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An investigation on the presence and characteristics of microplastics in freshwater sediment in the Vaal River



UNIVERSITY OF THE
WITWATERSRAND,
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by

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A dissertation submitted to the Faculty of Science, University of the Witwatersrand, in fulfilment of the requirements for the degree of Master of Science

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Co-supervisor: Prof H Tutu

Date: September 2022

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I would also like to thank my family and friends for their prayers, love, and support.

I would like to dedicate this dissertation to my mother who has been my biggest cheerleader, pillar of strength, and greatest support.

DECLARATION

I declare that this dissertation is my own work, unaided work. It is being submitted for the Degree of Master of Science at the University of the Witwatersrand, Johannesburg, South Africa. It has not been submitted before for any degree or examination at any other university.



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Ms Michelle Ndlovu

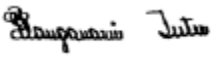
School of Chemistry, University of the Witwatersrand, Johannesburg 2022

This dissertation is submitted after examination and approval by the following supervisors



.....

Dr Dalia Saad



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Prof Hlanganani Tutu

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ABSTRACT

Microplastics (MPs) have become a bane on the environment for decades, and their impact on freshwater systems is still understudied. With the advancement in research techniques, MPs have been detected in the air, tap water, underground water, food, soil, and human stool. Their potential harmful impacts have drawn significant attention in recent years in the context of environmental protection. In comparison to marine waters, studies of MPs in freshwater sediment are limited. A thorough review of the literature on MPs in freshwater sediment also revealed a lack of standardisation in MP studies, ranging from the true definition of MPs to sampling and analytical methods.

In addition to the unavoidable and potentially irreversible ecosystem imbalances caused by MP pollution, the establishment of environmental standard benchmarks and coordinated responses is also hampered by a lack of knowledge on their abundance, distribution, and fate. As such, this study aimed at generating scientific evidence to provide evidence-based recommendations and risk-informed standards to influence and guide policymaking.

This project was designed to generate new data on the presence and characteristics of MPs pollution in South African freshwaters, as well as assessing the contribution of land-based activities to MPs pollution in freshwater bodies using the Vaal River as a study case. The main objectives were to determine the presence, abundance, and physical and chemical characteristics (size, shape, colour, and polymer composition) of MPs in sediment samples from the Vaal River.

Twenty-five sediment samples were collected from the Vaal River over 3 days using a 500 mL Van Veen grab sampler. Prior to analysis, samples were pretreated for effective MPs extraction and identification. Sample preparation and extraction were performed using modified National Oceanic and Atmospheric Administration (NOAA) laboratory methods for the analysis of the MPs. Samples were first oven-dried to remove moisture, digested using 10% potassium hydroxide (KOH) to remove organic and inorganic matters which may hamper MPs identification, after which, MP particles were separated based on their density. Density separation was conducted using saturated sodium iodide solution (NaI). For MPs analysis, optical microscopy (stereomicroscope) was used to detect and identify MPs in terms of size, shape, and colour. Scanning electron

microscopy (SEM) was used to study the surface morphology of the MP particles. The polymer composition was determined by Raman Spectroscopy to identify polymer type.

MPs were detected in all samples with varying abundances from 30 to 1096 particles/kg_dry weight (dw) and a mean abundance of 463 ± 284 particles/kg_dw. The examination of the physical properties of MPs revealed a predominance on fragments (63%) and fibers (35%), small-sized particles of less than 0.5 mm (32%), as well as the prevalence of coloured MPs (60%), mostly blue, white, and green. Detected MPs were identified as Polyethylene (PE) "both high and low density", polypropylene (PP), and polyethylene co-vinyl acetate (PEVA), polyester (PES), polyurethane foam (PU), and polyethylene/hexene-1-copolymer (PEH), according to Raman Spectroscopy analysis.

These findings reveal elevated levels of MP contamination within the Vaal, with the prevalence of fragments and fibers (98%) over pellets (2%) indicating that MPs pollution is from secondary sources. Fragments are formed by the breakdown of larger plastic pieces; fibers, on the other hand, are mostly attributed to domestic sewage, and, in this case, it is likely the protracted sewage input around the Vaal triangle. The prevalence of PE, PP, and PEVA is consistent with MPs from secondary sources as they are commonly used in single-use plastic, packing bags, textiles, and containers. These findings provide a benchmark for guiding future monitoring studies and identifying research gaps.

In general, anthropogenic activities, including heavy industrial and tourism activities in the area, agriculture, fishing, and wastewater discharge, were identified as potential sources of MPs in this study. The pollution profile, in terms of the physical and chemical properties of the detected MPs, indicates serious threats and health risks. For instance, small-sized MPs that were found to be predominantly abundant in the sediment samples, are considered to be more harmful to aquatic organisms due to their bioavailability (size similarity to natural preys). The large surface area of small MPs also increases the possibility of adsorbing and desorbing other pollutants from the surrounding environment. Coloured MPs may pose additional harm due to the toxicity of most colorant agents. Thus, the high prevalence of small-sized and coloured MPs within the Vaal River is therefore of a particular concern.

TABLE OF CONTENTS

ACKNOWLEDGEMENTS ii
DECLARATION ii
ABSTRACT iii
LIST OF FIGURES vii
LIST OF TABLES viii
LIST OF ABBREVIATIONS ix
Chapter 1 1
Introduction 1
1.1 Background 2
1.2 Problem Statement 3
1.3 Research Aims and Objectives 4
1.3.1 Aim 4
1.3.2 Objectives 4
1.3.3 Research Questions 4
Chapter 2 5
Literature Review 5
2.1 Plastic pollution 6
2.1.1 Plastic Types 6
2.2 MP Pollution 9
2.3 MP Sources 10
2.4 Pathways of MPs 11
2.5 Characteristics of MPs 12
2.5.1 Shape 12
2.5.2 Size 12
2.5.3 Colour 13
2.6 Environmental Impacts of MPs 13
2.7 Effects and Potential risks of MPs in Freshwater 13
2.8 Current direction in remedying impacts of MPs 14
2.9 Technical Approaches in MPs research 18
2.9.1 Sediment Sampling 18
2.9.2 Sample Pre-treatment and Analysis 18

2.10 MP studies in freshwater sediments "global, regional, and local review" 19
Chapter 3 22
Methodology 22
3. Methods 23
3.1 Study Site 23
3.2 Equipment Used 24
3.3 Sampling 24
3.3.1 Sample Acceptance Criteria 25
3.4 Sample Pretreatment 25
3.4.1 Drying 25
3.4.2 Digestion 26
3.4.3 Density Separation and Sieving 27
3.4.4 Filtration 28
3.5 MP Characterization 29
3.5.1 Visual Analysis 29
3.5.2 Polymeric identification 30
3.6 Quality Assurance and Quality Control 31
Chapter 4 32
Results and Discussion 32
4.1 MP Levels of Pollution in the Vaal River 33
4.2 Physical Characteristics of MPs 36
4.2.1 Shape 36
4.2.2 Surface Texture 37
4.2.3 Colour 38
4.2.4 Size 39
4.3 Potential Sources of MPs in the Vaal River 41
4.4 Effects of *in situ* parameters 43
4.5 Polymeric confirmation 44
4.6 Other Compounds Detected 48
4.7 Impact of MPs on Benthic Organisms and Deposit Feeders 51
Chapter 5 54
Conclusion 54

Chapter 6 57
References 57

LIST OF FIGURES

Figure 2.1 Ways in which MPs are transported into aquatic environments 11
Figure 3.1 Sampling area (Google Earth, 2021) 23
Figure 3.2 0.5 L Van Veen as used during sampling 25
Figure 3.3 Dry sediment sample after oven drying 26
Figure 3.4 Sample digestion 27
Figure 3.5 Air-drying of filter papers in the laminar flow cabinet 29
Figure 3.6 Nikon stereomicroscope for visual analysis 30
Figure 4.1 Abundance from sampling sites 35
Figure 4.2 MP shapes where a) is a pellet, b) is a fiber, and c) is a fragment 37
Figure 4.3 SEM images of a) a fragment, b) a fiber, and c) a pellet 38
Figure 4.4 Colours observed and their respective percentages 39
Figure 4.5 Size distribution in the class ranges 40
Figure 4.6 Spearman correlation plot of size and abundance 40
Figure 4.7 Shape distribution 43
Figure 4.8 HDPE Raman spectrum 44
Figure 4.9 LDPE Raman spectrum 44
Figure 4.10 Polyethylene co-vinyl acetate Raman spectrum 45
Figure 4.11 Polypropylene Raman spectrum 45
Figure 4.12 Polyester Raman spectrum 46
Figure 4.13 Polyurethane Raman spectrum 47
Figure 4.14 Polyethylene/Hexene-1 copolymer Raman spectrum 47
Figure 4.15 Carbon Raman spectrum 49
Figure 4.16 Vine black Raman spectrum 49
Figure 4.17 Orthoclase Raman spectrum 49
Figure 4.18 Microcline Raman spectrum 50
Figure 4.19 Cis-13-Docosanol Raman spectrum 50

Figure 4.20 Saffron Raman spectrum 51
Figure 4.21 Smalt Raman spectrum 51

LIST OF TABLES

Table 2.1 Frequently used types of plastic and their densities 8
Table 2.2 Effects of additives 14
Table 2.3 Sources and potential mitigation 15
Table 4.1 Sample dry mass, number of particles per sample and MP abundance 33

LIST OF ABBREVIATIONS

µm	micrometer
$3Na_2WO_4 \cdot 9H_2O$	sodium polytungstate
CCD detector	charge-coupled device detectors
CECs	contaminants of emerging concern
cm	centimeter
d	days
DDT	dichlorodiphenyltrichloroethane
ECHA	European Chemicals Agency
EPR	extended producer responsibility
FTIR	Fourier Transform Infrared spectroscopy
g/cm^3	grams per cubic centimeter
GESAMP	Group of Experts on the Scientific Aspects of Marine Environmental Protection
h	hours
HPLC	High Performance Liquid Chromatography
HQI	threshold hit quality index
IUCN	International Union for Conservation of Nature
KOH	potassium hydroxide
L	litre
LDIR	Laser Directed Infrared
m	meter

MERI	Marine and Environment Research Institute
min	minutes
mm	millimeter
MPs	microplastics
NaI	sodium iodide
NaOH	sodium hydroxide
nm	nanometer
NOAA	National Oceanic and Atmospheric Administration
^{o}C	degrees Celsius
PAHs	polycyclic aromatic hydrocarbons
Particles/kg_dw	particles per kilogram of dry weight
PBDE	polybrominated diphenyl ethers
PBTs	persistent bio-accumulative and toxic compounds
PCBs	polychlorinated biphenyls
PE	polyethylene
PET	polyethylene terephthalate
PP	polypropylene
PS	polystyrene
PU	polyurethane
PVC	polyvinylchloride
Pyr-GC-MS	Pyrolysis-Gas Chromatography-mass spectrometry

SEM	Scanning electron microscope
std dev	standard deviation
TED-GC-MS	Thermal extraction-desorption Gas Chromatography mass spectrometry
UNEP	United Nations Environment Programme
uPVC	unplasticised polyvinyl chloride
UV	ultraviolet
WWTPs	wastewater treatment plants
$ZnCl_2$	zinc chloride

Chapter 1

Introduction

This chapter contains a background of the study, defining microplastics and highlighting the general threats they are posing worldwide. It ends with a problem statement in which focus is paid to the problem of microplastics locally, and especially in freshwater systems where it has received less attention compared to marine environments.

1.1 Background

Over the last century, the use of plastics has grown extensively. Plastics have many outstanding features such as durability, lightweight, versatility, and low production cost (Ivleva et al., 2017; Pizarro-Ortega et al., 2022). Plastics are classified according to their size from: mega-plastics (larger than 1 m), macro-plastics (1 m – 2.5 cm), meso-plastics (2.5 cm – 1 mm), micro-plastics (1 µm – 5 mm), to nano-plastics (below 1 µm) (GESAMP, 2015). The focus of this project was on micro-plastics (MPs), and the study aimed at investigating MPs' presence in freshwater sediment taking the Vaal River as a study case.

MPs are defined as polymers with an upper size limit of 5 mm and without a specified lower limit (Yang et al., 2022). The lower size limit of MPs remains a contentious topic, scholars have failed to draw a consensus and this, consequently contributed to the lack of a universal definition of MPs as well as standardization of sampling, sample purification, and quantification methods (Arthur et al., 2009; Gambino et al., 2022; Hernandez et al., 2017; Thompson et al., 2009; Van Cauwenberghe et al., 2015).

MPs are divided into two groups namely, primary MPs and secondary MPs. Primary MPs are those which are manufactured to be < 5 mm and are found predominantly in medicine, personal care products, and textile products. They can be discharged from water treatment plants and transported by rivers; wind and surface run-off can also transport them into either freshwater and/or seawater environments. Secondary MPs on the other hand, are derived from the breakdown of large plastic particles due to degradation processes such as photo-degradation, physical, chemical, and biological interactions (Bertoli et al., 2022; Browne, 2015; Gall and Thompson, 2015; Nanthini devi et al., 2022; Thompson et al., 2009; Wang et al., 2021). With the high consumption of plastic materials, the accumulation of their debris in freshwaters is one of the most obvious yet least studied as compared to marine ecosystems (Wagner et al., 2014).

MPs have been identified as emerging pollutants of significant environmental and health impacts. However, there are no regulations or mitigation measures to reduce and control MP pollution. In some countries, they have in place regulatory and policy instruments that are associated with MPs in freshwaters. These include littering acts, carrier bag charge, deposit and return systems, waste management plans, and packaging regulation. In South Africa, the littering act implemented is the

White Paper on Integrated Pollution and Waste Management for South Africa 2000 (Department of Environmental Affairs, 2000).

1.2 Problem Statement

MPs are a growing global concern affecting both planetary and human health. In today's world, plastics can be found virtually everywhere in one form or the other where they continue to cause detrimental harm. MPs have been found to be in higher concentrations in main rivers, especially those close to residential and industrial areas than in tributary rivers and isolated freshwaters (Yang et al., 2021; Yonkos et al., 2014).

Wagner and Lambert (2018) found that less than 4% of MP-related studies were on freshwater systems. Despite the limited information, these studies have raised a concern, considering the possibility of bioaccumulation, which increases with time as their size decreases (Kuehr et al., 2022; Onoja et al., 2022; Wagner et al., 2014). Owing to their large surface-to-volume ratio and chemical composition, MPs cumulate waterborne contaminants including metals, organic contaminants, and persistent bioaccumulative and toxic compounds (PBTs) (Ashton et al., 2010; Bakir et al., 2012; Costigan et al., 2022; Koelmans et al., 2013; Liu et al., 2022; Mittal et al., 2022). There are also evidence of microorganisms developing biofilms on MPs, e.g. genus *Vibrio*, thus, acting as vectors for waterborne human pathogens influencing the hygienic water quality (Cholewińska et al., 2022; Lai et al., 2022). MPs have reported to reduce the lifespan of biota, affect reproduction, decrease biodiversity and pose threats to public health (Elert et al., 2017).

Research on the extent of MP distribution in freshwater is still in its infancy, and therefore the environmental impacts have not been thoroughly evaluated. MPs incorporate a broad range of polymers, with a range of sizes, shapes, and chemical compositions, which makes evaluating their impacts very complex (Scherer et al., 2018). Additionally, the methodologies on sample collection, sample pre-treatment, quantification, and identification are not standardized, presenting a challenge when comparing results between different studies (Li et al., 2017).

Studies on MP in freshwater sediment in South Africa are very few. Bouwman et al. (2018) and Weideman et al. (2019) reported MP pollution in the Vaal River, however, their studies were limited to surface water. Studying MPs in freshwater sediment is essential for understanding their

transport, distribution, fate, as well as their bioavailability to biota. The focus of this project was to investigate MPs in sediment samples from the Vaal River in Johannesburg.

1.3 Research Aims and Objectives

1.3.1 Aim

This project aimed at bridging the knowledge gap on MP pollution in South African freshwater systems. Taking the Vaal River in Gauteng "as a study case", the project was geared at generating new data on the presence, characteristics, and the potential sources of MPs pollution in freshwaters. This was achieved by addressing the following specific objectives and research questions.

1.3.2 Objectives

- To screen the presence of MPs in sediment samples from the Vaal River.
- To quantify the MPs present in the samples.
- To characterize the MPs detected in the samples, in terms of shape, size, and color.
- To identify polymer types/composition.
- To predict sources, pathways, and potential anthropogenic inputs.

1.3.3 Research Questions

- What is the abundance of MPs in the sediment samples?
- What types of MPs are present in terms of chemical composition and morphology?
- What are the potential sources of MPs around the Vaal River?

Chapter 2

Literature Review

This chapter presents a literature overview pertaining to MPs, including the general pollution situation and risk that they pose to water resources, human and aquatic life worldwide; their common sources; their physical and chemical characteristics; as well as analytical techniques commonly used for their characterization.

2.1 Plastic pollution

The United Nations Environment Programme (UNEP) predicted that plastic production will continue to rise exponentially (Fabres et al., 2016). Due to the desirable qualities of plastic materials such as durability and low production costs, the amount of plastics produced is growing each year, for example, plastic production has risen from 359 million tonnes in 2018 to 367 million tonnes in 2020 (PlasticsEurope, 2021). Plastics are nonbiodegradable and have long residence time in the environment, with limited recycling and poor waste management in most of the African countries, the plastic pollution may present insurmountable challenges.

Plastic waste from anthropogenic activities ranges from 60 – 80% of the produced quantity, with the continuous growth in plastic production this will lead to amass of plastic waste (Miloloža et al., 2021). Plastic pollution has detrimental effects on human health and the environment. Plastics have been reported to block sewers, and canals; form breeding grounds for mosquitoes; damage respiratory and digestive tracts in animals; affect the aesthetic quality of landscapes and touristic value (Nikiema et al., 2020b).

2.1.1 Plastic Types

Plastics are classified as thermosets and thermoplastics. Thermosets are chemically changed when heated, creating a three-dimensional network. They cannot be melted and reshaped repeatedly. Examples include polyurethane, silicone, acrylic resins, epoxy resins, and vinyl esters. Polyethylene, polystyrene, polypropylene, polyvinyl chloride, polyethylene terephthalate fall in the category of thermoplastics. These polymers melt when heated and harden when cooled, allowing them to be remoulded (PlasticsEurope, 2019).

Polyethylene is made of ethylene monomers and is used in packaging bottles for liquids and oils, cereal box liners, machine parts, irrigation and drain pipes, and cosmetic and medical equipment (Bond et al., 2018; Gidigbi et al., 2020; Rajendran et al., 2015). It is suitable for these uses due to its high ductility, tensile strength, low hardness, and is a good electrical insulator. Polyethylene is commonly reported in aquatic environments due to the unreactive -C-C- and -C-H- bonds. Its large molecular weight and hydrophobicity also play a great role in this regard (Bond et al., 2018).

Polystyrene is made of phenyl rings attached to every other carbon atom on the polymer chain. It is widely used for food containers, cups, trays, and packaging (Ho et al., 2018; Rajendran et al.,

2015). Polystyrene is lightweight and recyclable, although it is flammable, brittle, with a low melting range of 210 – 249°C, and glass transition temperature of more than 100°C, hence it softens when in boiling water (Bond et al., 2018).

Polypropylene consists of methyl groups on each monomer on the carbon chain. It has a high thermal resistance and mechanical properties. It is a good electrical insulator making it suitable for use in medical equipment, electronic parts, packaging, furniture, and textile industries (Arutchelvi et al., 2008; Auta et al., 2017; Bond et al., 2018). The high molecular weight and hydrophobic nature of polypropylene reduce its biodegradability but tends to be degraded by strong oxidants (Glaser, 2019; McLain, 2007; Rajendran et al., 2015).

Polyvinyl chloride contains a chlorine atom on every other carbon atom on the chain. It is used in manufacturing medical equipment and construction (Arutchelvi et al., 2008; Lieberzeit et al., 2022; Rajendran et al., 2015). It is known for acting as a barrier against oxygen and water making it excellent on packaged food as it lasts longer. However, it is prone to photodegradation (Miloložа et al., 2021).

Ethylene terephthalate ($C_{10}H_8O_4$) makes up polyethylene terephthalate, resulting in a semi-crystalline structure (Sharifian and Asasian-Kolur, 2022; Webb et al., 2012). It is used for packaging, in the textile industry, for tires, insulators, disposable medical clothing, and as a substitute to glass (Gong et al., 2018; Rajendran et al., 2015).

Semi-crystalline polymers exhibit high strength and stress while amorphous polymers have less strength and poor stress (Guo and Wang, 2019; Sysel, 2016). Examples include polymers are polyethylene, polyethylene terephthalate, and polypropylene. Their high degree of crystallinity results in them being easy to break during weathering and affects their ability to float, so they sink to the bottom in aquatic systems (Andrady, 2011). Table 2.1 below shows frequent types of plastics and their densities (Bouwman et al., 2018).

Plastics are manufactured to meet different consumer needs as exemplified by the polymers mentioned above. Commonly used thermosets and thermoplastics degrade to secondary MPs but are conjointly used in the production of primary MPs. This depends on the nature of the plastics such as tensile strength and degree of crystallinity. Plastics of high tensile strength and crystallinity such as PVC and PET may take longer to degrade resulting in high residence time in aquatic

environments. Semi-crystalline polymers such as PP and PE tend to degrade easily (Kim et al., 2014; Miloloža et al., 2021). Thermosets such as poly(methyl methacrylate) and polytetrafluoroethylene are used to manufacture microbeads used in personal care products that are part of primary MPs (Bråte et al., 2014).

Table 2.1 Frequently used types of plastic and their densities

Polymer type	Uses	Density (g/cm^3)
Natural rubber	Vehicle tires	0.29
Polyethylene* - low density	Plastic bags, outdoor furniture	0.91 - 0.93
Polyethylene* - high density	Bottles, pipes	0.94 - 0.97
Polypropylene	Rope, bottle caps, gear, strapping	0.85 - 0.94
Polystyrene (expanded)	Cool boxes, floats, cups	0.016 - 0.36
Polystyrene	Utensils, containers, microbeads	0.96 - 1.05
Polystyrene (high impact)	Shelves, printed graphics	1.04
Polyamide (Nylon)	Fishing nets, rope	1.12 - 1.14
Polycarbonate (bisphenol A)	CDs, glass alternative, lenses	1.2
Polyurethane	Foams	1.2
Methacrylate (acrylic)	Alternative for plate glass	1.19
Cellulose acetate	Cigarette filters, fabric fiber	1.28
Cellulose nitrate	printing inks, nail polish, foil	1.35
Polyvinyl chloride	Film, pipe, containers	1.38
Polylactic acid (biodegradable)	Packaging, cups	1.21 - 1.43
Polyethylene terephthalate	Bottles, strapping	1.34 - 1.39
Melamine	Flooring, dinnerware, dry boards	1.57

*Can be manufactured to meet required densities.

Sources: http://scientificpolymer.com/density-of-polymers-by-density/, (GESAMP, 2015) and https://www.engineeringtoolbox.com/polymer-properties-d_1222.html

2.2 MP Pollution

The International Union for Conservation of Nature (IUCN) attributes MPs to 7 main sources, namely, synthetic textiles (35%), tires (28%), domestic activities (24%), road making (7%), marine coatings (4%), personal care products (2%), and pellets (0.3%) (Boucher and Friot, 2017).

MPs are categorized depending on location, source, release patterns, and use, as well as shape, size, and polymer composition (Bouwman et al., 2018). They are defined as polymers with a maximum size of 5 mm with no prescribed lower limit (Frias and Nash, 2019; Hartmann et al., 2019; Thompson et al., 2009). The lower limit is not specified because MPs eventually become nano plastics (Bouwman et al., 2018). Some scholars used the term 'MPs' referring to particles above 20 µm, while others, expanded the scope to incorporate particles < 5 mm. Nevertheless, there is a concept in some studies to confine the upper limit of 'MPs' to 1 mm (1000 µm) (Arthur et al., 2009; Hernandez et al., 2017; Thompson et al., 2004; Van Cauwenberghe et al., 2015).

Properties of MPs such as size, shape, and density can affect their distribution patterns in aquatic media (Eerkes-Medrano et al., 2015). However, environmental conditions such as wind, geographical position, and currents may also influence their abundance, transport, and distribution in different environmental spheres (water column, sediment, and biota) (Bellasi et al., 2020). Environmental factors are likely to play a major role in large freshwater bodies such as riverine systems, but they are limited in smaller, isolated freshwater systems (Free et al., 2014).

The abundance of MPs in freshwater bodies depends on their residence time in the environment, the size of the water body, type of waste management, and the amount of sewage overflow (Eerkes-Medrano et al., 2015). There are waste management programs in place in South Africa, such as sorting waste for recycling, regular refuse collections, landfills, authorized dumping sites, etc. However, these programs do not cater to MPs. Due to their small sizes, they seep into streams and drainage pipes and make their way to freshwater bodies.

The residence time of plastic debris when released into the environment has been approximated to be in the tens to hundreds of years (Takahashi et al., 2022; Zbyszewski and Corcoran, 2011). High residence time results in plastics having exceptionally low degradation rates and a lengthy half-life under ambient circumstances (Eubeler et al., 2009). As MPs are insoluble in water, it means that they linger for a very long time in the environment which is partly why they are considered as contaminants of emerging concern (CECs) with severe hazard potential (Milološa et al., 2021).

2.3 MP Sources

Aquatic sediments are considered as a final sink for MPs, especially those with high density, as they would be more abundant in sediment than the less dense MPs. Whereas less dense MPs are normally found floating on the surface or in the water column (Yang et al., 2021).

MPs come from the land and ocean-based sources, where oceanic sources contribute 20% and terrestrial sources contribute the remaining 80% (Andrady, 2011; Cole et al., 2011; Hammer et al., 2012). When terrestrial MPs are released into natural waters, most of them would be transported to oceans by rivers while the remaining would stay in freshwater systems (Browne et al., 2010; Cook et al., 2020; Free et al., 2014).

Sewage sludge, fertilizers, compost, soil conditioners such as low-density polyethylene film, and polystyrene foam which are used in horticulture and composting additives, respectively, are the main sources of MPs found in soil. When irrigated, the degraded MPs then make their way to water systems (Do and Scherer, 2012; Duis and Coors, 2016; Lambert et al., 2014). Roughly 4 – 5 million tons of sludge is applied to agricultural lands each year (Horton et al., 2017).

Landfilling is a method of waste disposal that results in MPs leaching into the aquatic environment (Horton et al., 2017). South Africa produces 108 million tons of waste every year where 90% is disposed of in landfills. Reports show that the country's landfill sites are almost full. Gauteng province accounts for about 45% of these landfills (Alive2green, 2019; ResearchAndMarkets, 2021). The plastic particles in landfills are exposed to temperature changes, oxidation, acidic or alkaline conditions that change their chemical compositions and their additives. This may cause a detrimental effect on aquatic ecosystems (Xu et al., 2011).

Another source of MPs is car tires. A significant percentage of tires consist of synthetic rubber which is a plastic polymer, added to the natural rubber to provide rigidity and traction. Heat and friction with the road generate MPs as they wear down, this gives rise to minute particles that are usually nanosized (Kole et al., 2017; Wagner et al., 2018).

MPs in rivers and lakes come from different sources including on-water activities, tourism, and improper disposal of plastic waste on land. Notably, stormwater, rainwater drainage, flooding, and wind can collect and transport MPs from land to freshwater systems (Bellasi et al., 2020).

2.4 Pathways of MPs

As mentioned above, there are several ways in which MPs can be transported. One common route/ pathway is through wastewater treatment plants (WWTPs). The plants receive waste from landfills, domestic and industrial waste, and rainwater. From industry, MPs are released as wastewater or residues from plastic disposal. In domestic use, they are released as clothing fibers or personal care waste (Mateo-Sagasta et al., 2015).

WWTPs are currently not designed to remove MPs (Raju et al., 2018). About 95% of the removed MPs concentrate in sludge because MPs, as the name suggests, are very small (Mahon et al., 2017). Since WWTPs are generally not equipped to remove MPs, particles that are smaller than 10 µm remain and are discharged in effluent which ends up in aquatic environments. Figure 2.1 shows some pathways in which MPs travel from the sources to aquatic environments (Miloloža et al., 2021).

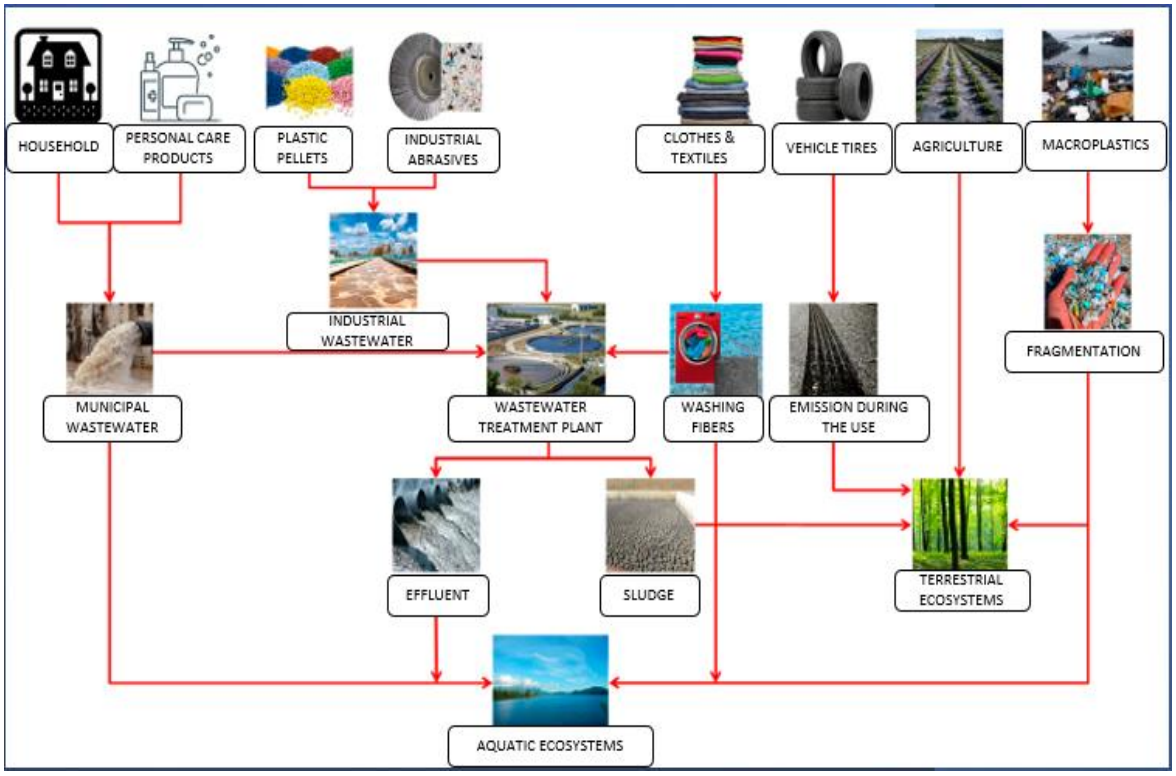

Figure 2.1 Ways in which MPs are transported into aquatic environments
https://www.mdpi.com/water/water-13-00056/article_deploy/html/images/water-13-00056-g002.png

2.5 Characteristics of MPs

2.5.1 Shape

MPs are found in different shapes including pellet, fragment, film, fiber, and foam (Hidalgo-Ruz et al., 2012; Su et al., 2016). They can be irregular, spherical, and fibrous. Sharp edges on the MP particles may indicate recent entry into the water body and/or could be because of a newly fragmented from a larger piece of plastic. Whereas, smooth and rounded edges may indicate repeatedly eroded by other particles or sediment (Doyle et al., 2011). The elongated shaped MPs are usually larger in size compared to circular ones. Factors such as erosion, degradation of the surface of the plastic, and residence time in the environment also affect the shape of the MP. For instance, the physical appearance of fragments and pellets such as grooves and cracks show that chemical weathering and mechanical wear have occurred to make that MP (Zhang et al., 2020). The rate of sorption of hydrophobic particles may be affected by the surface texture of MPs. This rate rises with the increase in surface area which is due to weathering enhancing the effective diffusivity of the sorbate in question (Mato et al., 2001).

Shape can deduce the original source of the MP. Fibers detected from the Changjiang estuary sediment, for instance, suggest that they were likely from textiles. Washing is a major route of MPs being released into freshwaters (Peng et al., 2017). Fragments could be from photodegradation or physical wear from macro-plastics (Wen et al., 2018; Xiong et al., 2018). Film comes from packaging and plastic bags whereas foam-shaped MPs are likely from Styrofoam (Xu et al., 2020; Zhang et al., 2020). Pellets are probably from spillages during manufacturing and transport (Corcoran et al., 2015). Beads are mostly from personal care products (Fahrenfeld et al., 2019; Hartmann et al., 2019).

2.5.2 Size

Size determines the transportation of MPs in the aqueous media, their distribution, as well as bio-availability to aquatic organisms (Li et al., 2020; Zhang et al., 2018). MPs that sink to sediment are more likely ingested by deposit feeders and benthic organisms (Yang et al., 2021). Studies show a general trend that MPs of 1 mm or less are more abundant in freshwater sediment. Eo et al. (2019) observed a similar trend in their study in the Nakdong River, South Korea, where 81% of the MPs were < 300 μm. In the Ciwalengke River, Indonesia, Alam et al. (2019) reported that

70% of the MPs were < 1000 µm (Alam et al., 2019). Abundance of MPs in sediment tends to decrease as the sizes increase (Corcoran et al., 2015).

2.5.3 Colour

Coloured MPs are commonly mistaken for food by aquatic biota compared to transparent MPs (He et al., 2020; Rodrigues et al., 2018). Frequently observed colours are black, blue, and green (Cole et al., 2014). Colour aids in visual identification where the analyte is in a sample matrix that has other particles. This however results in brightly coloured particles having a higher chance of being examined and the dull coloured ones overlooked hence introducing bias (Hidalgo-Ruz et al., 2012).

Colour may be used to predict possible sources of the MPs (Zhang et al., 2020). For instance, transparent is ascribed to single use plastics (Li et al., 2020; Prata et al., 2018). Coloured MPs are probably from plastics of long use (Li et al., 2020). Identifying MPs based on colour must be done cautiously and preferably followed by a qualitative method of analysis for polymer confirmation.

2.6 Environmental Impacts of MPs

MPs have been found to function as transmitters for hazardous materials such as toxic chemicals, trace metals, and organic pollutants. Owing to their high hydrophobicity and their small size, MPs interact with these co-occurring pollutants through sorption and desorption processes. Such interaction may alter the environmental behavior of the pollutants, for instance, their transport, degradation, and bio-accumulation (Fang et al., 2019; Prata et al., 2018).

Studies show that polyethylene, polypropylene, polystyrene, and polyvinylchloride adsorb hexachlorocyclohexane, chlorinated benzenes, polychlorinated biphenyls (PCBs), and polycyclic aromatic hydrocarbons (PAHs). This ability is influenced by physiochemical properties, size, and shape (Prokić et al., 2019).

MPs can also adsorb organic contaminants such as organochlorine pesticides, Polybrominated diphenyl ethers (PBDE), and dioxins. In freshwaters, it is assumed that their effects will be more as these chemicals are expected to be in greater quantities than in marine due to the closeness to their release sources (Dris et al., 2015).

2.7 Effects and Potential risks of MPs in Freshwater

MPs ingestion by various organisms is reported to cause pathological stress, false satiety, reproductive issues, and reduce growth rate (Batel et al., 2016). They can also affect the growth of

aquatic plants (Guo and Wang, 2019). This, in addition to their role as vectors for pathogens and pollutants and their adverse effects to humans and the environment. For instance, phthalates, the additives that make polyvinylchloride into pliable vinyl have been noted to be endocrine disruptors. MPs comprise of various plasticizers, additives, resins, stabilizers, lubricants, and colourants, which means that they have a wide range of reactivities, physical and chemical properties emanating from both the monomers that make up the polymer and the additives (Bonefeld-Jørgensen et al., 2007; Ivar do Sul, 2021). A brief description of the effects of some additives is given in Table 2.2, below (Issac and Kandasubramanian, 2021).

Table 2.2 Effects of additives

Additive	Properties	Effects	Reference
UV Stabilisers	Stops photolysis	Mutagenic, toxic, bioaccumulated, and show estrogenic activity	(Hammer et al., 2012)
Antioxidants	Slows oxidation, prevents fading	Estrogenic effects	(Hermabessiere et al., 2017)
Plasticisers	Makes the product flexible	Kidney, reproductive, cardiac system, and neurotoxicity	(Rowdhwal and Chen, 2018)
Flame retardants	Reduce flammability	Endocrine disruptors	(Fred-Ahmadu et al., 2020)
Pigments	Colour	Food copying resulting in intestinal blockage	(Hammer et al., 2012)
Surfactants	Modification of surface properties	Destroy mucus layer, damage gills	(Rani et al., 2015)

2.8 Current direction in remedying impacts of MPs

MP pollution is a growing concern and many studies have been conducted to explore effective measures to curb it. Once they enter natural water bodies i.e., lakes, rivers, oceans, MPs are very

difficult to remove and require an upstream intervention (Eriksen et al., 2018). Upstream intervention requires identifying and quantifying terrestrial MP sources; scale zero waste strategies; pursuing policy-driven extended producer responsibility (EPR) and developing novel business solutions. EPR is a form of "product stewardship" where the manufacturer and/or producer is responsible for lowering the risk to the health, safety, environmental and social impact of a product through its lifecycle (Lifset et al., 2013). Preventing the manufacture of new plastics is another way of ensuring that MPs do not find their way to freshwater systems. This is achieved by recycling and reusing plastics, some of which have been incorporated in clothes, shoes, sunglasses, skateboards, and so on (Bureo, 2016; Vincent, 2016). On the technical side, some upstream methods for MP treatment include improving the design of quality textiles, household or laundromat treatment by using better machines with better filters, stormwater retention ponds, stormwater gully pot, and stormwater infiltration basins (Nikiema et al., 2020a).

Shifting from single use plastics to other environmentally friendly materials, for example, fabric shopping bags can significantly reduce plastic pollution. Of the 368 million tonnes of plastic produced annually, approximately 50% is from single use plastics (Condor Ferries, 2022; Plastic Oceans, 2021; PlasticsEurope, 2020). Reusable fabric bags are offered globally in many shops as an alternative for plastic bags (Bouwman et al., 2018). Table 2.3 outlines some sources and potential mitigation measures for MPs (Eriksen et al., 2018).

Table 2.3 Sources and potential mitigation

Category	Source	Potential Mitigation
Production	MPs in cosmetics	Removing them from products and replacing them with benign alternatives
	Mismanaged preproduction pellets	Regulate pellet handling. Operation clean sweep

Commerce	Industrial abrasives	Improve containment and recovery and require alternatives
	Laundromat exhaust	Improved filtration
	Agriculture-degraded film, pots, and pipes	Improve recovery, biodegradable plastics
Consumer	Tire dust	Technological advances, road surface
	Littering of small plastic items	Enforcement of fines for littering, consumer education, EPR on design
	Domestic laundry, wastewater effluent	Wash with top-load machines. Wastewater containment, single-fiber woven textiles. Textile coatings
Wastewater management	Fragmentation by vehicles driving over unrecovered waste	Improved waste management
	UV and chemically degraded terrestrial plastic waste	Improved waste management
	Sewage effluent (synthetic fibers)	Laundry filtration, textile industry innovation
	Sewage overflow	Infrastructure improvement
	Mechanical shredding of roadside waste during regular cutting of vegetation	Better legislation and law enforcement; valorization of waste products

In terms of downstream interventions, there are several studies that investigated the removal of MPs from the environment. Most of these studies focused on biological removal using different types of bacteria and fungi. Biological degradation and digestion of MPs by bacteria and fungi results in loss of weight of the MPs, and destruction of the surface leading to a different physical appearance. It is reported that a change in the chemical structures of some MPs due to the removal of some functional groups such as the carbonyl bond in polyethylene using *Bacillus cereus* (Yuan et al., 2020).

According to the European Chemical Agency (ECHA) and the Norwegian Environment Agency, the available data is insufficient for precise risk assessment. More knowledge on the environmental occurrence, fate, and impacts of MPs is required for comprehensive risk assessment (Lusher et al., 2021). Such data is also needed to develop measures for contaminant level guidelines and limits. However, the ECHA recommended restrictions on the use of MPs in consumer products, agriculture, and manufacturing industries (ECHA, 2020). The European Strategy for Plastics in a Circular Economy presented by the European Commission has been working to transform the way that plastic products are produced, used and recycled (European Commission, 2018).

The laws and regulations on the limit for single use plastics and MPs were reviewed in a UNEP report that was published in 2018; 127 countries out of 191 have plastic bags legislation. From the 127, 91 have bans in place or some form of restrictions on distribution, importing, and producing plastic bags. 27 out of the 191 countries have adopted bans or restrictions on single use plastics. 9 countries out of 191 have implemented legal practices on the production, import, and distribution of microbeads (Environment, 2018).

The South African National Environmental Management: Waste Act (Act No. 58, 2008) states the right to an environment that does not harm human health and the need to protect the environment. The scope of the Act is to promote environmental conservation; engage sustainable use of natural resources, and prevent pollution and environmental degradation (Bouwman et al., 2018). With this in mind, the Vaal River was selected as a case study so as to contribute meaningfully to environmental conservation and pollution prevention.

2.9 Technical Approaches in MPs research

2.9.1 Sediment Sampling

Corer and grab samplers are commonly used for sediment collection. What determines the choice of the equipment is the nature of the sampling site. Factors include type and depth of the waterbody (sea, deep lake, estuary), whether the bottom of the waterbody is hard or soft, and the volume of the required samples (Klemm et al., 1990).

Grabs have jaws that close once they hit the surface of the sediment. The depth of sample collection depends on the size and mass of the grab, they are usually used for collecting surface sediment. Examples of grabs frequently used are the Van Veen, Ponar, and Ekman. They can be used for sampling any type of sediment such as sand, gravel, and firm clay, meaning they can be applied in any aquatic environment that is marine, rivers, lakes, or estuaries. The disadvantage is that they cannot be effectively used in shallow water (Campanale et al., 2020; U.S.EPA, 2001).

Corers on the other hand, are for studies where it is vital that the integrity of the sediment profile is maintained. They are normally used for very thick sediment samples. They are likely to plug or rod due to friction caused by the sediment moving through them. There are different types of corers including hand-held, gravity, box, and vibracorers. Of these, the box corer is mostly reported in various studies. The boxcorer is used in studies where sediment and water are to be analysed, for large volumes of sample, *in-situ* studies with interstitial water characterisation. They also allow for subsampling by inserting a tube into the desired area of the sediment. However, they are quite heavy and difficult to operate (U.S.EPA, 2001).

2.9.2 Sample Pre-treatment and Analysis

The methods used in collecting samples, pre-treating, quantifying, and identifying are not yet been standardised (Almuhtaram and Andrews, 2022; Li et al., 2017; Prata et al., 2018). These variations result in making comparisons challenging (Van Cauwenberghe et al., 2013). Discrepancies could be due to the size and representativeness of the sample selection; the sensitivity of the extraction technology used and non-uniform reporting units because of the variations in sampling techniques (Ivleva et al., 2017). There are various methods of analysing and quantifying MPs that have been published, for instance, the National Oceanic and Atmospheric Administration (NOAA) standard MP protocol and Corcoran (Corcoran et al., 2015; Masura et al., 2015). Yet, these methods are not standardised and have varying procedures. Depending on the nature of sediment samples that is

clay or sandy, these methods include drying, sieving, digestion, density separation, and filtration for pretreatment (Horton et al., 2017; Yang et al., 2021). For quantification, light microscopy is commonly used. For identification of MPs, the methods employed usually fall under microscopy based, spectroscopy based, and chromatography based. Commonly used microscopy based method is SEM (Mehdinia et al., 2020). Laser Directed Infrared (LDIR), Raman, and FTIR are examples used in spectroscopy-based methods (Horton et al., 2017; Li et al., 2017; Rodrigues et al., 2018). For chromatography, HPLC, Pyrolysis-Gas Chromatography-mass spectrometry (Pyr-GC-MS), and Thermal extraction-desorption Gas Chromatography mass spectrometry (TED-GC-MS) are frequently used (Käppler et al., 2018; Li et al., 2017). Many studies show that these techniques are usually used in combination with each other (Miloloža et al., 2021).

2.10 MP studies in freshwater sediments "global, regional, and local review"

MPs research in freshwater bodies is limited, however, with more rivers, lakes, reservoirs, and estuaries being studied around the world, more data is expected to be available. On a global scale, Africa had 4 lakes and 10 rivers studied according to a review conducted in 2021 (Aragaw, 2021). A review by Bellasi et al. (2020) indicated that MPs in water are studied more extensively compared to MPs in sediment.

On a global scale, there have been many studies conducted particularly in Europe and Asia. For example, Klein et al. 2015 studied MPs presence and abundance in the Rhine River and Main River in Germany, reporting an abundance of 228 – 3763 particles kg_dw and 786 – 1368 particles/kg_dw for the two rivers, respectively. The authors concluded that inland pollution was the major factor to MPs in German rivers resulting in rivers being instrumental in transporting MPs to the ocean (Klein et al., 2015). In Spain, an abundance of 1 – 2630 particles/kg_dw was reported in the Mediterranean rivers. Their results revealed strong correlation between MPs abundance and proximity of the water body to urban and industrial areas, they estimated that 1 x 10^{10} MPs are discharged yearly into the river catchment through both treated and untreated wastewater (Schell et al., 2021). A total number of 4500 ± 702 particles/kg_dw was reported in sediment samples from the Atoyac River basin in Mexico; MP abundance was reported to be higher downstream as a result of dense population, industrial activities, and proximity to WWTPs (Shruti et al., 2019).

River Alaknanda, a major tributary to River Ganga in India was reported to have 389 particles/kg_dw. They noted that MP abundance was heavily influenced by improper disposal of domestic waste, washing clothes, untreated sewage, construction, and commercial waste. On examining the surface of the MPs they found that sodium, potassium, aluminum, calcium, titanium, magnesium were absorbed on the surface of MPs, which shows the toxicity potential to human and aquatic life (Chauhan et al., 2021). A study in Iran on the Hashilan wetlands showed similar results; lead, zinc, copper, and iron were detected on the surface of MP particles (Abbasi, 2021).

In China, several studies have been conducted in freshwater sediments. An abundance of 460 – 1380 particles/kg_dw was reported in Taihu Lake, with a dominance of fragments (Zhang et al., 2021). A study by Peng et al. (2018) reported a mean abundance of 802 particles/kg_dw in Shanghai urban districts. They confirmed the notion that abundance of MP is greater in densely populated areas. He et al, (2021) studied the dispersal patterns and transport of MPs in sediment. They found that polyethylene and polypropylene are likely to move for longer distances whereas polyethylene terephthalate and polyamide would accumulate close to source points. They also confirmed that sediments are a sink for MPs (He et al., 2021). In South Korea, Eo et al. (2019) studied the Nakdong River, the study revealed high concentration of MPs (1970 particles/kg_dw). The authors observed that more than 50% of the detected MPs were fragments, with 24.8% polypropylene and 24.5% polyethylene as the major polymers.

In Africa, few studies have been reported MP presence in Freshwater sediments. For examples, a study on Lake Ziway in Ethiopia reported 0.05 – 36 particles/kg_dw, with polyethylene, polypropylene, and alkyd varnish being the dominant polymers. Recreational activities such as boating, restaurants, resorts and fishing, and agricultural practices were considered as main contributors to the high abundance (Merga et al., 2020). In Tunisia, on the lagoon of Bizerte, the abundance reported was 2340 – 6920 particles/kg_dw, and the major shape observed was fibers. The high abundances of MPs in this study was attributed to effluent discharges from both residential and industrial areas (Toumi et al., 2019). Another study by Abidli et al. (2017) assessed MPs occurrence in a lagoon channel in Tunisia, an abundance of 704 – 1483 particles/kg_dw was reported. The dominant polymers were polyethylene and polypropylene, with fibers (91%), fragments (5%), films (3%) as the noted shapes (Abidli et al., 2017).

A study conducted in Oxbow Lake in Nigeria, revealed varied abundance of 347 to 4031 particles/kg_dw and 507 to 7593 particles/ kg_dw in the dry and rainy season, respectively (Oni et al., 2020). This variation was attributed to the different feed sources of the MPs to the lake in the two seasons.

A few studies have reported MPs in South African freshwaters. Dahms et al. (2020) reported a mean of 167 particles/kg_dw in sediment samples from Braamfontein Spruit, Johannesburg. According to their findings, MPs tend to sink into the sediment in areas of increased depth and decreased flow (Dahms et al., 2020). A mean abundance of 160.1 particles/kg_dw was reported in sediment samples from the Bloukrans River system in the Eastern Cape (Nel et al., 2018). Another study reported MPs in 5 estuaries in Durban. They reported a total of 13680 particles/kg_dw (Naidoo et al., 2015).

Chapter 3

Methodology

This chapter presents a detailed account of the methods followed and equipment used from site selection, sampling, sample pretreatment, analytical techniques used, and measures taken to prevent cross-contamination.

3. Methods

There is a vast range of protocols for sampling and quantifying MPs. With the growing research efforts on MP pollution, there has been modifications to analytical procedures in order to increase precision and accuracy in polymeric confirmation (Bouwman et al., 2018). In general, methods reported in literature follow a rough outline of bulk or volume reduced sampling, digestion and density separation, filtration or sieving, and lastly, identifying polymer type (Yang et al., 2021).

The protocols and procedures carried out in the study are detailed in this chapter. Methods for sampling and analysis were adapted from several studies (Hidalgo-Ruz et al., 2012; Hurley et al., 2018; Sedlak et al., 2017; U.S.EPA, 2001).

3.1 Study Site

Samples were collected from the Vaal River between the Lethabo power station and the Vaal barrage. Sampling was done on 26 April 2021, 29 – 30 June 2021. The Vaal River is fed by 9 tributaries with the major ones being Klip, Wilge, Vals, Vet, and Riet rivers, which come from various locations in Gauteng, Free State, North West, and Northern Cape provinces, respectively. The area of the Vaal River between Bloemhof Dam and the Vaal Dam receives polluted waters from southern Gauteng's streams (InfoSA, 2021). As such, the Vaal then becomes a source of pollution as it feeds into the Orange River which leads to the Atlantic Ocean (New World Encyclopedia contributors, 2015). Figure 3.1 shows the sampling site.



Figure 3.1 Sampling area (Google Earth, 2021)

The Vaal River is an essential part of South Africa's economy, it provides water for drinking, industrial use, and irrigation. The Vaal marks the boundary between Mpumalanga, Gauteng, Free State, and North West provinces. It runs for about 1300 km, from Breyten in Mpumalanga to Kimberley in the North Cape where it meets the Orange River. Hence, the Vaal is a tributary to the Orange River leading to the Atlantic Ocean (Infogalactic, 2015).

A section of the Vaal is owned by Rand Water which provides drinking water to Gauteng province. It is also a major source of water for irrigation under the Vaal-Hartz scheme. A region of the river called the Upper Vaal is popularly known for recreational activities such as fishing, boat cruising, and water skiing (InfoSA, 2021).

3.2 Equipment Used

The equipment used was chosen based on cost-effectiveness, local availability, and materials used (stainless steel and/glass) to minimize contamination of samples. For sampling, a 500 mL Van Veen grab was used. For analysis, stereomicroscope, scanning electron microscope and Raman spectrometer were used for physical and chemical characterization, respectively.

3.3 Sampling

A total of 25 samples were collected using a 500 mL Van Veen grab sampler (Eijkelkamp, Netherlands) in Figure 3.2. A rope was tied to the hanger of the Van Veen and slowly lowered into the river from the side of the boat. Once it reached the bottom, the Van Veen closed and was pulled up carrying inside the sediment sample. At each sampling site, 3 replicates were scooped and mixed in a 2 L glass beaker using a stainless-steel spoon. The replicates were taken to collect representative samples since the distribution of MPs is largely affected by environmental factors. A 325 mL composite sample was then placed in precleaned glass jars with lids lined with aluminum foil to prevent contamination. The jars were transferred to the laboratory in a cooler box and stored in the refrigerator at 4°C until analysis.



Figure 3.2 0.5 L Van Veen as used during sampling

3.3.1 Sample Acceptance Criteria

Not all grab samples were accepted, they were rejected if:

- There was a rock or matter wedged between the jaws of the Van Veen allowing the sample to wash out.
- The sample was mostly made of rocks and other matter with very little sediment.
- The surface of the sample was in contact with the jaws of the Van Veen, signifying overpenetration of the grab and possible loss of sediment around the jaws (Sedlak et al., 2017).

3.4 Sample Pretreatment

3.4.1 Drying

Drying is a mass transfer process of removing water molecules from a sample. This could be done using various techniques such as air drying, freeze-drying, and oven drying. In this study, sediment samples were oven-dried.

Oven drying is one of the fastest and most effective methods for sediment drying, however, high temperatures of more than 60°C should be avoided to prevent heat distortion and retains the physical properties of MPs (Nuelle et al., 2014). The sediment samples were oven-dried at 40°C

for 10 d until a constant mass was reached. Figure 3.3 shows sediment sample before and after drying.



Figure 3.3 Dry sediment sample after oven drying

3.4.2 Digestion

Digestion is the removal of organic matter in the sample matrix to reduce interference, particularly, during visual inspection and analysis of MPs (Yang et al., 2021). The main methods of digestion are oxidative, acidic, alkaline, and enzymatic digestion.

In alkaline digestion, sodium hydroxide (NaOH) and potassium hydroxide (KOH) are widely used. Compared to KOH, NaOH is known to be harsher on polymers, it is reported to damages nylon fibers, melts polyethylene, and causes yellowing in unplasticized polyvinylchloride (uPVC) (Bellasi et al., 2020; Campanale et al., 2020; Cole et al., 2014). In this study, alkali digestion was performed using 10% KOH, hence it has been reported to have minimal damage to the MPs and is recommended for samples with high organic matter (Karami et al., 2017a).

KOH was purchased from Sigma-Aldrich, South Africa. Solutions of KOH (10% w/w) were prepared by dissolving pellets in ultra-pure distilled water. Digestion was accomplished inside a fume cupboard by adding 10% KOH solution to dry sediment at a volume ratio of 1:3 (w/v), the mixture was stirred for 5 min, covered with aluminum foil, and heated on a hot plate at 40°C for 24 h. Figure 3.4 shows samples undergoing digestion before being placed on the hot plate.



Figure 3.4 Sample digestion

3.4.3 Density Separation and Sieving

MPs are usually separated based on their density in a method known as density separation (Ivleva et al., 2017; Prata et al., 2018). In this method, the sample is mixed with a high-density salt solution where low-density particles, that is the MPs, float (Li et al., 2017).

Salts such as sodium iodide, sodium polytungstate, and zinc chloride have been noted to have high extraction rates due to their high densities, that is, 1.81 g/cm^3, 1.40 g/cm^{3,} and 1.6 g/cm^3, respectively (Campanale et al., 2020; Dekiff et al., 2014; Ivleva et al., 2017; Van Cauwenberghe et al., 2013). The major disadvantage of using these salts is that they are costly, in addition, NaI and $ZnCl_2$ are toxic.

In this study, NaI has been used in density separation. As mentioned above, it is expensive and toxic to the environment however it is effective in separating high density MPs (Ivleva et al., 2017; Masura et al., 2015).

NaI used was purchased from Merck, South Africa. 80 g powder was dissolved in 100 mL ultra-pure distilled water to prepare a saturated NaI solution. This solution was then added to the digested sample in a volume ratio of 1:3, stirred for 5 min, and left for 24 h. Prior to this, a 5 mm sieve was used to separate large debris such as twigs and large leaves from the previously digested sample.

NaI was recycled to limit its environmental impacts and to reduce the cost, while taking the advantages of a complete and effective separation. Recycling was performed in the fume hood, used NaI solution boiled in a metal pot on a hotplate. The recycled NaI was stored as a salt, because it is relatively unstable in solution (McDonnell and Russell, 1999).

3.4.4 Filtration

The top layer that is formed during density separation, which is suspected to contain MPs is filtered onto a filter paper and placed in a petri dish. Filtration can either be gravity or vacuum filtration. Filter papers used are made of different materials such as nylon, cellulose acetate, and polyamide (Cutroneo et al., 2020). The pore size of the choice of filter papers ranges from 0.2 µm to 300 µm, usually, with a diameter of 45 mm or 47 mm (Setälä et al., 2016; Syakti et al., 2018). When the supernatant liquid is filtered, the filter papers are rinsed with deionized or ultrapure water. This is to prevent salt crystals from forming on the filter papers once dry (Palatinus et al., 2015). These are then stored in pre-cleaned glass petri dishes. The wet filter papers can be air-dried or oven-dried normally between 40 – 70°C (Cutroneo et al., 2020).

In this study, the supernatant liquid was vacuum filtered using Nalgene flask, through GF/A filter papers Whatman®: 47 mm diameter, pore size: 1.6 µm. The filter papers were placed in glass petri dishes and air-dried in the laminar flow cabinet for 24 h (Figure 3.5).



Figure 3.5 Air-drying of filter papers in the laminar flow cabinet

3.5 MP Characterization

3.5.1 Visual Analysis

Visual inspection is based on size, colour, absence of cellular or organic structures visible, and shape. In terms of shape, MPs are classified as fibers, pellets, fragments, film, and foam (Hidalgo-Ruz et al., 2012).

For visual analysis, a stereomicroscope (Nikon MET SMZ745T, Japan) at 0.67 to 5x magnification was used to identify MPs based on their shape and colour. It was also used for counting the number of MPs in each sample as well as measuring the size of the particles. The guidelines for identification used were as described by the Marine and Environment Research Institute (MERI) guide (MERI, 2015). The imaging software used to capture the MPs was the NIS Elements-D imaging software version 5.30 with a The Imaging Source (TIS) USB 3.0 camera (Nikon Cooperation, Japan). The Nikon stereomicroscope is shown in Figure 3.6.



Figure 3.6 Nikon stereomicroscope for visual analysis

Scanning electron microscopy (SEM) enables morphological characterization of MPs down to the nanometer scale (Fries et al., 2013). Surface features such as fractures, grooves, and pits are considered to be the result of mechanical weathering, whereas granules, flakes, and solution pits are regarded to be the result of oxidative weathering (Wu et al., 2018).

SEM analyses was carried out in order to examine the surface morphology of MPs using the TESCAN Vega. The selected MPs were dried, transferred onto the double-sided adhesive carbon tabs on aluminum stubs, gold-coated and subjected to variable pressure in secondary electron mode.

3.5.2 Polymeric identification

Raman spectroscopy is one of the most preferred techniques in identifying MPs. It is coupled with an optical microscope and has a high spatial resolution (Rodrigues et al., 2018), allowing particles of as small as 500 nm to be viewed (Anger et al., 2018). It is a non-destructive, non-contact technique that generates data by optical image analysis, qualitative analysis, and chemical identification. This is accomplished by matching the resultant spectra with that of a reference

library. Another advantage is that wet samples can be analysed and has a better response to nonpolar functional groups (Lv et al., 2021).

However, it is affected by the interference of fluorescence (Erni-Cassola et al., 2017). This can be from MP pigments, additives, and organic and inorganic contaminants which hampers the identification of MPs (Eerkes-Medrano et al., 2015; Ivleva et al., 2017).

In this study, all suspected plastic particles were analyzed using the Horiba LabRAM HR Raman spectrometer with the Olympus BX41 microscope, and a 514.5 nm line of a Lexel Model 95-SHG argon-ion laser (Horiba, France). The incident beam was focused on the particles and the backscattered light was dispersed through a 600 mm grating on a liquid nitrogen cooled CCD detector. The data acquired was analysed using LabSpec v5 software. The obtained spectra were compared to existing polymer spectra from the KnowItAll (Bio-Rad Laboratories, Inc., South Africa) reference software, at a threshold hit quality index (HQI) of more than 80% similarity.

3.6 Quality Assurance and Quality Control

Quality assurance and quality control were adhered to avoid contamination, sample loss from leakages during sieving, and interference during analysis (Zobkov and Esiukova, 2017). Only metal and glass apparatus and containers were used during sampling, and glassware were in the laboratory to avoid cross-contamination introduced by the use of plastic.

In order to reduce procedural contamination, cotton laboratory coats were worn. All samples pretreatment steps were carried on in a laminar flow cabinet. Glassware was cleaned with soap and rinsed with ethanol (purchased from Merck, South Africa) before use. Filtered deionized water was used. Blanks (made from filtered deionized water) were run throughout the pretreatment and analysis procedures. MPs found in the blank samples were characterized and MPs of the same type and morphology were excluded (blank corrected) from the other samples to account for procedural contamination.

Chapter 4

Results and Discussion

This chapter presents the findings of the study and discusses the results in terms of abundance, shape, and colour. It also addresses questions raised in connection with sources of MPs in the Vaal River and possible environmental implications of the contaminants.

4.1 MP Levels of Pollution in the Vaal River

MPs were prevalent in all sediment samples, with abundances ranging from 29 to 1096 particles/kg_dw, and a mean abundance of 463 ± 284 particles/kg_dw (average ± std dev). Abundance was determined as particles per kg of dried weight of the sediments. The mass and MP abundance per sample is given in Table 4.1.

Table 4.1 Number of MP particles per sample and MP abundance

Sample	Dry mass/kg	Particles counted	Abundance particles/kg_dw
S1	0.25	68	271
S2	0.08	75	896
S3	0.13	115	862
S4	0.14	82	590
S5	0.12	83	675
S6	0.14	79	563
S7	0.09	47	526
S8	0.18	44	241
S9	0.11	76	666
S10	0.18	86	471
S11	0.37	28	75
S12	0.03	12	463
S13	0.05	4	84
S14	0.41	23	56
S15	0.27	8	29
S16	0.09	55	617
S17	0.14	98	694
S18	0.07	25	377
S19	0.08	19	253
S20	0.06	24	397
S21	0.34	28	81
S22	0.04	19	475
S23	0.06	44	704
S24	0.07	72	1096
S25	0.10	40	419

The results above are an indication of MP pollution in the Vaal River. The values in the table show considerable amount of MPs in all samples. The sampling area is located between Vereeniging and Vanderbijlpark, where potential sources of MPs exist. Potential sources in the area include water and wastewater treatment plants (e.g., Rand Water and Emfuleni Municipal wastewater

treatment plant), industrial activities (e.g., Lethabo Power Station and AccelorMittal) tourism (e.g., fishing and boat cruising), and waste generated from surrounding residential areas (e.g., Sedibeng and Metsimoholo). It is well documented that urban centres are major sources of plastic waste (Chauhan et al., 2021; Klein et al., 2015; Schell et al., 2021; Shruti et al., 2019; Toumi et al., 2019).

Upstream, sampling spots S1 to S4 were close to the Lethabo Power Station, which draws water from the river for electricity generation (Eskom, 2022). Recreational activities (e.g., fishing, houseboats, hotels, a golf course, picnicking areas, and resorts) observed along the river where samples S5 to S12 were collected could be major sources of MPs. Paint from houseboats may chip and form part of the MPs that settle at the bottom of the river. A squatter camp beneath a bridge with tents, plastic waste, and burnt plastic fragments from fires was also observed in that area (close to S9). This is consistent with studies carried out by Miloloza et al. (2021) and Shruti et al. (2019) which reported that anthropogenic activities contribute heavily to MP pollution.

Further down the river, S18 to S22 were located near a residential area, where some buildings are under construction. Household waste and building materials may have contributed to the MP pollution. Solid waste has been reported to have disastrous effects on aquatic ecosystems (Dehghani et al., 2021).

Additionally, some samples were collected from spots near confluences of the Vaal with its tributaries. Tributaries are known for transporting pollution from populated areas to rivers. The major tributaries feeding into the Vaal are Klip River and the Leeuspruit. The Klip River flows from some densely populated areas such as Soweto and Lenasia (Pheiffer et al., 2016). Whereas, Leeuspruit drains Sasolburg, the home to Sasol which is well known as an integrated energy and chemical company.

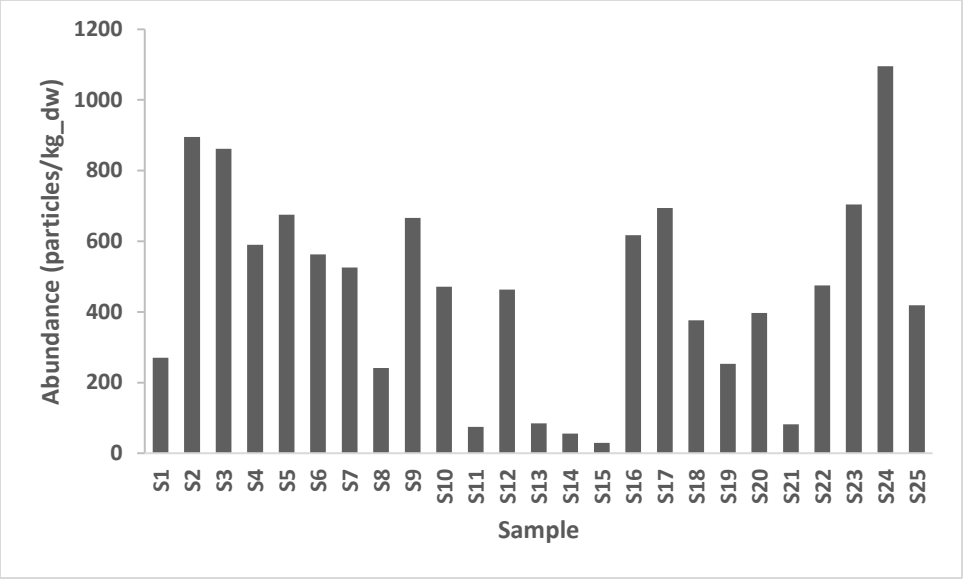

Figure 4.1 Abundance from sampling sites

Gray et al. (2018) and Lahens et al. (2018) reported that globally, higher MP abundance correlates to rivers within the most populous urban environments as exemplified by the Vaal River. According to the findings of this study, MP abundance in the Vaal River is significantly higher than that of the Qinghai-Tibet Plateau (QTP) in Tibet. Abundance was reported to vary from 10 to 90 particles/kg_dw, with a mean value of 42 ± 22 particles/kg_dw. Their study showed that greater intensity of anthropogenic activity could increase MP abundance (Feng et al., 2021). A study conducted on 18 streams in and around Auckland, New Zealand has also reported lower abundance of MPs, with an average of 80 particles/ kg_dw. However, they observed high variation in MP abundance across streams (Dikareva and Simon, 2019).

Some studies reported similar findings to the MPs abundance reported in this study. For instance, a study conducted in Taihu Lake, China, showed similar pollution level, an average abundance of 893 ± 246 particles/kg_dw. It is worth noting that, Taihu Lake is situated downstream of the Yangtze River. Both, Vaal River, and the Yangtze River are exposed to discharges from industrial and agriculture activities, this could explain the similarity in their pollution status.

Another study of comparable findings was conducted in Wei River in China, where an abundance of 360 – 1320 particles/kg_dw was reported (Ding et al., 2019). The high abundance was also attributed to the agricultural and anthropogenic activities from the surrounding regions. In South

Africa, Dahms et al. (2020) reported a varying abundance of 4 to 1348 particles/kg_dw with a mean of 167 particles/kg_dw in the Braamfontein Spruit in Johannesburg, South Africa.

4.2 Physical Characteristics of MPs

Physical characteristics of MPs significantly influence their effects and fate. The dispersion of MPs in aquatic environments is primarily due to particle-fluid interaction, which determines their settling or buoyancy. Likewise, morphology strongly influences the behaviour of plastic particles in aqueous media (Khatmullina and Isachenko, 2017; Kowalski et al., 2016). As such, studying the morphology provides information about the possible sources of MPs, as well as insights to predict their fate in aquatic environments (Rosal, 2021). In this study, the morphological characteristics of MPs were observed under a stereomicroscope and recorded in terms of shape, colour and size. Surface texture was examined using a scanning electron microscope.

4.2.1 Shape

MPs were classified into three morphotypes, namely, fragments, fibers, and pellets (Figure 4.2). Particles with a slender and elongated appearance were defined as fibers; irregular particles were defined as fragments, and round particles with spherical shape were classified as pellets (Su et al., 2016). Fragments and fibers were the most dominant shapes accounting for 63%, and 35%, respectively. This is consistent with other freshwater studies (Abbasi, 2021; Alam et al., 2019; Alava et al., 2021; Dikareva and Simon, 2019; Egessa et al., 2020b; Eo et al., 2019; Rodrigues et al., 2018). Pellets were found to be less prevalent forming 2%. The shape of MPs gives an indication of probable sources, in terms of primary and secondary microplastics.

The dominance of fragments and fibers over pellets clearly indicate that MPs contamination in the Vaal is of secondary sources. In this case, fibers may originate from synthetic textiles and fishing equipment, pellets could be from wastewater, and personal care products, and fragments from effluent discharge and degradation of large debris.

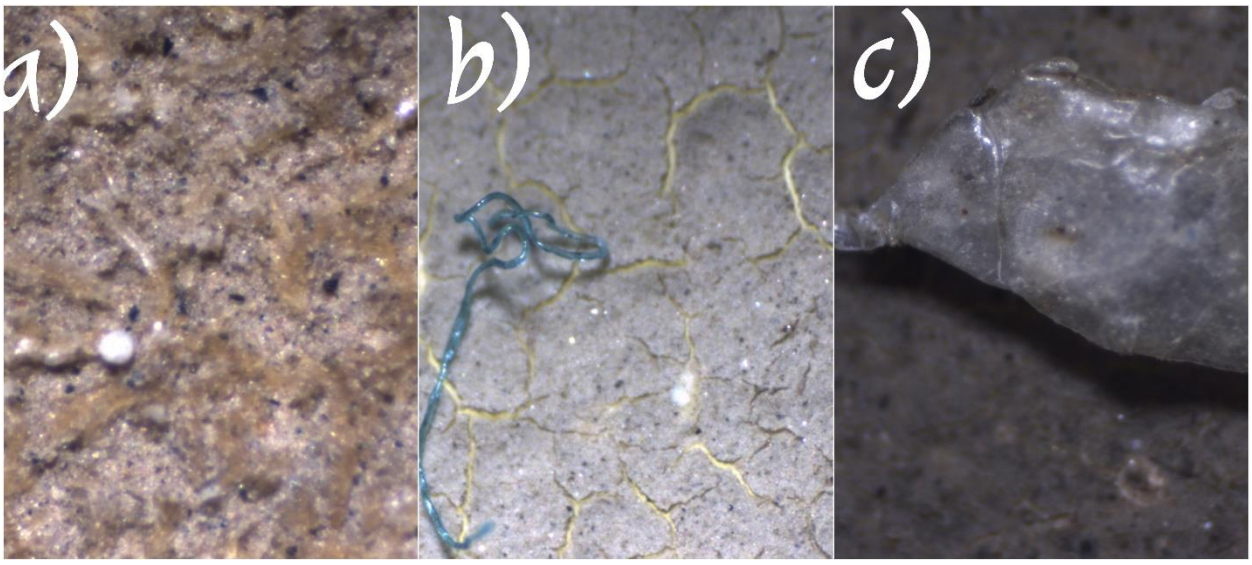

Figure 4.2 MP shapes where a) is a pellet, b) is a fiber, and c) is a fragment

4.2.2 Surface Texture

The surface texture of selected MPs of different shapes was examined for signs of wear and tear. The scanning electron micrographs of surface morphology showed scratches, flaking, fracturing, and pitting on the surfaces of the MPs (Figure 4.3). Mechanical abrasion, and exposure to chemical, and biological processes in aquatic environments (in this case, the Vaal River) could have resulted to the reported observations.

The roughness of the surface of MPs that results from physical erosion and chemical weathering in the presence of ultraviolet (UV) light, air, and humidity, is reported to facilitate contaminant adsorption (Zhang et al., 2021). Similar findings were reported in the Hashilan Wetland, Iran and wastewater treatment plants in Ireland (Abbasi, 2021; Mahon et al., 2017). Both studies observed grooves, flakes, blistering and fracturing on the surfaces of the MP particles.

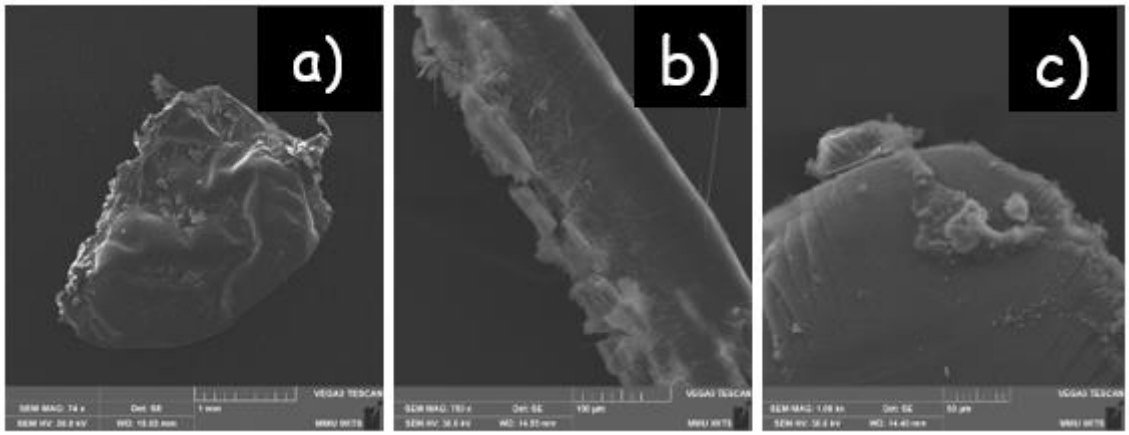

Figure 4.3 SEM images of a) a fragment, b) a fiber, and c) a pellet

4.2.3 Colour

Several colours were observed, and the results were sorted as coloured and non-coloured/transparent MPs. Coloured MPs were more abundant contributing 60% of the total MPs, of which, blue (18%), white (12%), and green (10%) were most dominant. Brown, pink, black, yellow, and grey were observed in small portions. The transparent MPs contributed the remaining 40%. Figure 4.4 shows the colour distribution of MPs in all samples.

Colours of MPs may be used to identify their sources. For instance, transparent MPs are assumed to be from packaging materials and single-use plastics (Li et al., 2020; Prata et al., 2018). The coloured MPs come from the degradation of macro-plastics that are dyed, such as clothing (Shruti et al., 2019). The dominance of coloured MPs is frequently reported in literature (Feng et al., 2021; Rodrigues et al., 2018; Simon-Sánchez et al., 2019; L. Zhang et al., 2020).

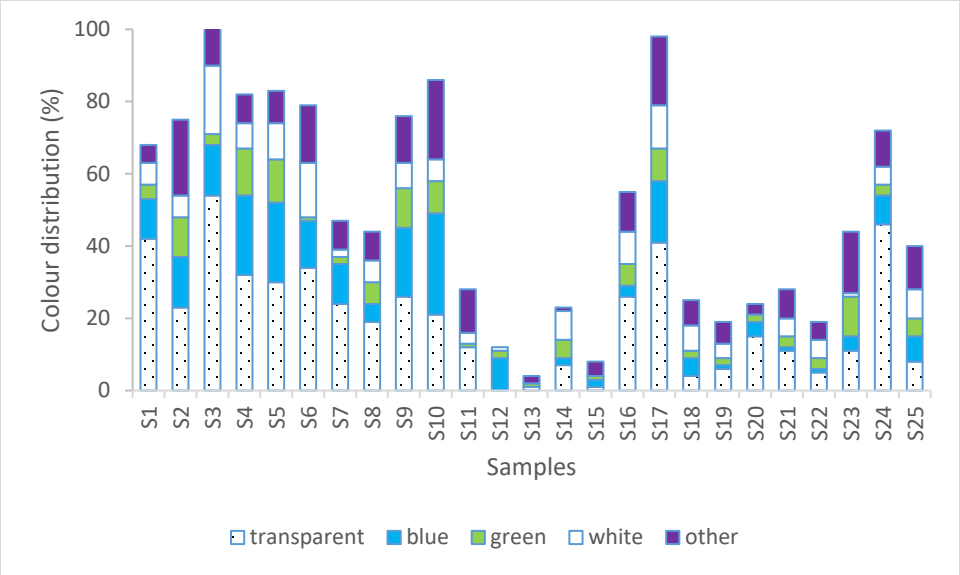

Figure 4.4 Colours observed and their respective percentages

4.2.4 Size

MPs were grouped into size ranges according to their sizes that is 0 – 500 µm, 500 – 1000 µm, 1000 – 2000 µm, 2000 – 3000 µm, 3000 – 4000 µm, and 4000 – 5000 µm. It was noted that the majority of the MPs were in the 0 – 2000 µm range forming 82% of the total MPs. The largest frequency of MPs was found in the 0 – 500 µm range, accounting for 32%. Figure 4.5 shows the size distribution in the various size ranges.

The dominance of small-sized MPs of < 500 µm in sediment was reported in several studies (Abbasi, 2021; Dikareva and Simon, 2019; Ding et al., 2019; Feng et al., 2021; Peng et al., 2018; Zhang et al., 2021). This could be due to their surface area, which was favourable to the mass accumulation of MPs via bio-fouling and other matter attachment, thus reducing the buoyancy and further enhancing the settling capability (Fazey and Ryan, 2016; Porter et al., 2018).

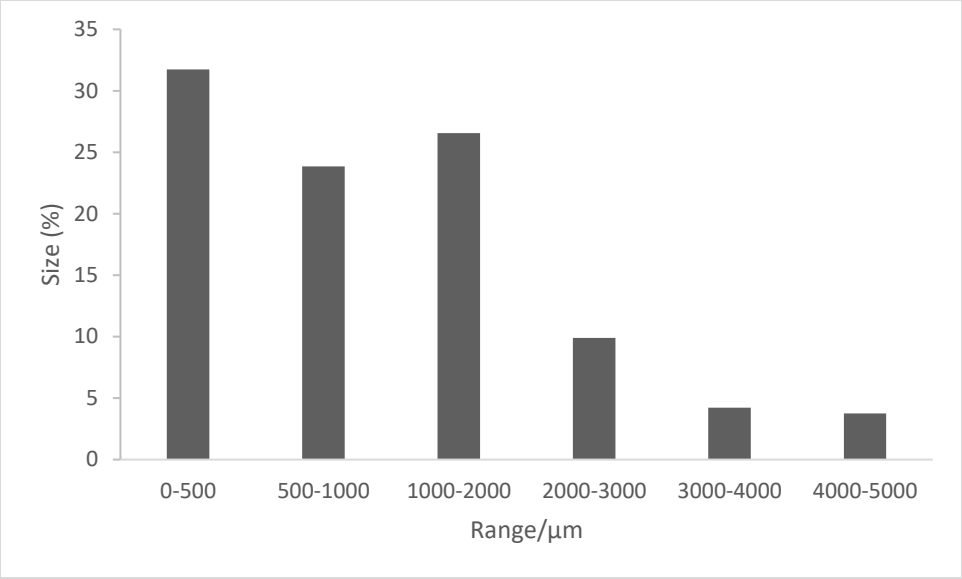

Figure 4.5 Size distribution in the class ranges

The relationship between MPs size and abundance was examined by Spearman correlation as shown in Figure 4.6. The results indicated significant positive correlation with a p-value of 0.03158. This means that the abundance increases with the small size of the MPs. This could be due to the frequent fragmentation as a result of natural environmental conditions. Thus, the quantity of smaller MPs increases without the introduction of additional plastics (Bouwman et al., 2018; Egessa et al., 2020a)

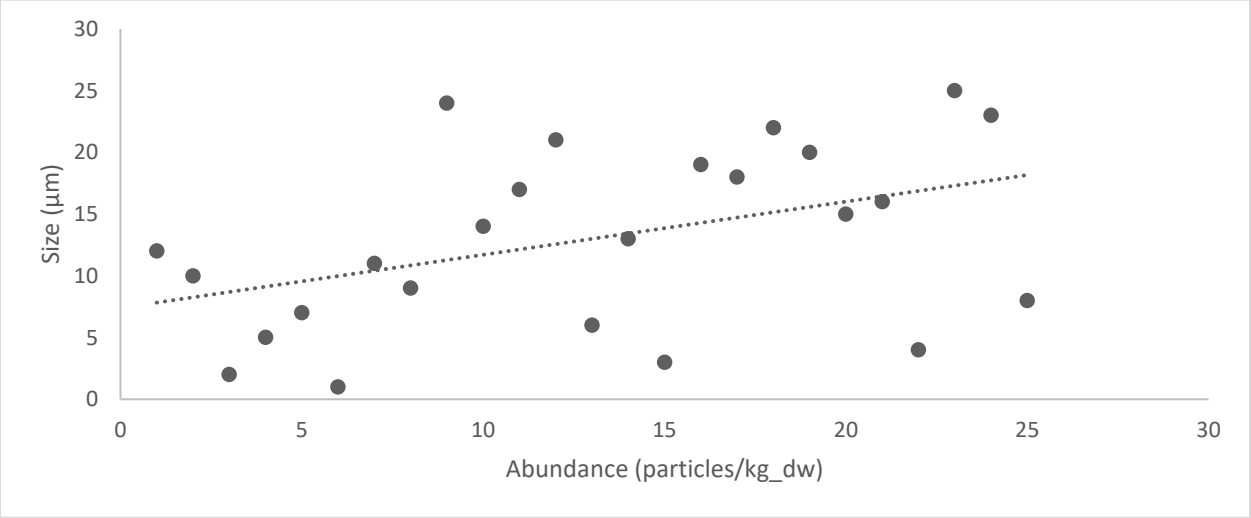

Figure 4.6 Spearman correlation plot of size and abundance

4.3 Potential Sources of MPs in the Vaal River

There are many potential sources associated with the morphology observed in this study. Morphological properties observed were used to narrow down the sources to those within the context of the Vaal and its tributaries.

The dominance of fragments and fibers in this study clearly indicates that MP pollution in the Vaal River is of secondary sources. Fragments could mostly be attributed to different anthropogenic activities around the Vaal, notably, the section of the river sampled is well known for a variety of recreational activities. Consequently, picnics, water sports, waste generated from the hotels and resorts may contribute to MP pollution. Furthermore, pieces of plastics from fishing rods, nets, and boats are directly introduced to the river. Once in the river system, the relatively larger surface area of fragments facilitates the adsorption of other contaminants from the surrounding environment which enhances their sedimentation (Porter et al., 2018). Additionally, domestic, and industrial waste are also documented as main sources for MPs, mainly fibers. According to the International Union for Conservation of Nature (IUCN) 24% of MPs originate from domestic and industrial activities (Boucher and Friot, 2017). From the collected data, it was noted that fragments were dominant across all size ranges, as shown in Figure 4.7. The dominance of fragments was reported in several studies, for example, in Qinghai-Tibet Plateau, Tibet, in Lake Taihu, China, and in Lake Ziway, Ethiopia, to mention a few (Feng et al., 2021; Merga et al., 2020; Zhang et al., 2021).

Fibers, on the contrary, are mostly generated from the textile industry and laundry services from both commercial and domestic activities. According to Boucher and Friot. (2017), approximately 35% of MPs released in aquatic environments globally are from synthetic textiles. However, a report by the United Nations Environment Programme (UNEP) estimates this figure to be around 16% (UNEP, 2020). Washing machines contribute greatly to fibers, approximately 120 – 730000 fibers are released into wastewater per one washing cycle (Cesa et al., 2020; Kärkkäinen and Sillanpää, 2021; Vassilenko et al., 2021). Some studies have reported that domestic wastewater from washing machines contains a vast quantity of artificial and synthetic fibers (Cesa et al., 2020; Kärkkäinen and Sillanpää, 2021; Sillanpää and Sainio, 2017; Vassilenko et al., 2021). Fibers in this study could therefore be attributed to domestic sewage from residential areas around the Vaal, namely, Sedibeng and Metsimoholo district.

It is important to note that this region of the Vaal River serves as a recipient of wastewater effluent from the above potential sources, predominantly, from the Emfuleni Municipal wastewater treatment system. There are reports of sewage spills in the Vaal between Vereeniging and the Vaal Barrage, including Vanderbijlpark. This was reported to cause the death of yellowfish, a common fish species found in the Vaal River (Evans, 2021). Substandard wastewater treatment results in significant discharge of various synthetic and natural fibers, which then sink to sediment, depending on their physical properties (Herzke et al., 2021). Fibers have an elongated shape whose physical properties however differ from the shapes of other MPs. This in turn influences forming, sedimentation, transportation, and degradation patterns (Bagaev et al., 2017).

Pellets made up 2% of the total MPs in this study. They are primary MPs produced by ultrafine grinding in mills and are widely used in cosmetics, primarily in small (100 μm) sizes (Fahrenfeld et al., 2019; Hartmann et al., 2019; Kalčíková et al., 2017). This is consistent with the findings of this study, as they were only found in the 0 – 500 μm size range (Figure 4.7). Pellets are found in approximately 72% of sunscreens (Kleida, 2020). These can easily enter the Vaal as people engage in water activities/sports like boat cruises and houseboats, rafting, tubing, flyboarding, kayaking, and river boarding, all of which are popular in the Vaal. According to the IUCN, pellets accounted for 0.3% of MPs in aquatic environments worldwide (Boucher and Friot, 2017). Pellets are known to enter the aquatic environment as both primary and secondary MPs from industrial and domestic discharges. Through photooxidation, the formation of various functional groups, weathering, and aging, pellets tend to acquire an inherent surface charge and a larger surface area (Turner and Holmes, 2011). As a result, trace metals and organic pollutants adsorb onto the surface of the pellets (Turner et al., 2015). The Vaal is lined with hotels, resorts, and private residences that could be potential sources of pellets.

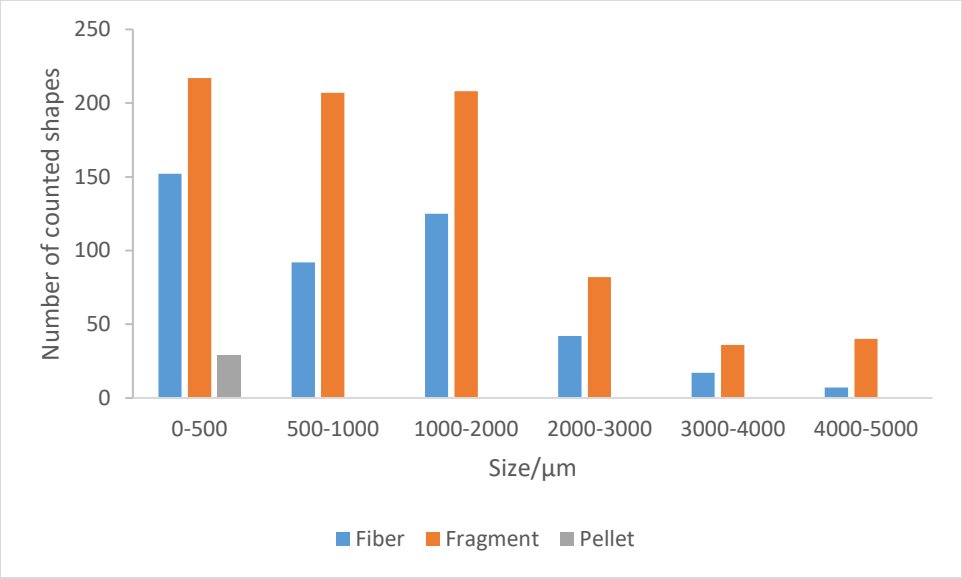

Figure 4.7 Shape distribution

4.4 Effects of *in situ* parameters

In-situ is the measurement of physical and chemical parameters in a water body at the time of sampling. These parameters include temperature, pH, conductivity, turbidity, flow rate, depth, and dissolved oxygen (Queensland and Department of Environment and Heritage Protection, 2018). They are important for the monitoring of aquatic and surrounding ecosystems and predicting the impact on environmental and human health (Frondiest Environmental, 2022).

Based on data collected from the Rand Water database, the flow rate of the Vaal River on the sampling dates of this study was 16 m^3s^{-1} and 18 m^3s^{-1}, for the 26th of April and 29 – 30 June 2021, respectively. For the barrage, it was 44 m^3s^{-1} and 10 m^3s^{-1} for the aforementioned dates. This could possibly affect the movement of the top layer of the sediment and also the rate at which the MPs settle at the bottom of the river. Differences in polymer densities, physicochemical state of the waterbody, and biofouling on the surface of MPs are reported to affect the rate at which MPs settle on the sediment (Graca et al., 2017). Apart from this, it should also be considered that the environmental conditions prevailing in the given region such as daily discharge, anthropogenic activities, developmental programs, and flow velocity affects the mobilization of sediments and previously settled particles thereby, altering the quantity of MPs (Ballent et al., 2016; Naden et al., 2016; Walling, 2009).

4.5 Polymeric confirmation

Raman spectrometry was used to determine the polymeric composition of the MPs. There were 7 polymers detected, namely, high-density polyethylene (HDPE), low-density polyethylene (LDPE), polyethylene co-vinyl acetate (PEVA), polypropylene (PP), polyester (PES), polyurethane foam (PU), and polyethylene/hexene-1-copolymer (PEH) with PE, PP, and PEVA as the predominant polymers (Figures 4.8 to 4.11). The blue spectrum in the Raman spectra presented in the following figures, is resulting from the MPs, while the red spectrum is the best identification match to the KnowItAll software reference library.

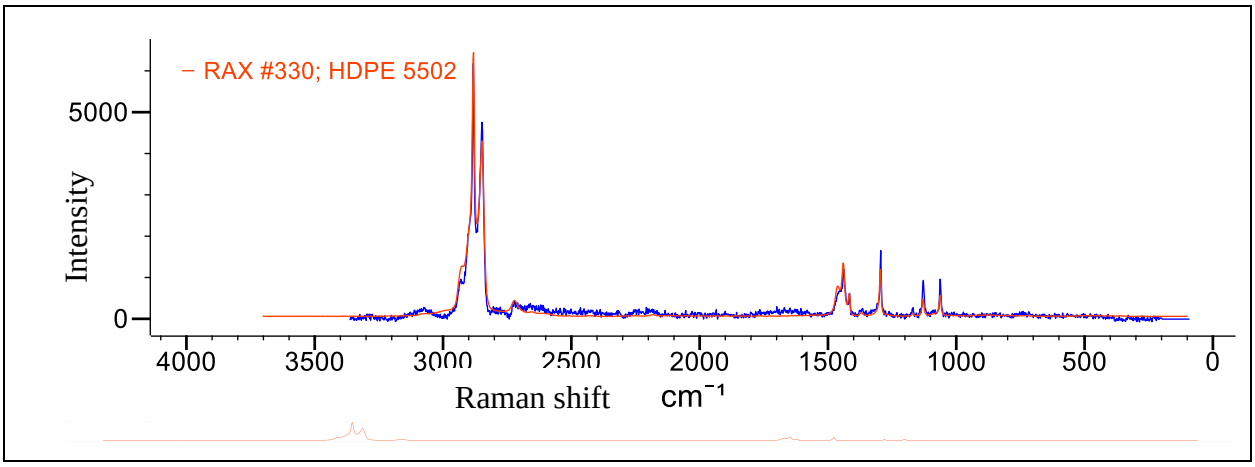

Figure 4.8 HDPE Raman spectrum

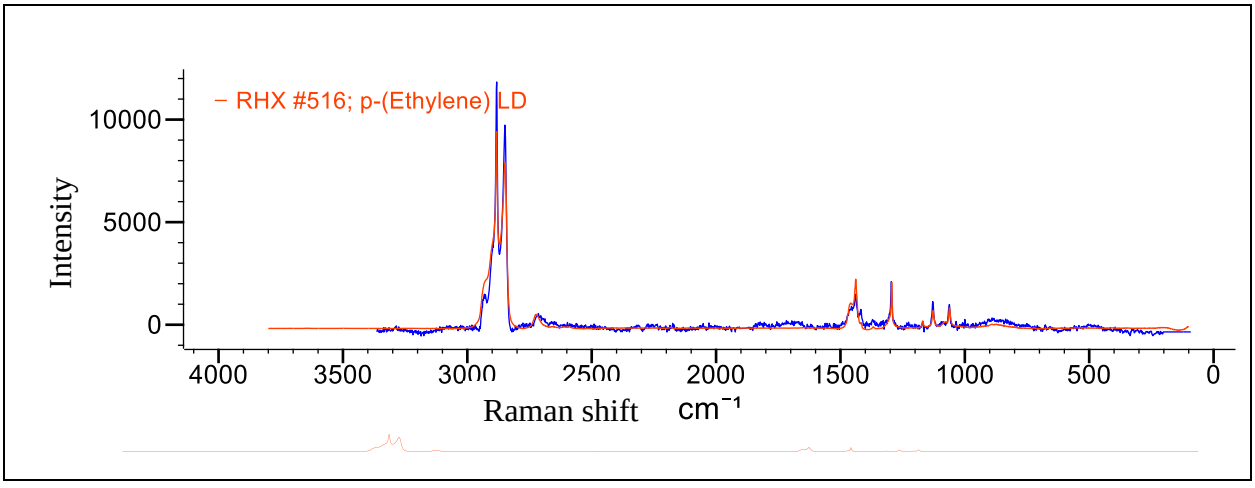

Figure 4.9 LDPE Raman spectrum

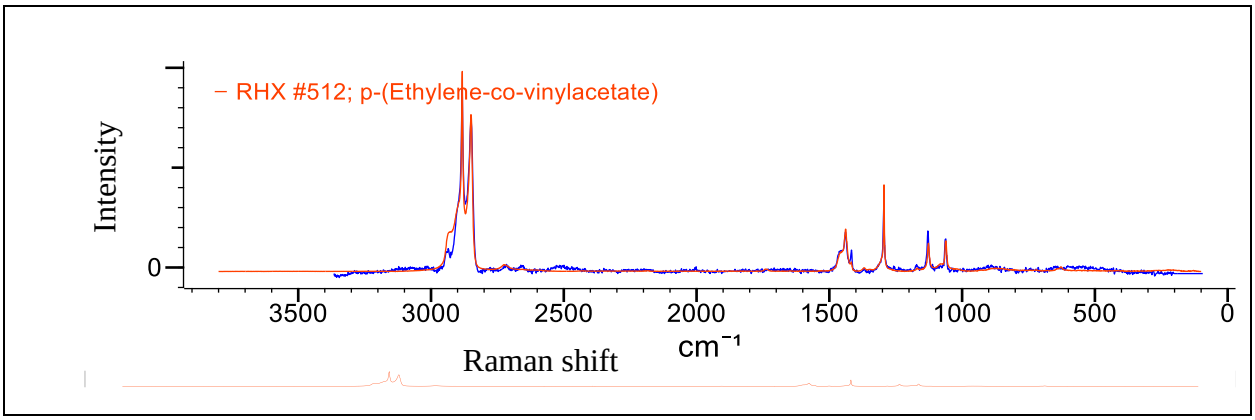

Figure 4.10 Polyethylene co-vinyl acetate Raman spectrum

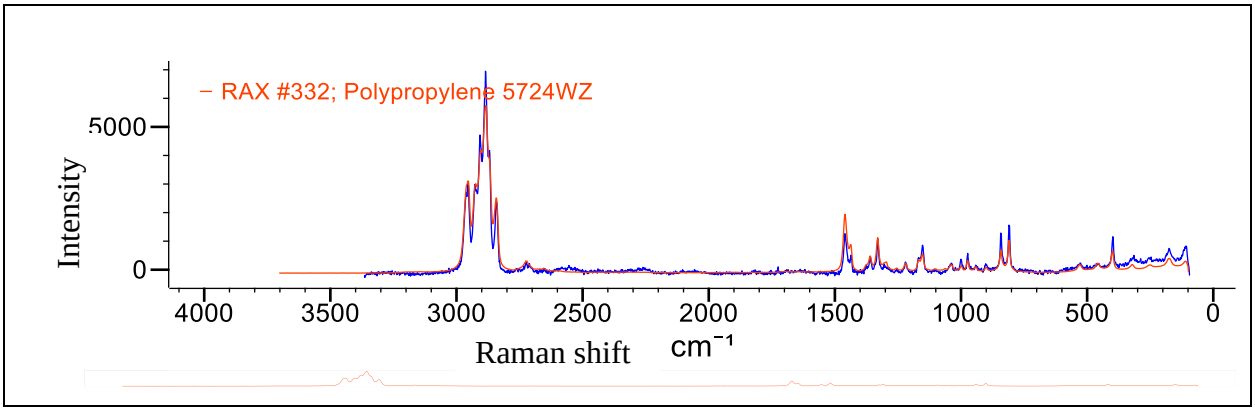

Figure 4.11 Polypropylene Raman spectrum

PE and PP are the most reported dominant polymer types, with widespread distribution in aquatic environments (Erni-Cassola et al., 2017; Horton et al., 2017). Their prevalence is associated with their wide use in packaging materials, storage containers, food packaging, water bottles, plastic bags, fishing nets, and boat ropes (Auta et al., 2017; Bond et al., 2018; PlasticsEurope, 2020; Rajendran et al., 2015). Physical characteristics of polymers and environmental conditions for example plastic density and residence time impact their transport and distribution in aquatic environments (Bakir et al., 2014; Sooriyakumar et al., 2022). PE has a density of 0.91 – 0.97 g/cm^3 and PP has a density of 0.85 – 0.94 g/cm^3 (Bouwman et al., 2018). MPs of high density tend to sink into sediments, whereas MPs with low density are easily transported by tides, waves, currents, and rivers (Zhang et al., 2017). However, density is not the only contributor affects MPs distribution and sedimentation, MPs are subjected to different environmental conditions, biofouling, and the adsorption of other compounds on their surfaces (Fazey and Ryan, 2016; Graca et al., 2017). This may also influence their sedimentation, leading to particles with low density to sink into the sediment, which may explain the presence of PE and PP in the sediment samples.

PEVA is used as a sealant, adhesive, and for coating; it is combined with a petroleum wax and a resin tackifier to form the foundation of many hot melt adhesives (Chalykh et al., 2009). It is also used as a form of plastic wrap. As a result, its presence in the Vaal would be due to anthropogenic activities and repair jobs performed on the river's boats and houses.

PES is another commonly encountered MP in aquatic environments (Figure 4.12). It is used for packaging, picnic blankets, disposal face masks, fishing gear such as nets, insulators, and as an alternative to glass (Chellamani et al., 2013; Gong et al., 2018; PlasticsEurope, 2020; Rajendran et al., 2015). Its abundance could be described by several transport processes in aquatic systems. Polyester is nonbuoyant however adsorption of matter onto its surface and biofouling impact its transport and sedimentation (Klein et al., 2015).

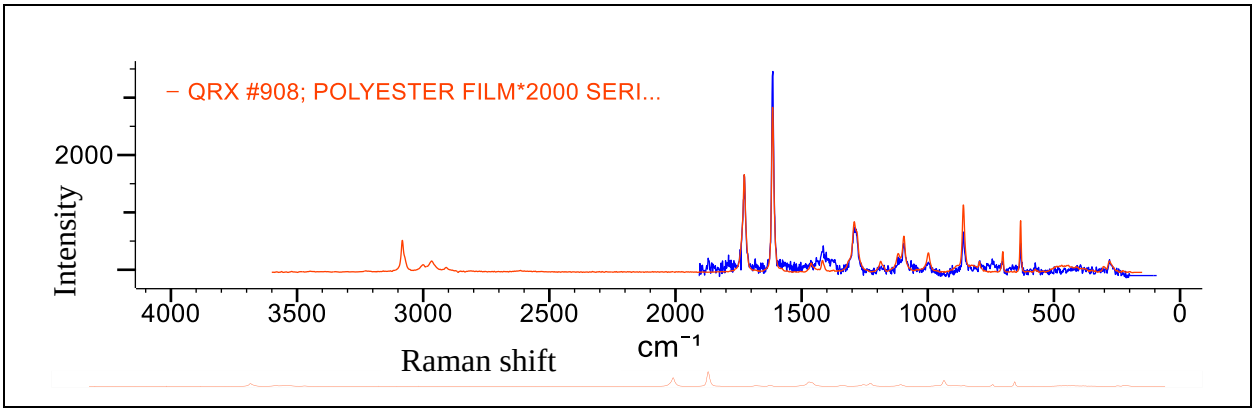

Figure 4.12 Polyester Raman spectrum

PU (Figure 4.13), is widely used in medical applications such as catheters and industrial products, particularly as foams (Islam et al., 2019). PU foams, which are commonly used in pharmaceutical and cosmetic industries, eventually end up as waste in the water cycle (Sharma and Chatterjee, 2017). Additionally, it is widely used in tires, sponges, insulation, coats, paints, adhesives, and fibers (Howard, 2002; Matías, 2022; Shah et al., 2008). Sewage leakage into the Vaal could be a potential source of PU in the river as it may be present in the wastewater.

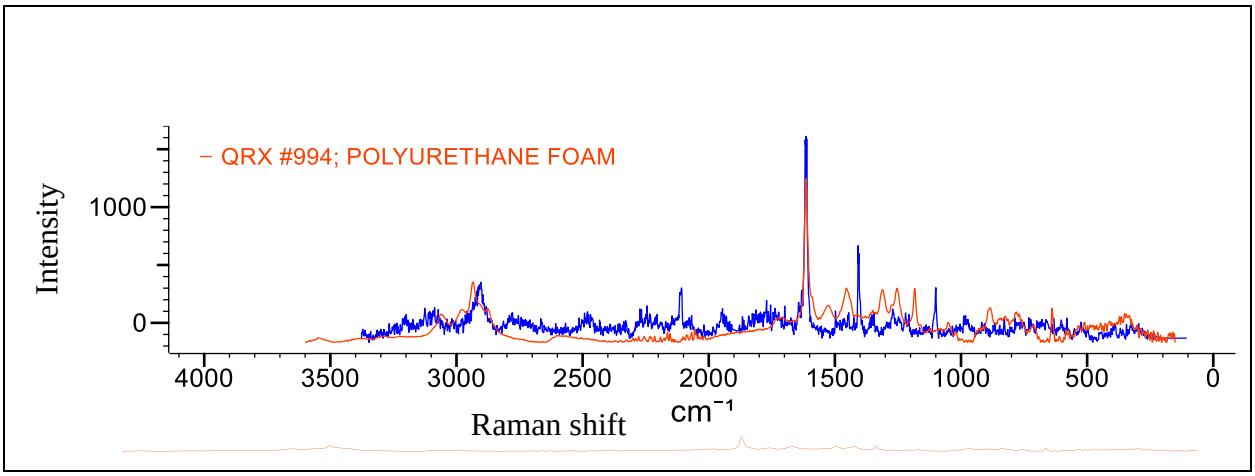

Figure 4.13 Polyurethane Raman spectrum

Polyethylene/hexene-1-copolymer is a plastomer (Figure 4.14). A plastomer is a polymer that has both elastic and plastic properties. Hexene is usually added to polyethylene to produce a low-density plastomer with desired specifications, for example, mechanical and thermal properties (Chaichana et al., 2010; Hanifpour et al., 2019; Jongsomjit et al., 2005).

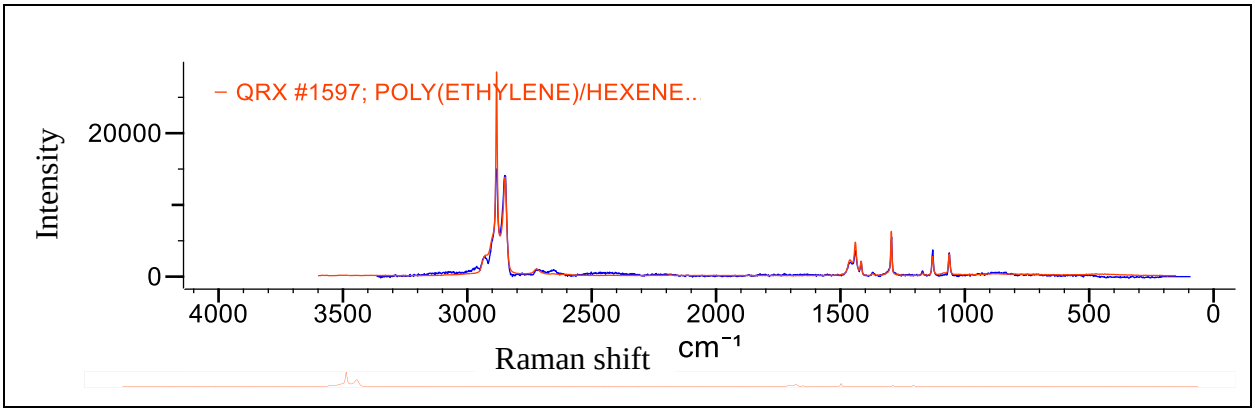

Figure 4.14 Polyethylene/Hexene-1 copolymer Raman spectrum

Klein et al. (2015) reported PE, PP, and PS as the dominant polymers in the Rhine-Main River, Germany. The authors argue that their abundance could be attributed to the considerable degree of economic value of PE, PP, and PS, as they cover 57.9% of the plastic demand in Europe (PlasticsEurope, 2020). The relatively low densities of PE and PP, as well as increased PS's floating capacity, enable spatial dispersal in aquatic conditions. They may easily be carried by rainwater and rivers, where they accumulate inshore sediments. As a result, these three polymers are among the most frequently identified polymers in freshwater sediment research. (Hidalgo-Ruz et al., 2012). Other studies that also reported similar findings as this study were Abbasi et al. (2021) and Peng et al. (2018).

The sediment samples exhibited a lot of fluorescence hence the spectra were subjected to baseline correction using LabSpec to clean up the spectra. During analysis, the very small particles were difficult to analyse due to interference of the surrounding matrix and the fluorescence. This also affected fibers and thin transparent film-like fragments. The resultant spectra for some samples had peaks that were difficult to see because of that interference.

4.6 Other Compounds Detected

The concerns on microplastics pollution include, in addition to their possible health risks, the potential hazard associated with their constituent additives such as flame retardants, plasticisers, pigments, stabilizers, and so on. Furthermore, MPs are known to adsorb and desorb toxic elements and organic contaminants from the surrounding environment, depending on the prevailing environmental conditions. It is therefore, expected that other compounds associated with MPs will be detected when studying MPs. In this study, in addition to the 7 polymers presented above, 3 minerals, 3 dyes, and 1 additive were identified, according to Raman analysis. The minerals identified were orthoclase, carbon, and microcline; vine black, smalt, and saffron were the 3 pigments/dyes detected; and the additive identified was cis-13-docosanol.

Carbon was mostly detected in the upstream samples (S1 – S5) as shown on Figure 4.15. This area is close to Lethabo Power Station, which uses water from the river to generate electricity. The station burns 50000 tons of coal to produce approximately 23000 tons of ash per day (Eskom, 2022). The detection of carbon in these samples could be due to the MPs being coated with carbonaceous matter. Additionally, soot from fires and incineration of plastics may also contribute to that effect. Figure 4.16 shows one of the pigments identified in this study. Vine black has a spectrum that is almost identical to that of carbon black as the peaks show. Traditionally, vine black is made of carbonaceous materials, which explains their spectra similarity.

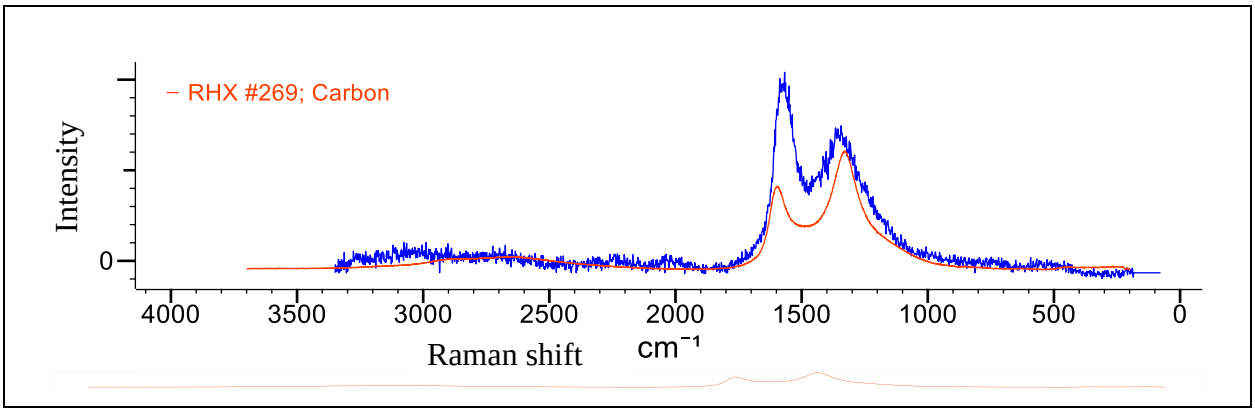

Figure 4.15 Carbon Raman spectrum

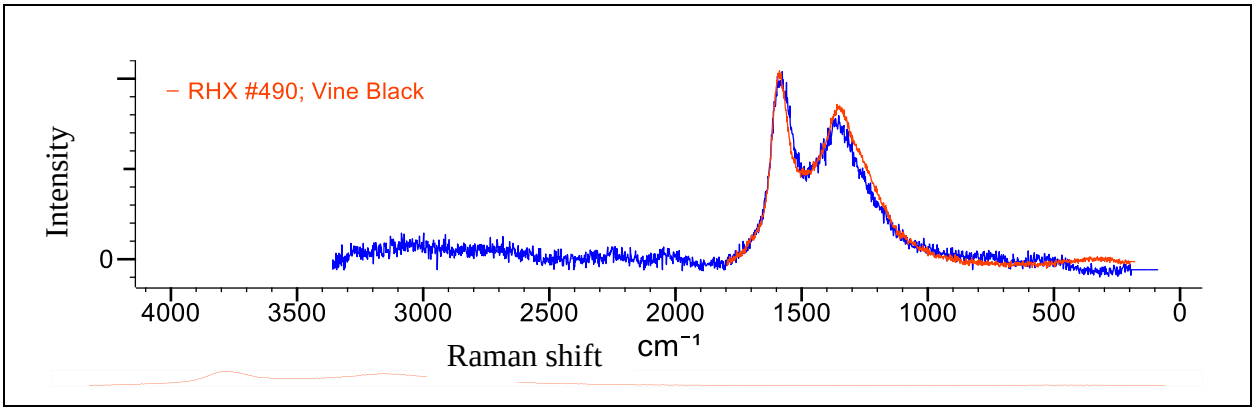

Figure 4.16 Vine black Raman spectrum

Orthoclase and microcline (Figures 4.17 And 4.18) are alkali feldspar minerals that are used in ceramics and glassmaking (Geology Science, 2019; King, 2022). These minerals were mostly detected in samples S18 – S22, which were close to the private residences along the river. Some of the houses were under construction thus they could have been the sources of the minerals.

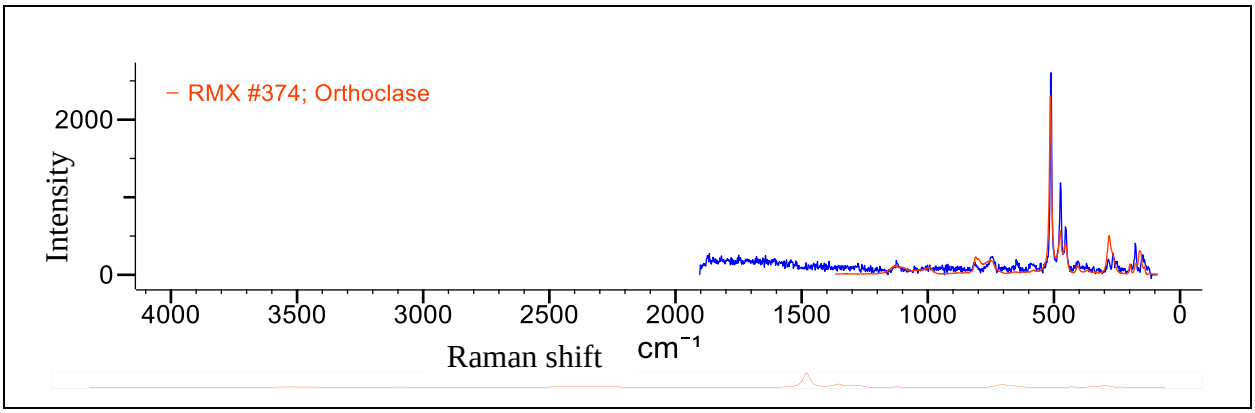

Figure 4.17 Orthoclase Raman spectrum

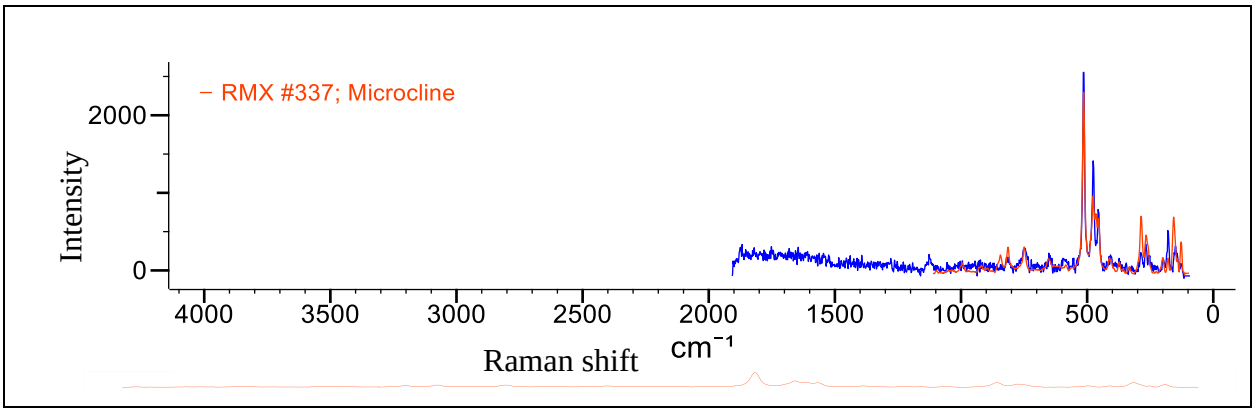

Figure 4.18 Microcline Raman spectrum

Cis-13-docosanol is found in a variety of consumer and industrial products, as well as pharmaceuticals (Figure 4.19). It is used in a wide range of applications and product sectors as thickener, emulsifier, emollient, and binder. In addition, the additive is used as a reactant in the manufacture of plastic materials and resins, soap, cleaning compounds, and toilet preparation, paper manufacturing, paint, and coating. Cis-13 docosanol is used in numerous industrial applications, including oil and gas drilling, plastics, and rubbers. It does, however, show aquatic toxicity, environmental persistence, and bioaccumulation (USEPA, 2020). Of concern, is that such chemicals could be leached/desorbed from MPs into the river.

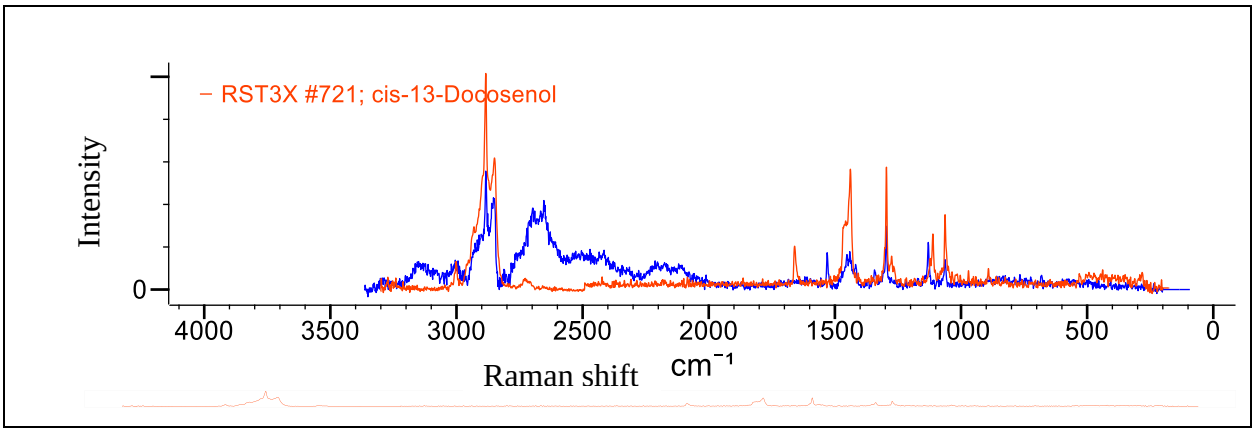

Figure 4.19 Cis-13-Docosanol Raman spectrum

Saffron is a yellow pigment (Figure 4.20). It is used in inks, paint, and coatings. This suggests that the pigment may have leached from paint chips that may have made their way to the Vaal River. Saffron is also used as a spice. The kitchens from the nearby resorts and hotels may incorporate the spice in their meal preparations.

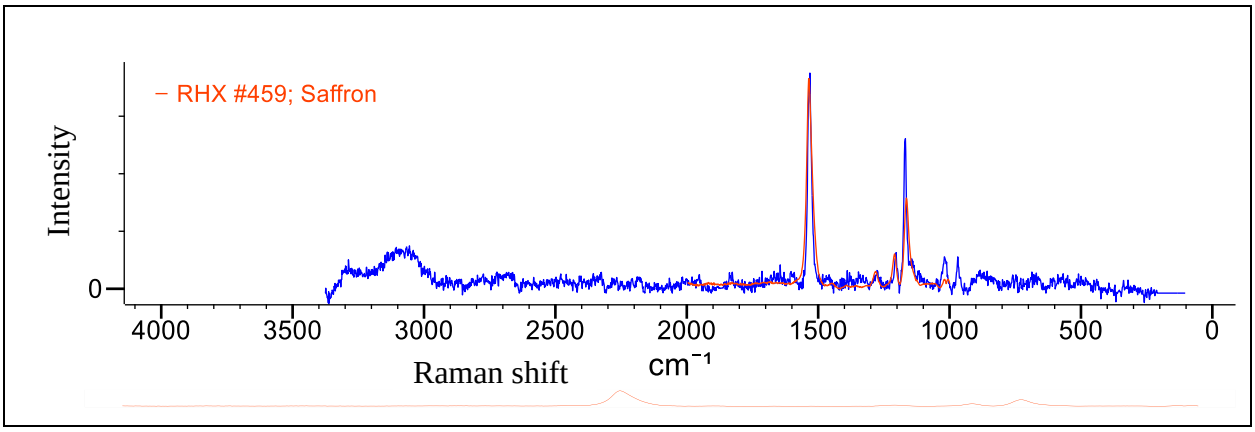

Figure 4.20 Saffron Raman spectrum

Smalt is a blue dye made from crushed cobalt glass (Figure 4.21). It is commonly added to PVC as a colourant during manufacturing, to enhance the polymer chemical stability (管文琴 et al., 2014). The possible leaching of these additives from MPs is of major concern due to their potential toxicity to the environment and both aquatic organisms and humans. For instance, pigments have been reported to resemble food particles which result in gut blockages in aquatic organisms (Hammer et al., 2012; Karami et al., 2017b; Lu et al., 2016).

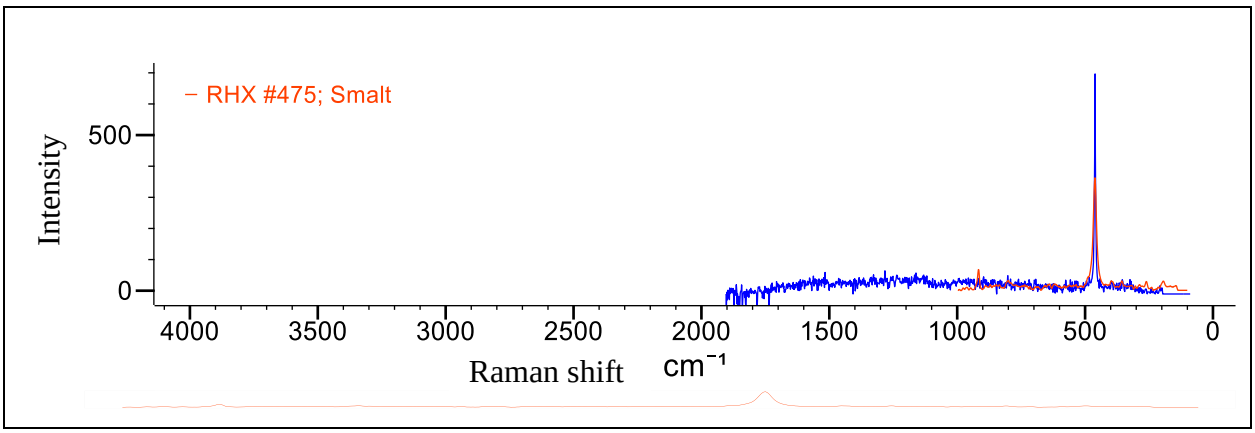

Figure 4.21 Smalt Raman spectrum

4.7 Impact of MPs on Benthic Organisms and Deposit Feeders

The prevalence of MPs in aquatic environments has raised concerns about their bioavailability and health risks. Their various physical and chemical properties render interactions with biota via multiple pathways probable. For instance, due to their small size and resemblance to natural food items, MP particles are readily consumed by aquatic biota incidentally or intentionally.(Van Cauwenberghe et al., 2013; Zhang et al., 2018). The Vaal River is a habitat to a large range of

aquatic life at various levels along the food chain. Consequently, the presence of MPs in sediment poses a threat to aquatic life in the Vaal.

Various studies have reported adverse effects of MPs on aquatic biota (Akindele et al., 2019; Li et al., 2020; Nan et al., 2020; Scherer et al., 2018). Studies of the ecotoxicological effects of MPs have mainly focused on marine organisms with limited studies on freshwater organisms (Li et al., 2020). However, there have been some studies on the effect of MPs on benthic organisms and deposit feeders. It is reported that MPs are primarily accumulated by wild freshwater mussels and benthic crustaceans from sediments.

Laboratory studies have further confirmed that MPs can amass in substantial quantities in zooplankton *Daphnia magna* (Besseling et al., 2017; Nasser and Lynch, 2016; Rehse et al., 2016; Rosenkranz et al., 2009). Some polymers may have calamitous impacts on benthic organisms and deposit feeders. For instance, PVC and PU are reported to cause acute toxicity to *Daphnia magna* (Lithner et al., 2009; Zimmermann et al., 2020). An exposure laboratory study revealed gene alterations on developing *D. rerio* larvae when exposed to 480 particles L^{-1} of PE for 14 days (LeMoine et al., 2018). It was also reported to impact the microbiome of *D. rerio* larvae (Wan et al., 2019). As for fully grown *D. rerio*, different MP polymers, such as PE, polyamides (PA), PP, and polyvinyl chloride (PVC) were observed to damage the intestine of adults (Lei et al., 2018).

The commonly ingested shape is fiber, which was shown to impact the absorption capacity of *Gammarus fossarum*, an amphipod collected from the stream Dorenbach near the city of Basel, Switzerland (Blarer and Burkhardt-Holm, 2016; Mateos-Cárdenas et al., 2019). MPs accumulate in the digestive tract and reproductive systems of various benthic organisms such as *Hyalella azteca*, *Lumbricus variegates,* and *Oryzias latipes* (Au et al., 2015; Imhof et al., 2013; Rochman et al., 2013). Studies have shown that MPs are quickly excreted by goldfish (*Carassius auratu*s), preventing them from accruing in their intestines (Grigorakis et al., 2017). This implies that MPs accumulate differently in freshwater organisms of different species. However, it should be noted that the uptake of MPs by aquatic organisms can occur indirectly via the consumption of other organisms that contain microplastics. As a result, MPs can be increased through the food chain, and humans may unknowingly consume aquatic species that have collected MPs, which can build in the human body depending on the size of the organism (Li et al., 2020).

Chironomus spp. larvae from the Bloukrans River in South Africa, were found to ingest MPs, and that the MP abundance within these organisms is broadly reflective of those in the sediment in which they reside. Therefore, the high abundance of MPs in the sediment samples from the Vaal River is of great concern. of special concern, is that MPs are considered vectors that concentrate water-borne pollutants; as well as having the potential to leach toxic monomers originating from the particles themselves, such as the dyes, additives and minerals that are reported in this study (Nel et al., 2018).

Chapter 5

Conclusion

This chapter summaries the analysis results and observations made throughout the study. It also highlights the knowledge gaps and recommendations for future monitoring programs and curbing the impact of MP pollution in freshwaters.

Research into microplastics (MPs) in freshwater sediment is significantly limited, particularly in South Africa. This study was aimed at investigating the presence and characteristics of MPs in freshwater sediment in South Africa, namely, in the Vaal River. MPs were observed to be 100% prevalent in sediment samples from the Vaal.

An average abundance of 463 ± 284 particles/kg_dw was recorded with fragments and fibers being the dominant shapes. The majority of the MPs were noted to be coloured, up to 60%, the remaining 40% were transparent. Anthropogenic activities for example boat cruises and houseboats, rafting, tubing, flyboarding, kayaking, and river boarding; inadequate wastewater treatment systems; and waste generated from surrounding residential and industrial areas were identified as potential sources of MPs. According to the findings, 82% of MPs were less than 2 mm in size. The small size represents greater possibility for other compounds, such as persistent organic pollutants (POPs) and heavy metals, to adsorb onto the MPs; this represents higher potential for health risks and higher level of toxicity.

Polyethylene (PE), polypropylene (PP), and polyethylene covinyl acetate (PEVA) were the most common polymers found among the MPs. However, it should be noted that analysis of the spectra for sediment samples was hampered by fluorescence and matrix interference. Sediment sample fluorescence was a significant challenge; as a result, LabSpec was used to adjust the spectra's baseline. Fibers and thin transparent film-like fragments were also affected by this.

A detailed literature review pertaining to MPs in freshwater sediment, showed a lack of data and standardization in MP studies starting from the true definition of MPs to sampling and analytical methods. This in turn affects widespread reporting and forecasting of the wider impact of MPs pollution. There is a clear lag in comparing results and collaboration between research communities, government agencies, and other key stakeholders. In addition to inevitable and possibly irreversible ecosystem imbalances due to MPs pollution, setting of environmental standard benchmarks and synergized responses is also constrained.

Rivers have been established as the transportation system for terrestrial MPs to be moved to marine waters. However, there are very few studies that have conducted transportation modeling, particularly for freshwaters. To determine potential sources of the elevated level of pollution in the investigated area, a detailed analysis of the spatial variation of MPs is required. This would help

efforts to reduce pollution from both macro and microplastics not only on the Vaal and its catchment areas, but also on other bodies of freshwater. Furthermore, the mobility of MPs from river to river emphasizes the significance of rivers as probable pathways. This was exemplified by the tributaries namely the Klip River, Reitspruit, and Leeuspruit, feeding into the Vaal River.

Additionally, MPs have greater surface area for possible adsorption of other pollutants and the release of those contained in the particles, which pose additional health hazard associated with the possible release of additives and other pollutants contained in the MP particles are being investigated. However, exposure studies should be conducted within the South African context, with relevant environmental conditions and climate in South Africa. In addition, research should be expanded to more freshwater systems including estuaries where there are vulnerable ecosystems. This would provide more data and set a baseline for MP pollution within the country.

To mitigate MPs contamination of the aquatic environment, it is necessary to increase monitoring of freshwater systems, determine sources, pathways, and dispersal patterns. Furthermore, when developing environmental policies to combat MPs pollution, *in-situ* data and legitimate estimations should be incorporated as part of the practice. However, when managing regions affected by intensive human activities, it is essential to incorporate economic consideration together with environmental concerns. This is essential for effective policy making as well as for successful adoption by communities.

Chapter 6

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