

Thesis Report

MICROPLASTICS IN URBAN STORMWATER SYSTEMS OF WESTERN SYDNEY

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11/2021

DECLARATION

This thesis is submitted in fulfilment of the requirement for the Master of Philosophy at the School of Engineering, Design and Built Environment of Western Sydney University. The work presented in this thesis is, to the best of my knowledge and belief, original except as acknowledged in the text. I hereby declare that I have not previously submitted this material, either in whole or in part for a degree at this or any other institution. Unless otherwise stated, all the data and observations presented here are the results of my work.

Signature: 

PROJECT SUMMARY

This study assessed the extent of microplastic (MP) pollution in the stormwater catchments of Western Sydney. Studies on microplastics in Australian stormwater systems and the lack of generally accepted methods for sample collection and the isolation and quantification of microplastics, were identified as opportunities for exploration.

One of the objectives of this study was to identify and develop an acceptable method for separating microplastics from water samples. A novel procedure was developed to collect microplastics by filtering stormwater using a purpose-built single sieve (48.5 μm) mini-filtering device and cascade filtration setup, which included four steel filters with pore sizes of 48.5, 170, 2500 and 5000 μm . Additionally, the six most commonly used microplastic separation methods were selected to assess their organic matter degradation efficiency and polymer degradation potential. The method involving shaking with 30% H_2O_2 at 65 $^\circ\text{C}$ and 80 rpm for 72 h had the highest degradation efficiency (93%) with no observable polymer degradation and was selected for application to terrestrial water samples. Based on previous publications, optical microscopy and ATR-FTIR spectroscopy were determined as two reliable methods of classifying microplastics. The procedure for quantifying the microplastics retained on the filter paper was selected following a series of tests using an analytical standard polystyrene monodisperse suspension (30 μm , 1.3×10^6 MP/mL). The

results indicated that a random analysis of at least 255 mm² (26%) of the filter paper was required for accurate quantification of the microplastics.

This research also presents the first results regarding microplastics pollution in Western Sydney stormwater catchments. Sample collection and analysis were carried out in two steps: preliminary sampling and secondary sampling. Preliminary sampling was carried out in the urban lake of Woodcroft using the mini-filtration device to test the practicality of the pre-identified procedures. Woodcroft and Wattle Grove were selected as the study areas for secondary sampling. The developed methodology was applied to quantify and characterise microplastics from two retention ponds. An average concentration of 2,233 MP/m³ was observed for the preliminary samples. Polyester was identified as the most common type of microplastic (67%), and fibres were identified as the most common form (93%). During the dry and wet periods, the average microplastics concentration was 2233 and 2225 MP/m³, respectively, indicating that the difference in microplastics concentration between the wet and dry seasons was insignificant ($p > 0.05$).

Similar microplastics concentrations were observed in secondary sampling for both sites. Average concentrations of 2,067 and 2,133 MP/m³ were observed for dry and wet periods, respectively, at the Woodcroft sampling site. Similar concentrations were observed for the Wattle Grove site. The results showed a slight increase in the microplastic concentration for the wet period. Most microplastic particles were in the size ranges of 48.5–170 µm and 170–2500 µm. Polyester was significantly more abundant than other plastic types among the microplastic particles (78–94%), which was also a similar observation to that from preliminary sampling. The proportion of fibres, fragments and pellets was estimated to be 88%, 5% and 7%, respectively, for the Woodcroft site and 93%, 3% and 4% for the Wattle Grove site.

From a comparison of the data obtained in this study with those in the literature, it was apparent that the stormwater originating from these two urban catchments was considerably contaminated with microplastics. This was attributed to anthropogenic activities in urban areas. Microplastic particles in stormwater can adversely impact aquatic life present in the receiving water bodies. Also, the presence of microplastics could suggest the presence of nanoplastics in urban stormwater. These findings have implications for urban stormwater management and highlight the need for comprehensive and in-depth studies to evaluate micro- and nanoplastics in the inland water bodies of Australia.

JOURNALS ARISING FROM THIS THESIS

- 1) Microplastics in Urban Stormwater –Developing a Methodology for its Monitoring (This paper is published in Environmental Monitoring and Assessment journal (HERATH, S., HAGARE, D., SIDDIQUI, Z. & MAHESHWARI, B. 2022. Microplastics in urban stormwater—developing a methodology for its monitoring. Environmental Monitoring and Assessment, 194, 1-15))
- 2) Microplastics in Sydney Urban Stormwater catchments (Lake Woodcroft) (This is being prepared.)

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LIST OF ACRONYMS

FTIR	Fourier-transform infrared	PE	Polyethylene
HQI	Hit quality index	PMMA	Polymethyl methacrylate
IR	Infrared	PP	Polypropylene
MPs	Microplastics	SEM	Scanning electron microscope
NPs	Nanoplastics		

CHAPTER 1. INTRODUCTION

1.1. BACKGROUND

Plastic pollution has become a grave environmental concern in recent years. Accumulation of plastic and plastic particles in the aquatic systems is called plastic pollution of waters. Plastics are low-weight, flexible and versatile synthetic organic polymers that are extracted during gas and oil production (Derraik 2002). Plastics are economically profitable and the plastics industry is growing faster than ever before. In 2019, total plastics production exceeded 365 million tons globally (Statista 2021), and 40% of this is used as single-use plastic (Wright & Kelly 2017). This situation is leading to end-of-life plastic disposal problems. Polystyrene, polyethylene, polypropylene, nylon, polyvinyl chloride, polyethylene terephthalate and polymethyl acrylate are considered to be the most common plastic pollutants currently present in the environment (Gillibert et al. 2019) and it is estimated that 10% of global municipal solid waste contains discarded plastics (Barnes et al. 2009). So, plastic pollution, including plastic pollution of water—which is the accumulation of plastic and plastic particles in aquatic systems—is one of today’s most growing environmental concerns.

The ubiquitous nature of plastics in every aspect of modern society has led to the growth of the plastics industry and increased plastic disposal. Disposed plastics in the environment can break down into smaller particles by environmental and meteorological factors such as sunlight, wind, water, wave action and microbial activity (Andrady 2011). As a result of these processes, minute fragments of plastic debris are created, called microplastics (MPs) and nanoplastics (NPs). The size ranges for these particles vary from one study to another. According to Thompson et al. (2004) and Moore, Lattin and Zeller (2011), the size ranges for NP and MP particles can be 0.001 μm - 0.1 μm and 0.1 μm - 5000 μm , respectively. Imhof et al. (2013) divided plastic particles into mega (> 20 mm), macro or meso (20–5 mm) and micro (< 5 mm). Koelmans et al. (2019) classified small plastic particles from 1 nm to 5 mm into two categories: particles in the range of 1 nm to 1 μm were classified as NPs, while those from 1 μm to 5 mm were classified as MPs. This classification was used in the present study.

In urbanised or commercial areas, plastic particles can enter the water through established stormwater drainage and overflows from sewerage systems (Browne, Galloway & Thompson 2010, Browne et al. 2011). Considering the current plastic usage and disposal rate, it appears that

the accumulation of MPs in marine environments is unavoidable. This poses a potential threat to marine organisms and human health (Du et al. 2020). Abbasi et al. (2018) stated that there is a possibility of MPs accumulating in the human body through seafood consumption. World Health Organisation (WHO) has recognised the anthropological health risk of MPs in drinking water as a function of both hazard and contact. It also has recognised the prospective risks associated with MPs are as physical, chemicals (additives, and attached compounds from the environment), and microbes that may settle on MPs (Marsden et al., 2019). It has been suggested that the uptake of MPs can damage the digestive tract and cause toxicity, resulting in adverse human health effects and even death (Abbasi et al. 2018). Hidalgo-Ruz et al. (2012) stated that MPs provide a vehicle for persistent, bio-accumulative and toxic compounds (PBT) and can cause serious human health effects if they enter the human body.

The above research suggests that it is imperative to understand the presence of MPs in inland water bodies. Table 2.2 summarises the MP concentrations in water bodies reported around the globe, with most studies detecting MP particles larger than 10 μm . There was an extensive range of concentrations reported, starting from a few particles per m^3 to a few million per m^3 . One of the reasons for the dissimilar concentrations was attributed to the significant variations in the lower cut-off size used in these studies; very few included smaller cut-off sizes of between 10 and 50 μm (Table 2.2; Liu et al. 2021; Piñon-Colin et al. 2020; Järslskog et al. 2020; Liu et al. 2019; Olesen et al. 2019; Hu et al. 2018; Di & Wang 2018; Wang et al. 2017). Most of the studies (Anderson et al. 2017; Baldwin, Corsi & Mason 2016; Su et al. 2016; Fischer et al. 2016; Mani et al. 2015; Dris et al. 2015; Free et al. 2014; McCormick et al. 2014; Lima, Costa & Barletta 2014; Eriksen et al. 2013; Moore, Lattin & Zeller 2011) quantified MPs in terrestrial water samples using manta trawls, and neuston and plankton nets, with an average mesh size of 300 μm . These methods did not retain particles smaller than 300 μm and were also associated with contamination of the samples as the nets used were plastic. Some studies (Liu et al. 2019; Piñon-Colin et al. 2020; Wang et al. 2017) used single-layer 10, 25 or 50 μm steel sieves. These studies used smaller volumes of water samples due to the problem of filter clogging when a large volume of water samples was filtered. The studies presented in Table 2.2 mainly cover North American, European and Asian regions.

Direct overflow which originates from impermeable surfaces and waterlogged soil is acknowledged as stormwater runoff (Ferguson, 1998). Urban impervious surfaces transform rainfall to stormwater runoff, which causes water quality complications (Berland et al., 2017).

Urban and highway stormwater runoff provides a direct pathway for MPs to enter other terrestrial water systems and is a primary contributor to marine MPs (Liu et al., 2019). As shown in Table 2.2, some studies (Järnskog et al. 2020; Pinon-Colin et al. 2020; Olesen et al. 2019; Su et al. 2016) reported close to or over a million MP particles in one m³ of stormwater; indicating high levels of MPs in storm and lake waters. In contrast, river water was reported to contain relatively lower MP levels, ranging from 58 to 12932 MP/m³ (Rodrigues et al. 2018; Moore, Lattin & Zeller 2011).

It is evident from all these studies that the three critical parameters for quantifying MP pollution are size, concentration and type. Researchers have implemented different techniques and methods to determine these parameters (Liu et al. 2019; Wang et al. 2017; Rodrigues et al. 2018; Fischer et al. 2016) and there are no universally accepted procedures. Hence, the identification or development of efficient methods for isolation, identification and quantification of MPs is urgently needed.

The literature review revealed some shortcomings of the existing body of research. First, most studies did not use a cascade of filters for collecting MP particles from the water sample. Using one filter with a small pore size can minimise the removal of plastic particles due to clogging, which is most significant if the MPs being collected are smaller than 50 µm. Second, there is no comparative analysis of the various treatment methods that can be used to remove potential interfering contaminants. Third, there are no benchmarking studies on the filtration process, which needs to be considered for manual counting of MPs particles. Fourth, there are no studies on the presence of MPs in Australian stormwater systems. And finally, as shown in Table 2.2, very few studies determined the type of MPs.

Hence, widespread in-depth studies are urgently needed to bridge these knowledge gaps and enable the more comprehensive risk assessment of MPs in inland waters. These will support the relevant authorities in policy development to address this issue. Therefore, this study aimed to identify and develop methods for sampling, isolation, identification and quantification of MPs to understand the extent of MP pollution in Australian urban stormwater systems under dry and wet weather conditions. Australian stormwater retention ponds are designed to capture runoff from fully-developed urban areas. They are designed considering ecosystem health, flooding and drainage control, public health and safety, economic considerations, recreational opportunities, social considerations and aesthetic values (Australian Guidelines for Urban Stormwater Management,

2021). Thus, the stormwater from these retention ponds could potentially contain significant concentrations of MPs resulting from anthropogenic activities in the urban area.

1.2. AIMS

This study aims to recognize and develop acceptable methods to isolate, identify and quantify the MPs found in the terrestrial water samples. Furthermore, the study aims to investigate MPs in Western Sydney urban stormwater catchments to identify future research needs relating to Australian terrestrial water MP contamination.

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1.3. SCOPE

Initially, a comprehensive literature review on freshwater MP studies was conducted and the findings summarised. The MP isolation, identification and quantification techniques used in various studies were identified. The most commonly used MP isolation methods were tested to select the most efficient technique to apply in field sampling. The most suitable MP identification and characterisation methods from previous studies were applied in the present work and laboratory experiments were conducted to develop a standard quantification method for MPs.

Two sampling locations were identified to cover Western Sydney stormwater catchments. These stormwater catchments were Lake Woodcroft, in the Sydney suburb of Woodcroft, New South Wales, Australia, and Wattle Grove Lake, in the Sydney suburb of Wattle Grove, New South Wales, Australia. Based on the selected water sampling technique, the sampling and filtration apparatus were fabricated. Preliminary sampling was conducted at one sampling site and samples were analysed using the pre-identified isolation quantification, and identification techniques to evaluate these procedures. The results were documented and analysed. Secondary sampling was then conducted at the identified sites and samples were subjected to treatment and analysis procedures. Analysis of the results was carried out to characterise the presence of MPs in Sydney surface water catchments.

The characterisation was undertaken at the Advanced Materials Characterisation Facility (AMCF) of the Western Sydney University (WSU) via optical microscopy and ATR-FTIR spectrometry.

CHAPTER 2. LITERATURE REVIEW

A literature review on the topics of MPs and NPs was performed using Google Scholar and the UWS library databases. Some of the other areas explored were the physical and chemical characteristics of MPs and NPs, contamination methods, interaction with aquatic flora and fauna, and the effects of MP and NP pollution on humans. Studies on MP identification and quantification were also retrieved and the procedures were documented and summarised for preliminary testing. The literature search was carried out using keywords such as microplastics (MPs), nano plastics (NPs), plastics breakdown, plastic classification, plastic contamination, microplastics sampling techniques, marine microplastics, microplastics isolation techniques, microplastics identification, FTIR, optical microscopy, raman spectroscopy, plastics in freshwater, microplastics and effect on human, plastic effect on flora and fauna and a combination of these terms. More than 140 scientific publications were considered and 100 papers were included in this work.

2.1. PLASTICS POLLUTION

Since 1600 BC, when the ancient Mesoamericans first processed natural rubber into balls, humans have benefited from polymers (Hosler, Burkett & Tarkanian 1999). In the following years, man has become increasingly dependent on plastics and rubber, experimenting with applications of natural rubber, resins, natural polymers and waxes. The initial expansion of the plastics industry occurred in the first half of the twentieth century during which at least 15 new classes of polymers were created (Andrady & Neal 2009).

At present, plastics are mainly prepared by the polymerisation of monomers derived from the gas and oil industries, and usually with the addition of various chemical additives (Thompson et al. 2009). Plastics have properties such as corrosion resistance, versatility, light weight, strength, durability, bendability and high insulation. These properties facilitate the manufacture of a vast range of products with various economic and social benefits (Derraik 2002; Andrady & Neal 2009) and, together with the low cost of plastics, have driven an annual worldwide demand for plastics exceeding 320 million tons globally in 2017 and 368 million tons in 2019 (Statista 2021). Although hundreds of plastic polymers are available today, only a small number of these meet the requirements of commodity plastics in terms of their high volume and relatively low price (Andrady & Neal 2009). Low-density polyethylene (LDPE), high-density polyethylene (HDPE), polypropylene (PP), polyvinyl chloride (PVC), polystyrene (PS) and polyethylene terephthalate

(PET) account for approximately 90% of the total demand for commercial plastics (Andrady & Neal 2009). Applications of plastics are only expected to increase as more innovative plastics and products are developed to meet demands.

The surging use and manufacture of plastics in developing and emerging countries have also become a global concern (ENV, 2011). It is estimated that 8.3 billion tons (Bt) of plastics were produced from 1950 to 2015 and 5.7 Bt were discarded as waste (Barnes et al. 2009), including 4.9 Bt that was discarded into landfills or the natural environment such as oceans and waterways (Barnes et al. 2009). According to Gordon (2006), plastics are considered the most common type of marine debris, constituting 60% to 80% of all marine debris and over 90% of all floating particles. Based on the current plastic use and disposal rate, MP accumulation in marine environments is unavoidable. This poses potential threats to the survival of marine organisms and human health (Du et al. 2020).

Table 2. 1 Common plastic polymers and their densities (adapted from Hidalgo-Ruz et al. 2012)

Plastic Polymers	Density (g/cm³)
Polypropylene (PP)	0.9–0.91
Polyethylene (PE)	0.917–0.965
Polyamide (PA)	1.02–1.05
Polystyrene (PS)	1.04–1.1
Acrylic	1.09–1.20
Polymethyl acrylate (PMA)	1.17–1.20
Polyurethane (PU)	1.2
Polyvinylchloride (PVC)	1.16–1.58
Polyvinyl alcohol (PVA)	1.19–1.31
Alkyd	1.24–2.3
Polyester	1.24–2.3
Polyethylene terephthalate (PET)	1.37–1.45
Polyoxymethylene (POM)	1.41–1.61

2.2. TYPES OF MPs AND PLASTIC BREAKDOWN

MPs found in water originate from diverse sources and are categorised as primary MPs or secondary MPs, depending on their origin.

2.2.1 PRIMARY MPs

Primary MPs are engineered to be small in size. Synthetic fibres, polystyrene beads found in personal care products, industrial scrubbers used in abrasive cleaning agents and plastic powders used for moulding are some of the common primary MPs (Boucher & Friot 2017)

2.2.2 SECONDARY MPs

Usually, plastics do not fully degrade but break down into smaller fragments (Auta et al. 2017b). Some of these plastic particles are called MPs (Cole et al. 2011). Secondary MPs results from the fragmentation of larger plastic debris after being released into the environment (Mani et al. 2015). Disintegration also can occur during the use of plastic products such as tyres, paint and textile materials (Anderson et al. 2015). When the particles are in the range of to 5 mm to 1 μ m they are called secondary MPs (Gillibert et al. (2019).

2.2.3 PLASTIC BREAKDOWN AND MPS

Broken down plastic particles are called mesoplastics when the particles are larger than 5 mm (Andrady 2011; Cole et al. 2011). These mesoplastics further degrade into smaller particles called MPs and NPs (Andrady 2011; Cole et al. 2011). Degradation results in a chemical change that significantly decreases the average molecular weight of the polymer. Since the mechanical integrity of plastics is significantly dependent on the average molecular weight of their polymer constituents, degraded plastics are brittle and fall apart into powdery particles on handling (Andrady 2011). The degradation of plastics is usually categorised based on the cause; that is, biodegradation, photodegradation, thermooxidative degradation, thermal degradation, chemical degradation—including hydrolysis—and physical degradation. Biodegradation is due to the actions of living organisms, usually microorganisms such as phytoplankton, bacteria and fungi (Jahnke et al. 2017). Photodegradation occurs when the sunlight comes into contact with plastic. Thermooxidative degradation is the slow oxidative breakdown of plastics at moderate temperatures. Thermal degradation occurs when plastics are exposed to high temperatures. Chemical and physical degradation processes are driven by factors such as physical stress, ultraviolet (UV) radiation, fluctuating temperatures, salinity and oxidising conditions (Jahnke et

al. 2017). Hydrolysis is the process of reacting plastics with water and is not considered an environmental degradation mechanism (Andrady 2011)

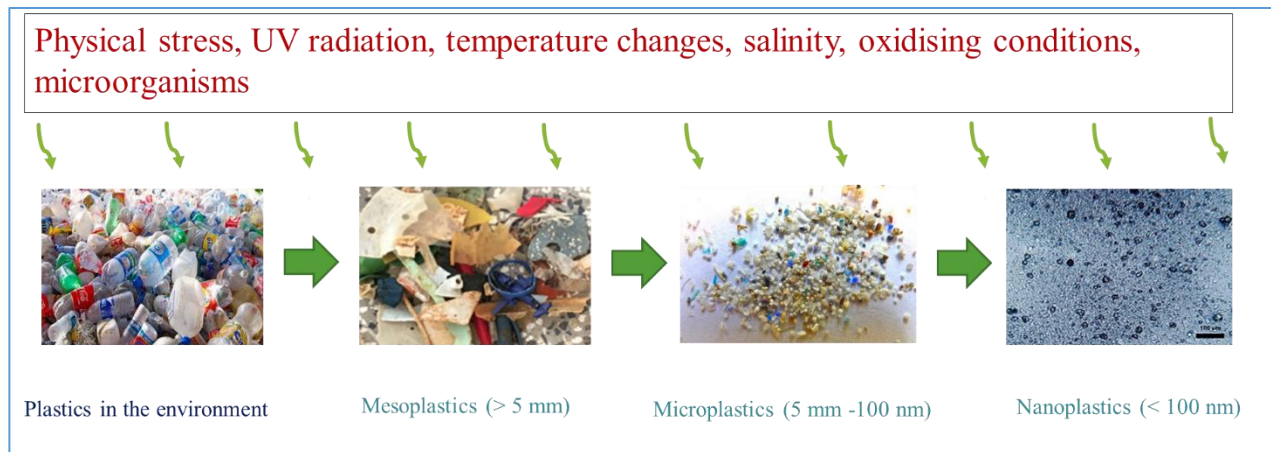


Figure 2.1 Degradation of plastic (Adapted from Jahnke et al. 2017)

2.3. SIZE-BASED CLASSIFICATION OF PLASTIC PARTICLES

A universal scale for the demarcation of MP and NP particles is still to be confirmed, and scientists have different opinions on this matter. This is apparent in research on MPs and NPs, where different studies have used different size categories. According to Thompson et al. (2004) and Moore, Lattin and Zeller (2011), the sizes of NPs and MPs are 0.001 to 0.1 μm and 0.1 μm to 5 mm, respectively. Some scientists divide plastic particles into mega debris (> 20 mm), macro (meso) debris (20–5 mm) and micro debris (< 5 mm) with an indeterminate lower limit for the microparticle size (Imhof et al. 2013).

According to Gillibert et al. (2019), MPs are divided into three categories. Particles in the range of 5 to 1 mm are called large MPs, while particles in the range of 1 mm to 20 μm and 20 μm to 1 μm are called small and sub-20 μm MPs, respectively. The International Organization for Standardization (ISO; ISO 2015) defines the term ‘nanomaterial’ as a material with any outer measurement or internal surface assembly on the nanoscale; that is, in the range of 1 to 100 nm (Dolez 2015). Considering the references, we suggest delimiting MPs and NPs as being in the range of 5 mm to 100 nm and 100 to 1 nm, respectively.

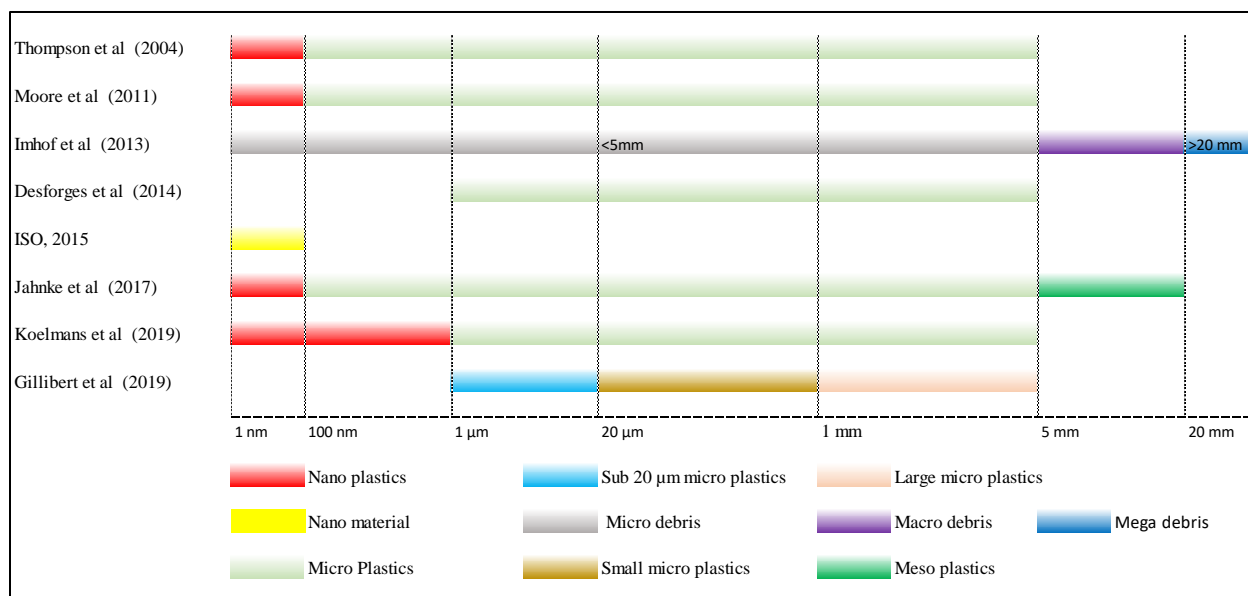


Figure 2.2 Size-based definition of plastics, proposed by different authors (Thompson et al. 2004; Moore, Lattin & Zeller 2011; Imhof et al. 2013; Desforges et al. 2014; ISO 2015; Jahnke et al. 2017; Koelmans et al. 2019; Gillibert et al. 2019)

2.4. ENVIRONMENTAL PRESENCE OF MPS

Primary MPs have been identified as a significant input of MPs to terrestrial environments (Boucher & Friot 2017). MPs from personal care products designed for gentle friction, such as soap, hand and facial cleansers, toothpaste, shower gels and deodorants, the mixtures used for sandblasting and shot blasting, MPs employed as pharmaceuticals vectors and in 3D printing are some examples of primary MPs (Fendall & Sewell 2009; Picó & Barceló 2019).

MPs enter freshwater environments in many ways. The primary way is from surface runoff and wastewater effluent (both treated and untreated), but other ways include combined sewer overflows, industrial effluent, sewage treatment runoff during high-volume rainfall episodes, degraded plastic waste and atmospheric deposition (Horton et al. 2017; Browne, Galloway & Thompson 2010; Browne et al. 2011). In isolated and undeveloped areas, MPs are more likely to be introduced through the degradation and destruction of plastic consumer products that are gusted or washed into the water from shore (Coe & Rogers 2012; Ryan et al. 2009). MPs have been detected in superficial water columns and sea sediments, globally (Van Cauwenberghe et al. 2015). Various studies have also confirmed the worldwide presence of MPs in rivers and lakes, and at very high levels (Auta et al. 2017a). Details of some of the studies carried out on terrestrial water MPs are listed in Table 2.2.

Table 2.2 Recent studies on Micro-plastics in freshwater systems

Reference	Location	Sampling technique	Sampling depth	Cut-off size (μm)	Purification technique	Filters for substrate separation	Identification technique	Level and nature of pollution
Liu et al. (2021)	Surface water of the Qinghai-Tibet Plateau	Sampling bottle and 20 μm stainless steel mesh	0.5 m	20	30% H_2O_2 solution at 70 °C for 72 h	0.45 μm (GF/F, 47 mm \emptyset , Whatman)	Stereo microscopy	856 MP/m^3
Piñon-Colin et al. (2020)	Stormwater runoff in Tijuana, Mexico	Grab samples collected in 1 L bottles	Stormwater runoff	25	–	Glass fibre filter (Whatman 696)	Optical microscopy and FTIR-ATR spectroscopy	6.6×10^4 to 1.95×10^5 MP/m^3
Järnskog et al. (2020)	Runoff from pavement in Gothenburg, Sweden	Automatic ISCO sampler	–	20				20–100 μm : 1.5×10^6 to 6×10^6 MP/m^3 >100 μm : 1×10^3 to 2×10^3 MP/m^3
Liu et al. (2019)	Retention ponds, Denmark	10 μm stainless steel mesh	0.2 m	10	500 mL of SDS solution + 50 mL of 50% H_2O_2 + ultrasonic treatment; particles collected into 200 mL of SDS solution + (Cellubrix + Viscozyme) at 50 °C for 3 days + Alcalase at 50 °C for 3 days + 146 mL of 50% H_2O_2 , 63 mL of 0.1 M FeSO_4 and 65 mL of 0.1 M NaOH (15–19 °C) for 4 h	10 μm stainless steel	μ -FTIR imaging	490 – $22,894$ MP/m^3 , 85 – $1,143$ $\mu\text{g}/\text{m}^3$ (10–2000 μm)
Olesen et al. (2019)	Stormwater retention ponds in Viborg, Denmark	5 L sampling bottles	0.5 m	10	60 mL of 5 M KOH per 1 g (dry weight) of sample	–	FTIR imaging	2.7×10^5 MP/m^3

Reference	Location	Sampling technique	Sampling depth	Cut-off size (μm)	Purification technique	Filters for substrate separation	Identification technique	Level and nature of pollution
Gilbreath et al. (2019)	Bioretention rain garden located in San Francisco Bay Area, USA	Two stacked sieves (355 μm and 125 μm)	Samples from inlet and outlet	125	–	500 μm and 106 μm sieves and 20 μm polycarbonate filter	Visual observation and Raman spectroscopy	1,600 MP/m ³
Hu et al. (2018)	Small water bodies from the Yangtze River Delta, China	5 L glass bottle	0–0.1 m	20	100 mL of 30% H ₂ O ₂ at 65 °C and 80 rpm for no more than 72 h	47 mm diameter polycarbonate filter with a 5 μm pore size	SEM and ATR-FTIR spectroscopy	480–21,520 MP/m ³
Rodrigues et al. (2018)	Antuã River in Portugal	Pump and nylon mesh net (0.01 m ²)	Surface and bottom	55	30% H ₂ O ₂ with 0.05 M Fe(II) catalyst at 75 °C for 5/10 min, until boiling, then continued at room temperature for 15 h.	0.45 μm membrane filter	ATR-FTIR Stereomicroscopy	5–8.3 mg/m ⁻³ or 58–193 MP/m ⁻³ in March and 5.8–51.7 mg/m ⁻³ or 71–1,265 MP/m ⁻³ in October
Wang et al. (2017)	Urban waters of Wuhan, China	Stainless steel sieve	0–0.2 m	50	30% H ₂ O ₂ , room temperature in the dark for 24 h	0.45 μm (GF/F, 47 mm Ø, Whatman)	SEM, FT-IR (MCT detector in a wavenumber range of 8000–50 cm ⁻¹)	1,660.0 ± 639.1 MP/m ³ to 8,925 ± 1,591 MP/m ³ ; fibres, granules, films and pellets

Reference	Location	Sampling technique	Sampling depth	Cut off size (μm)	Purification technique	Filters for substrate separation	Identification technique	Level and nature of pollution
Di and Wang (2018)	Three Gorges Reservoir (TGR), China	Teflon pump with stainless steel sieve	1 m	48	30% H_2O_2 for 12 h	0.45 μm glass microfibre filter	Optical microscopy and micro-Raman spectroscopy	1,597–12,611 MP/m^3
Anderson et al. (2017)	Lake Winnipeg, Canada	manta trawl 61 cm wide by 18 cm high 3 m long	0–0.3 m	333	20 mL of 0.05 M Fe (II) solution, 20 mL of 30% H_2O_2 at 75 °C for 30 min, covered loosely with tin foil for 24 h	250 μm brass sieve	Microscopic visualisation + SEM-EDS	Mean abundance 193,000 MP/km^2
Wang et al. (2017)	Hanjiang River, Yangtze River of Wuhan and Bei Lake of central China	Teflon pump and stainless steel sieve	0–0.2 m	50	30% H_2O_2 , room temperature in the dark for 24 h	0.45 μm glass microfibre filter	Stereoscopic microscope visualisation and FTIR	1,660.0 \pm 639.1 to 8925 \pm 1,591 MP/m^3
Baldwin, Corsi & Mason (2016)	29 Great Lakes tributaries, USA	Neuston net (100 cm \times 40 cm)	0.2–0.35 m	333	30% H_2O_2 in the presence of an iron (II) catalyst	125 μm mesh sieve	Microscopic visualisation	0.05–32 MP/m^3 ; 72% were in 0.355–0.99 mm range and 26% were in 1.0–4.75 mm range
Su et al. (2016)	Taihu Lake China	Nylon plankton net diameter 0.65 m, length 1.55 m Bulk water 5 L	0–0.3 m	333	30% H_2O_2 in a glass bottle in a shaking incubator at 65 °C and 80 rpm for 72 h	100 μm polycarbonate filter 5 μm polycarbonate filter	Microscopic visualisation and μ -FT-IR or SEM/EDS	0.01 \times 10 ⁶ to 6.8 \times 10 ⁶ MP/km^2 ; 100–1,000 μm 3.4–25.8 MP/L

Reference	Location	Sampling technique	Sampling depth	Cut off size (μm)	Purification technique	Filters for substrate separation	Identification technique	Level and nature of pollution
Fischer et al. (2016)	Lake Bolsena and Lake Chiusi, Italy	Manta Trawls (60 cm \times 18.5 cm)	0–0.3 m	300	HCl for 48 h at room temperature and 70 °C for 1 h, 0.7–2.5 mL of a lipophilic dye (1 mg/mL Nile red in acetone)	5–13 μm qualitative filter (413, VWR International)	Optical microscopy, SEM	Lake Chiusi: 2.68–3.36 MP/m ³ ; Lake Bolsena: 0.82–4.42 MP/m ³ (43% in the 1.0–5.0 mm range)
Estahbanati & Fahrenfeld (2016)	Raritan River, USA	Plankton nets (0.2 m diameter, 0.51 m long)	0–0.3 m	153	20 mL of 0.05 M Fe (II) solution and 20 mL of 30% H ₂ O ₂ at 75 °C for 30 min; NaCl ₂ added to increase mixture density	4000, 2000, 500, 250, 125 and 63 μm sieves	Optical microscopy	–
Mani et al. (2015)	Rhine River along the 820 km stretch	Manta net (60 x 18 cm)	–	300	H ₂ O ₂ + enzymes (protease, amylase, lipase, cellulase)	300 μm mesh	FTIR, resolution of 4 cm ⁻¹ , 32 scans, gain range radius of 40 and sensitivity of 1	Mean value of 892,777 MP/km ⁻²
Dris et al. (2015)	Greater Paris	Plankton net	0–0.35 m	80	-	1.6 μm glass fibre GF/A Whatman filters	Visualisation (Histolab image analysis software)	3–108 MP/m ³
		Manta trawl	0–0.3 m	330	-	1.6 μm glass fibre GF/A Whatman filters	Visualisation (Histolab image analysis software)	0.28–0.47 MP/m ³
Free et al. (2014)	Lake Hovsgol, in the mountains of northern Mongolia	manta trawl with a rectangular opening	0 - 0.3 m	333	30% H ₂ O ₂ in the presence of an iron (II) catalyst.	Tyler sieve	Optical microscopy	20,264 MP/ km ²

Reference	Location	Sampling technique	Sampling depth	Cut off size (μm)	Purification technique	Filters for substrate separation	Identification technique	Level and nature of pollution
McCormick et al. (2014)	North Shore Channel, Chicago, USA	Neuston nets (0.92×0.42 m and 0.36×0.41 m)	0–0.3 m	333	30% H_2O_2 in the presence of an iron (II) catalyst, 75°C	2 mm and $330 \mu\text{m}$ stacked sieves	Optical microscopy, SEM	0.73×10^6 to 6.698×10^6 MP/Km ²
Lechner et al. (2014)	Austrian Danube between Vienna and Bratislava	Stationary conical driftnets (0.5 m diameter, 1.5 m long, mesh)	0.5 m	500	–	–	Optical microscopy (Zeiss Axio Imager M1 with Axio Vision 4.8.2 software)	0.3168 MP/m ³ , 0.0048 ± 0.00242 g/m ³
Lima, Costa & Barletta (2014)	Goiana Estuary, Brazil	conical plankton net ($\varnothing 0.6$ m; 2 m long)	Superficial and bottom	300	–	$45 \mu\text{m}$ mesh	Optical microscopy	0.2604 MP/m ³ , mean size 2.23 ± 1.65 mm
Eriksen et al. (2013)	Laurentian Great Lakes, USA	Manta trawl $16 \text{ cm} \times 61 \text{ cm} \times 3 \text{ m}$	0–0.3 m	333	2 M HCl for 24 h	0.355 , 1.00 and 4.749 mm Tyler sieves	SEM-EDS	$43,157$ MP/km ² ; 81% in 0.355 – 0.999 mm range; 17% in 1 – 4.749 mm range; 2%
Moore, Lattin & Zeller (2011)	Los Angeles River, San Gabriel River, Coyote Creek, USA	Manta net, handheld nets	0–0.3 m	800, 500, 333	–	4.75 , 2.8 and 1.0 mm Tyler sieves	Optical microscopy	$12,932$ MP/m ³ 411 MP/m ³ 153 MP/m ³ 4.75 mm in size

2.5. MPs AND ENVIRONMENTAL POLLUTION

MPs have recently been acknowledged as an evolving global problem that affects marine organisms and even humans (Auta et al. 2017a). As the particle size decreases, the availability and potential to accumulate in the food chain increases (Scherer et al. 2017). MPs are abundant in water bodies and are consumed by various aquatic organisms (Murphy et al. 2016). According to Wu, Yang and Criddle (2017), the top 1 mm of the sea surface microlayer (SML) accumulates more light MPs (< 330 µm), including alkyd, poly(acrylate/styrene), PS, PE and polyester. Laboratory trials have demonstrated that aquatic invertebrates can consume these microscopic plastic particles due to diverse feeding habits. It is identified that polychaetes, bivalves, echinoderms and copepods all—in at least one life stage taking up MPs from the environment (Graham & Thompson 2009). MPs are also ingested by a variety of marine organisms, from invertebrates to fish, which has many implications (Lusher, McHugh & Thompson 2013). Low numbers of MPs were recovered from tissue from a laboratory experiment performed on *Mytilus edulis* and *Crassostrea gigas*. The average MP load in an organism of *M. edulis* was 0.36 ± 0.07 particles per gram of soft tissue (wet weight, WW) and in *C. gigas* was 0.47 ± 0.16 particles per gram of soft tissue (WW) (Van Cauwenberghe & Janssen 2014).

2.6. MPs AND HUMAN HEALTH

Existing knowledge of the effect of plastic particles on humans is still primitive (Vethaak & Leslie 2016). Due to their broad range of sizes, the effects of MPs and NPs on organisms can be diverse. Existing studies show that plastic particles can cause lung and gut injury, and the smallest particles can cross cell membranes, the blood-brain barrier and the human placenta (Vethaak & Leslie 2016). MPs can also adsorb persistent, bioaccumulative and toxic compounds (PBT; Hidalgo-Ruz et al. 2012). Scientists at the Austrian Environment Agency and the University of Vienna analysed stool samples of people from eight countries and found that every sample contained MPs. In some cases, nine different plastic types were found in a single sample. On average, 20 MP particles ranging in size from 50 to 500 µm per 10 g of human waste were found (Parker 2018). Recently, a group of researchers have analysed six human placentas, collected from females with pregnancies to witness the existence of MPs. In this study, in total, 12 MPs particles (from 5 to 10 µm) were observed in placentas (Ragusa et al., 2021).

Another recent study revealed the existence of PP particles in media (Dulbecco's Modified Eagle Medium method). Particularly, those particles below 20 μm , were observed to be cytotoxic to Peripheral blood mononuclear cells (Hwang et al., 2019). Another study showed that nylon fibres and high-density polyethylene (HDPE) can disrupt the epithelial barrier. It also has revealed that luminal exposure to polystyrene particles (1 and 10 μm) and pristine HDPE fragments ominously decline human colon tissue functionality (Donkers et al., 2022).

Due to the way plastic commodities are produced, plastic particles can potentially contain chemical additives (Wright & Kelly 2017). These particles and their additives, potentially including persistent organic pollutants (POPs), endocrine-disrupting chemicals (EDCs), carcinogens and heavy metals, can enter the human body via direct contact, ingestion or inhalation. These substances can have a range of adverse health impacts. (Wright & Kelly 2017). Therefore, plastic pollution has become a cascade of concerns.

2.7. SAMPLE COLLECTION FOR MPs AND NPS

Since plastic pollution is found in various terrestrial and marine environments, MP and NP contamination can be found in various locations (Schwaferts et al. 2019). The analytical points of significance include the type of sample, the plastic particle concentration and size, the mass of plastic particles and the volume of the sample. Samples can range from sediments, terrestrial waters, marine waters, drinking water, wastewater treatment plant (WWTP) effluent and biota tissue, which contain considerably different concentrations and diversity of MP and NP particles (Wang & Wang 2018). However, as plastic particles are pervasive in the environment, there is a high possibility of sample contamination throughout sample collection and preparation. Therefore, appropriate procedures to minimise contamination during these processes are required.

Sample collection from water can be from the surface or at specific depths, and researchers have employed numerous methods in this process. Most techniques are based on volume-reduced methods (Wang & Wang 2018). For the collection of samples from surface water, manta trawls and neuston nets are frequently used, while for sampling from the water column, plankton nets, bongo nets, multiple opening-closing nets and near-bottom trawls are the primary techniques (Wang & Wang 2018; Anderson et al. 2017; Baldwin, Corsi & Mason 2016; McCormick et al. 2014). Other tools have occasionally been employed for surface water sampling, such as water intake pumps, water collection bottles and handheld nets (Di & Wang 2018; Su et al. 2016; Moore, Lattin & Zeller 2011). The filter (mesh) size of sampling tools

differs from microns to millimetres, with 333 μm being the most common aperture size used by researchers (Dris et al. 2015; Free et al. 2014; Eriksen et al. 2013; McCormick et al. 2014). The mesh size of the sampling tool directly influences the abundance of MPs recovered from the water medium. For example, it was determined that an 80 μm net could retain up to 250 times the concentration of plastic fibres than a 330 μm mesh (Dris et al. 2018). As the majority of the current sampling procedures are only appropriate for collecting MPs within specific size ranges, the use of various sampling tools with different mesh sizes makes it challenging to compare the observed data (Wang & Wang 2018).

2.8. SAMPLE PREPARATION FOR MP AND NP ANALYSIS

2.8.1. REMOVAL OF ORGANIC FRACTION FROM THE SAMPLE

The density of organic matter is similar to that of most plastics and needs to be removed separately as organic compounds can impede MP analysis. The separation methods used to separate NPs from the sample are similar to those used for MP separation (Schwaferts et al. 2019) and include the following.

Acid treatment

- a) Samples are treated with HNO_3 (65%, 1 mL) at 70 °C for 2 h and then diluted with deionised (DI) water to a final volume of 5 mL (Eriksen et al. 2013).
- b) Samples are treated by soaking in HCl (2 M) for 24 h at room temperature (Eriksen et al. 2013).

Oxidising agents (H_2O_2)

- a) Samples are treated with aqueous 0.05 M Fe(II) solution (20 mL), which is prepared by adding $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (7.5 g) to water (500 mL) and concentrated sulphuric acid (3 mL). Then, H_2O_2 (30%, 20 mL) is added and the solution is heated to 75 °C for 5–10 min until it boils. The reaction is continued at room temperature for 15 h (Rodrigues et al. 2018).
- b) Samples are treated with H_2O_2 (30%) in a conical glass flask left in a shaking incubator at 65 °C and 80 rpm for 72 h (Su et al. 2016).
- c) Samples are treated with H_2O_2 (30%) at room temperature in the dark for 24 h (Wang et al. 2017).
- d) Samples are stirred in with Fe (II) solution containing H_2O_2 (30%) at 75 °C for 30 min then covered loosely and left for 2 h at room temperature (Anderson et al. 2017).

Alkali digestion

- a) Samples are treated with NaOH (1 M) for 1 h at 60 °C (Catarino et al. 2017).

Enzymatic digestion

- b) Samples are treated with proteinase K at 50 °C for 2 h (Cole et al. 2014).

2.8.2. PRE-CONCENTRATION BEFORE CHARACTERISATION AND IDENTIFICATION

Even though a sample volume can be very large, the number of plastic particles present in the sample can be meagre (Ter Halle et al. 2017). Therefore, to enable the presence of plastic particles in most types of samples to be accurately estimated, a preconcentration step is required (Schwaferts et al. 2019).

Membrane filtration

Filtration of the sample using a series of membrane filters is called membrane filtration. Membrane filters made from diverse materials (e.g., aluminium oxide, ceramics, polycarbonate, glass fibre, stainless steel) are commercially accessible with pore sizes ranging from a few mm to 0.01 mm (Schwaferts et al. 2019). Sometimes these membranes are used in a sequence of pore sizes, and this filtration cascade can help avoid rapid clogging of the pores (Hernandez, Yousefi & Tufenkji 2017).

Ultrafiltration

Ultrafiltration is a form of membrane filtration in which hydrostatic pressure forces a liquid against a semi-permeable membrane. Suspended particles and solutes of high molecular weight are retained, while water and low molecular weight solutes pass through the membrane. Ultrafiltration uses nanoporous films that have a molecular weight cut-off in the range of 10e100 kDa (which roughly corresponds to 5–50 nm). This method has a high potential for the processing of environmental samples because it can process large volumes of water up to the m³ range (Schwaferts et al. 2019).

Ultracentrifugation

Ultracentrifugation is a specialised technique used to spin samples at exceptionally high speeds. As it relies on mass and the fundamental law of gravitation, it has broad applicability (Laue &

Stafford 1999). Modern ultracentrifuges can spin as rapidly as 150,000 rpm and can be used to deposit suspended particles as a pellet. The high centrifugal force of ultracentrifuges is essential to deposit tiny plastic particles on the sub-micron and NP scale, as their densities are near that of water. This procedure is readily accessible and straightforward to use but can only process small sample volumes (Schwaferts et al. 2019).

Evaporation of solvent

Solvent evaporation at reduced pressure, usually with a rotary evaporator, is a method from nanoparticle synthesis and is particularly useful for organic solvents (Vauthier & Bouchemal 2009). As this method does not eliminate dissolved material and is inefficient for removing large volumes of water, it may primarily apply to pre-concentrated suspensions (Schwaferts et al. 2019).

2.8.3. METHODS FOR CHARACTERISATION IMAGING AND IDENTIFICATION OF MPs AND NPS

Some of the methods for the pre-concentration, separation, characterisation, imaging and chemical identification of MPs and NPs are tabulated in Tables 2.3, 2.4 and 2.5.

Table 2.3 Methods for the pre-concentration and separation of MPs and NPs. (Adopted from Schwaferts et al. 2019)

Task	Technique	Range	Advantages	Disadvantages
Pre-concentration	Membrane filtration	> 10 nm	Easily available, cheap	Low flow rates with small pores, small volumes
	Ultrafiltration	10–100 kDa, ca. 5–50 nm	Large volumes, minimal sample damage/aggregation, minimal membrane clogging/fouling	Interaction with membrane Setup not plastic-free
	Dialysis	5–50 nm	Mild conditions	Slow, large volume of counter dialysing medium Risk of microbial contamination
	Ultracentrifugation	Any	Simple washing of particles with centrifugation and redispersal	Harsh conditions, no separation from the particulate matrix Difficult to obtain a complete separation
	Analytical ultracentrifugation	1 nm–1 µm	Can provide much information, multiple detectors	Best for small particles
	Evaporation of solvent	Any	Cheap, easy	Does not remove dissolved matter Superheating
Separation	Asymmetric flow field-flow fractionation	1 nm–1 µm	No stationary phase, sample focusing, online coupling	Operation difficult, interaction with membrane, steric inversion
	Hydrodynamic chromatography	5 nm–1.2 µm	Less interaction with a stationary phase Coupled detectors	Infrequently used
	Size exclusion chromatography	1 nm–100 nm	Coupled detectors	Stationary phase, small range
	High-performance liquid chromatography	1 nm–40 nm	Coupled detectors	Stationary phase, small size range
	Capillary electrophoresis	5 nm–500 nm	High separation resolution, coupled detectors, fast	Charge required, electrolyte/surface modification, interaction with capillary/clogging, may damage the sample, complex matrices difficult

Table 2.4 Techniques for the characterisation and imaging of MPs and NPs (Adopted from Schwaferts et al. 2019)

Task	Technique	Information	Range/Limits	Advantages	Disadvantages
Characterisation	Dynamic Light Scattering	Size, particle size distribution, aggregation behaviour	1 nm–3 mm conc. 10^{-6} e 10^{-1}	Fast, cheap, in situ, non-invasive, aggregation, direct coupling	Large particles, polydispersity, complex matrix, non-spherical particles
	Electrophoretic Light Scattering	Surface charge, stability	1 nm–3 μ m	Fast, cheap, non-invasive, with DLS	Electro-osmotic effect Sensitive to environment
	Multi-Angle Light Scattering	Size (d_g), particle size Distribution	10 nm–1,000 nm	Online coupling	Requires clean samples
	Laser Diffraction	Size	10 nm–10 mm, conc. 10^{-5} e 10^{-1}	Large size range, easy, fast, automated	Only spherical model
	Nanoparticle Tracking Analysis	Size (d_h), PSD, concentration	30 nm–2 μ m	Better with polydisperse samples Complex media, particle corona	Complex in operation, spherical model
Imaging	Transmission Electron Microscopy	Size, shape, aggregation, imaging	< 1 nm	High resolution, precise size information	Quantification difficult, sample preparation, expensive
	Scanning Electron Microscopy	Size, shape, aggregation, imaging, surface morphology	ca. 3 nm	High resolution	Quantification difficult, sample preparation, charging effects
	Environmental Scanning Electron Microscopy	Size, shape, imaging, surface morphology	ca. 30 nm	Wet samples, environmental conditions, non-conductive samples	Reduced resolution
	Energy Dispersive Spectroscopy	Elemental composition	nm range	Complementary to EM	Elemental information not sufficient
	Optical microscopy and Fluorescence Microscopy	Size, shape, morphology, particle location	> 1 μ m	Non-destructive, cheap, easy to handle, sub-diffraction variants	Diffraction-limited, environmental plastic is not fluorescent
	Atomic Force Microscopy	Size, shape, topography, aggregation	ca. 0.1 nm	High resolution, AFM-IR TERS, in liquid	Slow, small area, artefacts due to particle movement
	Scanning Tunneling Microscopy	Size, shape, topography, aggregation	ca. 1 nm	High resolution	Conductive samples, slow, small area
	Confocal Laser Scanning Microscope	Size, shape, location in	> 0.2 μ m	Fluorescence imaging	Small area, diffraction limit
	Near-field Scanning Optical Microscopy	Size, shape,	30 nm	Fluorescence	Slow, small area

Table 2.5 Techniques for chemical identification and characterisation of MPs and NPs. (Adopted from Schwaferts et al. 2019)

Technique	Information	Range	Advantages	Disadvantages
FPA-FT-IR (focal plane array FT-IR)	Vibrational spectrum, Pigments, Additives, Ageing	> 10 μm	Non-destructive, automated	Not applicable for single MPs and NPs Strong interference from water
ATR-FT-IR (attenuated total reflection FT-IR)		Bulk	Simple, fast	
AFM-IR (atomic force microscopy infrared spectroscopy)	Spectrum, imaging	> 50 nm	High resolution, chemical imaging	Slow Small area
RM (Raman microspectroscopy)	Fingerprint spectrum, bulk pigments, additives	> 0.5 μm , bulk	Non-destructive, easy sample preparation, fast, no interference from water	Fluorescence
XPS (X-ray photoelectron spectroscopy)	Binding energies of orbitals	Bulk	Surface characterisation	UHV, laborious
Py-CG-MS (pyrolysis gas chromatography-mass spectrometry)	Mass, polymer type, additives	Bulk, ng– μg e.g., PS: LOD: 4 mg/L	Minimal sample preparation	LOD dependent on polymer type, some polymers complex, dry sample needed, pre-concentration necessary
Thermal extraction desorption gas chromatography-mass spectrometry (TED-GC-MS)			Measurement with matrix, fast, larger sample masses	Dry sample needed

2.9. DIFFICULTIES IN DETECTING MPs

Understanding the abundance of plastic particles in the environment is vital for evaluating their likely risk to the ecosystem. Research on MPs is complicated because the particle size, shape, density and charge continually change over time (Galloway, Cole & Lewis 2017). Some polymers, such as PS, PVC and PET have greater density than water and have higher settling rates (Table 2.1), whereas others, such as LDPE, HDPE and PP, have lower densities and are presumed to mainly float in the water column (Duis & Coors 2016; Auta et al. 2017a). These differences in density make the isolation of MPs challenging.

According to previous studies, concentrations of MPs can be as low as 3 MP/m³ in water (Doyle et al. 2011) and 8 MP/kg in sediment (Thompson et al. 2004), to very high concentrations of 102,000 MP/m³ in water (Norén & Naustvoll 2010) and 621,000 MP/kg in sediment (Liebezeit & Dubaish 2012). Therefore, high-volume samples are required to capture particles from lightly polluted catchments.

MPs analysis can be problematic due to the contamination caused by airborne particles (Hidalgo-Ruz et al. 2012). According to Prata et al. (2019), the quality and quantity of the recovered MPs vary with environmental conditions, so samples should be collected in both wet and dry seasons to evaluate this proposition. Furthermore, all plastic devices and laboratory equipment must be replaced with non-plastic materials to avoid contamination. Three blank tests should be conducted to mitigate experimental error.

2.10. RESEARCH GAPS AND SIGNIFICANCE

According to Horton et al. (2017), MPs research is rapidly increasing. However, although research on marine MPs is developing rapidly, few studies have been conducted on freshwater environments in recent years (Dris et al. 2015; Wagner et al. 2014). Horton et al. (2017) believe that much of the current information about the environmental presence of MPs reflect terrestrial environments only as sources and transport corridors of MPs to the ocean. However, considering that most plastics are used and disposed of on land, the probability of MP pollution of terrestrial waters is high (Horton et al. 2017).

Nets are the most used devices for marine MPs sampling and the types of nets are included neuston nets, plankton nets, manta nets, continuous nets, and manual nets (Cutroneo et al., 2020). The majority of methods used nets with an average mesh size of ~330 µm (Barrows et al., 2017). The

nets with smaller mesh sizes are found to be challenging to operate because they can get clogged up with ease (Löder and Gerdt, 2015) leading to an underestimation of MPs profusion of the sampled water. Nets are typically manufactured with plastics which can contribute to the contamination of the extracted sample (Cutroneo et al., 2020).

Pumping systems are also used in taking samples from marine waters but they used less commonly than nets (Cutroneo et al., 2020). These pumping systems allow the filtering of seawater and usually, intake systems of the vessel are used for the pumping (Morgana et al. 2018). Hence, the pumping and filtering systems used in the assessment of marine MPs are impractical for terrestrial water MPs studies.

According to the available studies, MPs in water create numerous environmental and health impacts. Several studies conducted in recent years identify the MPs are present at hazardous levels within marine ecosystems (Cole et al. 2011). Their miniature size can endow MP particles with some unique features such as a high surface area and hydrophobic characteristics (Wright & Kelly 2017).

The exposure of aquatic organisms to MPs can affect the ecosystem directly and indirectly. Therefore, the importance of understanding MP release rates, transport and availability in terrestrial waters—including rivers, lakes, reservoirs and stormwater catchment ponds—has been highlighted in the recent past. However, the number of available studies on MPs in terrestrial waters is limited and most studies have been conducted in North America, Asia, and Europe; no evidence of research on Australian terrestrial MPs was found in the literature review. A robust understanding of the worldwide distribution of MPs is essential to undertake a comprehensive risk assessment that can be adopted globally. Therefore, this study aimed to understand the extent of MP pollution in Sydney terrestrial waters.

2.11. OBJECTIVES

This study aimed to determine the extent of the presence of MPs in urban stormwater. Therefore, the objectives of this study were twofold:

- a) To develop an appropriate sampling technique and filtration system for collecting water samples from the terrestrial waters, develop an efficient MP isolation technique to separate MPs from contaminants and develop a quantification technique that can be applied to the field samples to accurately identify and quantify MPs.

- b) To determine the extent of the presence of MPs in Australia's stormwater system by analysing samples from two stormwater retention ponds in Western Sydney, Australia.

CHAPTER 3. RESEARCH METHODOLOGY

Past studies (Table 2.2) were reviewed to find an acceptable method for quantifying MPs in terrestrial water samples. It was soon discovered that there was a lack of universally accepted methods for quantifying MPs in water and an attempt to fill this gap was made in the present study. A method for analysing the MPs in terrestrial waters was developed, considering some of the past references (Table 2.2). This method was based on the studies conducted by Su et al. (2016), Mani et al. (2015), Liu et al. (2019) and Wang et al. (2017), is shown schematically in Figure 3.1 and is explained in detail in the following sections. The terrestrial water samples were subjected to the developed method to determine the extent of MP contamination in Western Sydney stormwater catchments. Samples were collected from Lake Woodcroft and Wattle Grove Lake and tested. The results were analysed, discussed and recommendations presented.

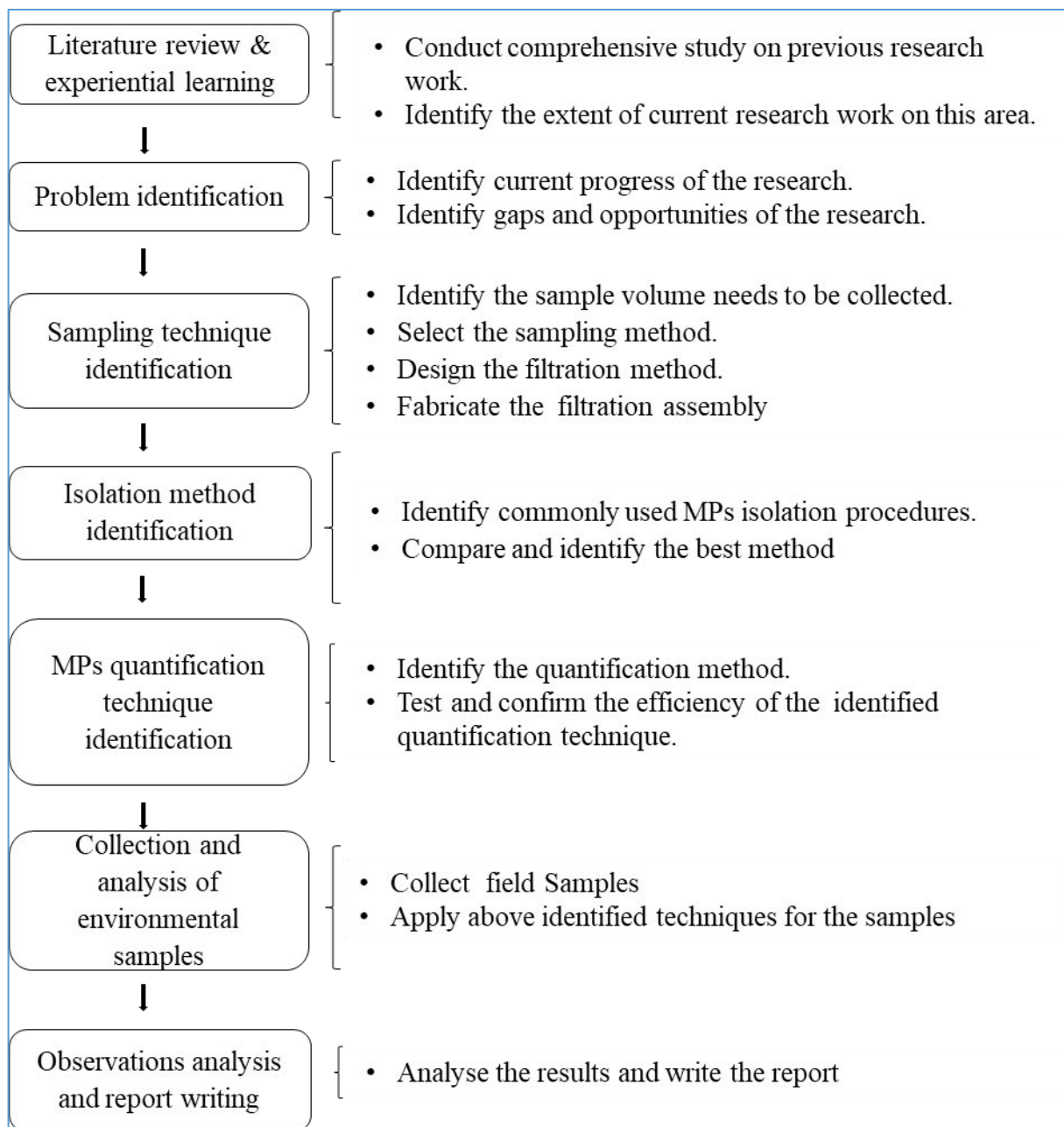


Figure 3.1 Flow diagram of the research methodology.

Table 3.1 Summary of primary sampling plan

Sampling Site	Number of samples	Period	Time of day
Lake Woodcroft	4 (2 wet, 2 dry) x 1	01/2020–04/2020	10.00–12.00
	1 (dry) x 3	06/2020	10.00–16.00

Table 3.2 Summary of secondary sampling plan

Sampling Sites	Number of Samples	Period	Time of day
Lake Woodcroft	4 (2 wet 2, 2 dry) x 2	01/2020–09/2020	R1: 10.00–12.00
			R2: 14.00–16.00
Wattle Grove Lake	4 (2 wet, 2 dry) x 2	01/2020–09/2020	R1: 10.00–12.00
			R2: 14.00–16.00

3.1. ANALYTICAL METHODS

Past studies (Table 2.2) were reviewed to find an acceptable method for quantifying the MPs in stormwater samples. It was soon discovered that there was no universally accepted method for the quantification of MPs in water. Therefore, a methodology for determining the MPs in the stormwater was developed considering the learnings from the past literature (Table 2.2). This methodology also based on the studies conducted by Su et al. (2016), Mani et al. (2015), Liu et al. (2019) and Wang et al. (2017), is schematically outlined in Figure 3.2 and is explained in detail in the following sections.

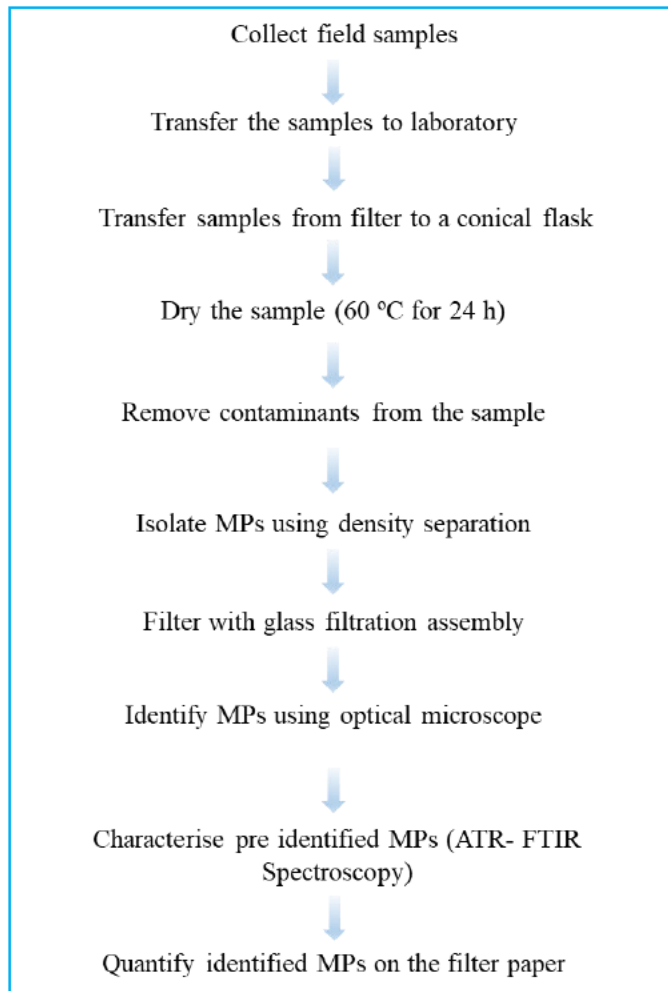


Figure 3.2 Methodology for analysing MPs in water samples.

3.1.1 SAMPLE EXTRACTION METHOD

Sample collection was conducted in two steps: preliminary and secondary. A hand-held sampler was fabricated with a 1 m long non-plastic handle and 500 mL metal cup to collect samples, as shown in Figure 3.3.

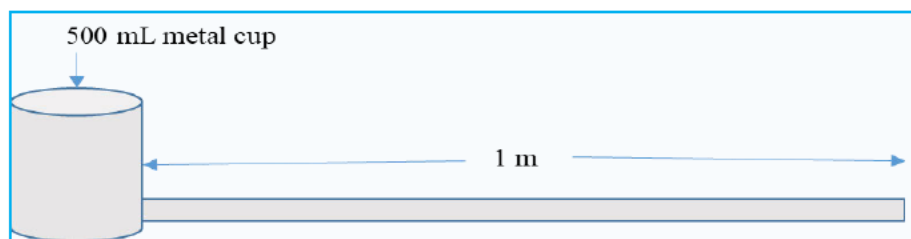


Figure 3.3 Hand-held metallic sampler

Preliminary sample collection

Preliminary sample collection and filtration were conducted with a fabricated sampler and a purpose-built mini-filtration device, all fabricated from non-plastic materials. As shown in Figure 3.4, the filtration system was designed with a metal cylindrical funnel, a cylinder head, 48.5 μm stainless steel sieve and cellulose fibre gaskets. The metallic sampler collected lake water samples from 30 cm below the surface water and 1 m from the edge. Twenty litres of water was filtered at the sampling location using the fabricated iron filtration assembly with a 48.5 μm stainless steel filter. After completing the filtration, the assembly and filters were covered with aluminium foil and transferred to the laboratory. Four samples were collected with no duplicates as the sampling was an elaborate process, but the fifth sample was collected in triplicate to assess the accuracy of the sampling procedure. The preliminary samples were collected from Lake Woodcroft with the following objectives:

- a) To assess the sampling mechanism before fabrication of the secondary sampler.
- b) To assess the pre-identified MP isolation, quantification and characterisation techniques.
- c) To review the MP concentration at the sampling site and determine the required volume of secondary samples.

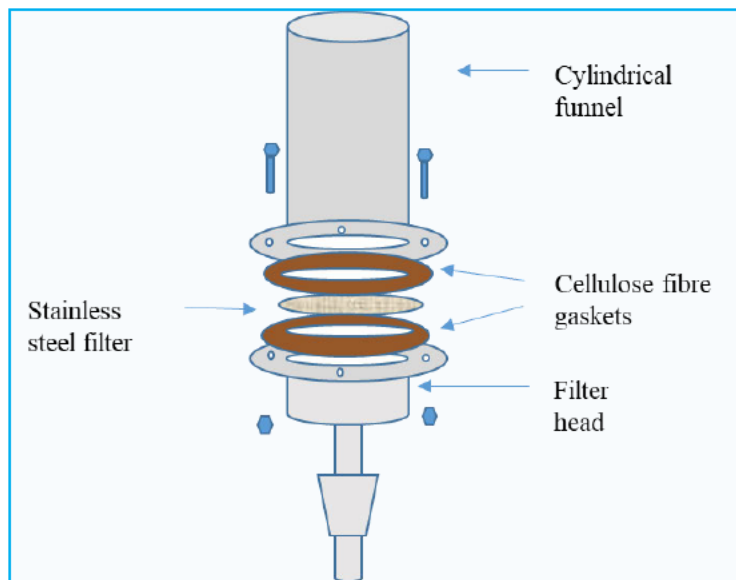


Figure 3.4 Diagram of the preliminary filtration assembly.

Secondary sample collection

Secondary sample filtration was conducted with a sampler fabricated from non-plastic materials. All the pipes and sieve assemblies were fabricated with steel, gaskets were designed with 0.8 mm

red fibre vulcanised gasket sheets and filters were made from stainless steel sieves (48.5 μm , 170 μm , 2500 μm , 5000 μm). Water flow was recorded using a water flow meter. The filtration system was fabricated as shown in Figure 3.5 and sample collection was conducted with the following objectives.

- a) To assess the concentration of MPs at the sampling sites.
- b) To assess the MP concentrations of the sampling sites (Sydney stormwater catchments).
- c) To identify and quantify the various MP polymer types at the sampling sites.

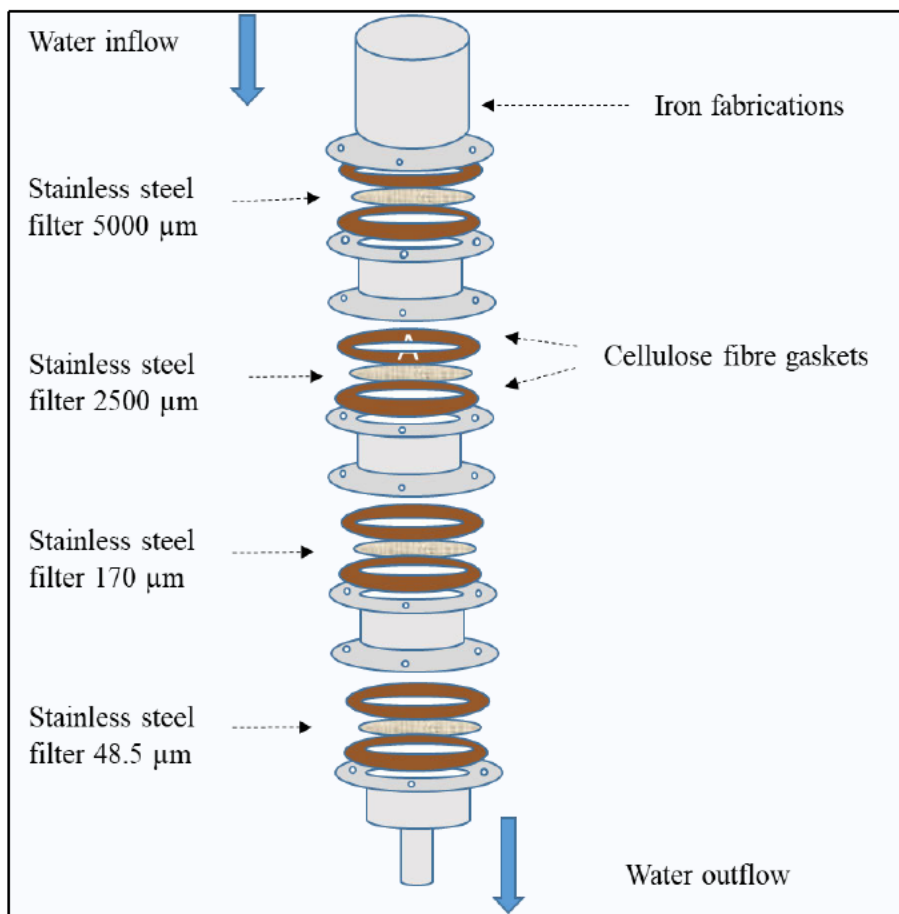


Figure 3.5 Details of the secondary filtration assembly

Secondary sampling procedure

Samples were collected from Lake Woodcroft and Wattle Grove Lake. Four samples were collected from each of the sites with duplicates. Two samples were collected in wet weather and two were collected in dry weather (at least two days without rain before sample collection). After filtration of the samples, the assembly openings were covered with aluminium foil and transferred

to the laboratory. The filters were removed from the assembly at the laboratory and stored in Petri dishes in the cool room for later treatments.

3.1.2. ISOLATION TECHNIQUE FOR MPS

MPS isolation technique verification

Over the past ten years, there has been progressive development in the knowledge and understanding of methods to extract MPs from samples (Prata et al. 2019). However, researchers have used several techniques with varied success rates due to the absence of generalised procedures (Prata et al. 2019). Most methods resulted in polymer degradation, destruction, or a change in the colour of the MPs particles. From the comprehensive literature review, five commonly used techniques for separating MPs from the organic matter component in the sample were identified. These techniques were assessed for their organic matter degradation efficiency and the best two methods were selected to evaluate their polymer degradation potential.

Assessment procedure

Organic matter for the experiment was prepared by collecting, washing, drying and grinding floating organic solids from Woodcroft Lake. The degradation efficiency was compared by weighing the organic matter before and after treatment. An analytical PS suspension (30 μm , 1.3×10^6 MPs/mL) was used to represent the MPs in the assessment of the polymer degradation potential of the treatment. Samples were monitored using Olympus BH2-UMA upright microscope and FlexSEM1000ii electron microscope for colour and shape changes.

Treatment methods

Oxidising agents

- a) The sample was treated with H_2O_2 (30%) at room temperature in dark conditions for 24 h to digest organic matter, including biological and non-biological materials (Wang et al. 2017).
- b) The sample was treated with H_2O_2 (30%, 20 mL) and 0.05 M Fe(II) catalyst (0.05 M, 20 mL) at 75 °C for 5–10 min until it started to boil. If all the visual organic matter was not fully oxidised, further H_2O_2 (20 mL) was added and the reaction continued at room temperature for 15 h (Rodrigues et al. 2018)
- c) The sample was stirred with Fe (II) solution (0.05 M, 20 mL) and H_2O_2 (30%, 20 mL) at 75 °C for 30 min and left covered loosely with aluminium for 24 h to continue the digestion (Anderson et al. 2017).

- d) The sample was treated with H₂O₂ (30%) in a glass conical flask, loosely covered with aluminium foil and left in a shaking incubator at 65 °C and 80 rpm for 72 h (Su et al. 2016).

Acid digestion

The sample was treated by soaking in HCl (2 M) for 24 h at room temperature (Eriksen et al. 2013).

Alkali digestion

The sample was treated with NaOH (1 M) for 1 h at 60 °C (Catarino et al. 2017).

3.1.3 IDENTIFICATION AND CHARACTERISATION OF MPs

The separation and identification of MPs from environmental samples are challenging due to the persistence of other natural materials that may be mistaken for plastics (Shim, Hong & Eo 2017). The various shapes, polymers and sizes of MPs increase the difficulty in differentiating them from indigenous environmental materials (Shim, Hong & Eo 2017). This indicates the importance of using at least two identification techniques to confirm the identity of isolated material.

Identification (optical microscopy)

Optical surveillance of the treated filter paper was conducted as the initial identification process. According to Shim, Hong & Eo (2017), using a microscope to identify MPs is quick and straightforward.

Procedure

- a) The sample on the filter paper was observed with the naked eye and suspected plastic pieces were separated using forceps for later examination.
- b) The remaining sample was studied under the optical microscope and potential plastic particles with the same morphological characteristics were counted and recorded.

Elimination of non-plastics

- a) The forceps were dragged across the particles to rule out grass sheaths, diatoms, salt crystals and pine needles of similar appearance to plastics. If a powder formed or the material broke down, the particles were determined to be non-plastic (Masura et al. 2015).
- b) Suspected plastic particles were checked for visible organic or cellular structures, as plastics do not have such structures (Norén 2007).

- c) MP fibres should be uniformly thick, not entirely straight, not narrowing towards the ends, clear and consistently coloured (Norén 2007). These characteristics were considered in the differentiation of plastic particles.
- d) Transparent particles were inspected further under higher magnification for potential organic origin (Norén 2007).

Characterisation of MPs

The use of FTIR spectroscopy for the identification of polymers is considered to be a reliable method (Shim, Hong & Eo 2017, Thompson et al. 2004). Accordingly, the MP particles identified by optical microscopy were subjected to attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy to identify the plastic polymer.

Filter papers with treated samples were stored in Petri dishes and transferred to the Advanced Materials Characterisation Facility (AMCF) at the Parramatta campus of Western Sydney University. A Hyperion 1000 mid-infrared microscope attached to a Bruker Vertex 70 spectrometer was used to characterise the MPs. Dried samples were subjected to optical surveillance using the Olympus BH2-UMA upright optical microscope. Twenty-six per cent of the filter paper was photographed using a UCMOS03100KPA digital camera. Possible MP particles were identified and counted using the above procedure. Identified MP particles were verified via the secondary method of FTIR. Based on past studies (Mani et al. 2015; Gal, Sandor & Karoly 2007), the spectral range was set at 4,000–675 cm^{-1} at a resolution of 4 cm^{-1} and the collection time was set at 32 co-scans for each measurement. All spectra were compared with those of the Hummel polymer additives and Aldrich polymers libraries for corresponding peaks of similar intensities. The OPUS 7 software was used to characterise the MP polymers.

3.1.4. QUANTIFICATION OF MPs

Quantitative research is imperative in this field as it generates data that can enable a broad understanding of the issue (Onwuegbuzie et al. 2005). However, to produce valid conclusions from these data, they need to be logically and scientifically accurate. Hence, it is essential to develop an analytically acceptable technique for quantitatively determining the number of MP particles in a sample.

Quantification technique

A sequence of assessments was performed to determine the best quantification technique for the MPs identified in the water. This experiment used monodisperse PS (30 μm , $\sim 1.3 \times 10^6$ MPs/mL) to represent the MPs identified in the terrestrial water samples.

Validation of the procedure

Using a verified quantification procedure was considered a vital aspect of this experiment for the reliability of the results. Hence, the below experimental procedure was followed to assess the accuracy of the proposed quantification technique.

- a) A 50 μL aliquot of the suspension was taken from the analytical PS sample and a series of dilutions were performed to prepare the chosen concentrations (~ 13000 , ~ 2600 , ~ 560 , ~ 260 MPs/L).
- b) 100 mL of each dilution was filtered using a glass filtration assembly with 0.45 μm 47 mm glass fibre filter papers.
- c) The filter papers were placed in Petri dishes and dried in the oven at 60 $^{\circ}\text{C}$ for 24 h.
- d) Fifty random photographs were taken of each filter paper under the optical microscope.
- e) The area of each photograph was calculated using software calibrated to the scale of the selected objective lens magnifications.
- f) The number of PS beads on the designated area of each photograph was calculated and recorded.
- g) Five groups of images (10, 20, 30, 40, 50) were created by selecting images randomly from the pool of 50 from each concentration using Microsoft Excel.
- h) The recovery percentage for each group was calculated and recorded.
- i) The standard deviation for each image group was calculated and recorded.
- j) The recorded standard deviations were plotted in a graph with an exponential relationship and a forecast of 100 images (300 mm^2 of the filter paper area).
- k) The accuracy of the proposed MP counting method was assessed based on the experimental results.

3.2. SAMPLING SITES

Lake Woodcroft

Lake Woodcroft is surrounded by the Woodcroft Reserve and contains precious biodiversity. An aerial image of the lake is shown in Figure 3.6. This ecological system is situated in the suburb of Woodcroft, which is part of Sydney, in New South Wales, Australia. Woodcroft is located 42 km west of the Sydney central business district.

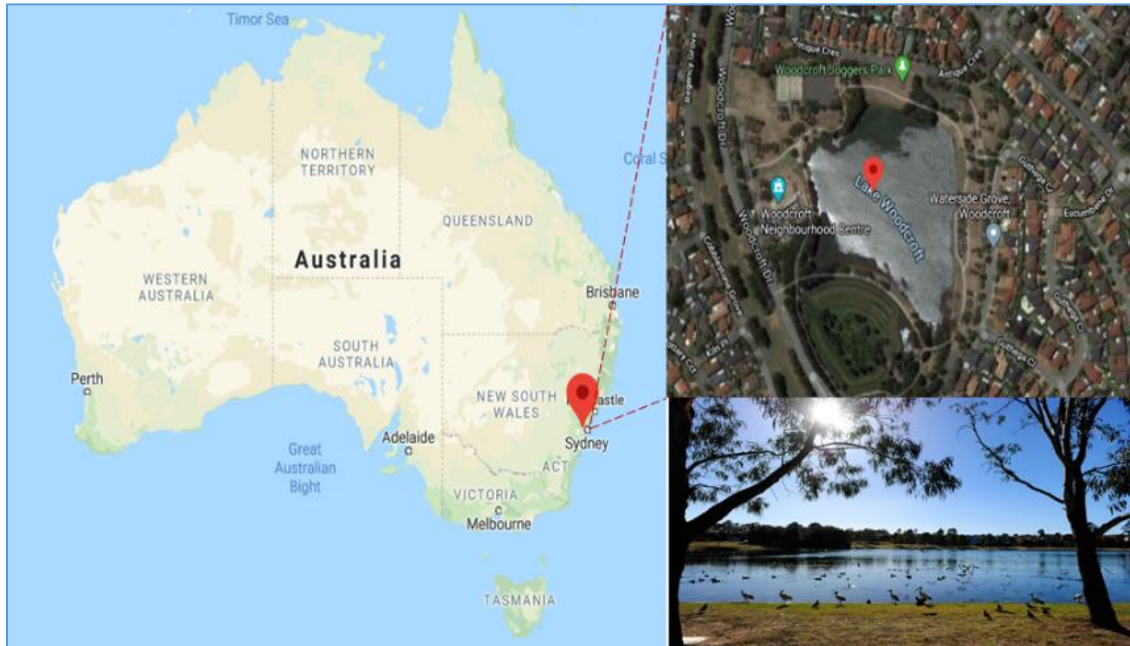


Figure 3.6 Aerial view of Lake Woodcroft.

Wattle Grove Lake

Wattle Grove Lake is an artificial pond in Wattle Grove, New South Wales, Australia, surrounded by the Wattle Grove residential development. An aerial image of the lake is shown in Figure 3.7. This lake acts as a wildlife reserve, providing a home for various water birds and fish species, including ducks, swans and eels.



Figure 3.7 Aerial view of Wattle Grove Lake.

3.3. ADDITIONAL RESOURCES AND TRAINING

Training on ATR-FTIR spectroscopy, optical microscopy and electron microscopy was undertaken at the AMCF in Parramatta.

3.4. VALIDATION EXPERIMENTS AND RESULTS

The fabrication of sampling equipment and filtration devices and the development of validation experiments to identify suitable MP isolation, identification and quantification techniques were performed.

3.4.1. FABRICATION OF SAMPLING APPARATUS

Metal filtration assemblies were fabricated as shown in Figures 3.8 and 3.9. The filter head and cylindrical funnel were fabricated from metal, filters were steel and gaskets were cellulose fibre sheets.

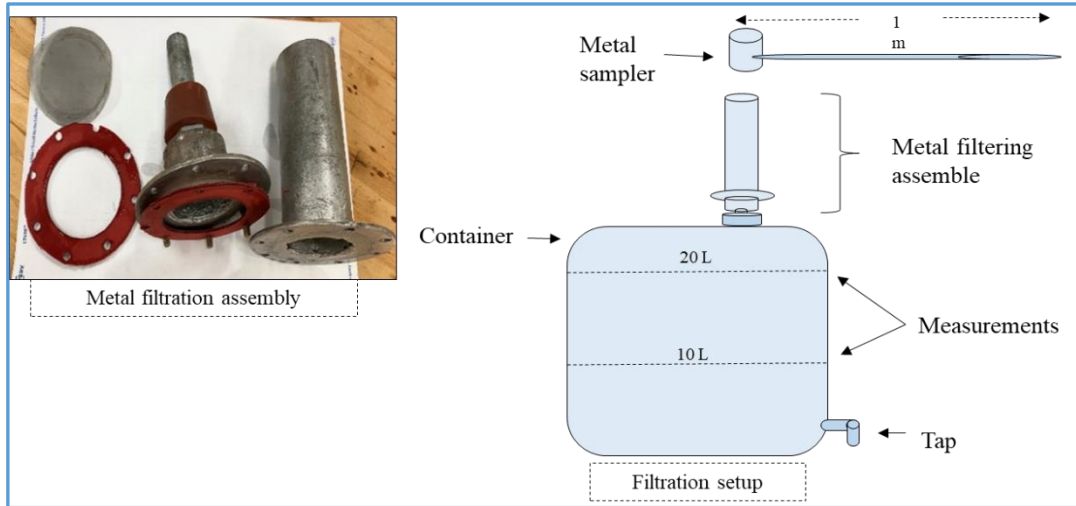


Figure 3.8 Preliminary metal filtration assembly and filtration setup

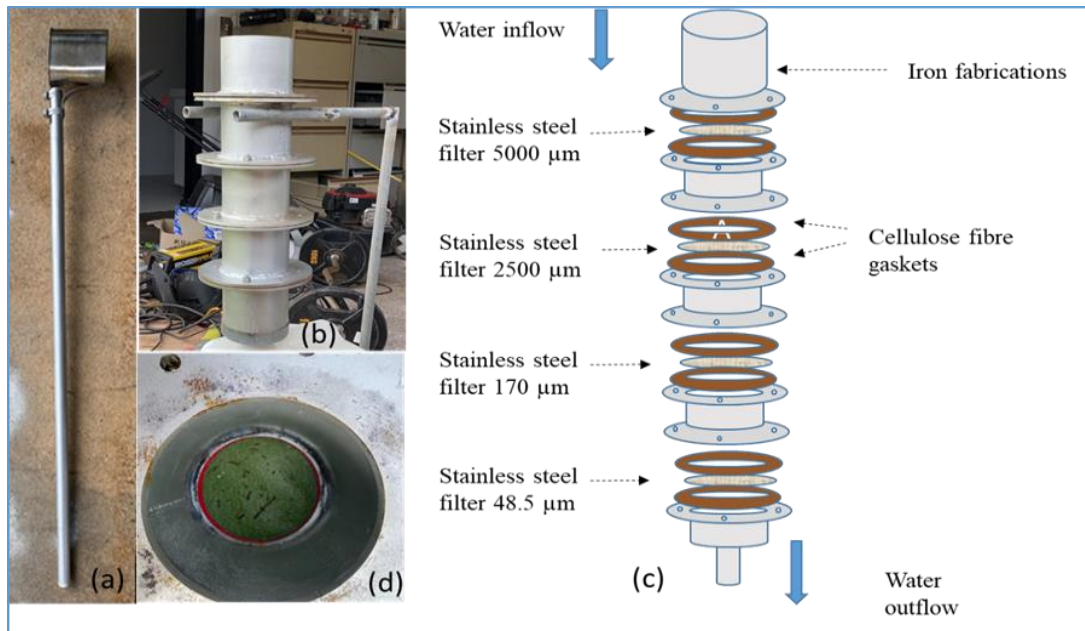


Figure 3.9 Sampler and filtration assembly for MPs sampling:(a) sampler; (b) filtration setup; (c) details of filtration assembly; (d) filter after filtration.

3.4.2. IDENTIFICATION OF MPs ISOLATION TECHNIQUE

Five regularly used MP isolation techniques were selected for testing, as mentioned above. These techniques were also tested for their organic matter degradation efficiency. The outcome summary is tabulated in Table 3.3, with the best treatment technique being the one with the highest degradation efficiency. The comparison of procedures began with the preparation of organic matter samples to represent environmental bioorganic substances, as described below.

- a) Floating organic solids were collected from the Lake Woodcroft using a steel net with a 5 mm sieve.
- b) Green matter and organic matter that were visible to the naked eye were separated.
- c) The collected solids were washed with water and dried in the oven at 60 °C for 48 h.
- d) The dried organic matter was ground and sifted through a 1 mm steel sieve.

Assessment of the organic matter degradation efficiency of the selected treatment methods

- a) Fifteen clean and dry 250 mL beakers were selected.
- b) Around 0.1 g of pre-prepared organic matter was added to each beaker.
- c) The beakers were separated into five groups with triplicates and allocated for each treatment method.
- d) The treated samples were rinsed with deionised water through glass microfibre filters (2 µm, 47 mm) using the glass filtration assembly.
- e) The filters were placed in covered glass Petri dishes and left in the oven for approximately 48 h at 60 °C.
- f) The weights of the filter papers, the weights of the samples before the treatments and the weights of the dried filter papers with the samples were measured and recorded.
- g) The best two treatment methods were selected based on their superior organic matter degradation efficiency.
- h) These two methods were employed in the subsequent polymer degradation experiments.



Figure 3.10 Glass filtration assembly.



Figure 3.11 Filter paper with particles.

Experimental procedure to assess the polymer degradation potential of the selected treatment methods

- a) Two monodisperse PS samples (1.3×10^4 MPs/mL, 30 μ m, 50 mL) were prepared in duplicate in beakers using the analytical standard monodisperse PS suspension (1.3×10^6 MPs/mL).
- b) The beakers were left in the oven at 60 °C until the samples were dehydrated.
- c) Each beaker sample was treated separately with the pre-selected treatment methods.

- d) The liquid in the beakers was filtered using the glass filtration aperture and glass fibre filter papers (0.45 μm , 47 mm).
- e) Each filter paper was placed in a Petri dish and dried in the oven for 24 h at 60 °C.
- f) One blank experiment was also conducted in duplicate.
- g) The filter papers with polystyrene beads were analysed for possible polymer degradation or destruction by scanning electron microscopy (FlexSEM 100II; Figure 3.13).

Confirmation of the isolation treatment to apply on the field samples

The two treatment methods with the highest degradation efficiencies were selected for assessment of their polymer degradation efficiency (Table 3.3). It was identified that treating the samples with 30% H_2O_2 in a shaking incubator at 65 °C and 80 rpm for 72 h had the best organic matter degradation efficiency (93%) and that treating the samples with 30% H_2O_2 at room temperature in the dark for 24 h had the second-highest degradation efficiency (50%; Table 3.3).

These two treatment methods were subjected to the experimental procedure to assess the likelihood of MP polymer degradation when applied to the field samples. After completing the procedure, the filter papers with treated monodisperse polystyrene samples were subjected to scanning electron microscopy. Images of the treated polystyrene beads were compared for changes in their shape or possible polymer degradation (Figure 3.13). However, no shape alteration or observable degradation of the plastic polymer was identified.

Since treating the samples with 30% H_2O_2 in a shaking incubator at 65 °C and 80 rpm for 72 h resulted in the best organic matter degradation efficiency with no observable polymer degradation, this isolation technique was applied to the field samples.

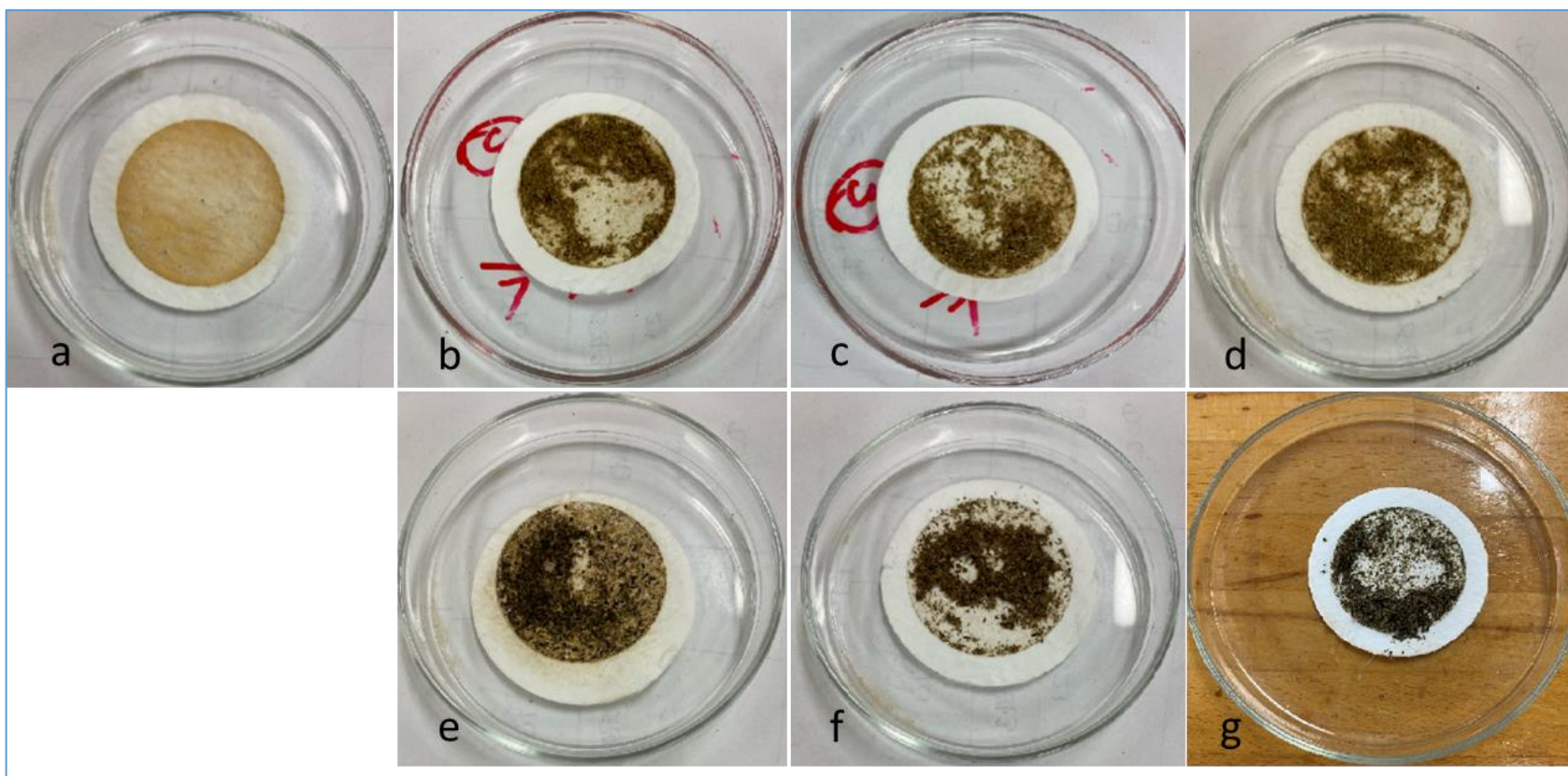


Figure 3.12 Filter papers after filtration of the treated samples:

- a) H_2O_2 , 65 °C, shaking incubator for 72 h, b) H_2O_2 , 75 °C for 30 min and 2 h at room temperature, c) H_2O_2 , Felton reagent, 75 °C for 5–10 min and 15 h at room temperature, d) H_2O_2 , 24 h in the dark at room temperature, e) 50 mL of 1 M NaOH, 1 h, f) 50 mL 2 M , HCl, 24 h; g) control.

Table 3.3 Details of calculations

Treatment	Chemicals and method	Replicate	Organic matter before treatment (g)	Filter paper weight (g)	Filter paper + organic matter (g)	Organic matter after treatment + filter paper (g)	Weight of residue on filter paper (g)	Degradation (g)	Degradation efficiency (%)	Average degradation efficiency (%)	SD for treatments	SD
Oxidising agent	(T1) 30% H ₂ O ₂ in a glass bottle in a shaking incubator at 65 °C and 80 rpm for 72 h	1	0.1012	0.2130	0.3142	0.2198	0.0068	0.0944	93.28	93.08	1.01	24.6
		2	0.1013	0.2127	0.3140	0.2188	0.0061	0.0952	93.98			
		3	0.1010	0.2131	0.3141	0.2212	0.0081	0.0929	91.98			
	(T2) 30% H ₂ O ₂ , room temperature in the dark for 24 h	1	0.1016	0.2135	0.3151	0.2623	0.0488	0.0528	51.97	50.02	1.69	
		2	0.1012	0.2122	0.3134	0.2638	0.0516	0.0496	49.01			
		3	0.1021	0.2113	0.3134	0.2633	0.0520	0.0501	49.07			
	(T3) 30% H ₂ O ₂ with 0.05 M Fe(II) catalyst at 75 °C for 5/10 min, until it started to boil; reaction continued at room temperature for 15 h	1	0.1013	0.2129	0.3142	0.2637	0.0508	0.0505	49.85	49.21	0.69	
		2	0.1026	0.2135	0.3161	0.2655	0.0520	0.0506	49.32			
		3	0.1015	0.2122	0.3137	0.2645	0.0523	0.0492	48.48			
	(T4) Fe (II) solution with 30% H ₂ O ₂ at 75 °C stirring on a hotplate for 30 min; covered loosely and left for 2 h at room temperature	1	0.1002	0.2133	0.3135	0.2650	0.0517	0.0485	48.40	46.59	1.84	
		2	0.1014	0.2125	0.3139	0.2666	0.0541	0.0473	46.65			
		3	0.1011	0.2128	0.3139	0.2687	0.0559	0.0452	44.71			
Alkali	(T5) 1 M NaOH for 1 h at 60 °C	1	0.1016	0.2125	0.3141	0.2720	0.0595	0.0421	41.44	44.44	2.63	
		2	0.1012	0.2132	0.3144	0.2675	0.0543	0.0469	46.34			
		3	0.1019	0.2133	0.3152	0.2688	0.0555	0.0464	45.53			
Acid	(T6) 2 M HCl for 24 h in room temperature	1	0.1016	0.2134	0.3150	0.2772	0.0638	0.0378	37.20	37.49	0.71	
		2	0.1012	0.2121	0.3133	0.2759	0.0638	0.0374	36.95			
		3	0.1026	0.2122	0.3148	0.2755	0.0633	0.0393	38.30			
Blank (untreated)		1	0.1010	0.2130	0.3140	0.3104	0.0974	0.0036	3.56	4.55	1	
		2	0.1015	0.2112	0.3127	0.3081	0.0969	0.0046	4.53			
		3	0.1024	0.2133	0.3157	0.3100	0.0967	0.0057	5.57			

- T1, T2, were the treatment methods with the highest organic matter degradation efficiency.
- Among these, T1 has the best degradation efficiency (93.1%)

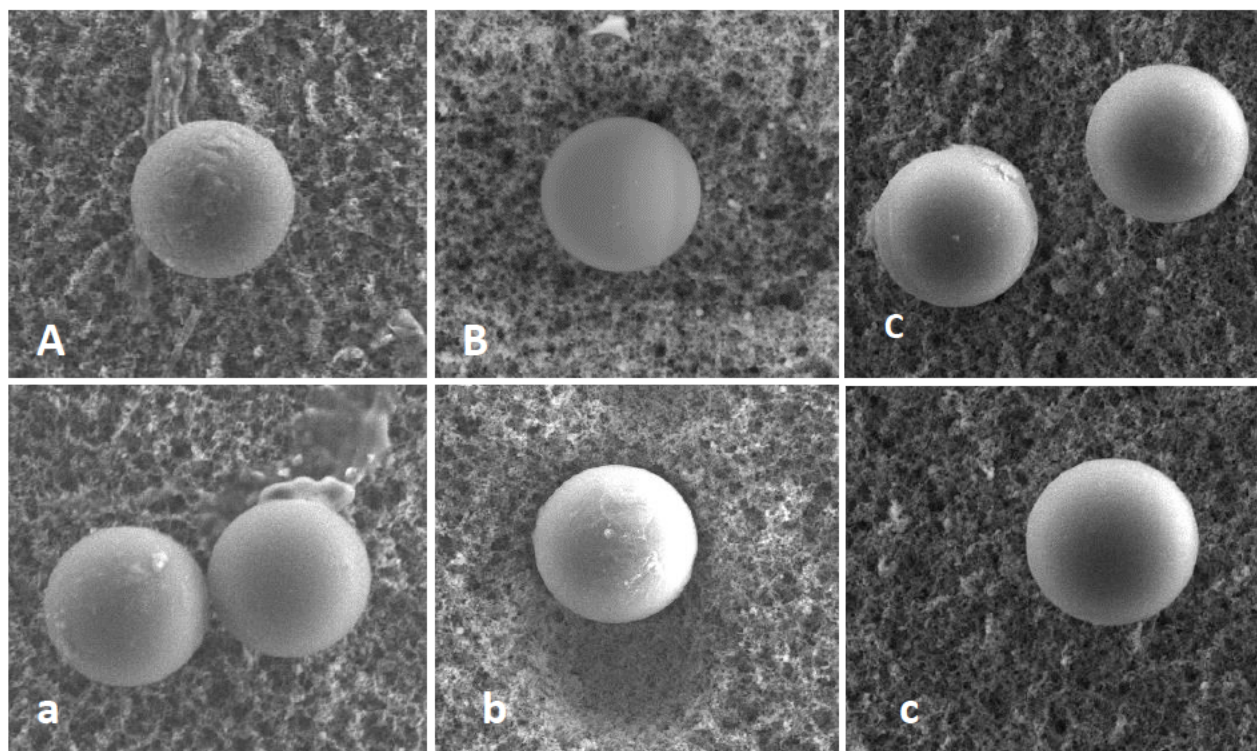


Figure 3.13 Scanning electron microscope images of the 30 μm monodisperse polystyrene beads after the treatments:

A, a) 30% H_2O_2 in a glass bottle left in a shaking incubator at 65 $^\circ\text{C}$ and 80 rpm for 72 h; B, b) 30% H_2O_2 , room temperature in the dark for 24 h; C, c) blank experiment. [Images A, a, C and c were taken under vacuum (50 Pa), 10.0 kV accelerating voltage, magnification 470 using an ultra variable-pressure detector (UVD). Images B and b were taken under vacuum (50 Pa), 15.0 kV accelerating voltage, magnification 470 and UVD.]

3.5 EXPERIMENTAL ERROR MANAGEMENT

A blank sample of 30 L of Milli-Q water was filtered through the filtration assembly using separate filters and subjected to the same treatment and analysis procedures to reduce contamination and experimental errors. Blanks were found to be free of MP particles. Before sampling, all the glassware and filtration assembly were cleaned following the method suggested by Liu et al. (2019). Natural fibre lab coats and gloves were worn and equipment and glassware were kept covered all the time using aluminium foil. The transfer and treatment of samples were performed in the laboratory under a laminar flow hood. The treated sample extracted on the filter paper was kept in a covered Petri dish and optical inspection and ATR-FTIR Spectroscopy were performed in a dust-free room.

CHAPTER 4. RESULTS AND DISCUSSION

4.1. MP QUANTIFICATION PROCEDURE

A series of tests were performed before selecting a standard MP quantification technique. An analytical polystyrene suspension (30 μm , 1.3×10^6 MP/mL) was used to represent the MPs found in the environmental samples. The experiment was performed as it was mentioned in section 3.1.4 and the standard deviation for each image group (Table 4.1). The recorded standard deviations were plotted in a graph with an exponential relationship and a forecast of 100 images (300 mm² of filter paper area; Figure 4.1).

Table 4.1 The recovery percentage calculated against the number of images taken.

Particle concentration (MP)	Images 10	Images 20	Images 30	Images 40	Images 50
260	0	61.7	82.2	92.5	98.7
520	123.3	92.5	82.2	92.5	98.7
2,600	111	104.8	102.8	98.7	93.7
13,000	76.5	88.8	83.0	86.9	91.3
Standard deviation	55.5	18.2	10.1	4.5	3.7
Area considered	30 mm ²	60 mm ²	90 mm ²	120 mm ²	150 mm ²

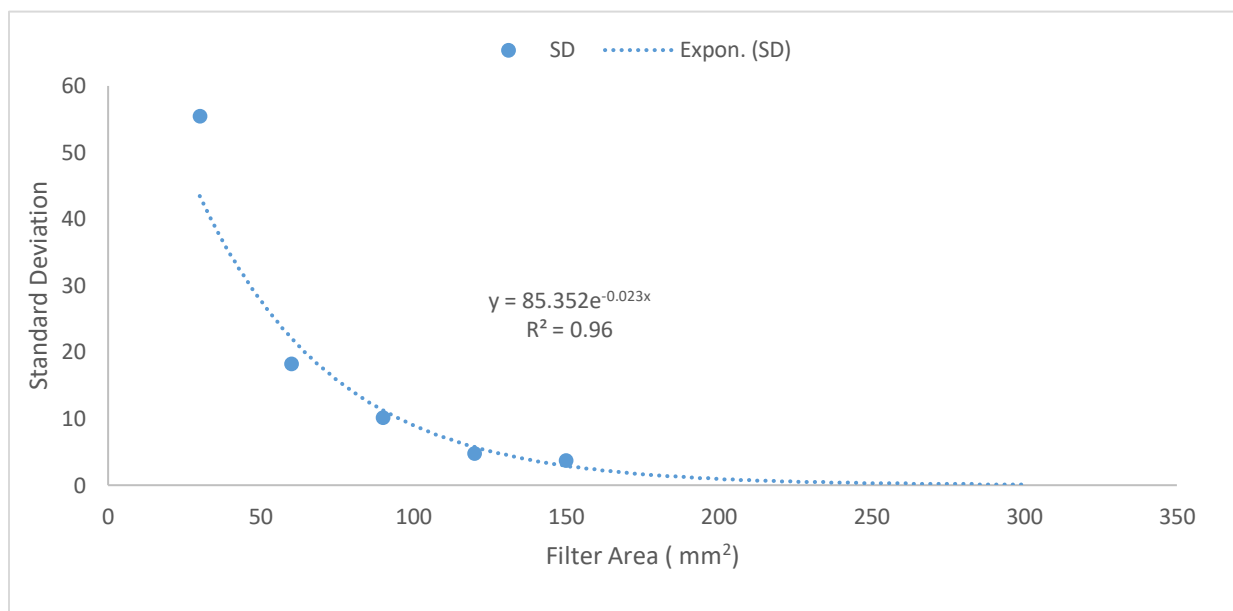


Figure 4.1 Relationship between standard deviation of recovery percentage and area considered.

R-squared (R^2), which is known as the coefficient of determination, represents how much variance of the data is explained by the model. According to the results of the data modelling, $R^2 = 0.9585$, indicating a strong relationship between the standard deviations of the test groups. The resulting graph (Figure 4.1) shows that at 255 mm^2 , the standard deviation of the test groups approached zero. This revealed that random analysis of at least 255 mm^2 (26%) of the filter paper was required to provide an accurate count of the MPs on the filter paper.

Some important considerations were as follows:

- An all-glass filter holder 47 mm filtration assembly was used for the filtration (Figure 3.10).
- Gridded $0.45 \mu\text{m}$, 47 mm glass fibre filter papers were used for filtration (Figure 3.11).
- The diameter of the usable filtration area was measured by Vernier callipers and was recorded as 35 mm (Figure 3.11)
- The area of the usable filtration area was calculated as 962.11 mm^2 .

4.2 MPs IDENTIFICATION AND CHARACTERISATION

The procedure that was implemented to identify MPs on the filter paper comprised two steps: optical surveillance and ATR-FTIR spectroscopic characterisation.

Optical surveillance of sample on the filter paper

The dried samples on the filter paper were subjected to optical surveillance using various magnifications of the Olympus BH2-UMA upright optical microscope. Particles that were similar to plastic particles were identified using their morphological features. Identification was conducted with reference to the approach of Norén (2007) following the guidelines mentioned in section 3.1.3.

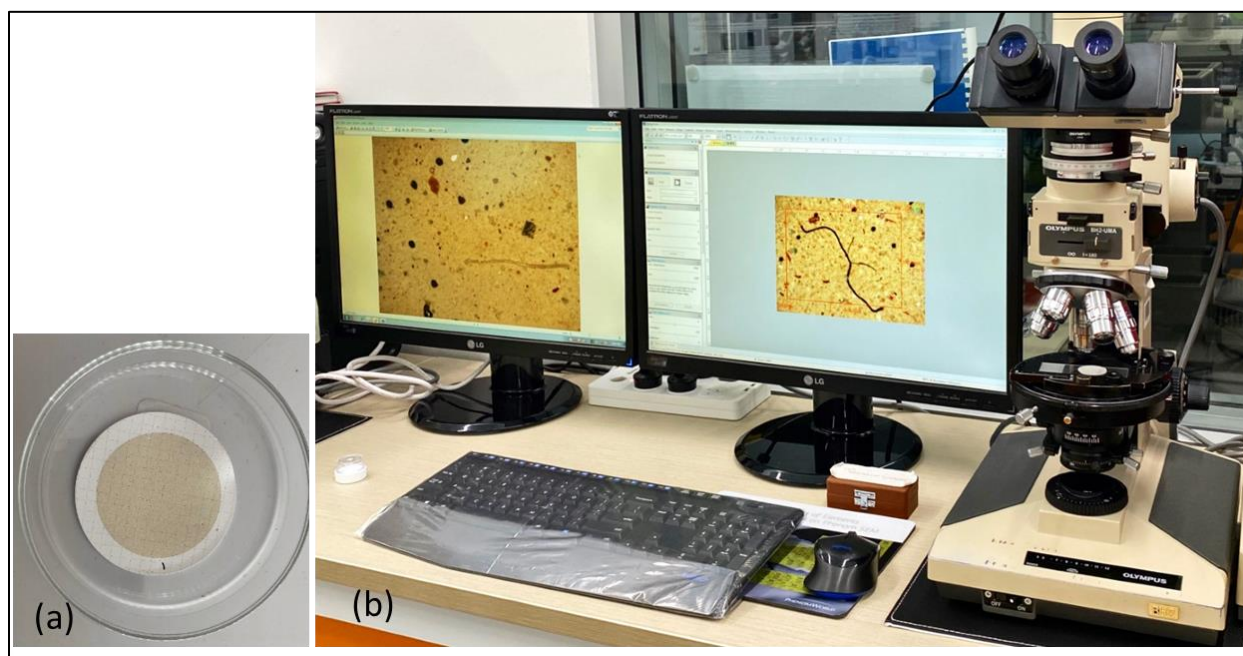


Figure 4.2 Sample on the filter paper and the Olympus BH2-UMA upright optical microscope

Chemical characterisation by ATR-FTIR spectroscopy

Secondary optical surveillance of the sample on the filter paper was carried out using HYPERION 1000 high-performance infrared microscope, which was equipped with a nose piece with a 15x Cassegrain objective, 4x visual objective and binocular and video viewing. The pre-identified

particles were located visually and images were captured at all stages of the optical surveillance process.

According to Thompson et al. (2004), FTIR spectroscopy enables the identification of plastic polymer particles based on their representative IR spectra (Figure 6.11). Accordingly, the chemical characterisation of MP particles were conducted using ATR-FTIR spectroscopy.

Pre-identified potential MP particles were subjected to further optical analysis using the 20x ATR objective to precisely locate each particle on the filter paper. The located particle was investigated in situ by direct contact of its surface with the germanium ATR crystal, which was achieved by lifting the microscope stage with the filter paper. The resulting spectrum was matched to reference libraries of Hummel polymer additives and Aldrich polymer spectra using computer installed OPUS 7 software. The hit quality index (HQI) was used to determine how well the resulting spectrum matched against each reference library spectrum.



Figure 4.3 FTIR with HYPERION 1000 high-performance infrared microscope.



Figure 4.4 ATR objective with germanium crystal.

The HQI was established using various mathematical procedures (Boruta 2012). In the assessment of spectra, the highest-ranking hit is considered the best match and the substantial gap until the next hit reflects an excellent match (Boruta 2012). The absence of a significant gap between the first two or more hits creates difficulties for matching. For example, when there is a cluster of spectra with similar HQI scores followed by a spectrum with a substantial gap, this can be indicative of a group of spectra that are similar but not exact matches. (Boruta 2012). Based on these criteria, the plastic particles present on the filter paper were identified.

MPs quantification

Once identification and characterisation were complete, the number of MPs present on the filter paper was calculated using the pre-identified quantification technique (see Section 3.4.3). The various plastic polymer types were also recorded (Figure 4.8).

ATR-FTIR spectroscopy and spectrum comparison

Each chemical substance has a chemical signature. It releases and absorbs different wavenumbers of energy depending on its chemical bonds. FTIR spectroscopy applies the same principle, enabling the identification of plastic polymer particles based on their representative IR spectra (Thompson et al. 2004). FTIR uses invisible infrared light. When IR radiation is passed through a sample, some radiation is absorbed by the sample and some is transmitted. The resulting signal that is detected is a spectrum representing a molecular ‘fingerprint’ of the sample. The position

and intensity of the measured absorption bands can be used to identify and quantify samples and mixtures vial comparison to a reference database of thousands of spectra using a computer.

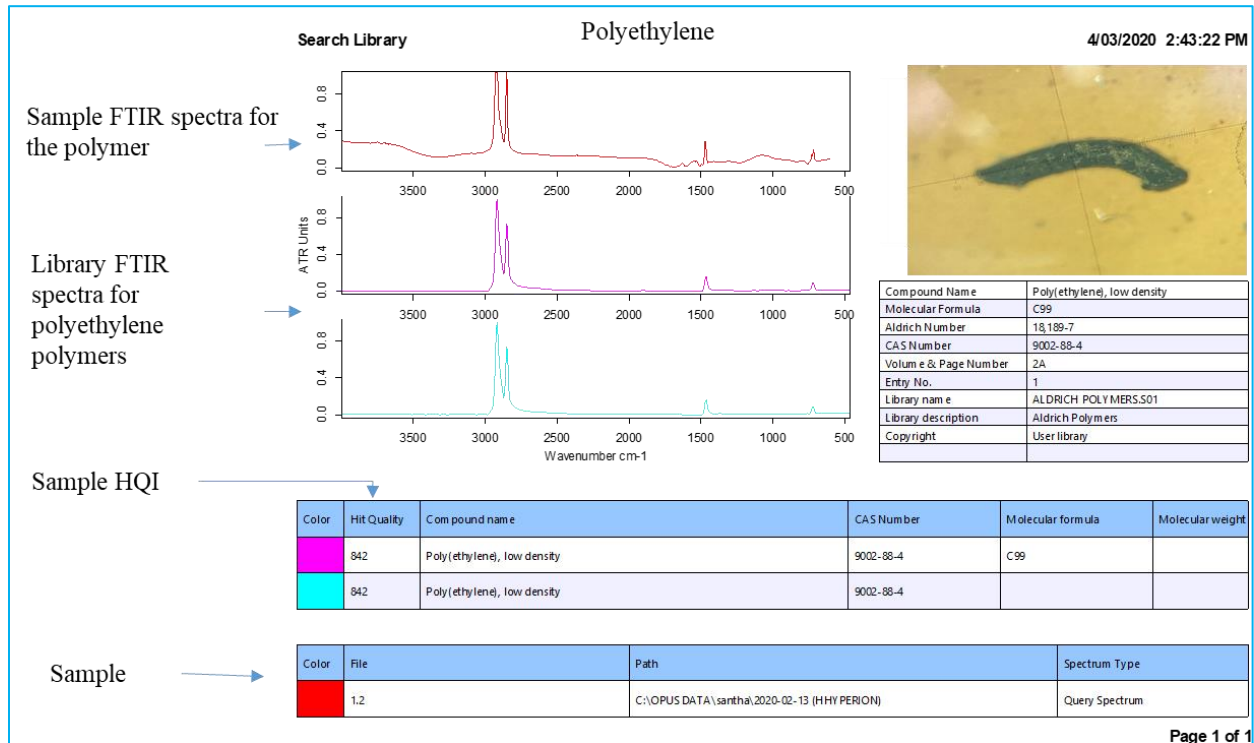


Figure 4.5 Comparison of FTIR library spectra with the sample spectrum.

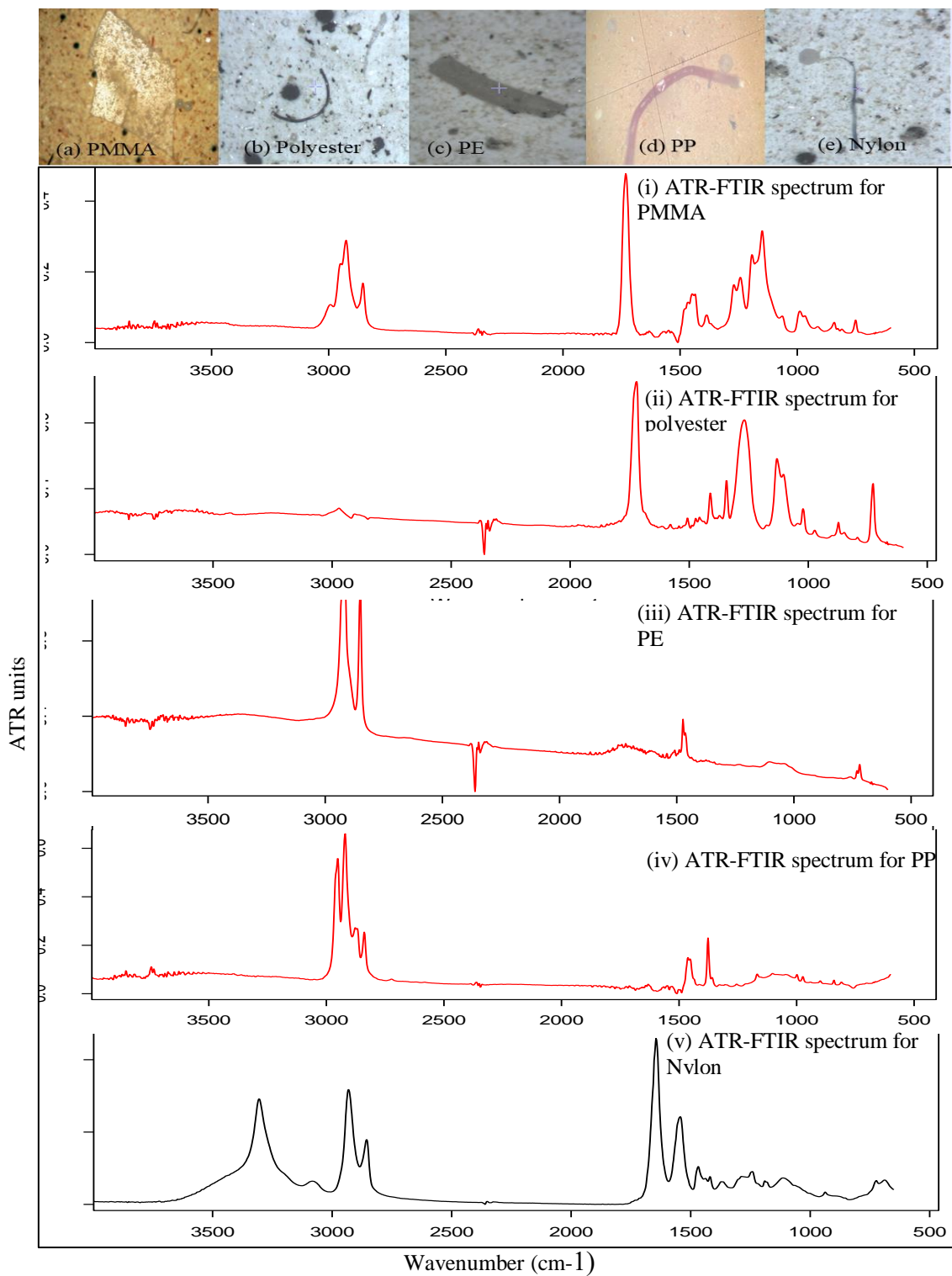


Figure 4.6 Images and FTIR spectra of some of the identified MPs:

a) PMMA, b) polyester, c) PE, d) PP, e) nylon; ATR-FTIR spectra of extracted MPs: i) PMMA, ii) polyester, iii) PE, iv) PP, v) nylon.

Interfering particles make the identification of MPs by optical microscopy more challenging. For example, some non-plastic microscopic materials can be easily mistaken for MPs, such as silicon particles. Nonetheless, in this study, it was possible to identify many MP particles using an optical microscope and to confirm these via FTIR (Figure 4.3).

4.3 PRELIMINARY SAMPLINGS (WOODCROFT LAKE)

4.3.1 DATA OF SAMPLE ANALYSIS

In this study, five samples were collected for the preliminary sample analysis. While collecting these samples, no duplicates were collected for the first four samples as the sample collection and analysis was an elaborate process. The last sample was collected with two duplicates to assess the precision of the procedure. Three samples were collected in the dry season and two samples were collected in the wet season. Each sample was subjected to the nominated separation and identification procedures. The identified MPs in each sample were counted and recorded (Table 4.2, Figure 4.8).

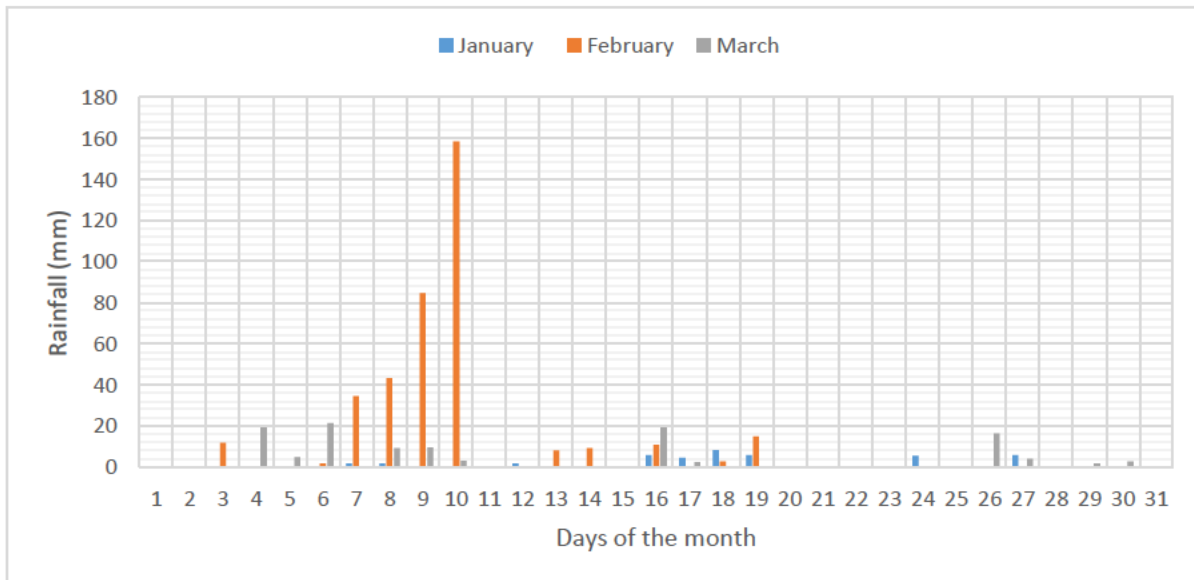


Figure 4.7 Annual rainfall recorded at Seven Hills (Collins St) Bureau Station (4.9 km from the sampling site).

Table 4.2 Number of MPs identified (preliminary sampling).

Sample No.	Rainfall	Date of sampling	Particle Size Range	Concentration (MP/m ³)
1 (Dry)		24/01/2020	48.5 µm–2.5 mm	2,150
2 (Dry)		31/01/2020	48.5 µm–2.5 mm	2,350
3 (Wet)	158.4 mL on 10/02/2020	11/02/2020	48.5 µm–2.5 mm	2,150
4 (Wet)	21.2 mL on 06/03/2020	07/03/2020	48.5 µm–2.5 mm	2,300
5 (Dry)		11/06/2020	48.5 µm–2.5 mm	2,200* (87)
Average				2,233 (91)

Note: Value in parentheses is the standard deviation * Sample 5 was sampled and analysed in triplicate.

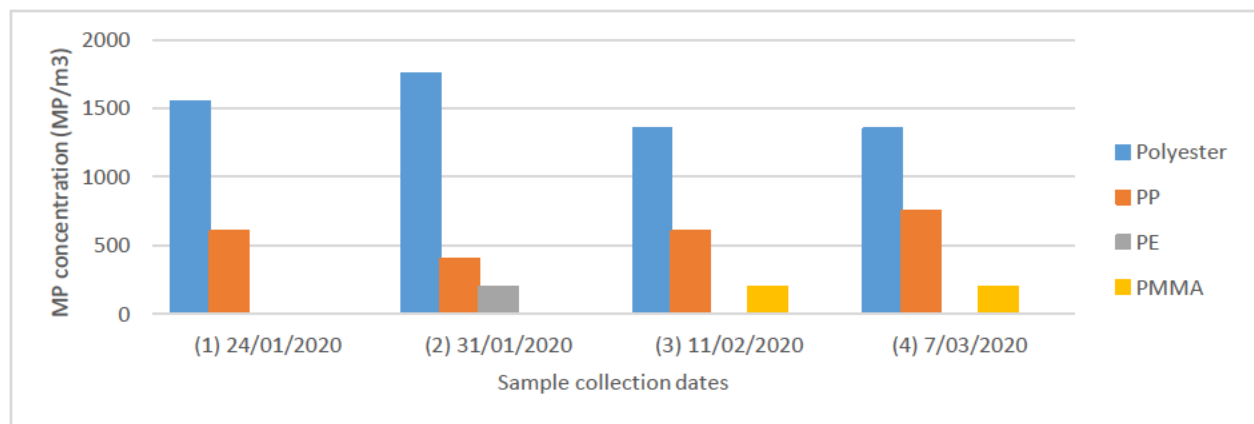


Figure 4.8 Composition of sampled MPs (preliminary sampling, Lake Woodcroft)

4.3.2 DATA ANALYSIS

In this study, five samples were collected from January to June 2020. As shown in Table 4.2, the average MP concentration was 2,233 MP/m³ with a standard deviation of 91 MP/m³. This result gave a coefficient of variation (CV) of 4%, which was indicative of low variability between the samples.

To check the possibility of sampling error, triplicate sampling was performed for sample number 5. As shown in Table 4.2, the mean MP concentration for sample number 5 was similar to that of the first four samples. Even the standard deviation for sample number 5 (87 MP/m³) was identical to the overall standard deviation. These results yielded a coefficient variation of 4%, which is

statistically acceptable. Thus, it was concluded that the sampling and analysis methodology adopted in this study was reliable and could be used to determine the concentration of MPs in stormwater. The types of plastic polymers and their concentrations in sample 5 are not given as this sample was only used to confirm the reliability of the analytical procedure applied in this study.

Three samples were collected in the dry season and two samples were collected in the wet season. During the dry and wet periods, the average MP concentration was found to be 2,233 MP/m³ and 2,225 MP/m³, respectively. These results indicate that the differences in MP concentrations between the wet and dry seasons are insignificant ($p > 0.05$).

It should be noted that the size range for the particles detected in this analysis was between 48.5 μm and 2.5 mm. Comparable observations were reported for Wuhan, China's urban surface waters (Wang et al. 2017) and retention ponds in Denmark (Liu et al., 2019). The relative abundance of smaller MP particles was possibly due to the degradation of large plastic debris by environmental factors (Jahnke et al. 2017)

In the current study, the MP concentration was in the range of 2,150–2,350 MP/m³ (with a size range of 48.5 μm to 2.5 mm). The concentrations observed in this study appeared to match those of Wuhan's surface waters, which were reported to be in the range of 1,660–8,925 MP/m³ (Wang et al. 2017). The observed MP concentration range is also lies in the range of that reported in other global studies on urban stormwater catchments (Table 2.2). From a comparison of volume-based concentration studies, lakes and reservoirs had low MP concentrations while stormwater catchments had the highest concentrations (Table 2.2). Observations from area-based studies indicate that inland water bodies—including rivers, estuaries, lakes, reservoirs and urban stormwater catchments—are all subject to considerable MP pollution (Table 2.2). According to the literature, these concentrations can vary significantly depending on geographical location, climatic conditions, human culture and urbanisation (Wang et al. 2017). Thus, it is essential to generate more data on MP pollution in Australian waters to assess the nature of the pollution. It is suggested that, due to the miniature size of MPs, they can be easily ingested by aquatic animals and potentially result in the bioaccumulation of toxic chemicals in the food chain (Wright & Kelly 2017).

MP polymer classification

Polyester and PP were the most common polymers in the sampled water (Figure 6.10), with 67% of the identified MP being polyester. Fibres were the most frequently identified form of MPs (93%). These results were similar to observations reported by Liu et al. (2019). Picó and Barceló (2019) identified cloths as the likely source of polyester MPs in water. These fibres can be deposited from airborne MPs (Dris et al. 2015) or form the breakdown of fishing nets and lines (Cole et al. 2011). Since the present study was carried out on an urban stormwater catchment surrounded by a heavily populated area, domestic sewage may have acted as a carrier via discharge or surface overflow (Browne et al. 2011; Wagner et al. 2014). Lesser quantities of PE and PMMA particles were found in the samples. These particles may have resulted from the fragmentation of large plastics on land and transported to the water bodies with rain (Zhang et al. 2015). The polymer densities for the identified MPs ranged from 0.9 to 2.3 g/cm³ (Hidalgo-Ruz et al. 2012). Most of the particles had a higher density than water. According to Wang et al. (2017), various other factors also affect the buoyancy of MPs in water; for example, pressure, temperature and turbulence can resuspend benthic particles in the water column (Ballent et al. 2012; Sadri & Thompson 2014). Most importantly, according to Zhao et al. (2015), a higher surface to volume ratio enables small MP particles to be suspended in the water column.

4. 4 SECONDARY SAMPLING

4.4.1 DATA OF SAMPLE ANALYSIS

Lake Woodcroft (sampling site 1)

Four samples were collected with duplicates. Two samples were collected in the dry season and two samples were collected in the wet season. Each sample was subjected to the nominated separation and identification procedures. The number of identified MPs in each sample was counted and recorded (Table 4.3, Figure 4.9).

Table 4.3 Experimental MP data for sampling site 1 (Lake Woodcroft).

Sampling date (conditions)	Repeat	Number of MPs on the filter paper				MP concentration (MP/m ³)						
		48.5–170 µm	170 µm– 2.5 mm	2.5–5 mm	Total	48.5–170 µm	170 µm– 2.5 mm	2.5–5 mm	Total	For the Sample	For the Season	For the site
06/06/2020 (dry)	R1	35	31	0	66	1166.7	1033.3	0	2000	2133.3	2066.6	2100 (86)
	R2	35	27	0	62	1166.7	900	0	2066.7			
23/07/2020 (dry)	R1	35	27	0	62	1166.7	900	0	2066.7	2000	2133.3	
	R2	35	23	0	58	1166.7	766.7	0	1933.3			
29/07/2020 (wet)	R1	31	27	0	58	1033.3	900	0	1933.3	2066.6	2133.3	
	R2	39	27	0	66	1300	900	0	2200			
12/08/2020 (wet)	R1	35	27	0	62	1166.7	900	0	1066.7	2200		
	R2	39	31	0	70	1300	1033.3	0	2333.3			

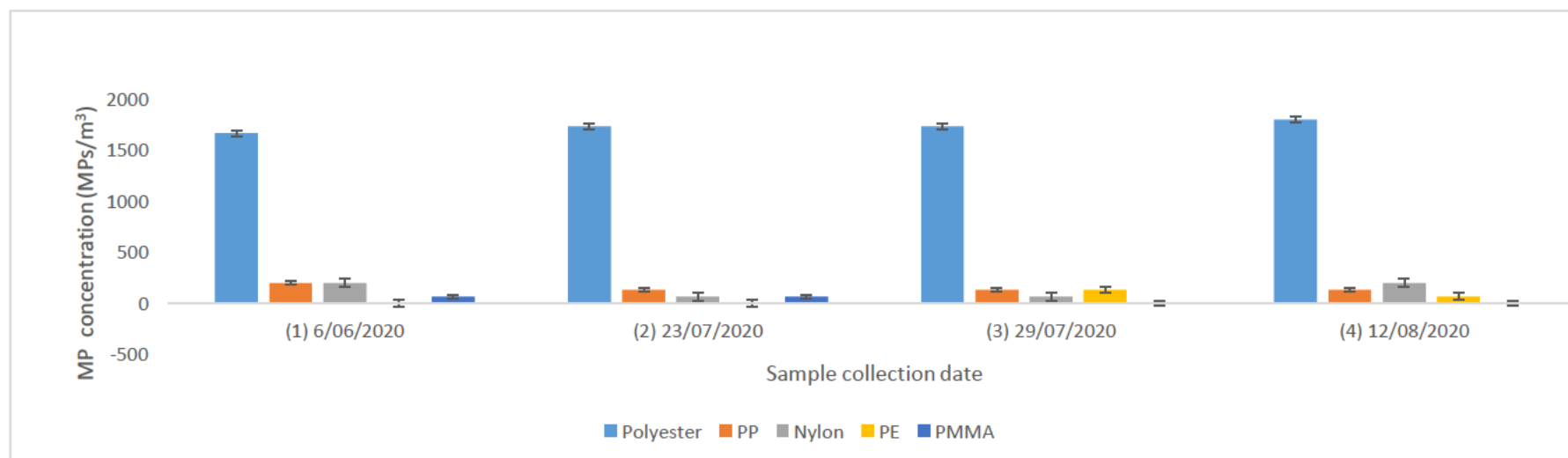


Figure 4.9 MPs composition of the sampled water (Lake Woodcroft)

Wattle Grove Lake (sampling site 2)

Four samples were collected with duplicates. Two samples were collected in the dry season and two samples were collected in the wet season. Each sample was subjected to the nominated separation and identification procedures. The number of identified MPs in each sample was counted and recorded (Table 4.4, Figure 4.10).

Table 4.4 Experimental MP data for sampling site 2 (Wattle Grove Lake).

Sampling date (conditions)	Repeat	Number of MPs on the filter paper				MP concentration (MP/m ³)						
		48.5–170 µm	170 µm–2.5 mm	2.5–5 mm	Total	48.5–170 µm	170 µm–2.5 mm	2.5–5 mm	Total	For a Sample	For the Season	For the site
05/06/2020 (dry)	R1	43	27	0	70	1433.3	900	0	2333.3	2200	2200	2266.6
	R2	35	27	0	62	1166.7	900	0	2066.7			
22/07/2020 (dry)	R1	35	31	0	66	1166.7	1033.3	0	2200	2200	2333.3	(94)
	R2	35	31	0	66	1166.7	1033.3	0	2200			
30/07/2020 (wet)	R1	39	31	0	70	1300	1033.3	0	2333.3	2266.6	2333.3	
	R2	39	27	0	66	1300	900	0	2200			
11/08/2020 (wet)	R1	43	27	0	70	1433.3	900	0	2333.3	2400		
	R2	43	31	0	74	1433.3	1033.3	0	2466.7			

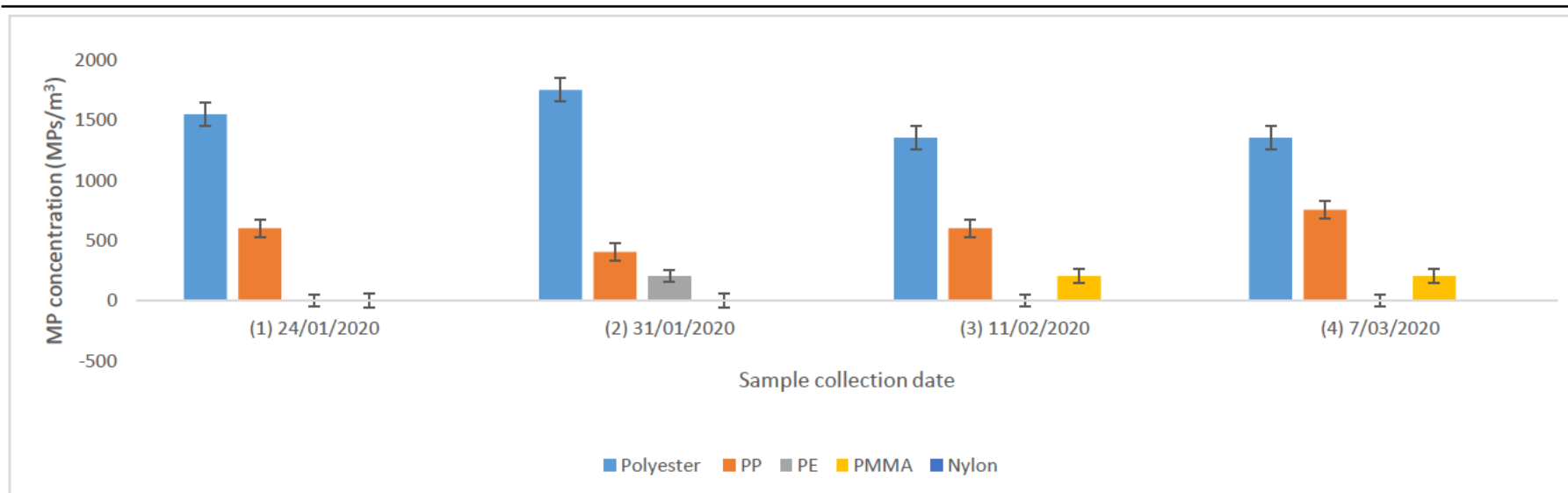


Figure 4.10 MPs Composition of sampled water (Wattle Grove Lake)

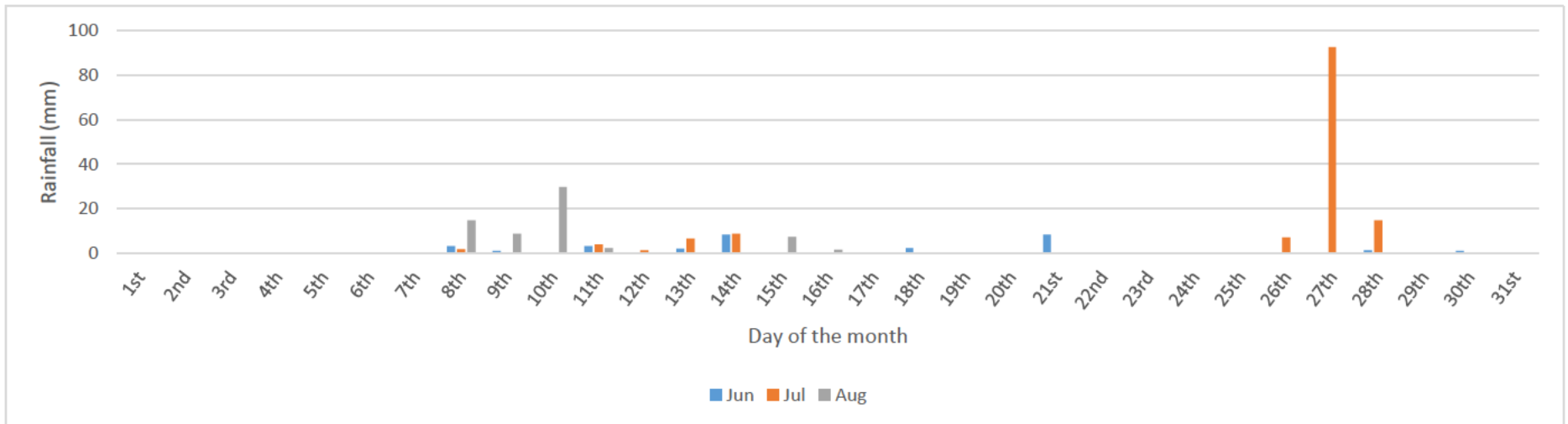


Figure 4.11 Rainfall recorded at Seven Hills (Collins St) Bureau Station (4.9 km from the sampling site).

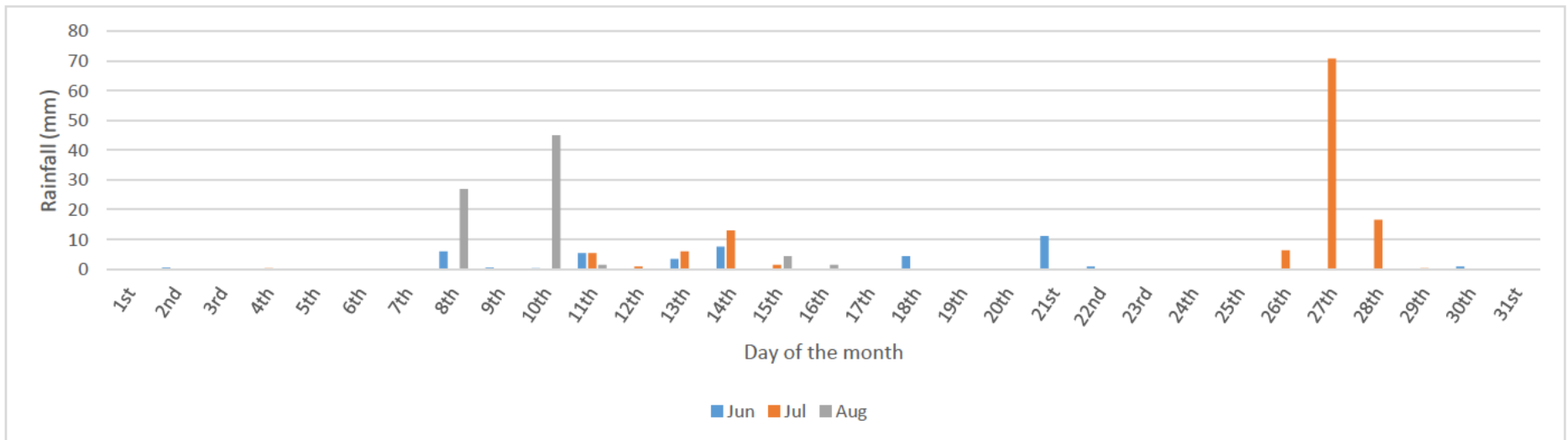


Figure 4.12 Rainfall recorded at Holsworthy Aerodrome AWS Bureau Station (3.7 km from the sampling site).

4.4.2 DATA ANALYSIS

The methodology outlined in Section 3 was applied to all samples collected from the two urban lakes. Table 4.3 shows the results of the analysis of the stormwater samples collected from Lake Woodcroft (site 1). The average MP concentration was 2,100 MP/m³ with a standard deviation of 86 MP/m³. This meant that the CV was 4% for site 1. Table 4.4 shows the MP concentration in the stormwater collected from Wattle Grove Lake (site 2). For sampling site 2, the average concentration was 2,267 MP/m³ with a standard deviation of 94 MP/m³ (CV of 4%). Both the standard deviation and CV values were generally low, indicating low variability between duplicates as well as between dry and wet periods.

The observed MP concentrations in this study were compared with those reported for small inland water bodies in the literature. The observed concentrations appeared to be within the range observed by Hu et al. (2018) and Liu et al. (2019; Table 2.2). Gilbreath et al. (2019) reported an anthropogenic MP concentration of 1,600 MP/m³ for a sample collected from a bio-retention rain garden in the San Francisco Bay Area, USA (Table 2.2). The lower concentration of MPs observed by Gilbreath et al. (2019) may be attributed to the larger cut-off size of 125 µm (Table 2.2) used in their sampling. Liu et al. (2019) and Hu et al. (2018) analysed MPs in the size range of 10–2,000 µm and 20–5000 µm and reported concentrations of 490–22,894 MPs/m³ and 480–21,520 MPs/m³, respectively. The observed MPs concentrations in the present study were within the range reported by these authors, even though the authors used smaller cut-off sizes in their sampling. However, Piñon-Colin et al. (2020) reported relatively high concentrations of MPs (66,000–191,000 MP/m³) for the stormwater runoff samples collected in Tijuana, Mexico (Table 2.2) and Olesen et al. (2019) reported a concentration of 270,000 MP/m³ for samples collected from stormwater retention ponds in Viborg, Denmark (Table 2.2).

On the other hand, significantly lower concentrations of MPs were reported for 29 Great Lakes tributaries located in six states of the USA (0.05–32 MP/m³), Lake Chiusi (2.68–3.36 MP/m³) and Lake Bolsena (0.82–4.42 MP/m³; Table 2.2). The lower concentrations in these lakes may be attributed to the lakes being freshwater bodies with limited human influence. Also, comparing the results obtained in the present study with those in the literature (Table 2. 2), it is suggested that the MP concentration can vary significantly from one place to another based on the geographical location, climatic conditions, human culture and urbanisation, smaller cut-off sizes and sampling

methods used, as proposed by Wang et al. (2017). Thus, it is vital to generate more data on MPs to assess the universal nature of MP pollution.

Tables 4.3 and Table 4.4 present MP concentrations during dry and wet sampling periods. For site 1, the average MP concentration for the wet period (2,133 MP/m³) was slightly higher than for the dry period (2,067 MP/m³). Similarly, for site 2, the respective concentrations were 2,333 MP/m³ and 2,200 MP/m³. Again, for site 2, there was a slight increase in the MP concentration in the wet period compared to the dry period. The increase in the concentration for wet periods over dry periods varied from 3 to 6%. Statistical analysis indicated that the difference in MP concentrations between the wet and dry periods was insignificant ($p > 0.05$). As the sampling included collecting water samples from the top 0–30 cm water layer, some of the MP particles may have sunk to the lake's bottom. As a result, not all the MPs particles were captured in the sampling. These results indicate that a better understanding of the extent of wet weather impacts on MP pollution of stormwater may be gained by sampling the entire column of the water, including lake sediments.

Based on the results of the secondary sampling in this study, about 56–57% of the MP particles appeared to be in the size range of 48.5 to 170 μm (Tables 4.3 and 4.4). The larger size range of 170 to 2,500 μm had a slightly lower number of particles (43–44%) and no MP particles in the size range of 2,500 to 5,000 μm were detected. This observation of low concentrations of larger particles appeared to agree with the previous literature (Wang et al., 2017; Fischer et al. 2016).

It should be noted that, in this study, some MP particles retained on the filter had elongated structures. For example, particles longer than 170 μm and with thicknesses of 5–15 μm were retained on a 48.5 μm filter. Thus, the size-based classification of MP particles may vary from one analysis to another. It was also possible that thin particles with an elongated structure may have escaped through the bottom filter and, therefore, that the concentrations determined in this study were underestimates of the actual concentrations. To overcome this error, it is necessary to repeat these sample collection and analyses trials often and for different stormwater samples. The proposed method of using a cascade filtration assembly for collecting different sized MP particles is preferred as using a single filter can overcrowd the filter, which will cause difficulties for manual counting and introduce additional errors to the determined concentrations.

MP polymer classification

The similar appearance of MPs can make their identification by optical microscopy challenging. To address this challenge, this study combined a treatment system to remove organic particles, observation of suspected MP particles by optical microscopy and then confirmation of the type of plastic particles using ATR-FTIR. This process aided in the confirmation and characterisation of MPs. As shown in Figures 4.9 and 4.10, all the MPs identified in this study were characterised as polyester, PP, PE, PMMA or nylon; optical microscope images of these are shown in Figures 4.6 a–e, respectively, while Figures 4.6 i–v present their respective ATR-FTIR spectra. These spectra were compared with those in the library databases., following which Opus 7 was used to classify the plastics into one of the five polymer types.

The number of MPs particles under each polymer type was determined by combining this identification process and the manual counting using the optical microscope. The results of this classification are plotted in Figures 4.9 and 4.10 for sites 1 and 2, respectively. At site 1, polyester, PP, nylon, PE and PMMA MP particles were identified in proportions of 83%, 7%, 6%, 2% and 2%, respectively. Similarly, at site 2, polyester, PP, nylon and PE were identified and were found to be in proportions of 86%, 4%, 7% and 3%, respectively. PMAA was found only at site 1. Figures 4.9 and 4.10 indicate that most of the MP particles identified in the stormwater samples were polyester (78–87% for site 1 and 84–94% for site 2). The likely source of these polyester MPs was fabric (Picó & Barceló 2019) and may have entered the stormwater from the deposition of airborne MPs (Dris et al. 2015). The polyester particles collected from the surface water samples were of various colours and sizes. As the source for polyester was attributed to fabric, it was construed that these polyester particles could be associated with various dyes and additives that are potentially harmful to human and aquatic animals' health if ingested.

The shapes of the particles in the sampled water were mainly fibres, fragments and pellets, with the shape categorisation performed as described in Di and Wang (2018). The proportion of fibres, fragments and pellets was estimated to be 88%, 5% and 7%, respectively, for site 1 and 93 %, 3% and 4% for site 2. These results indicated that the majority of MP particles were fibrous in shape. This was not surprising given that most of the MP particles were polyester and their most likely source was fabric.

CHAPTER 5. CONCLUSIONS AND FUTURE WORK

5.1 CONCLUSIONS

This study developed a unique methodology for identifying and classifying MP particles. The successful use of a cascade filtration assembly was demonstrated for the collection of MP particles of different sizes, with assisted in the isolation, counting and characterisation of the MP particles. The novel method included visual identification of MPs by optical microscopy followed by confirmation of the identity using ATR-FTIR spectroscopy. For manual counting, it was determined that 26% coverage of the filter would be sufficient to yield an accurate concentration of MP particles in the sample. Also, the use of the 30% H₂O₂-based pre-treatment method resulted in the removal of 93% of the organic contaminants, which could otherwise have interfered with the quantification and characterisation of the MP particles.

The MP concentration in two urban lakes was found to be in the range of 1933–2467 MP/m³. Comparing these observed concentrations with literature values revealed that the observed concentrations were within the range reported for stormwater systems worldwide and relatively higher than those observed for freshwater lakes. This was attributed to the fact that the collected water samples were stormwater that originated from urban areas, meaning that stormwater from urban areas can contain higher levels of MPs. This would be expected, as urban activities produce plastic waste, which can eventually degrade and disintegrate in the outside environment to yield MP particles.

The size of MPs measured in this study ranged from 48.5 to 2,500 µm and most of the MPs detected in the stormwater were polyester. One of the primary sources of polyester was likely to be fabric. This was also reinforced by the finding that the majority of the particles were fibrous in shape. As such, the dyes and additives used for manufacturing polyester material may enter humans and aquatic animals via MPs.

The methodology adopted in this study in quantifying MPs found in the water samples proved to be valid. The standard deviation was low with a COV of 4%. This indicated that the methodology developed in this study was reliable for quantifying and characterising MPs in urban stormwater. However, further studies are required to test the robustness of the proposed methodology. Furthermore, as the concentration of the MPs in water can vary considerably depending on the

location, climatic conditions, local culture, urbanisation and waste disposal methods, this study highlights the need for more monitoring studies to establish MP background levels in the inland environment.

5.2 RECOMMENDATIONS FOR FUTURE WORK

There are several future study options as extensions of this research. First, the analysis of stormwater catchments in other parts of Australia would provide a more comprehensive assessment of MP pollution in the stormwater system. Second, studies that investigate the presence of MPs in other Australian terrestrial waters, including stormwater runoff, lakes, rivers and drinking water reserves, is vital to make recommendations regarding MP pollution in Australian waters. Additionally, studies on water MPs could be further extended to assess MP concentrations in sediments of various terrestrial water bodies and beaches around Australia for a comprehensive MPs pollution assessment. Finally, the presence of MPs in aquatic systems is indicative of the presence of NP particles. Hence, it is imperative to monitor the presence of NPs in water systems as they could potentially be more harmful to human and animal health than MPs.

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Acknowledgement

Special gratitude should pay to the staff at AMCF, Western Sydney University, including Dr Richard Wuhler, Dr Laurel George and Dr Daniel Fanna, for their support and training for using various lab instruments, including FTIR, and SEM. In addition, appreciations to Mr Upul Jayamaha at Built Environment & Architecture, school of engineering Western Sydney University, and Mr Adam Hale, Technical Team Leader (Chemical & Biological Sciences) Western Sydney University, for the help and support provided during this research work.