quantification of these aggregates of tire wear would require the application of special techniques, which was not available to the researcher at the time of research. Tire wear is a major source of microplastic pollution in freshwater, hence, its quantification could have affected the microplastic loads of each sample reported.

4.2. Future work

This study has provided information about the microplastic loads and their sources in the South Saskatchewan River and storm ponds, however, further work is still needed to understand the microplastic contributions from tire wear particles that are important pollutants in the freshwater ways. Consequently, the level of microplastic accumulation in the aquatic species (especially fish) in Saskatchewan water is not yet known. Microplastic accumulation in fish and other aquatic species could severely impact their physiological and metabolic processes resulting in oxidative stress, clogging of digestive tracts, reduced food intake, reduced energy available for growth, and reduced reproductive successes.^{150,151} Further work on this would not only bring to our knowledge the measures to be taken for sustainable use of the waterways for its socio-economic benefits, but also for the sustainability of its aquatic species.

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APPENDIX

A.1: Total Particles distribution with seasonal changes.

Table A. 1.1: Total particles (both microplastics and natural textile fibers) identified and analyzed in all samples *N/A means sample not available for analysis.

S/N	Sample	May	June/July	Aug./Sept.	Total
1.	Miry Creek	13	32	4	49
2.	Outlook upstream	17	6	8	31
3.	Outlook downstream	6	46	6	58
4.	Fred Heal	5	5	6	16
5.	Beaver Creek	15	N/A	11	26
6.	Clarkboro	10	7	6	23
7.	St. Louis	9	13	18	40
8.	Evergreen	7	12	7	26
9.	Aspen ridge	8	9	N/A	17
10.	NE Swale	5	13	12	30
	Total	95	143	78	316

A.2.1 Morphology of microplastics identified

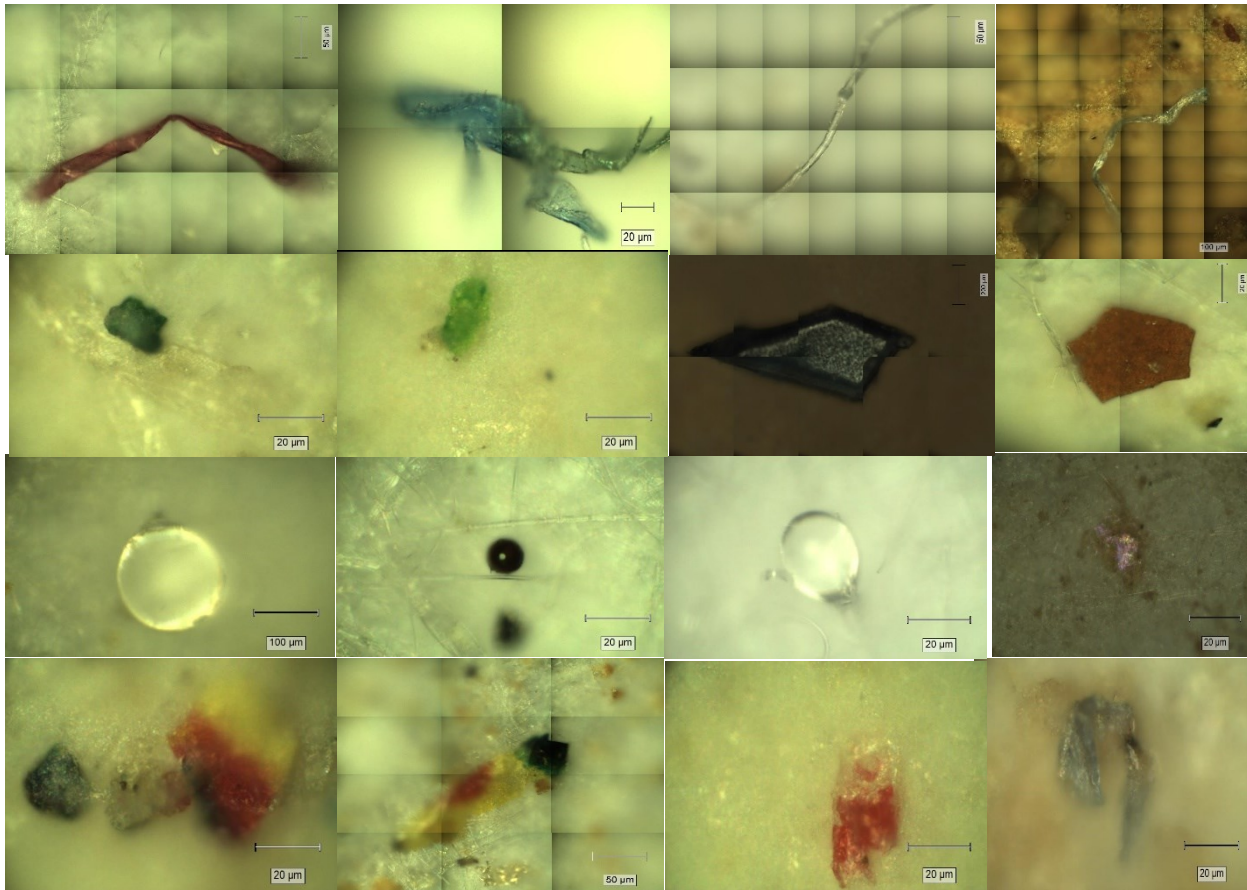


Figure A.2.1: showing some selected microplastics and natural textile fibers identified in the river and storm pond samples.

A.3.1. Representative spectra of microplastics samples acquired with their Raman band assignments.

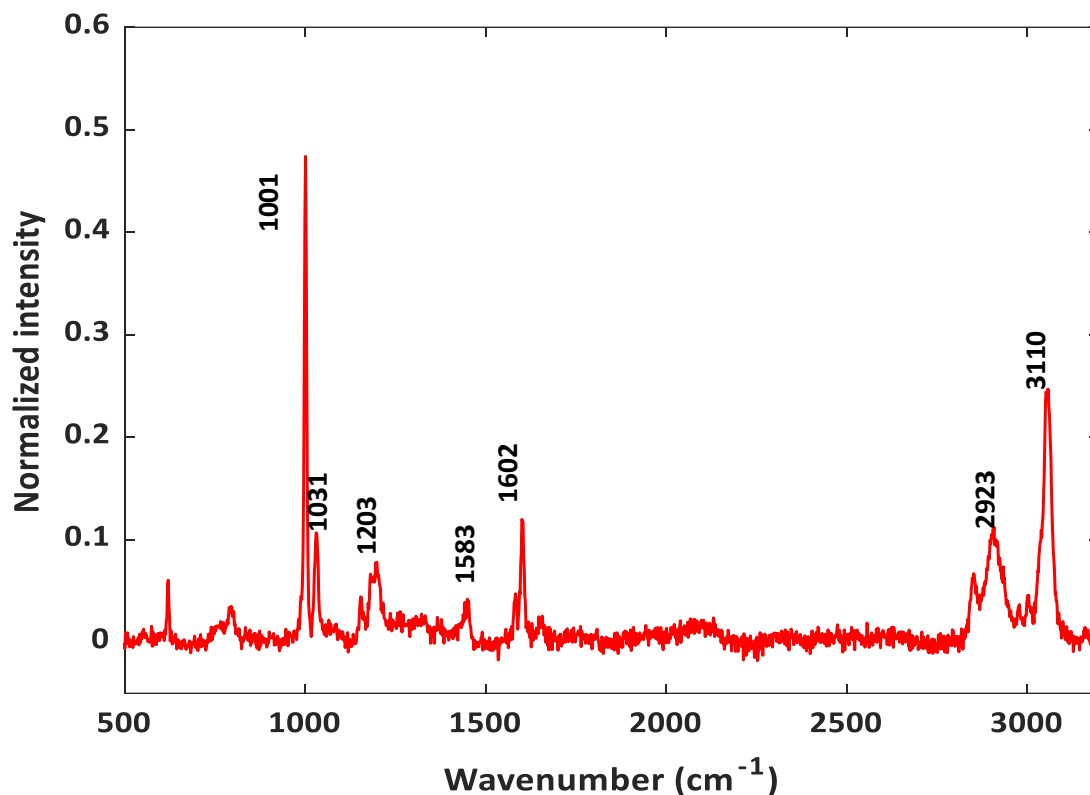


Fig. A.3.1: Raman spectra of polystyrene particles identified

Table A.3.1: showing the Raman band assignments for polystyrene

	Identified peaks (cm⁻¹)	Literature value (cm⁻¹)	Band Assignment
1.	975	975	CH out-of-plane deformation
2.	1001	1001	Ring breathing mode
3.	1031	1031	C-H in-plane-deformation
3.	1156	1155	C-C stretch
4.	1452	1450	CH ₂ scissoring
5.	1583	1583	C=C stretch
6.	1602	1603	Ring-skeletal stretch
7.	2923	2923	Methylene C-H backbone
8.	3110	3110	Aromatic C-H vibration.

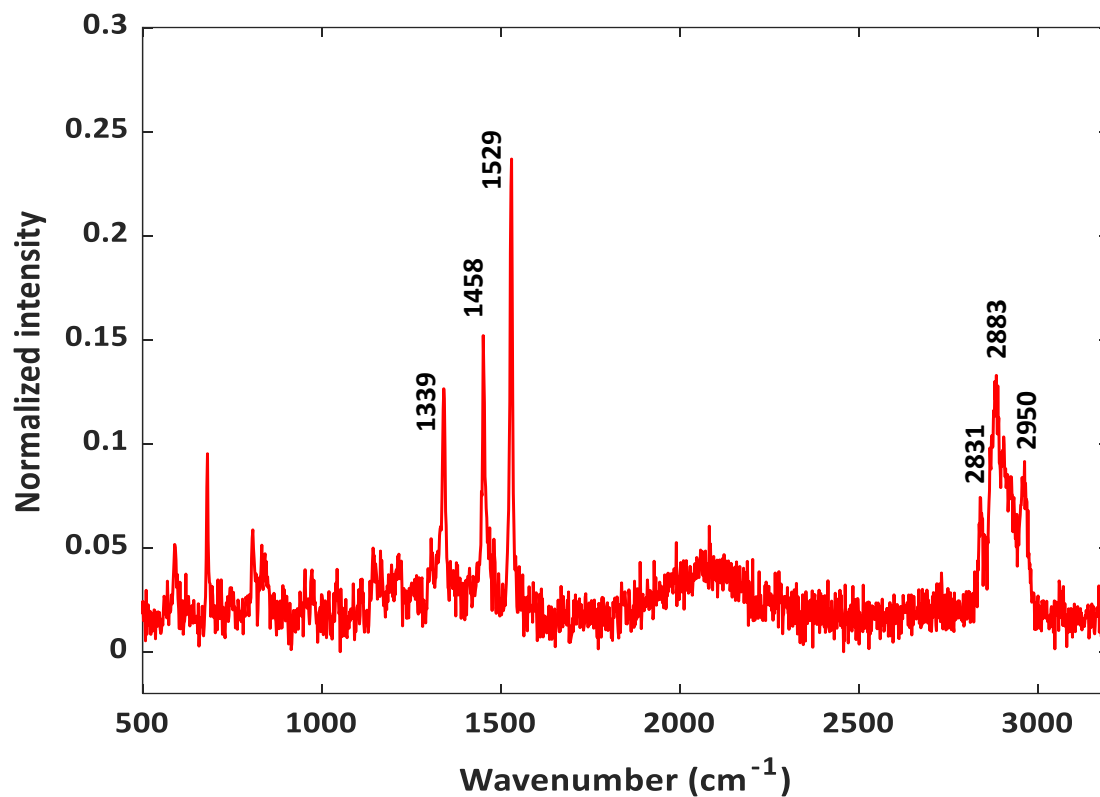


Fig. A.3.2: Raman spectra of polypropylene particles identified

Table A.3.2: showing the Raman band assignments for polypropylene

S/N	Identified Peaks (cm ⁻¹)	Literature value (cm ⁻¹)	Band Assignment
1.	808	808	CH ₂ rocking, C-CH ₃ and C-C stretching
2.	841	840	CH ₃ and CH ₂ rocking
3.	974	976	CH ₃ rocking and C-C stretching
4.	1152	1152	C-C and C-CH ₃ stretching, CH bending, and CH ₃ rocking
5.	1167	1167	C-C stretching
6.	1339	1338	CH ₂ twisting
7.	1458	1459	CH ₂ bending
8.	2832	2831	CH ₂ sym. Stretching
9.	2883	2444	CH ₃ sym. Stretching
10.	2921	2920	CH ₂ asym. Stretching
11.	2950	2952	CH ₃ asym. Stretching

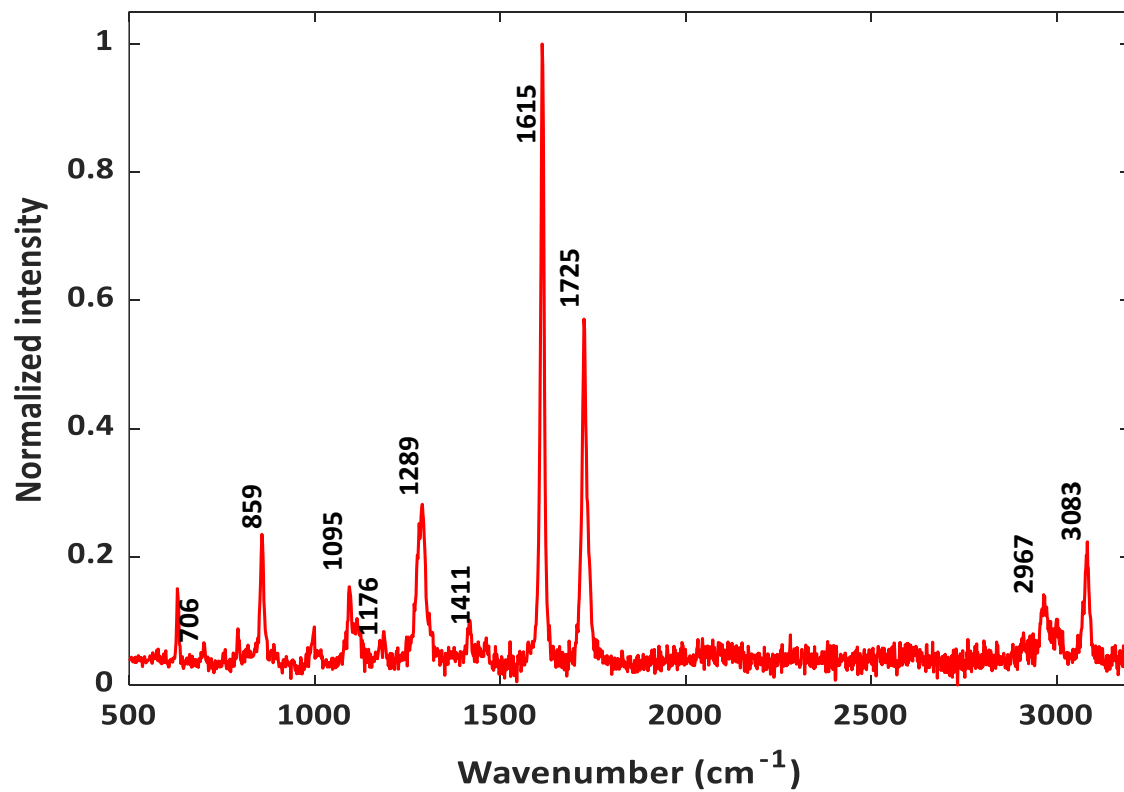


Fig. A.3.3: Raman spectra of polyethylene terephthalate (PET) particles identified

Table A.3.3. showing the Raman band assignments for polyethylene terephthalate

S/N	Identified peaks (cm ⁻¹)	Literature Values (cm ⁻¹)	Band Assignment
1.	706	706	Ring -C-C- stretching
2.	796	796	Ring torsion and C=O stretching
3.	859	857	Ring mode of C-C and C(O)-O stretching
4.	1095	1096	Ethylene glycol C-O, C-C stretching, and C-O-C bending
5.	1125	1126	Ester C(O)-O and ethylene glycol C-C stretching
6.	1176	1178	Ring in plane C-H bond and C-C stretching
7.	12 89	1290	C(O)-C stretching
8.	1308	1308	Ring CH in plane bending
9.	1411	1414	C-CH bending and OCH bending
10.	1452	1452	CH ₂ bending and OCH bending
11.	1615	1615	Ring mode 8a (in Wilson's notation)
12.	1725	1726	C=O stretching
13.	2895	2895	C-H bond of methylene sequences
14.	2963	2960	Methylene groups adjacent to oxygen atoms
15.	2967	2967	C-H stretching
16.	3080	3080	C-H stretching of ring alkene

A.4.1: Raman spectra of some selected dyed and undyed natural fibers identified

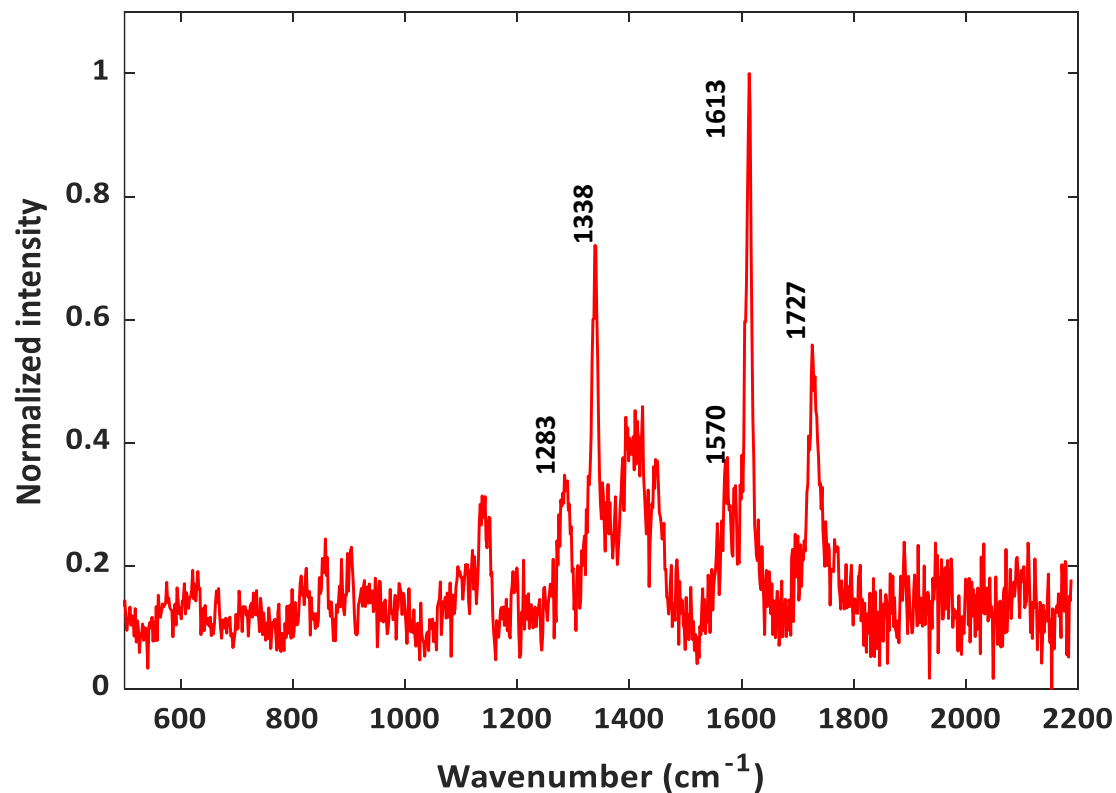


Fig. A.4.1: Raman spectra of polycotton (blended cotton) fibers identified. Peak at 1338 cm⁻¹ is typical of cotton material while peaks at 1727, 1613, and at 1283 cm⁻¹ are typical of PET material respectively.

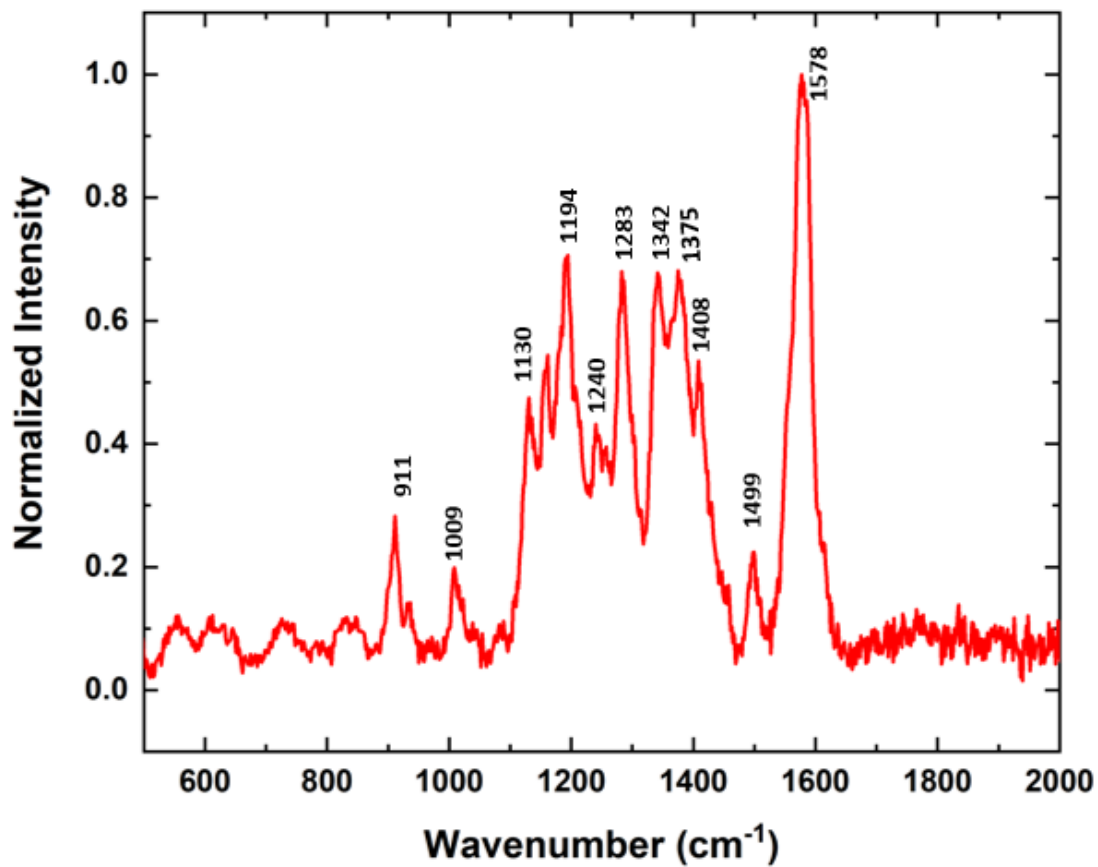


Fig. A.4.2: Raman spectra of reactive black 5 (RB 5) dye observed in some textile fiber samples. RB5 is applied in the textile industry for dyeing cellulosic fibers such as cotton, flax, rayon, and other materials such as polyamide, wool, silk, and acetate.

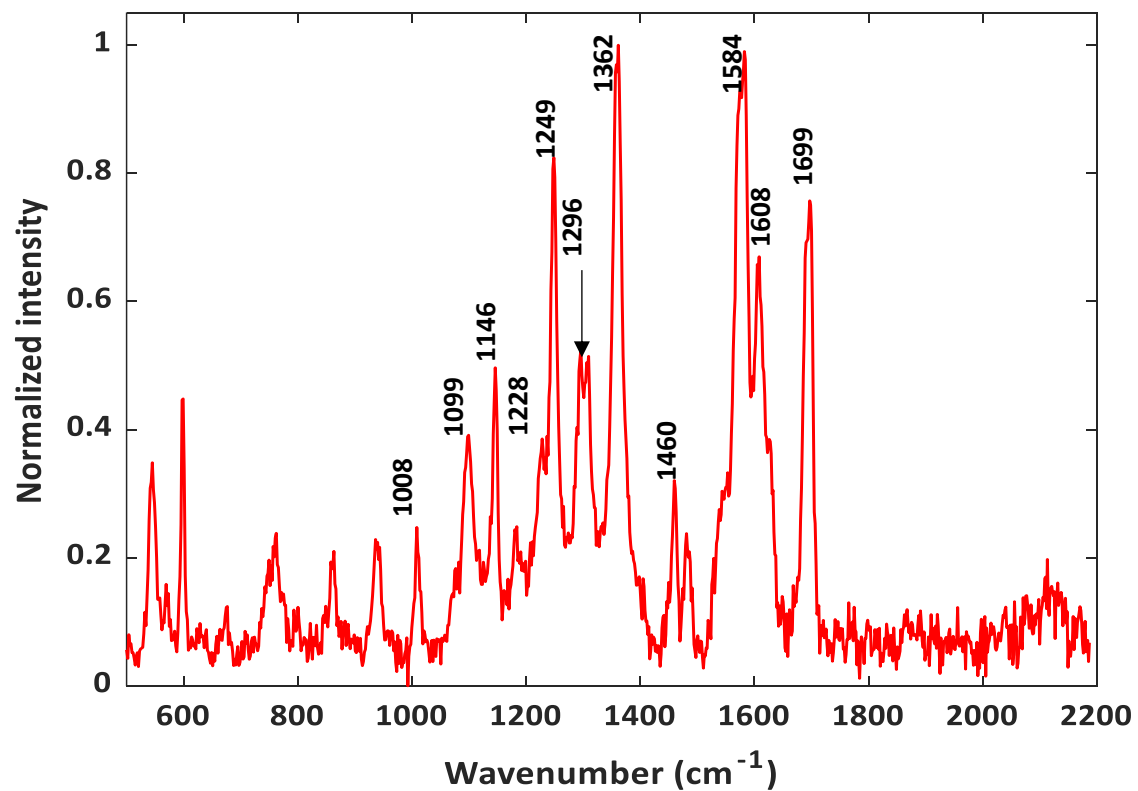


Fig. A.4.3: Raman spectra of vat indigo dye (Natural Blue 1) dye observed in some textile fiber samples. This dye is specifically used for dyeing denim (Jeans materials) with its typical peaks at 1608, 1584, 1575, 1460, 1481, 1362, 1249, 1146, 937, 755, and at 599 cm^{-1} .

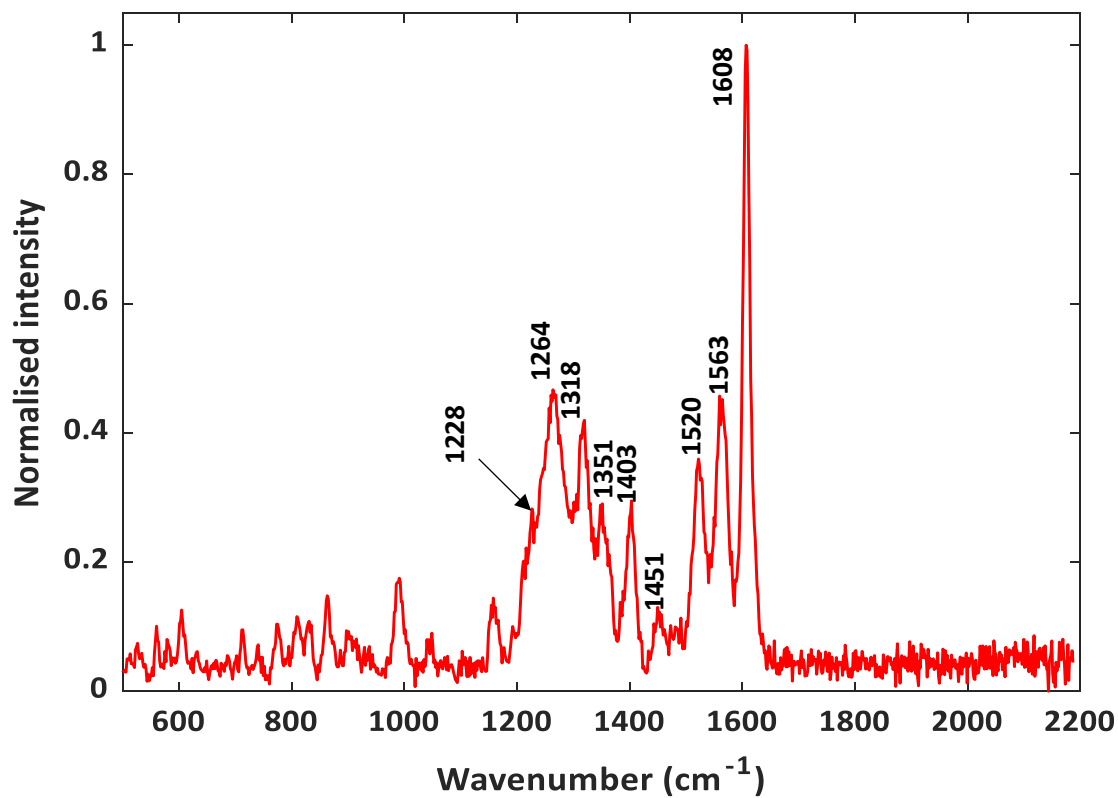


Fig. A. 4.4: Raman spectra of diarylide yellow (Pigment Yellow 83) showing its typical peaks at 1608, 1563, 1403, 1351, and at 1318 cm⁻¹ respectively

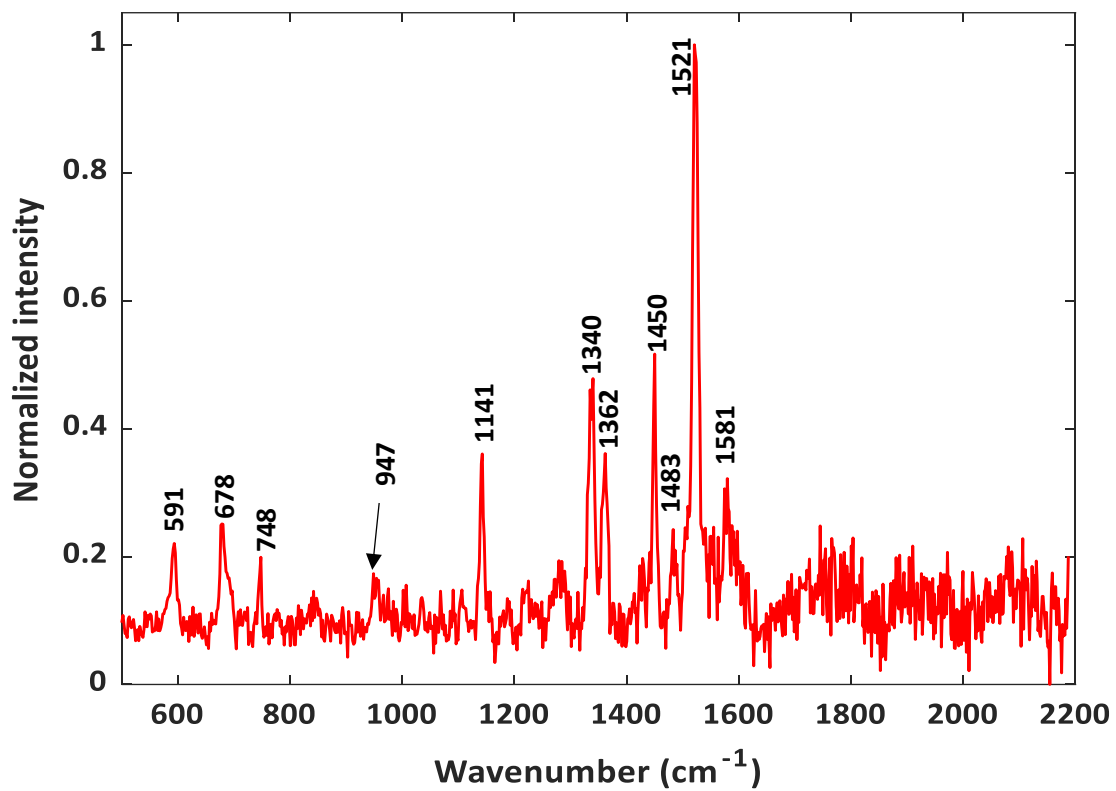


Fig. A. 4.5: Raman spectra of copper phthalocyanine (Pigment Blue 15:0) dyes majorly used for dyeing cellulose fibers, with its typical peaks at 678, 748, 947, 1141, 1446, and at 1521 cm⁻¹ respectively