

Microplastic pollution in the estuarine and river environment of the River Thames, UK

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Abstract

Microplastic pollution is ubiquitous globally and is considered a leading threat to ecosystems. As microplastic studies increase, key areas remain understudied, such as rivers, with new areas and sources of microplastics still being discovered. The overall aim of this thesis is to investigate the abundance of microplastics within the tidal river Thames, UK and identify potential sources of microplastics. In this thesis, I assess the current literature on microplastics, identify potential research gaps within current known knowledge, and show the range of laboratory methods used in studies worldwide to identify and quantify microplastic abundance within the environment. Through surface water samples collected along the river Thames from May 2019 - May 2021, I demonstrate that microplastics are present within the river Thames and vary between sites and samples, as well as identifying potential sources. I highlight how seasonality and rainfall impact microplastic abundance within this river system. During this study, the Covid -19 pandemic occurred, proving a unique sampling opportunity. As a result, this thesis acknowledges that this pandemic may have impacted microplastic abundance and provides valuable information on the short-term impacts of the pandemic on microplastic within this time. Finally, I highlight the effects of the New Year fireworks displays on microplastic abundance within water samples collected from the river Thames at Westminster. This data is novel as it had not previously been noted or identified when this study was published. The data and results presented within this thesis provide valuable information on the abundance, possible sources and accumulation of microplastics along the river Thames that can be used as a baseline for future studies. This data and results can also be used by stakeholders such as the Environment Agency, Thames Water and non-profit

organisations to inform possible decisions on the removal of microplastic pollution from the river.

Declaration

I hereby declare that the work presented in this PhD thesis is my own original work, and information derived from other research works has been appropriately cited.

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Ria Devereux

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Abbreviations

ABS – Acrylonitrile Butadiene Styrene

ALDFG - Abandoned, lost or discarded fishing gear

ALK - Alkyd resin

Bio - PE – Bio polyethylene

BPA – Bisphenol A

CA - Cellulose acetate

DDT – Dichloro-diphenyl-trichloroethane

EDS - Energy-dispersive X-ray spectroscopy

EU - European Union

Fe(II) - Iron(II)

FTIR – Fourier Transform Infrared Spectroscopy

GC/MS - Gas chromatography mass spectroscopy

H₂O₂ – hydrogen peroxide

HCl - Hydrochloric acid

HDPE – High density polyethylene

HNO₃ – Nitric acid

LDPE - Low density polyethylene

mmt - million metric tons

MP – Microplastic

MPF – Microplastic fibers

MPP – Microplastic particles

MPT - Microplastic Total

MSW – Municipal solid waste

NaCl- Sodium chloride

NaOH - Sodium Hydroxide

PA - Polyamide (nylon)

PBTs – Persistent, bioaccumulated and toxic

PC – polycarbonate

PCBs – Polychlorinated biphenyls

PCP - Personal care products
PE - Polyethylene
PES - Polyester
PET - Polyethylene terephthalate
PLA – Poly lactic acid
PLA – Port of London Authority
PMMA- Poly(methyl methacrylate)
POP's – Persistent organic pollutants
PPE – Personal Protective equipment
PPE – Personal protective equipment
PP - Polypropylene
PS - Polystyrene
PUR – Polyurethane
PVA – Polyvinyl alcohol
PVC – Polyvinyl chloride
Py – GC/MS - Pyrolysis–gas chromatography/mass spectrometry
SDS solution - Sodium dodecyl sulfate in distilled, deionized water
SEM -Scanning electron microscope
SUP – Single use plastic
TWP – Tire wear particles
UV – Ultraviolet
WPO- wet peroxide oxidation
WWTP – Wastewater treatment plant
ZnCl₂ -Zinc chloride

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Dedication

This PhD is dedicated to Grandad John, a man who laid the foundation for my love of water and saw me start but never finish this PhD.

“More than a substance, plastic is the very idea of its infinite transformation; as its everyday name indicates, it is ubiquity made visible. And it is this, in fact, which makes it a miraculous substance: a miracle is always a sudden transformation of nature.”

— Roland Barthes, *Mythologies* (1957)

Chapter 1 Introduction

Scientists are starting to refer to the period after the 1950s as the "Dawn of the plasticine age" due to the build-up of a plastic layer within the environment (Harram *et al.*, 2020). Our reliance on plastics and consumerist nature, exhibited with over 390.7 mmt million metric tons (mmt) (2021) (Statista, 2022; Vom Saal *et al.*, 2008) of plastic being produced annually, is causing substantial environmental problems, with plastic being a significant contributor to pollution, especially with regards to freshwater and marine pollution due to plastics taking anywhere 10 - 1000+ years to degrade (Chamas *et al.*, 2020).

1.1 History of Plastics

Plastics are considered a relatively new material; however, natural plastics such as rubber have been used since 1600 BC (Tarkanian and Hosier., 2011). Recent technological advances have led to modern-day plastic, and this advanced plastic is causing considerable damage to the environment (Andrady and Neal., 2009; Hosler, 1999). The origin of plastics started with discovering the vulcanisation process by Charles Goodyear in 1839 (Martin-Matinez., 2002). Vulcanisation is when rubber is heated with sulphur to give it more rigidity and durability (Nair and Joseph., 2014). The

invention of cellulose-based semi-synthetic plastic followed this process, much like the bioplastic being explored and developed today. This included celluloid (chemically modified cellulose) and the first synthetic textile, Chardonnet silk, a mixture of cellulose nitrate strands and artificial fibre, and Parkesine, all invented between 1850-1860 (American Chemical Society, 2022; Brydson,1989). The birth of modern-day plastics occurred in 1907 when Leo Hendrik Arthur Baekeland (the father of the plastics industry) invented Bakelite (the first synthetic polymer) (Figure. 1.1). The development of other synthetic polymers followed this in the late nineteenth and early twentieth centuries, such as Polyethylene (PE), polyvinyl chloride (PVC), polystyrene (PS) and nylon (Andrady and Neal., 2009; Bryson.,1989; Chandran *et al.*, 2020).

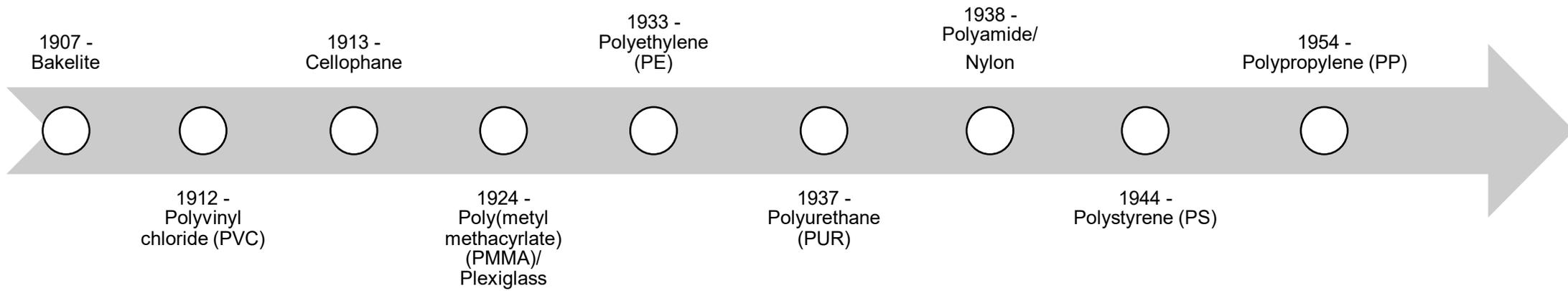


Figure 1.1 Early history of plastic polymer production (Andrady and Neal., 2009; American Chemical Society., 2022; Bryson., 1989; Chandran *et al.*, 2020)

It was not until World War II that the need for a quick and cheap material led to the mass production of modern-day plastic. For example, 32 times more polystyrene was produced by the end of the war compared to when it started (Breskin,1947). Annual production was approximately five mmt in the 1950s (Figure. 1.2). Their evident properties, such as being lightweight, inexpensive, durable, and chemical and light-resistant, have replaced more traditional materials such as glass, wood, paper, and metal. As a result, annual production reached over 390.7 mmt (Statista, 2022) since World War II. There have only been three periods since the 1950s that plastic production did not increase. This was due to the global oil crises and the great recession, which caused a slight dip in plastic production in 1975, 1980, and 2008 (Chandran *et al.*, 2020). Plastic production significantly increased due to the emergence of Covid-19 in 2019 (Figure. 1.2), resulting from extremely low oil prices and a worldwide increase in personal protective equipment (PPE) use worldwide. This caused a knock-on effect in 2020 as plastic production decreased from the previous year purely because of the significant increase in 2019 that was

unexpected. The situation in Russia (2022) may mean that plastic production will decrease further in 2022 to 2023 due to the sanctions placed on Russian oil.

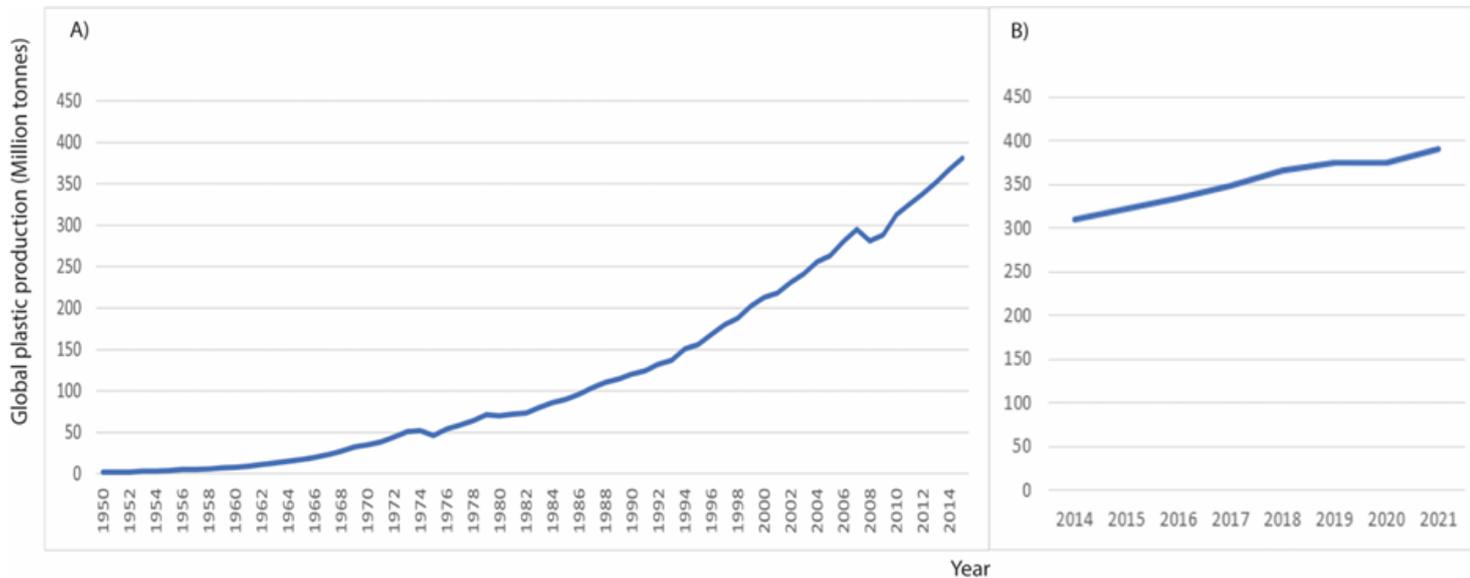


Figure 1.2 Global plastic production (Million metric tonnes) from A) 1950-2014 data gathered from Geyer *et al.*, 2017 and B) 2015 - 2021 data gathered from PlasticsEurope., 2021

*Plastic Europe (2022) includes Thermoplastics, Polyurethanes, Thermosets, Elastomers, Adhesives, Coatings and Sealants and Polypropylene - Fibers. Not including PET-, PA- and polyacryl - Fibers (estimated data)

1.2 Plastic production process

Plastics are now defined as synthetic or semi-synthetic polymers, primarily made from carbon atoms and mainly derived from crude oil or natural gas (fossil fuels) (Cole *et al.*, 2011). As a result, plastic is causing massive environmental issues throughout its life cycle (cradle to grave) and not just how it is disposed of after use.

The production of plastic begins with the fractional distillation of crude oil, which separates it into smaller and lighter components that are a mixture of hydrocarbon

chains differing in size and structure (Baheti, 2022). The most important of these fractions to produce plastic is Naphtha, fractioning at temperatures <60 - 180°C (Figure. 1.3), which contains a mixture of C₅ and C₁₀ hydrocarbons, including ethane and propane raw material for some plastic products (Jeswani *et al.*, 2021). Naphtha is then converted into monomers, for example, ethylene and propylene (Geyer, Jambeck

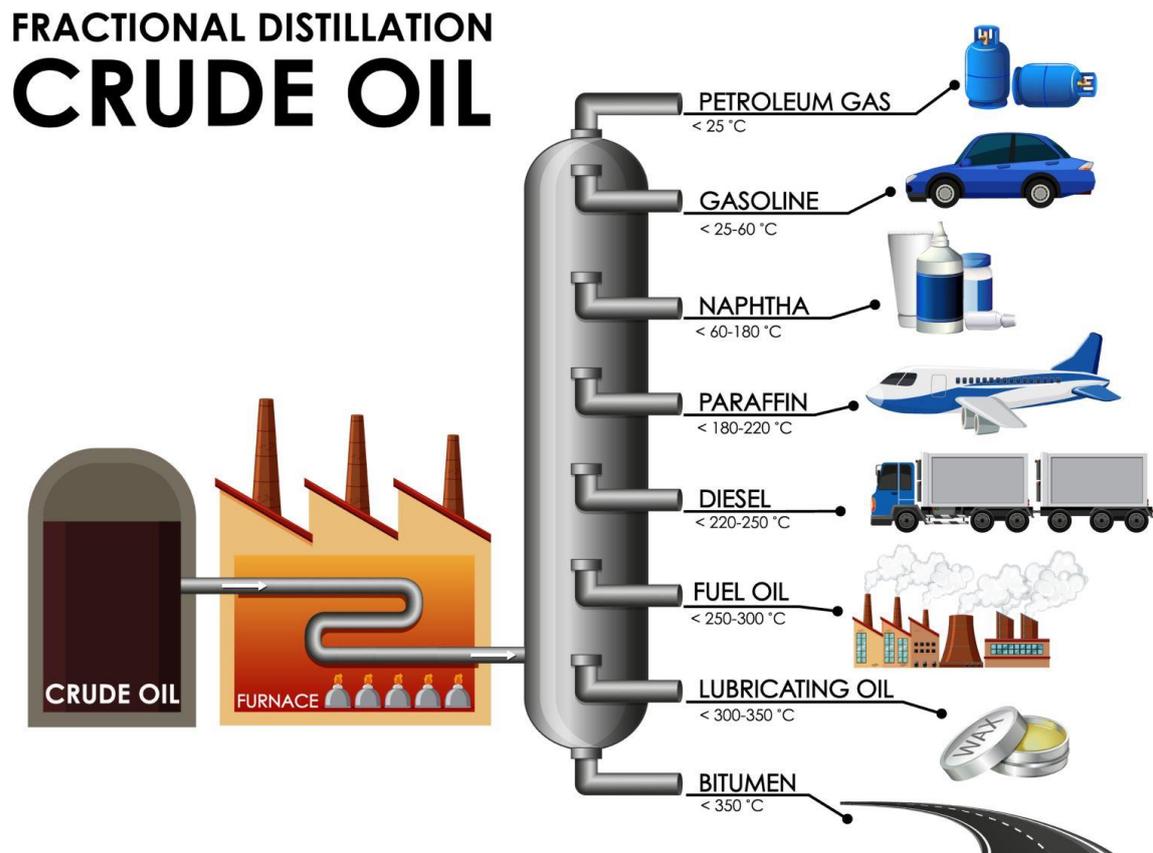


Figure 1.3 Fractional distillation of crude oil into smaller fractions (Baheti., 2021)

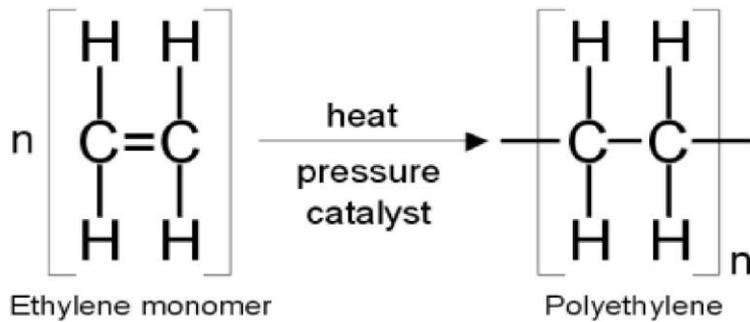
and Law, 2017; Jeswani *et al.*, 2021).

These monomers can react to form polymers by polymerisation, by either addition or condensation (Figure. 1.4). The monomer's double bond breaks during both processes creating an open bond. In addition, the monomers join due to a catalyst, or another initiator molecule and no by-products are formed. An example is when the

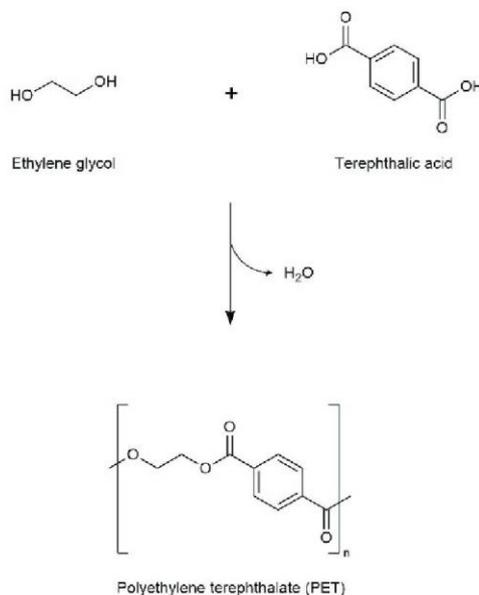
monomer styrene joins with another styrene to become the polymer polystyrene (Baheti, 2022) (Figure. 1.4).

Polycondensation forms polymers by combining chemically distinct monomers and removing water, alcohol, or hydrogen halides, e.g., ethylene glycol + terephthalic acid

A)



B)



= Polyethylene terephthalate (PET) (Jenkins *et al.*, 2020; Ni *et al.*, 2015) (Figure. 1.4).

Figure 1.4 Examples of forming polymers through; A) Polymerisation, combining Ethylene monomers to form a Polyethylene (PE) monomer (Kingshill Science, 2016), B) Polycondensation, combining Ethylene glycol with Terephthalic acid to form

Polyethylene terephthalate (PET) with a by-product of water (Figure 4 from Carr *et al.*, 2020)

1.3 Properties of plastic

Plastics can be separated into two groups: thermoplastics and thermosets. Thermoset plastics can be solid or liquid at room temperature; however, they cannot be reshaped or remoulded once heated. Thermoset plastic includes silicone, epoxy resins, and polyester. However, most plastics are thermoplastics, with over 84% of the thirty thousand different polymer materials recognised as this type by the European Commission (Postle *et al.*, 2012). Thermoplastics can be repeatedly melted, hardened, and reshaped, making them widely used daily. Examples include food containers and fishing equipment; however, there are multiple applications in different industries, mainly as this group consists of the most common types of plastic, including PE, Polypropylene (PP) and PVC (Table 1.1). As a result of the ability to be melted and reshaped, these plastics, in theory, are recyclable. However, the ability to recycle depends on multiple factors, including global use and recycling policies and practices.

Polymer	Global production (Million metric tonnes)	Plastic use examples
Polypropylene (PP)	68	Packaging, i.e., bottles for cleaning products, ropes, carpets, plastic furniture, and clothing
Low-density polyethylene (LDPE)	64	Computer components, packaging, i.e., bin bags, bottle lids, and toys
Polyester, polyamide e and acrylic fibres (PP and A)	59	Textiles – clothing, curtains, blankets, and pillowcases
High-density polyethylene (HDPE)	52	Plastic bottles, i.e., shampoo bottles, Toys, pipes
Polyvinylchloride (PVC)	38	Pipes for water plumbing, flooring, clothing
Polyethylene terephthalate (PET)	33	Packaging, i.e., bottles, sleeping bags, construction material
Polyurethanes (PUR)	27	Automotive – bumpers, building and construction, electronics, packaging foam
Polystyrene (PS)	25	Insulation, food packaging, electronics

Table 1.1 Top 10 most produced plastic polymers in 2015 and some examples of their uses (Geyer *et al.*, 2017)

Additives	25	Anti-microbial, anti-counterfeiting, flame retardants
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1.4 Plastic pollution

With a rise in plastic production and types of plastic, plastic debris worldwide in all environments has become ubiquitous, partially due to a lack of correct or standardised end-of-life processes. New global concerns have increased in the public eye and the scientific community, especially regarding the ecological impacts of plastic waste within marine or freshwater environments. Plastic pollution is concerning as it originates from many sources.

Since the first reporting of plastic pollution over 50 years ago, plastic studies have increased, as has knowledge regarding this topic. Studies on plastic pollution show a variety of shapes and sizes. As a result, plastic debris has been categorised according to size, including macroplastic, mesoplastics, microplastics and nanoplastics. A new category has also been added in recent years in the form of picoplastics which are the size of bacteria (Bilsby and Ferrera., 2021). This study will focus on the most predominant form of plastic debris, microplastics (MPs), which are potentially more harmful to the environment (Desforges *et al.*, 2014; Thompson., 2015). There are discrepancies between the size range of MPs as there is no standardisation. However, many studies define MPs as having a diameter of 1 μm – 5 mm (Barboza *et al.*, 2015; Goldstein *et al.*, 2012). Microplastics can either be primary or secondary. Primary MPs include microbeads manufactured to be small and used in a wide range of cosmetics (Ivar do Sul and Costa., 2014; Xanthos and Walker., 2017). It was their use in cosmetics that led to a “ban the bead” campaign. Secondary MPs, on the other hand, result from the fragmentation of larger plastic debris called macroplastics (>5 mm) as a result of physical, chemical, or biological processes such as wave action (Ivar do Sul and Costa., 2014).

Plastic debris of varying sizes can enter the environment through many sources, including but not limited to; wastewater treatment systems, tourism, or inadequate waste management procedures (An *et al.*, 2020). Most plastic originates from the land, with river pathways being the most significant transport pathway of plastic pollution into the marine environment. When plastic fragments become MPs, the particles can act like sediment. Adapting transport models for a plastic material can help understand retention and release within these systems. Microplastic's small size has resulted in the mass transport of plastic pollution around the world's water systems (Kooi *et al.*, 2018). However, data must be obtained within the different systems to understand MP sources and transport systems. Even though there may be similarities, multiple factors can impact these systems. As a result, two rivers may not transport MPs the same.

The spread of plastic pollution has caused multiple problems in the ocean as well as river environment. It is important to understand sources of plastic and how MP abundance varies within a river system. Previously macroplastics in oceans and larger bodies of water have been the main focus of plastic pollution studies. In recent years this focus has shifted as knowledge and technology improved and resulted in MPs becoming the focus of many studies to further our understanding of MPs impacts and transport systems (Birch *et al.*, 2020; Horton and Dixon, 2018; Peterson and Hubbart, 2021). Rivers or freshwater have become a vital system to study, although it is still understudied compared to the ocean environment.

While plastic consumption is rising, international, regional, and national legal and policy frameworks are becoming necessary to curb the growing plastic tide. These frameworks vary worldwide and potentially add to plastic proliferation.

Policies have been introduced worldwide that impact plastic life cycles from production through consumption to disposal with the main aim of reducing plastic consumption and attempting to create a circular economy via a closed loop of production and recycling chains (Abril Ortiz., 2020). These policies include bans or taxes on plastic products. They range from Rwanda's total ban on plastic bags, where shop owners can face a one-year jail sentence if they are caught selling them (Dagan, 2011), to 10p bag taxes in the UK (Nielsen *et al.*, 2019; Thomas *et al.*, 2019). As the public interest grows around plastic pollution and the impacts become wider known, some countries have taken it further. India pledged to eliminate all single-use plastics (SUPs) by July 1st, 2022, by implementing a nationwide ban on the production, sale, importation, use and handling of SUPs (PIB Delhi, 2022).

However, whilst these policies may reduce the amount of plastic that enters the environment, plastics were designed to be durable. As a result, all plastics made since the 1950s are still in the environment in varying sizes or forms, resulting in 6.3 x 10⁹ mmts of waste from the 1950s to 2017 (Geyer *et al.*, 2017).

This study will focus on MPs within the river Thames, UK. The tidal Thames starts in Teddington, runs through London and joins the North Sea at Southend-on-Sea. The river has been used as a waste transport system for centuries and, in the past, has been heavily polluted with trace metals (Johnstone *et al.*, 2016). Whilst these historic pollutants have decreased, some studies report that the river Thames is the cleanest it has ever been since records began. However, new pollutants such as MPs have not been considered. Whilst studies have been undertaken to research MP pollution within the Thames; there does not appear to be one continuous study to investigate MP abundance along the length of the tidal Thames.

This PhD research focuses on the sources, presence, distribution, and movement of MPs along the river Thames in London and its estuary, contributing to understanding the river as a conduit of MPs.

Research aims and Objectives

Aim: To evaluate plastic pollution in the river Thames and variations due to pollution sources as well as seasonal influences, thus increasing our understanding of plastic pollution within river systems.

The objectives of this study are:

- 1) Determine the extent of microplastic abundance along the tidal section of the Thames river and estuary and obtain a baseline of data on microplastic abundance within the river;
- 2) Determine potential microplastic sources along the Thames and the effect they may have on the microplastic abundance;
- 3) Changes in plastic pollution quantities depending on site or influences such as rainfall and seasonal effects as well as through the Covid-19 pandemic: and
- 4) Use this information to highlight similar issues and preventative measures that are already used to control the flow of plastic pollution into rivers, from wastewater treatment plants and industrial sectors.

This research will highlight the contamination of water in the river Thames and its estuary by microplastics and yield valuable information on the potential impacts on the ecosystem and human health, where it accumulates, which may be used to help the

removal of plastic waste. This research could be used by possible stakeholders such as the Environment Agency, Thames Water and non-profit organisations.

Thesis structure

Chapter 2: Literature review

This thesis investigates MP abundance within the Thames estuary and reviews previous literature with estuaries focusing on the river Thames. This first chapter is dedicated to a literature review. It will also define aspects important to understand the content, e.g., plastic types and environmental issues associated with MPs. Definitions will include plastic sizes (macro, micro, nano and pico), types, sources, impacts and occurrences within the environment.

Chapter 3: Description of study sites and methods used to quantify and characterise plastics

This chapter has two sections; the first will give a detailed analysis of the river Thames, focusing on the study sites. The second focuses on methodology, including how water samples were collected and the steps carried out to filter samples and analyse of MPs. Although filtering and MP analysis were the same throughout the study, the sample dates and locations used in further chapters may vary.

Chapter 4 – River Thames “the great source” Microplastic abundance along the river Thames

This chapter focuses on the river Thames, UK, specifically the tidal section from Teddington to Southend-on-Sea-on-Sea, based on the sampling timeframe of May 2019 - May 2021. It was conducted to provide a baseline dataset for the presence and abundance of MPs within the river's surface water. The focus is to use this dataset

and generate data on the morphology, including polymer types present, to identify potential sources of MPs in the river.

Chapter 5: Seasonality, i.e. rainfall and high rain events and impact on MP

This section looks at the data gathered from water samples collected along the river Thames from 2019 - 2021, focusing on seasonal variation and possible sources. It will look at the impacts of rainfall, wastewater treatment plants, and flow within areas of the Thames.

Chapter 6: Impact of Covid-19 on MP abundance

As the Covid-19 pandemic occurred six months into water sampling, it provided a unique opportunity to explore the impacts of the pandemic and subsequent lockdowns on MP pollution. This chapter will focus on how MP abundance changed from pre-Covid-19 to during Covid-19. During the pandemic, the UK had lockdowns where non-essential workers were required to stay home. As a result, this chapter will also compare non-lockdown to lockdown MP abundances. It will also explore its impact on polymer types and colours of MPs found.

Chapter 7: Microplastic abundance in the Thames River during the New Year period

This chapter looks at the impact of the New Year celebrations held at Westminster, London, in 2019 on the MP abundance within water samples collected from the area over the course of nine days following the firework event, focusing on a source of potential MP pollution that has not been previously looked at in depth (fireworks) whilst also considering other possible sources of MPs within the area.

Chapter 8: Discussion/conclusions – including limitations

This chapter will conclude this thesis. It will present a summary of the main findings regarding the specific objectives set out for this project. It will also reflect on challenges and limitations that presented themselves over the course. As well as present the relevance and knowledge gained that will benefit the topic of microplastics within a river and estuarine environment. The end of this chapter will present recommendations for further work.

Chapter 2 Literature review

Abstract

Plastic use and production is increasing, resulting in an increasingly growing environmental problem from plastic waste. Plastic pollution significantly impacts many aspects of modern-day life, from environmental and human health to the economy and livelihoods. A growing volume of studies on plastic pollution shows these impacts are becoming more evident. The research is expanding into different sizes of plastic (macro, micro, nano and pico) found within the environment. These studies advance knowledge relating to sources, distribution and impact, covering a range of locations, mainly aquatic systems, with a focus on marine habitats. The expanding range of studies has led to various methods to assess microplastic presence, leading to a lack of standardisation within studies that make comparisons between studies difficult.

Furthermore, most microplastic studies focus on marine environments, whilst studies on freshwater or estuarine systems appear to be lacking or scarce. Riverine and estuarine systems are arguably the essential systems to focus on as most plastic debris originates from terrestrial sources. Therefore, investigations should focus on the sources, distribution and mobility of microplastic particles to develop prevention methods and strategies to reduce the discharge of pollution into the sea, rivers, estuaries and marine environments.

2.1 Introduction

Since the creation of modern plastic, plastic pollution has become pervasive in all environments: terrestrial, marine, freshwater, and even space (Clormann and Klimburg-Witjes, 2021; Rochman, 2018). The plastics industry in Europe alone consists of over 60,000 companies, and it is an industry that has created 1.5 million

jobs and bought in 350 billion euros of revenue (Phung, 2019). Due to the adaptability and versatility of plastics, it is hard to find an industry that they have not permeated, ranging from packaging, which is 40% of the plastics market, to construction, and to the medical field (Groh *et al.*, 2019). Although 2020 saw a decrease in production, the industry is booming, and due to its popularity, plastic production is expected to double within the next 20 years (Lebreton and Andrady, 2019).

Studies have shown that plastics are present in varying types and sizes, making it one of the significant societal challenges of the 21st century (Galloway *et al.*, 2017) mainly due to our reliance on them as a society (Galloway *et al.*, 2017; Silva *et al.*, 2019), and the complex nature of removing plastics from the environment (Mendenhall, 2018). Whilst large (> 25mm) pieces of plastic may be visible by the naked eye, plastic degrades overtime resulting in fragments and smaller pieces ultimately resulting in a larger concentration of plastic that are difficult to identify and even harder to remove. One teabag, for example, can release over 20,400 microplastic particles (Busse *et al.*, 2020)

Due to plastics' desirable properties, being lightweight, durable, versatile, robust, with high thermal and electrical insulation, and inexpensive to make, society has become highly dependent on them. However, although these properties are desirable, they are causing massive environmental issues mainly due to their extreme resistance to degradation, as well as plastic being primarily single-use and designed for immediate disposal (Jambeck *et al.*, 2015). Plastics' resistant to degrade coupled with an insufficient and varied waste management programme worldwide has led to an estimated 5.25 trillion pieces of plastic entering into the world's oceans, with 4.8-12.7 million metric tons (mmt) being introduced annually (Eriksen *et al.*, 2014; Haward,

2018). Plastics' lightweight and buoyancy mean they can quickly travel long distances carried by wind and currents, and hence, have become ubiquitous in the environment.

Marine plastic debris was first reported in the 1970s (Carpenter *et al.*, 1972; Carpenter and Smith, 1972) when a mixture of marine debris and macroplastic was observed due to its size, and primarily identified as abandoned fishing equipment or litter from boats. The concern on plastic pollution may be more evident due to its accumulation and impacts, especially within oceans. For example, patches of plastic debris accumulate within rotating ocean currents (gyres) and convergence areas (Egger *et al.*, 2020; Eriksen *et al.*, 2014; van Sebille *et al.*, 2015), also referred to as garbage patches. In total, there are six gyres: 1) the North Atlantic, 2) the South Atlantic, 3) the East Pacific, 4) the North Pacific, 5) the South Pacific, 6) the Indian Ocean (Lebreton *et al.*, 2018; Leal Filho *et al.*, 2021). The largest is the Great Pacific garbage patch (North Pacific Gyre) which is approximately three times the size of France, with an estimated 80,000 tons of debris (Lebreton *et al.*, 2018; Filho *et al.*, 2021). The smallest is the South Atlantic Plastic Gyre, approximately 0.7 million km² (Leal Filho *et al.*, 2021).

Unlike oceans, where there are patches of high plastic abundances or sinks with rivers and estuaries, this seems to vary due to physical factors (flow velocity, water depth and substrate type) as well as temporary factors such as rainfall, tidal cycles and season. For example, riverbed sediment in low-flow areas will be higher than in water samples due to sinking, however in high-flow areas, sediment may be less than water due to resuspension (Eerkes-Medrano *et al.*, 2015; Yang *et al.*, 2021). Riverbed substrate in the intertidal section will have a higher concentration of MP during low tide than high tide (Yang *et al.*, 2021). Plastic debris in marine and freshwater environments, especially macroplastics, negatively impact social, economic, and

ecological structure and dynamics. The environmental implications alone fall into two categories: 1) physical harm to organisms via ingestion (damage to digestive system), or by entanglement (risk of strangulation) (Mallory, 2008; Mascarenhas *et al.*, 2004), and 2) chemical harm: production of plastic, requires many chemicals and additives, and plastic waste can leech or adsorb into the environment and organisms (Teuten *et al.*, 2009). As a result, these chemicals can travel long distance through the environment or transported by organisms that ingest the chemicals.

Although the main focus on plastic pollution has so far been in marine habitats, recent developments have found that marine sources of litter contribute to a small percentage of plastic waste. These studies point to 80% of plastic originating from terrestrial sources (Andrady, 2011; Van Sebille *et al.*, 2016) and entering the marine environment via rivers and waterways. As plastic has become a necessary product for human use, higher plastic waste is observed in high population density areas such as major cities (Tibbetts *et al.*, 2018; Yin *et al.*, 2020). Anthropogenic sources such as the release of clothing fibres from washing machines (Dalla Fontana *et al.*, 2020; De Falco *et al.*, 2019; Kelly *et al.*, 2019; Napper and Thompson, 2016) or particles from car tyres (Ziajahromi *et al.*, 2020) also contribute to plastic abundance within rivers.

Pollution studies have highlighted a threat to the environment, biota, and human health (Arias-Andres *et al.*, 2019; Sharma and Chatterjee, 2017). This threat, publicity and increased awareness of the growing production and accumulation of plastic pollution worldwide have increased the need for the development of policies and management strategies on local, regional, national and global levels (Borrelle *et al.*, 2020; Syberg *et al.*, 2018; Willis *et al.*, 2021). The strategies emphasised the need for further studies and generated data on the abundance, distribution, and composition of polymer debris, which are still widely unknown (Chae and An, 2018; Earn *et al.*, 2021). These

studies have led to the discovery of plastics of assorted sizes: macroplastic, microplastics (MPs), nanoplastics and picoplastics (Thompson *et al.*, 2004; Bermúdez and Swarzenski, 2021). However, with increasing number of studies, a lack of standardisation between studies has become evident from the methods used to collect samples, define sizes, and measure abundances, therefore making it essential to follow standardised practices. This would allow for comparisons between studies, which would ultimately lead to a better estimate of how much plastic in each size fraction has contaminated the environment, and its sources, allowing for appropriate policies and regulations to be effectively implemented.

This introductory chapter aims to review the literature on plastic pollution, MP pollution and its role within freshwater and estuarine environments, especially the Thames river. It will include the impacts, sources, and methods currently used for sampling and analyses, to identify inconsistencies or knowledge gaps where further investigations could be explored.

2.2 Plastics and classification of sizes

Reviewing the literature on plastic studies shows a lack of standardisation (ambiguity), from the definition of plastics to size characterisations as plastic litter occur in a range of sizes. This lack of uniformity makes it hard to compare data and fully assess the impact and abundance of plastic pollution that has reached the marine environment (Ryan *et al.*, 2009). The term plastic pollution incorporates a wide range of topics within its spectrum, i.e., different plastic types, locations, chemicals within plastic particles, and even size, including everything from macroplastic such as ghost nets, to nanoparticles.

The term plastic also has many different definitions. The Cambridge dictionary defines it as “an artificial substance that can be shaped when soft into many different forms and has many different uses” (Cambridge University Press, 2022). However, in science, it is described as a synthetic or semi-synthetic organic polymer that is lightweight, durable, and low cost. It is designed to meet the needs of a range of products (van Emmerik, 2021; van Eygen *et al.*, 2017).

These definitions cover many sizes that plastics can be manufactured in or broken down into. Due to the global distribution of plastic and its broad range of particle size, multiple size classifications have been used in studies (Figure. 2.1). The most common groups stated within the literature are macroplastic and microplastic (MP) (Cyvin *et al.*, 2021).

Although sizes have been proposed such as: macro = >1 mm, meso = 1 - 10 mm, micro = 1 - 1000 μm , and nano = 1 - 1000 nm (Stark, 2019). This brings into question about which size group to assign particles on the border between for e.g., microplastic (max 1 mm) and mesoplastic (minimum 1 mm).

The definitions get murky when looking at microplastics (MP) specifically: the Group of Chief Scientific Advisors (2019) states that MPs should be no more than 5 mm at their longest dimension and nanoplastics as between 1 - 100nm (Thompson *et al.*, 2004). Other definitions within the literature on MP include: 1) Particles are smaller than 500 μm , or 2) 1 μm - 5 mm (Frias and Nash, 2019). This leaves a wide range of sizes described within studies and may mean a potentially significant range of plastics are left out of studies, thus resulting in undetected or unreliable plastic pollution levels.

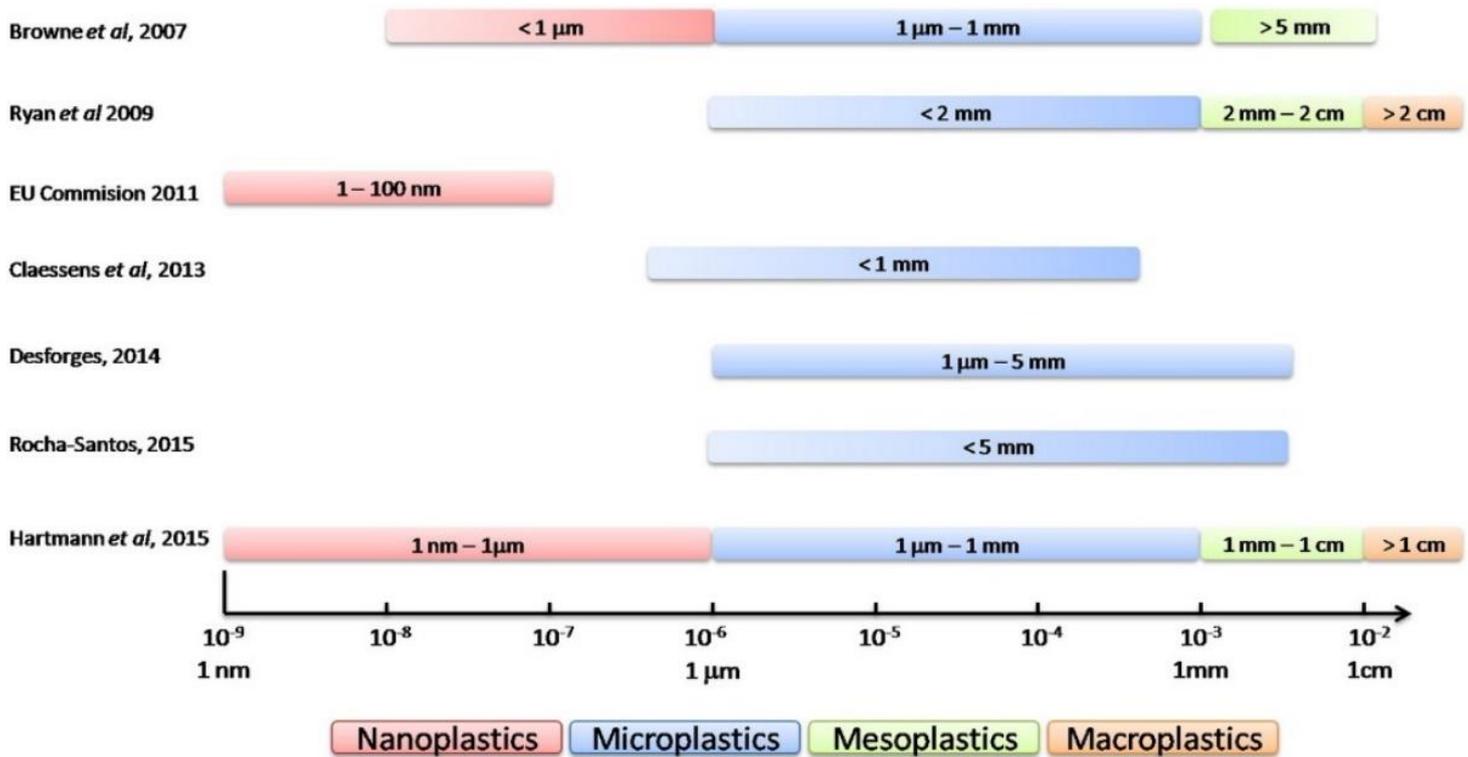


Figure 2.1 Size-based definitions of plastics proposed by different authors 2015-2017 (Fig.1 in Da Costa *et al.*, 2016)

2.3 Microplastic classifications

2.3.1 Primary microplastics

Depending on their source, MPs fall into two categories - primary and secondary. Their source can affect their shapes and composition. Primary MP are purposely manufactured to be small for the products or applications they are used for. Primary MP account for 3 mmt of plastics released annually into the environment globally (UNEP, 2018), with 145,000 tonnes produced in Europe (ECHA, 2021).

Primary MP are mainly pre-production pellets or nurdles (also known as resin pellets or mermaid tears) which come in various shapes and colours (Avio *et al.*, 2017). They form the raw material used to make plastic moulds in industries. They are known for their smooth surfaces, which differentiate them from other primary MPs, and their

lightweight and buoyancy, which means they can travel vast distances in ocean environments (Fernandino *et al.*, 2015). However, smaller powders called fluff can also be produced, which can be irregular in shape (Karlsson *et al.*, 2018). Nurdles have been entering waterways since the 1940s, with reports of being found on beaches since the 1970s (Carpenter and Smith, 1972; Carpenter *et al.*, 1972; Jambeck *et al.*, 2015).

Accidental industrial spills during production or transport account for 5 - 53 billion pellets per annum in the UK, making it the most common way nurdles enter the environment, according to Cole and Sherrington (2016). However, this could be greatly underestimated as, concentrations of nurdles lost through accidental spills are primarily unknown or under-reported (Karlsson *et al.*, 2018). These pellets have also been called virgin plastic, criticised by some researchers who believe they should have their own group (Andrady, 2011; Costa *et al.*, 2009).

Virgin plastic is resin pellets that are easier to transport before manufacturing plastic objects. These pellets are made from petrochemical feedstock, e.g., natural gas or crude oil, which has never been processed. However, they are the same size and shape as resin pellets (Kershaw, 2015). Biobeads are similar to nurdles, and sometimes mistaken for them, as shown in the report by CPPC (2018) where 90% of primary MPs found in an English Channel beach near France and Belgium were bio-beads instead of the suspected resin pellets. Bio-beads are used as part of the filtration process in some wastewater treatment plants (WWTP). Each reactor in the plants can contain up to 5.4 billion bio-beads; these can make their way into the environment if the steel mesh holding the beads splits (CPPC, 2018).

Another example of primary MPs are scrubbers, first patented in the 1980s and are most often found within the cosmetic industry and personal care products, such as lipsticks, toothpaste and sun lotions (McDevitt *et al.*, 2017). Often referred to as microbeads in the media, their size, shape, and polymer type depend on the cosmetic product they are found in (Fendall and Sewell, 2009). The most common polymers used for microbeads are polyethylene (PE), nylon, polypropylene (PP) and polyethylene terephthalate (PET). These beads were banned in cosmetic products from the UK in 2018 due to an estimated 4,000 tonnes a year being released into the marine environment (Europe) (Carrington, 2019; Jinhua and Guangyuan, 2014; Sundt *et al.*, 2014). Scrubbers are also used in other industries such as oil and gas exploration, plastic blasting, grit and sandblasting at shipyards, offshore maintenance, or car parts (Boucher and Friot, 2017). Microscopic dust is also a result of scrubbers, the dust originates from the techniques above as scrubbers which can be used several times, but each time breaks down into smaller particles (Laskar and Kumar, 2019). It is unknown how many particles enter the atmospheric environment this way, due to a lack of data and studies.

2.3.2 Secondary microplastics

The term secondary MPs is used to describe small plastic pieces (e.g., fibres, fragments, films) that are formed by fragmentation and the breakdown of larger plastic items (macroplastics) (Auta *et al.*, 2017). The items that break down include, but are not limited to, textiles, paints, tyres and plastic bags released into the environment. Moret-Ferguson *et al.* (2010) found that irregularly shaped fragments are abundant in intertidal and oceanic habitats, with most plastic debris trending toward smaller pieces. The study suggested that most of these irregularly shaped pieces came from the degradation and breakdown of larger objects into smaller fragments by various ways

(Figure. 2.2). Thompson *et al.* (2004) have even suggested that synthetic polymers may be the remnants of macroplastics, and Andrady (2011) has speculated that these remnants could begin to degrade into nanoplastics over time.

Over extensive exposure to physical, biological and chemical processes, plastics break into small pieces due to a reduction in structural integrity, resulting in fragmentation. In theory, plastic fragments can keep degrading and getting smaller, thus going from one plastic size classification to the next as the process is ongoing (Fendell and Sewell, 2009).

Plastics can break down through various ways such as road (Andersson-Sköld *et al.*, 2020) or tyre wear (Kole *et al.*, 2017), wave activity (Ryan *et al.*, 2009), temperature, exposure to acids and alkalis, and sunlight or ultraviolet (UV) (Cooper and Corcoran, 2010). Biological degradation can also occur through the presence of bacteria, fungus (i.e., *Aspergillus tubingensis*), or enzymes that can “digest” plastics, as well as the presence of organisms (Baker, 2018; Eriksen *et al.*, 2014; Lusher *et al.*, 2015) that consume and degrade plastic, for example, waxworms, mealworm and microbes. Over time, plastics degrade, turn brittle, form cracks, and become yellow, and hence become more susceptible to degradation (Andrady, 2011).

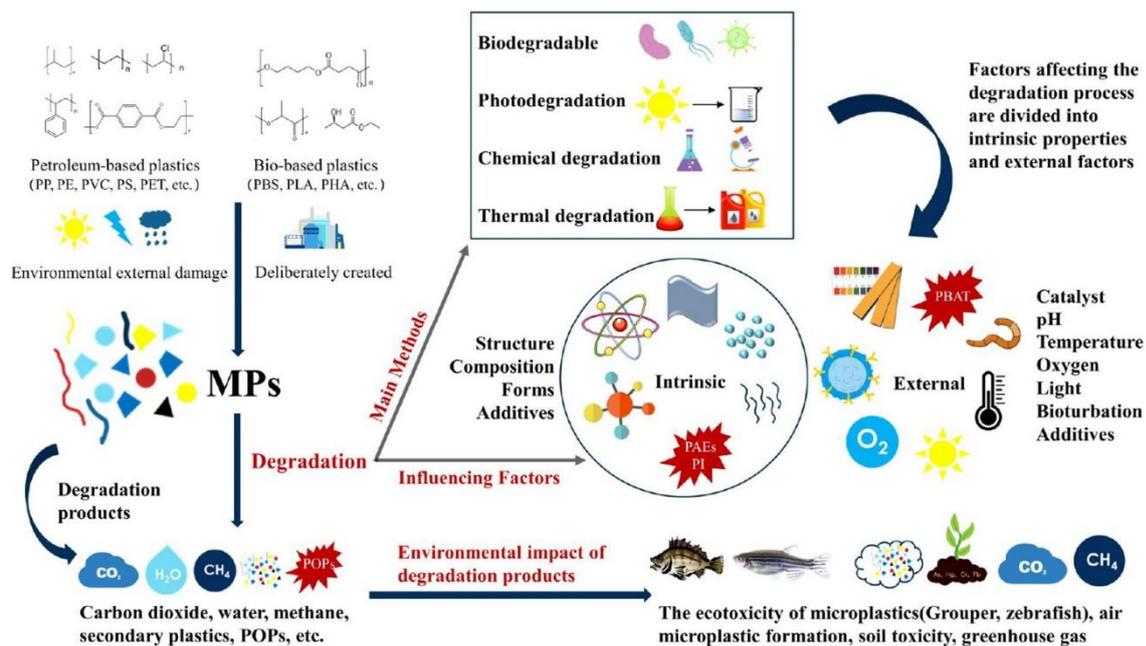


Figure 2.2 Types of degradation experienced by plastics, particularly microplastics and influencing factors (graphical abstract from Liu *et al.*, 2022)

2.3.3 Alternative Plastics: bio-based plastic, biodegradable and compostable plastic

Due to increasing publicity on plastic pollution, alternatives to plastics such as bio- and compostable plastics have been developed and recently introduced for public use. This greener approach and bio-based research have offered alternatives to plastic. In 2021 they made up 1% of the global plastic production (European Bioplastics, 2022). They are biodegradable plastic and plastics produced from renewable sources such as feedstock (Di Bartolo *et al.*, 2021). Bioplastics are already being used as alternatives to plastics in different industries such as food (packaging and carrier bags), agriculture, automotive and electronics (George *et al.*, 2020). While the name bioplastic implies that the material breaks down and biodegrades, this is not the case in general.

There are three groups of bioplastics: 1) biobased and biodegradable such as polylactic acid (PLA) (Garlotta, 2001), 2) biobased but not biodegradable such as bio polyethylene (bio-PE) (Siracusa and Blanco, 2020), and 3) biodegradable bioplastic made from fossil fuels such as polyvinyl alcohol (PVA) (Aslam *et al.*, 2018) but specific conditions are needed for the breakdown of this material.

For bioplastics to be classified as biodegradable, it needs to be able to break down under specific conditions. Currently, biodegradability standards use well-defined conditions that biodegradability or compostability tests will achieve (Kale *et al.*, 2007; Narancic *et al.*, 2020). However, scientists have pointed out that these standards are not replicable within the natural environment where temperature and humidity fluctuate (Nandakumar *et al.*, 2021; Vardar *et al.*, 2022). This can result in an incomplete breakdown of material into MPs (Emadian *et al.*, 2017; Hubbe *et al.*, 2021), also hampered by the use of plasticisers, surfactants and polymer blends which can affect the biodegradability or can have harmful impacts on the environment (Hubbe *et al.*, 2021; Shen *et al.*, 2020; Tokiwa *et al.*, 2009). Whilst there are differences in their end-of-life degradability if disposed of incorrectly, bioplastics will have many similarities with plastics and MPs regarding environmental sources and potential impacts.

2.4 Microplastic sources within the environment

Plastics of varying sizes can be found within the environment with many studies (Gesamp 2016; Horton *et al.*, 2017; Wang *et al.*, 2018) showing that primary and secondary sources of MPs follow the same pathways (Figure 2.3) and are not dependent on the source or size. Hence MPs can be found in terrestrial, freshwater and marine environment as well as in the atmosphere (Zhang *et al.*, 2020). Primary MP will be lost through production or transport and subsequently enter the surrounding

area. Secondary MPs may enter the environment through sources such as illegal dumping, mismanaged waste or litter (e.g., lost shipping gear or damaged nets).

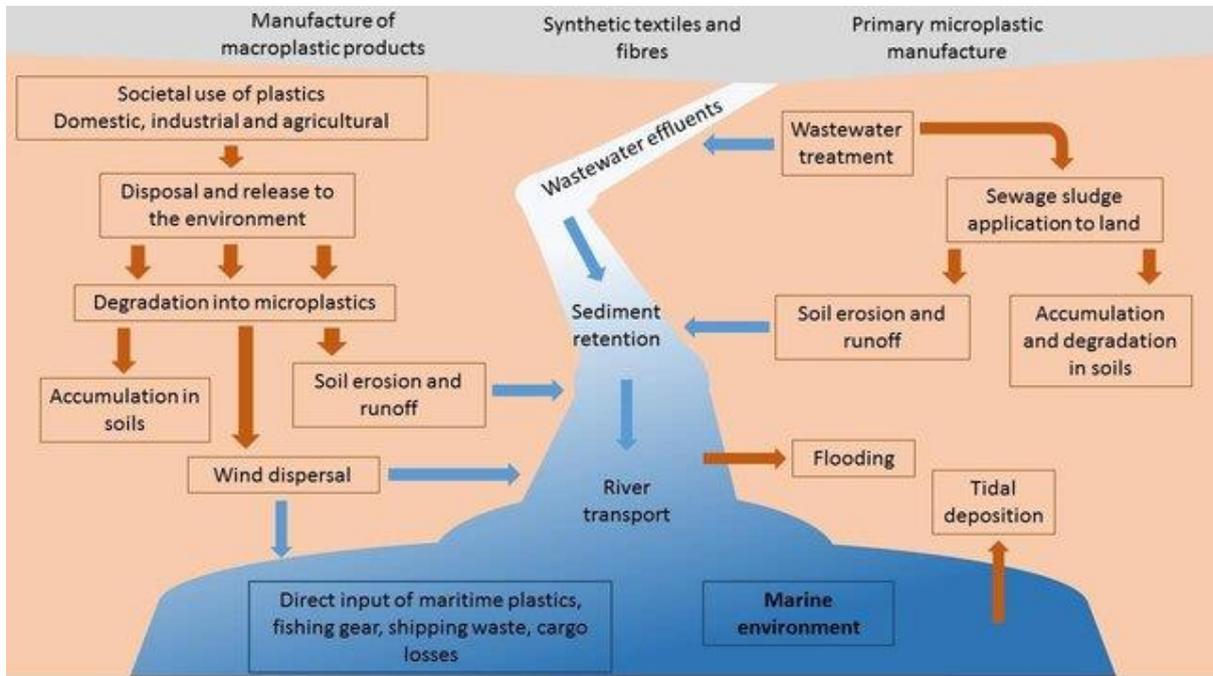


Figure 2.3 Sources and pathways of microplastics in terrestrial and marine habitats (Source: Horton *et al.*, 2017)

Table 2.1 Sources of plastic in the sea and amount released into the oceans per annum European Union (EU) and in the UK.

Origin	Source	EU/YEAR (Tonnes) [K= thousands M= millions]	UK/year (Tonnes)	Reference
Land Based- Inland	Sewage sludge	125-850 per M people	612-673	Environment and Land Reform, 2021; Nizetto <i>et al.</i> , 2016
	Personal care products	EU-3,125	"data not available"	Essel <i>et al.</i> , 2019
	Domestic and industrial cleaning products	"data not available"	"data not available"	
	Road Paint	80 K	"data not available"	Eunomia, 2016
	Tyre abrasion	EU-375 -693.75	63 K (UK passenger cars only)	Kole <i>et al.</i> , 2017 ; Essel <i>et al.</i> , 2019

	Synthetic textiles	“data not available”	2.3-5.9 K	Browne <i>et al.</i> , 2011 ; Essel <i>et al.</i> , 2019
	Plastic pellets loss	21 -210 K	105-1,054	Cole <i>et al.</i> , 2011 ; Essel <i>et al.</i> , 2019
	Litter/large plastic items	34 -57 M	10 -26 K	Essel <i>et al.</i> , 2019
	Packaging/municipal waste	75-80??	10-26 K	Andrady, 2011; OSPAR Commission, 2017
Land based-coastal	?? source	9 M	“data not available”	Jambeck <i>et al.</i> , 2015
At Sea	Fishing litter	1.15 K	“data not available”	Barnes, 2009
	Shipping litter	0.60 K	“data not available”	Barnes, 2009

2.4.1 Microplastics on Land

Plastics are manufactured on land and primarily used on land except for plastic use in the marine and fishing industries as well as goods on transit on ships. As a result, plastic pathways will be mainly affected by practices on land, including littering or inefficient waste management programmes, e.g., in water and solids in waste disposal systems and through industrial spills. Despite these facts however, studies are scarce on the sources of MPs on land. Malizia and Monmany-Garzia (2019) suggest that this may be because plastics are hidden from sight by vegetation or within soils inland, so they are less detectable. As a result, the soil could act as a long-term sink for MPs, meaning terrestrial environments could be the most plastic contaminated due to landfills, urban areas and the agricultural industry (Ng *et al.*, 2018; Tympa *et al.*, 2021).

2.4.2 Landfills

Increasing human population and plastic use, leading to increasing plastic production inevitably results in similarly increasing amount of plastic waste being generated. A lack of a global waste disposal scheme and inefficient recycling schemes have led to plastics becoming a significant contributor to municipal solid waste (MSW), the treatment of which varies depending on economic development of countries as well as commitment to environment sustainability (Nkwachukwu *et al.*, 2013; Rajmohan *et al.*, 2019).

According to Zhou (2014), landfills receive plastic waste of up to 20% of the MSW, including a range of plastic types and sizes. Even in the absence of light and oxygen in landfills, macroplastics will continue to fragment into much smaller sizes due to microbial activity, fluctuating temperatures and stress due to compaction (Zhang and Chen, 2020). Microplastics in landfills can also act as vectors for hazardous chemicals or pollutants that they contain if the MP finds its way into the natural environment

through landfill leachate; the adverse effects this may cause are only recently being studied (He *et al.*, 2019; Silva *et al.*, 2021; Xu *et al.*, 2020).

Whilst landfills contribute to MP pollution on land, data from five Pacific countries (China, Indonesia, the Philippines, Thailand, and Vietnam) (Conservancy Ocean, 2017) shows they also contribute over 1.1 - 1.3 mmt of plastic to marine environments annually. This is because landfills can be subjected to flooding from rivers or surface water flooding, especially in a flood hazard zone (Laner *et al.*, 2009). An increase in plastics within landfills may also contribute to the potential of flooding. Jahanfar *et al.* (2017) found that plastic layers may retain water and increase the risk of the landfill collapsing.

Even if a landfill is not currently in a flood hazard zone, due to the longevity of a landfill, growing plastic use and waste may pose a serious concern. Hence more studies should be made, and methods developed to prevent the mobilisation of pollutants in waste deposits (Laner *et al.*, 2009). England alone currently has over 1,200 historic landfills in coastal areas, which are at risk of flooding with sea levels rising (Brand *et al.*, 2018), and the risk is likely to increase with time.

Various physical barriers such as wall lining are in place globally to contain contaminants within a landfill. If a lining is used, then macroplastics and MPs will end up in treatment facilities for run-off and leachate, which are 70-100% efficient in removing them from the environment (Praagh *et al.*, 2018). However, if a lining is not used, MPs are transferred to the soil and accumulated in groundwater or travel deeper in the ground due to cracks and macropores (Yadav *et al.*, 2020), depending on soil conditions. However, preventative measures are not used worldwide and also do not exist in some historic landfills.

2.4.3 Urban areas

Urban areas have a high anthropogenic activity due to a high population density, and it could be regarded as a significant source of MPs in the terrestrial environment. Microplastics could be produced in several ways: from tire wear, construction, or industrial activity and products, littering, etc.

Car tyres, for example, release plastic through mechanical abrasion and general wear and tear. Some studies suggest this is a leading source of MPs in the environment (Sundt *et al.*, 2014; Prata, 2018), but this is disputed. The number of particles released varies depending on the temperature or climate, road surface, speed, and tire and road structure (Alexandrova *et al.*, 2007). Airplanes, conveyor belts, bikes and construction vehicles such as diggers also experience wear and tear. It has been noted that car parts can enter waterways through road runoff such as bumpers or hubcaps, even road markings that all eventually break down into smaller particles called tire wear particles (TWP) (Browne *et al.*, 2010; Tibbetts, 2015). Recycled car tyres are used on artificial grass for playing fields to increase grip. One study on artificial grass football pitches in Denmark found that the rubber in-fill enters the environment, each year equating to 380-640 tonnes (Environment protection agency, 2015). As a result, more urban places have a higher MP input than rural areas (Su *et al.*, 2020) for example average MP abundance in sediments in rural areas 83.20 ± 32.99 n/100g dry weight (dw/ dry weight) are lower than urban areas 182.67 ± 72.21 n/100g (dw) (Liu *et al.*, 2021).

2.4.4 Agricultural sources

As in other industries, plastics have also infiltrated agricultural processes, where materials and equipment made from plastic are used in natural products such as crops

or animal production. In 2019, use of plastics in agriculture reached 7.4 mmt globally (Plasticseurope, 2022). Polytunnels, plastic mulch, greenhouses, protective nets, and irrigation systems are just a few examples of equipment's and products made from plastic used within the crop production systems (Shah and Wu, 2020). Twin bale nets or stretch films that protect crops, or store fodder are examples in animal production systems. The most common types of polymers used in this industry are polypropylene (PP), low-density polyethylene (LDPE), polyvinylchloride (PVC), and polystyrene (PS) (Briassoulis *et al.*, 2013). To get a perspective of the quantity of plastic used in the agricultural industry, 1.5 mmt of film mulch (made of polyethylene – PE) alone is used annually and total plastic used worldwide within the agricultural industry is estimated at 7.4 mmt (FAO, 2021). A substantial percentage of this mulch is not recovered at the end of the season, leaving the plastic particles to accumulate in the soil (Zhang *et al.*, 2020).

Besides the equipment and tools used, biosolids or sewage sludge from wastewater and sewage systems are used on agricultural land as fertilisers and in irrigation (Table 2.1) (Nizzetto *et al.*, 2016). Plastic particles captured in the WWTP system can end up in sewage sludge. Many types of MP, such as fibres, beads, glitter and fragments, have all been found in sludge samples (Nizzetto *et al.*, 2016). Sewage sludge is used in the European Union (EU) predominantly as compost for arable land, whilst the rest is sent to landfills. Reports from DEFRA (2012) showed that the EU-27 produces 10 mmt of sewage sludge (dry solids) annually, and nearly 40% of this is added to agricultural land. Carr *et al.* (2016) state that up to 90% of all MPs entering the treatment plants will settle in the tanks and accumulate in the recycled sludge placed on arable land. According to the EU, 125-850 tonnes of MPs per million inhabitants

are added to agricultural land due to sludge application from WWTP (Nizetto *et al.*, 2016).

2.4.5 Sources in freshwater

Plastics can be introduced in freshwater systems directly from plastic sources used on land (e.g., combined sewage outflows (CSO)), as well as indirectly from WWTP sludge placed on agricultural land that may enter waterways through land runoff during rainfalls. Storms or extreme weather events can be another source of MP in freshwater environments. To prevent overflow of sewage during these events, WWTP industries can discharge water straight through the overflow pipes and into rivers, meaning that plastics accumulated in the sewers, or the street can be released into waterways without being filtered and removed. Plastics and debris are expected to be collected, treated and released by WWTP, especially in urban areas, except during periods of heavy rainfall, and possibly flooding, when sewers and plants cannot cope with the high volumes of water (Prata, 2018). After periods of heavy rainfall plastics of varying sizes may also be washed from land as the flood water recedes and can enter water environments as a result.

Wastewater treatment plants are considered a significant pathway of MPs into the aquatic environment (Kazour *et al.*, 2019; Talvatie *et al.*, 2015). WWTP treat industrial and domestic water containing MPs from various products and places. Gouin *et al.* (2011) reported that wastewater treatment in the river Clyde (Glasgow) emits 65 million microplastic particles into the river daily. Microbeads from personal care products (PCPs) or fibres washed off from clothes into household drainage systems and entering sewage systems are one of the primary MP pollution sources. Research by Napper and Thompson (2016) shows that 6 kg of washing can release over 700,000 fibres into the sewage system. Fibres in washing machine wastewater account for 35%

of primary MP released globally (Boucher and Friot, 2017). For example, during a 5 kg wash of polyester fabrics, De Falco (*et al.*, 2017) found that on average, 6 million microfibers were released depending on the detergent used. Currently, the suggested solution is the placement of filters in washing machines to collect MP fibres released during the washing process, to prevent introduction into the environment, specifically in rivers (Brodin *et al.*, 2018). In the UK, a bill was introduced in January 2022 (UK Parliament, 2022) in parliament that requires manufacturers to fit MP catching filters to washing machines. However, an argument can be raised as to what procedures will be put into place to prevent these filters and subsequent MPs from entering the environment through other means, such as the littering of filters.

Although strict practices are in place to remove pollutants from waste treatment plants, MPs can pass through the physical and chemical filtration systems due to their small size. Although 99% of MPs are supposedly trapped during the primary and secondary treatment processes, studies have shown that treatment plant processes need to be updated to efficiently remove 100% of MPs (Browne *et al.*, 2011; Mathalon and Hill, 2014; Murphy *et al.*, 2016). These processes currently cannot deal with certain pollutants such as heavy metals, pharmaceuticals, and MPs (Magni *et al.*, 2016; Magni *et al.*, 2017; Talvitie *et al.*, 2017).

Whilst the main inputs of MPs are from combined sewage outflows (CSOs) and WWTPs, other sources such as recreational facilities (e.g., boating, shipping in estuaries) can also be a source of MPs in freshwater environments. Estuaries for example with high levels of shipping and recreation boating use contain higher MP abundances than rivers with low or no shipping activities (Galagher *et al.*, 2016). Fishing or angling in rivers can also increase MP pollution. De Carvalho *et al.* (2021)

for example found a mean concentration of 17.4 pieces of MP kg⁻¹ in ground bait used by anglers to attract fish.

2.4.6 Sources in Marine Water

Plastics, including MPs, make their way from the terrestrial environment through the aquatic and freshwater environment and may eventually end up in the marine environment. Meijer *et al.* (2021) state that the primary source of plastic in the marine environment is plastic travelling through rivers, accounting to 80% of plastic globally. Data compiled (Table 2.2) from studies by Lassen *et al.* (2015), Magnusson *et al.* (2013), and Sundt *et al.* (2015) show that MPs of multiple sizes are found in the marine environment introduced from various sources.

Table 2.2 Sources of microplastics found in the environment, including the marine environment with the range of sizes commonly found within particles (Source: Lassen *et al.*, 2015; Magnusson *et al.*, 2013; Sundt *et al.*, 2015).

Source	Process	Microplastics (MP) Size (mm)
Personal care products (PCP)	Wastewater effluents	0.005-0.8
Laundry/household dust	Wastewater effluents	0.01-0.1
Plastic pellets	Plastic moulding	1-5
Exfoliation polymer paints	Urban/ industrial environments	0.05-1
Degradation/weathering/breaking down	Plastic litter in landfills/ recycling facilities	(MPs of all sizes)

		0.005-5
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Extreme environmental disasters such as floods, tsunamis, volcanoes can have significant ecological impacts by increasing plastic pollution. In 2011, the Tsunami in Tohoku, Japan, produced floating debris, which would have taken 3,200 years of regular debris input to reach the amount of waste entering the system within a few days (Lebreton and Borrero, 2013), thus also enhancing the movement of plastic through physical barriers to be washed into lower ground and the oceans.

Plastics can also be introduced directly into the sea from vessels. Rubbish from ships and boats may be accidentally released or blown off into the water, or purposely thrown overboard (e.g., lost or broken fishing equipment), contributing to marine litter. The fisheries industry refers to abandoned, lost or discarded items such as gloves, ground ropes and fishing gear as “abandoned, lost or otherwise discarded fishing gear” (ALDFG). Macfadyen *et al.* (2009) estimated this loss equates to more than 640,000 tonnes per year globally. Degradation or maintenance, such as painting hulls, resulting in paint flakes also contribute to plastic litter in the sea (Magnusson *et al.*, 2017); paint flakes were observed in higher quantities near shipyards or marinas (Turner, 2021). Waste from ships and fishing vessels accounts for 20% of current marine litter, even with several global, international and national regulatory and management legislation to prevent marine debris from ships and vessels (*European Parliament, 2019*).

2.4.7 Atmospheric Sources

Compared to studies on MPs on land and fresh and marine waters, investigations into atmospheric MPs are relatively more recent. Whilst a global perspective and long-term monitoring have yet to occur, there have been studies undertaken that report urban, rural and remote areas as well as indoor and outdoor pollution (Dris *et al.*, 2015; Dris *et al.*, 2017; Liu *et al.*, 2019; Yin *et al.*, 2019; Zhang *et al.*, 2020). In their study on MPs from textiles, Dris *et al.* (2017) reported that indoor MP concentrations appeared to be significantly higher (1 - 60 fibres m³) than those outside (0.3 - 1.5m³), suggesting that indoor MPs from textiles may be an important source of atmospheric plastic pollution. Atmospheric particles (< 100 µm) (Allen *et al.*, 2019) and fibres (between 100 - 500 µm) which made up 50 - 80% of samples (Dris *et al.*, 2017) tend to be smaller in size composition than those found in other environments. Moreover, studies have often shown that samples and experimental set ups can easily be exposed to atmospheric contamination from MPs, adding a challenge to controlled studies to prevent or limit the contamination level. The atmosphere is more likely to play an essential role within the transport system for plastics; however, studies have only recently started on the topic, and little is known about this process (Allen *et al.*, 2019; Dris *et al.*, 2017).

2.5 Microplastic impacts on the environment

Knowledge and awareness of the impact of MPs on the environment and organisms is only just emerging. The consensus is that their occurrence in the environment is causing harm to all living organisms in a range of ecosystems and habitats. Due to the small size of MPs and nanoplastics (100 nm), various organisms can ingest these fragments. Studies are also starting to show evidence of ingestion and being passed along in the trophic chain, thus raising concern about the organisms (Lozano and Mouat, 2009) as well as implications for human health (Lehel and Murphy., 2021; McIlwraith *et al.*, 2021; Van Raamsdonk *et al.*, 2020; Walkinshaw *et al.*, 2020).

It is not just organisms affected by this pollution problem; the aesthetics and economic cost of all the effects of plastic pollution globally have been estimated at between £4.6-14.8 billion per year in 2018 (marine environmental cost only) (Petten *et al.*, 2020). Based on 2011 ecosystem service values and marine plastic stocks, Beaumont *et al.* (2019) place the value of damage between £2,500-25,700 per tonne of marine plastic. Whilst numbers appear to be a rough estimate; both papers agree that the economic cost of the impacts of plastics will be far greater.

Physical obstruction, for example by plastic bags, can block waterways and may increase damage and destruction from natural disasters. Blocked waterways also increase the likelihood of infestation by pests and mosquitos, which increase cases of malaria and other vector-borne diseases, adding to impacts other than environmental ones, such as public health and socio-economic (Thiel and Gutow, 2005a).

2.5.1 Physical impacts on organisms

Plastics were first found in sea birds in the 1960s (Harper and Fowler, 1987) after which many studies were carried out on plastics in organisms. Plastic fragments have since been observed in freshwater and marine systems in a range of organisms such as molluscs (Polidoro *et al.*, 2022; Wright *et al.*, 2013), Cnidaria (Devereux *et al.*, 2021), sea cucumber (Iwalaye *et al.*, 2020) and nematodes (Kim *et al.*, 2020). Whilst ingestion of plastic can cause damage to the organisms themselves, plastics can also introduce invasive species to an area as they provide refuge or transportation to many organisms. Globally, 1,200 species are associated with natural and human-made debris (Noaa, 2017). These new species can then be transported to an area that can lead to ecological disturbance and the destruction of an ecosystem (Noaa, 2017; Thiel and Gutow, 2005a).

Ingested plastic can also result in being transferred up the trophic system, affecting food chains and the ecosystems (Egbeocha *et al.*, 2018). Following ingestion, some plastic will be excreted independently of feeding methods. For example, polychaete worms can egest faecal casts, which contain microfibers without causing harm to the organism (Browne *et al.*, 2008; Thompson *et al.*, 2004). Plastic that is not excreted can also build up in the guts of organisms which can cause pseudo-satiation, which makes the organism feel full, and as a result, they starve to death. Some particles can also translocate into other tissues in the organism, which can cause further damage (Browne *et al.*, 2008; Hall *et al.*, 2015). These problems include the sub-lethal effects of toxicology, such as reduced productivity, growth and fitness, ultimately causing the individual's death and potentially the species (Wright *et al.*, 2013a, b).

2.5.1.2 Chemical impacts on the environment

Plastics in landfills or littered on land leak chemicals and additives as they break down, affecting the environment. Plastic chemicals may accumulate in the soil, and organic pollutants potentially change the soil chemistry (Fuller and Gautam, 2016). However, further knowledge is required on their presence, transport across physical boundaries, and interaction with and effect on the environment. Many studies have shown how Bisphenol A (BPA - a synthetic oestrogen found in water bottles) can act as an endocrine disruptor in organisms such as fish, reducing fertilisation and affecting population sizes (Ivar Do Sul and Costa, 2014; Rochman *et al.*, 2013; Science Daily, 2015). These chemicals leak and enter the aquatic systems through run-off during rainfall or when the plastic breaks down.

Plastic products in today's commercial market vary greatly in type and chemical composition. However, 90% of the plastic products consist of the polymers LDPE,

HDPE, PP, PVC, PS or PET. Additives or resins are added to make plastics, enhance the performance of materials such as fire retardants, ultraviolet (UV) stabilisers or plasticisers, to improve flexibility, and prevent burning or degradation. According to the literature, not all additives are harmful (Hahladakis *et al.*, 2018). The effects depend on the additive used, e.g., plasticisers such as phthalates. While some phthalates, such as diisononyl phthalate, have a complete European risk assessment and can be used in applications, others, such as dibutyl phthalate, can only be used if risk-reduction methods are applied (European Chemicals Bureau, 2019).

Most reports (Gallo *et al.*, 2018; Murray and Cowie, 2011) on plastic and toxic chemicals conclude that plastic debris can be a source of harmful chemicals. They may also be a sink for toxic chemicals by either leaching the chemicals they gained during manufacture or for the substances they sorb from the environment (Gouin *et al.*, 2011). They act as vectors, providing a surface for hydrophobic organic compounds such as persistent organic pollutants (POPs) to adsorb to, and thus the plastic becomes heavily contaminated with toxic chemicals. Research suggests that this ability to sorb chemicals is a bigger problem than the chemicals released due to bioaccumulation in organisms and biomagnification (Wright *et al.*, 2013), known as the *plastisphere* (Zettler *et al.*, 2013). These chemicals can then get transferred through the food chain.

Some chemicals and substances are persistent, bioaccumulated and toxic (PBTs), e.g., polychlorinated biphenyls (PCBs) and dichloro-diphenyl-trichloroethane (DDT). PBTs do not degrade and accumulate in organisms and the environment (Muller *et al.*, 2001; Lomann *et al.*, 2005; Pascall *et al.*, 2005). They concentrate at the sea surface and sorb into plastics on contact. A common PBT compound, PE, is used to detect environmental chemicals in studies because it readily sorbs them (Ogata *et al.*,

2009). PBTs and DDT sorb chemicals 100 times more than naturally occurring suspended organic matter; however, plastics' environmental behaviour varies depending on the type and how degraded or fragmented they are. Virgin plastic sorbs fewer chemicals than fragmented plastic, due to weathering that increases the surface area and the extension of the pores' size in the pieces of plastic (Mato *et al.*, 2001). Polyethylene sorbs chemicals more readily than PP, possibly due to its higher surface area and free volume (Endo *et al.*, 2005; Mato *et al.*, 2001; Teuten *et al.*, 2009). Chemicals sorbing and leaching means that chemicals and pollution can travel to regions previously unaffected and affect habitats yet untainted.

2.5.2 Microplastic impact on human health

Studies on effects of plastics on the human body are quite limited, but there is a recent spike in interest. Such studies will inevitably have their challenges as strict research ethic issues must be observed, thus limiting the number and depth of potential studies. Whilst the limited number of studies on this topic show evidence of the uptake and contamination of the human body by plastic particles, much remains to be studied to establish cause and effect dynamics in the environment and organisms, and the transport and transformation of chemicals in various plastic sources through the ecosystems, affecting human consumption of plastics. It is also necessary to investigate how much accumulation of plastics occurs in humans in the general population worldwide.

2.5.2.1 Physical impacts on humans

Studies on the presence of MPs in food and water (Karami *et al.*, 2017; Liebezeit and Liebzeit, 2013; Obmann *et al.*, 2018; Van Cauwenberghe *et al.*, 2014) suggest that the primary source of MP uptake into the human body is through ingestion (Galloway,

2015). Due to variation in diet and lifestyle worldwide, it is hard to estimate how much MPs are consumed by an average person. Cox (*et al.*, 2019) estimated on an American diet, an average person will consume 39,000-52,000 pieces annually, rising to 74,000-121,000 pieces when MP inhalation is included in the calculation.

Amato-lourenco (*et al.*, 2021) have discovered MPs in lung tissue from inhalation of airborne MPs. The MP fibres were similar to those found in environmental studies, with PE and PP being the most common polymers observed. Anthropogenic microfibrils were also found such as cotton.

Once in the body, MPs can enter the bloodstream (Leslie *et al.*, 2022) and may be present in a quantifiable concentration of up to 1.6 µg/mL. This is concerning as blood travels around the human body to transport oxygen and nutrients to tissues and organs. Hence, plastic within the bloodstream can affect or be found in any part of the body. Although this study has confirmed that plastic is present in the blood, further studies need to be made on if and how the plastic can be excreted through the body's waste processes.

Other studies (Ragusa *et al.*, 2021) found MP in placentas after vaginal deliveries on the maternal and foetal side as well as the chorioamniotic membrane. Microplastics have also been found in the gastrointestinal tract (Arumugasaamy *et al.*, 2019), colon (Banerjee and Shelver, 2021) as well as in faecal matter (Scwabl *et al.*, 2019; Zhang *et al.*, 2021). Yan *et al.* (2021) found a potential link between the number of MP in faecal matter and inflammatory bowel disease in humans. Whilst some studies have found MPs in humans, studies on effects of MPs in humans are still few and far in between.

2.5.2.2. Chemical impacts on humans

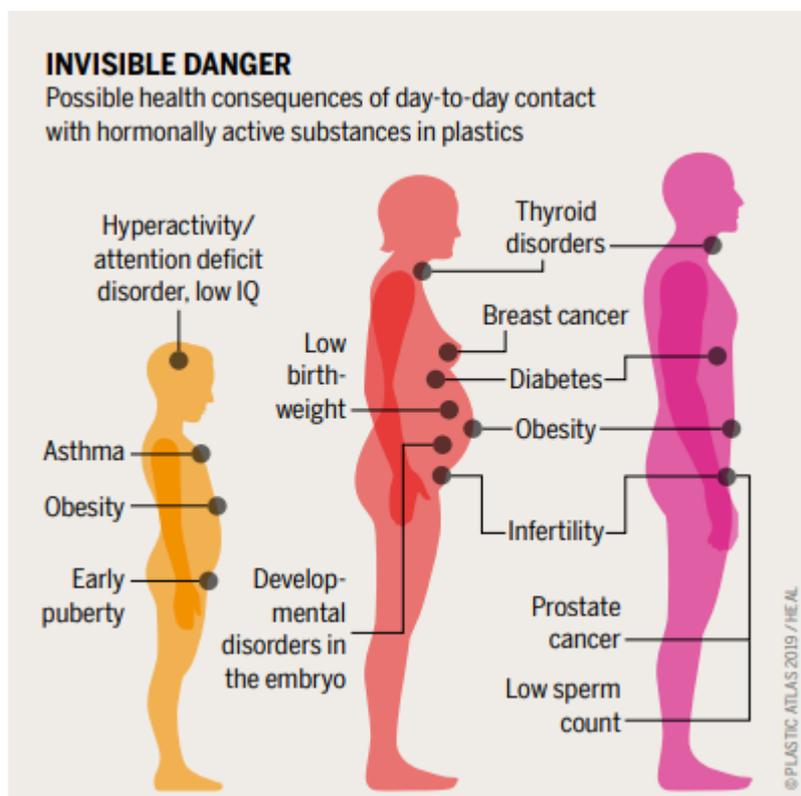
The presence of MPs in the human body may pose a significant risk to human health due to the chemical composition of polymers (Figure. 2.4). Many additives in plastic are harmful to organisms, and classified as carcinogenic or mutagenic, whilst many other chemicals used in plastic production are identified as endocrine disruptors (Koch and Calafat, 2009). The additives in polyvinyl chloride (PVC), polyurethanes, epoxy resins, and styrene polymers are reported to be highly hazardous to human health (Galloway, 2015; Lithner *et al.*, 2011; Yuan *et al.*, 2022).

For example, BPA used in food and drink packaging is linked to hormone or endocrine disorders in the human body (Almeida *et al.*, 2018; Rochester, 2013). Heavy metals such as cadmium, lead, mercury, tin, zinc and chromium are also used in plastic production to colour plastic (Meng *et al.*, 2021; Martin and Griswold, 2009). Whilst these heavy metals are classified as harmful to human health, some, such as cadmium and lead, are regulated by the European Union (EU, 1994; Martin and Griswold, 2009). However, they can still be found in plastic packaging exceeding the limits imposed (Turner and Filella, 2021; Van Putten, 2011).

Due to the many different types of chemicals used in polymers and the variations in composition, not all substances have been studied, or their potential impacts on human health analysed (Groh *et al.*, 2019). Also, whilst some countries have tried to regulate the most “harmful” substances due to the ability and ease of ordering items from across the globe, it is still possible to get items containing these chemicals even in regulated countries (Musoke *et al.*, 2015). As plastics can adsorb to and sorb pollutants, it is possible for plastics that did not previously contain these chemicals to become exposed, thus leading to the possibility of ingestion by humans (Filella and Turner, 2018). As a result, more studies on legacy chemicals that still exist within the

environment are required. In addition, recent plastic uptake needs to be investigated, primarily focusing on the effect on human health.

Figure 2.4 Potential short and long-term impacts of chemicals contained within polymers on human health (Figure taken from page 16 of Heinrich Boll Foundation, 2019).

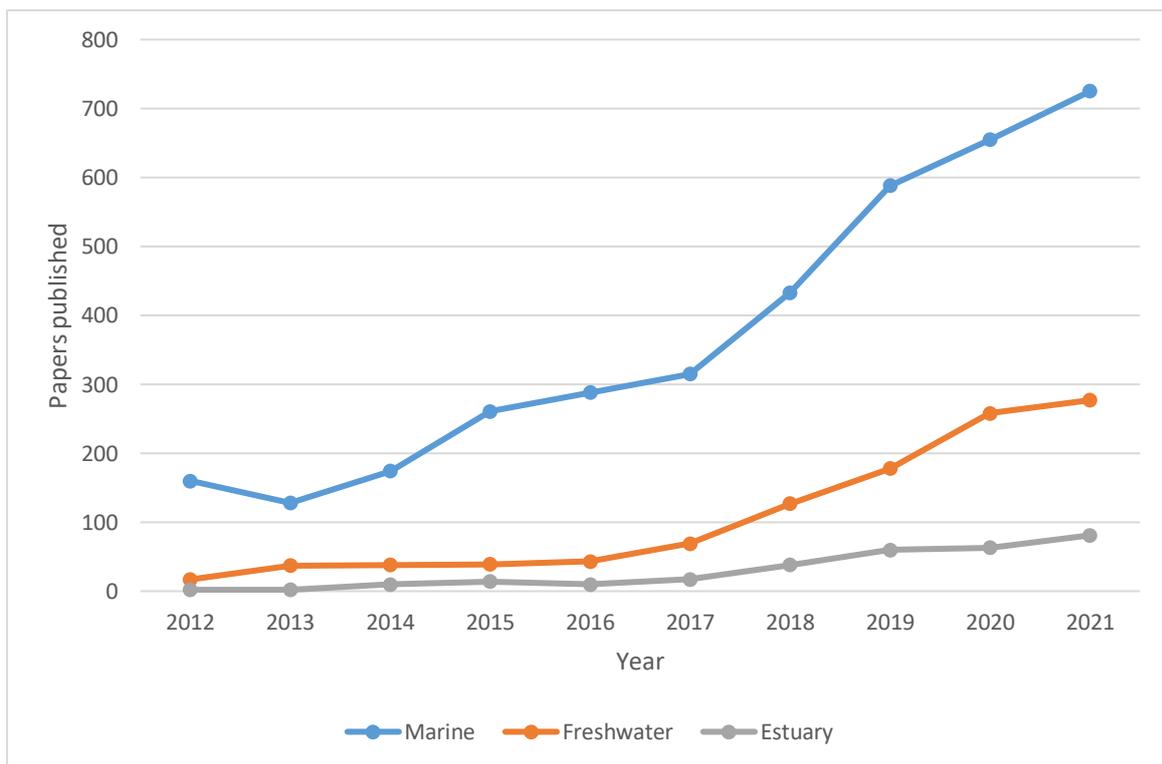


2.6 Microplastics in rivers

Rivers are the main transport pathway for MPs (Browne *et al.*, 2011; Wright *et al.*, 2013a). However, not much is known about the extent of plastic pollution in these environments. Fewer studies are conducted for MPs in rivers compared to marine

waters, and even lesser on estuaries (Figure. 2.5). Rivers, especially “main” rivers, are regularly monitored for pollutants to ensure guidelines are enforced and that levels stay at a previously stated “safe” level. However, newly emerging contaminants, including PCP’s, pharmaceutical waste, drugs and plastics, have only been recognised as pollutants recently, so procedures and “safe” levels have yet to be established (Tran *et al.*, 2018).

Figure 2.5 Comparison of papers published from 2012 – 2021 using Semantic Scholar. Papers were searched for using the phrases “Microplastic and Marine”, “Microplastic and Freshwater” and “Microplastic and Estuary”.



Studies focused on rivers, and freshwater systems consider estuaries a source and transport system for MPs in the ocean, but do not consider MP to affect these systems as much (Horton *et al.*, 2016). Based on results from these studies, it has been

suggested that riverbeds are likely to become sinks for MPs such as PE and PP, the most commonly used plastics (Table. 2.3). These are observed to be buoyant in the ocean (seawater density = 1.02-1.03 g per ml) as well as riverbed sediment in rivers (freshwater density = 1g per ml) (Horton *et al.*, 2017; Manning, 2001).

Table 2.3 Plastic types and associated density (g.cm⁻³) relating to virgin resins that does not consider biofouling or additive (Driedger *et al.*, 2015; Hidalgo-Ruiz *et al.*, 2012; Liu *et al.*, 2020)

Plastic Class	Abbreviation	Density (g cm⁻³)
Low-density polyethylene	LD-PE	0.89-0.93
High-density polyethylene	HD-PE	0.94-0.98
Polyester	PES	1.24-2.3
Polyethylene Terephthalate	PET/PETE	1.38-1.41
Polypropylene	PP	0.85-0.94
Polystyrene	PS	<0.05-1.00 /1.04- 1.08
Polyvinyl Chloride	PVC	1.16-1.58
Polycarbonate	PC	1.20-1.22
Polyamide (Nylon)	PA	1.02-1.05/1.13-1.16

Acrylonitrile Butadiene Styrene	ABS	1.04-1.06
Cellulose acetate (cigarette filters)	CA	1.30
Alkyd resin	ALK	1.42-2.20

About 80% of all MPs in water have a land-based source, and are transported mainly by rivers (Horton *et al.*, 2017); 70% of these sink to the bottom (Meng *et al.*, 2020) of the riverbeds or seabeds. A survey conducted by Hurley *et al.* (2018) found that the abundance of MPs in rivers dropped by 70% during flooding events, thus suggesting they were transported to the sea and that rivers play a crucial part in the storage and transport of plastics. This is supported by a study conducted by Mani *et al.* (2015) on the river Rhine that starts in the Swiss Alps and flows through German Rhineland and Netherlands, and eventually empties into the North Sea. The authors state that the river transports almost 10 tonnes of MPs annually to the surface waters of the North Sea. According to Peng *et al.* (2018), rivers that run through urban areas, especially megacities, appear to be subjected to more plastic pollution than rural areas. The authors also found that river sediments had a higher MP abundance than tidal flats due to being subjected to more human activities and becoming a plastic hotspot.

2.6.1 Rivers as transport pathways for plastic

Rivers are dynamic, constantly changing and always flowing as a result. They can either retain MP or transport it. Plastics, especially MPs, are subjected to the same transport processes as sediment. Hence, most plastics in rivers will settle to the bottom

and be buried on the riverbed with sediment deposition (Corcoran *et al.*, 2014), while some may reach the ocean due to wind and current movements. Plastic input from rivers still constitute a significant transport route as reported by Lebreton *et al.* (2017) who found 1.15-2.41 million tonnes of plastic waste are transported through rivers into oceans each year. Once in the ocean, plastic can travel across large areas depending on its buoyancy, density and shape (Khatmullina and Isachenko, 2017; Thompson *et al.*, 2004; Browne *et al.*, 2010). 70% of all plastic in the marine and freshwater is thought to be concentrated in sinks due to the fluid dynamics of rivers, estuaries and oceans, such as the tidal motion, Ekman pumping, upwelling, downwelling and turbulence-induced roll structures (Cozar *et al.*, 2014; Zhao *et al.*, 2019). However, due to the constantly changing hydrological factors (Van Emmerick, *et al.*, 2018) impacting rivers and estuaries as well as other factors such as vegetation (Van Emmerick *et al.*, 2019), and structures such as dams, MP settlement within rivers and estuaries varies dependent on the individual case. Recent studies (Drummond *et al.*, 2020; Gallitelli *et al.*, 2020; Horton and Dixon., 2018; Kumar *et al.*, 2021) show that MP retention within riverbeds is constant, with gravitational settling and hyporheic exchange of MPs evident within rivers. However, the average storage time scale of MP or percentage of MPs resuspended versus buried long term are currently unknown. A recent model (Drummond *et al.*, 2022) investigating MP settlement suggests that 3 - 8% of MPs per Km will remain within riverbed sediment long term whilst the other 92 - 97% of MPs that settle can stay in the sediment anywhere from 5 hours to 7 years depending on flow conditions.

Another way that MPs are transported through rivers is via ingestion by organisms.

2.6.2 Spatial and temporal distribution of plastic pollution

Quantitative estimates of global plastic abundance are limited, often controversial, and disputed primarily because of the lack of standardisation (Ryan *et al.*, 2009). Quantitative estimates mainly focus on marine plastic. For example, Erikson *et al.* (2014) worked out using data gathered from 24 expeditions from 2007 to 2013 that there were 270,000 tonnes of plastic across the five subtropical gyres. Data was collected with surface net tows and visual surveys. Using this data, researchers such as Van Sebille (2012) used an oceanographic model of floating debris, which accounted for vertical mixing caused by the wind, which increased to 5.25 trillion particles in these gyre regions alone. The data does not include information on a gyre believed to be located in the Barents Sea but not studied due to its location.

Studies suggest that 1% of the global marine plastic is found in surface water, whilst the remaining 99% of 'missing' plastic can be found in the deep sea (Kane *et al.*, 2020). However, the data is not confirmed, and it is also not known about the number of plastics that have reached the seafloor or riverbed. The seafloor appears to be a globally significant sink for plastic, however, the impact of processes and currents such as deep-sea and thermohaline currents on the seafloor remains unclear. This seems similar to studies (Drummond *et al.*, 2022; Rochman, 2018) that identified riverbeds as an important global sink for MP. Oceanographic processes such as storms and saline subduction assist in transferring MPs to the depth; bioturbation and hydrodynamic conditions can see these fragments remobilised into the water column. These processes make rough estimates of MP abundance hard to theorise or calculate (Claessens *et al.*, 2011; Avio *et al.*, 2017). Similar processes within estuaries and rivers thus cause the same issue within these studies, although many models have been altered or devised to help with the calculations. As this research highlights, there are many knowledge gaps on the number of MPs in freshwater environments.

A knowledge gap has also been highlighted in other studies (Law and Thompson, 2014; Lusher, 2015) on temporal and spatial trends of MPs, especially in rivers. Existing data (Browne *et al.*, 2011) suggest that the abundance of MPs is low in surface water and sediment, except for a few areas where abundance is exceptionally high such as shipyards. The authors also stated that spatial data shows that there may be a weak correlation between plastic abundance and population density. Browne *et al.*, (2011) found that areas where sewage sludge had been pumped in had a higher quantity of MPs. Shorelines downwind of potential pollution sources contained more MPs than sediment taken from up-wind shores (Browne *et al.*, 2013). Although some trends seem to appear concerning pollution sources, not enough is known about these sources and how physical processes such as wind or tides may affect these trends over time.

2.6.3 Microplastics in the River Thames

The river Thames is the longest river in the United Kingdom (215 miles) flowing through southern England and is home to over 950 species (NHM, 2019). It is one of the most studied rivers in the UK, with continuous monitoring of nitrates going back to the 1860s and water quality in the 1970s because the river is a significant source of London's drinking water (Powers *et al.*, 2016; Wright *et al.*, 2002).

The river and its estuary are ecologically diverse and provide essential habitats and nurseries for various species. Many biological studies have been made on phytoplankton, macroinvertebrates, and hundreds of other species, including short-snouted seahorses (*Hippocampus hippocampus*) (Lack, 1971). However, with MPs becoming a rising problem in the environment, a lack of studies on plastic in or around the river Thames is becoming evident (Table 2.4), especially whilst various reports are stating that the river is clean, healthy, and not polluted. However, pollution studies may

not consider MPs as pollutants (Environment Agency, 2019). For example, Morrill *et al.* (2014) recorded over 8,400 pieces of plastic litter over three months in the river between Crossness to Broadness Point. The survey used a fyke net programme; however, only macroplastics were collected, and the study did not consider or include MPs.

Table 2.4 Microplastic (MP) studies undertaken in or around the River Thames, UK

Location	Study	Abundance/ Outcome	Reference
Upper Thames Estuary between Crossness and Tilbury	Plastic in the Thames: A river runs through it	<ul style="list-style-type: none"> • 8490 submerged plastic (macroplastic) items were removed over three months. • Most contaminated sites were near sewage treatment plants. 	Morritt <i>et al.</i> , 2014
Tributaries in the Thames River basin	Large microplastic particles in sediments of tributaries of the River Thames, UK – abundance, sources and methods for effective quantification	<ul style="list-style-type: none"> • Fibres most common • Most MP were found to be secondary. • Sewage and land runoff influences microplastic abundance. 	Horton <i>et al.</i> , 2016
Erith and Isle of Grain/ Sheppey	Presence of microplastic in the digestive tracts of European flounder, <i>Platichthys flesus</i> , and European smelt, <i>Osmerus eperlanus</i> , from the River Thames	<ul style="list-style-type: none"> • Fibres were the most common. • Up to 75% of flounders ingested fibres. • Black fibres dominant 	McGowan <i>et al.</i> , 2017
Non-tidal section	The influence of exposure and physiology on microplastic ingestion by the freshwater	<ul style="list-style-type: none"> • The majority of MP were fibres (75%). • Polymers included polyethylene, polypropylene, polyester. 	Horton <i>et al.</i> , 2018

	fish <i>Rutilus rutilus</i> (roach) in the River Thames, UK		
Thames Estuary – Thamesmead, Erith and Isle of Sheppey Firth of Clyde	Ingestion of plastic by fish: A comparison of Thames Estuary and Firth of Clyde populations	<ul style="list-style-type: none"> • Microfibers were the most abundant • Polymers most abundant were polyester, nylon, polyamide and polypropylene. 	McGoran <i>et al.</i> , 2018
River Thames – precise location unknown	UK's most iconic rivers and lakes riddled with microplastics	<ul style="list-style-type: none"> • 84.1 pieces of plastic per litre 	Dunn, 2019
Hammersmith Bridge, Queen Caroline Drawdock, Crabtree Wharf, St Marys Church Battersea, Battersea Bridge, Vauxhall Bridge, Queenhithe, Cutty Sark, Newcastle Drawdock, Millenium Drawdock	Macro-plastic pollution in the tidal Thames: An analysis of composition and trends for the optimisation of data collection	<ul style="list-style-type: none"> • Focused on Macroplastic deposited on the foreshore • Hammersmith Bridge site had a high abundance of items (mean=64.64) – wet wipes. • Floating sites had more range in types of items found compared to sink sites. 	Benardi <i>et al.</i> , 2020
London – Hammersmith	The effects of wet wipe pollution on the Asian clam, <i>Corbicula fluminea</i> (Mollusca: Bivalvia) in the River Thames, London	<ul style="list-style-type: none"> • Maximum wet wipe density was 143 wipes m⁻². • Clams found close to the wet wipe reefs contained polypropylene (57%), polyethylene, polyallomer, nylon and polyester. 	McCoy <i>et al.</i> , 2020

Putney and Greenwich	London's river of plastic: High levels of microplastics in the Thames water column	<ul style="list-style-type: none"> • 24.8 pieces of MP m⁻³ at Putney, 14.2 m⁻³ at Greenwich (excluding microfibres) • Polyethylene and polypropylene were the most abundant polymers. • Increase in glitter particles found in July was potentially due to rainfall and pride festival. 	Rowley., 2020
Cricklade (Source) - Teddington Weir	Modelling Microplastics in the river Thames: Sources, Sinks and Policy Implications	<ul style="list-style-type: none"> • The model estimates a total load of 100 tonnes per year of MP entering the Thames estuary. • MP should be placed on the list of Potential toxic elements 	Whitehead, 2021
Westminster	Microplastic abundance in the Thames River during the New Year period	<ul style="list-style-type: none"> • Fibres were the most abundant (99%). • Polychloroprene and polyvinyl chloride were the most commonly found polymers. 	Devereux <i>et al.</i> , 2022

Microplastics may enter the system from many potential sources such as the historic landfill sites along the river Thames. The content of these landfills is mainly unknown as they have incomplete or no records of the disposed waste, and no monitoring or management requirements (O'Shea *et al.*, 2018). Many of these historic landfills were built in coastal zones due to the land's low value, especially if the land was a salt marsh. Many historic landfills (circa 50) (Cooper *et al.*, 2012) around the river Thames was constructed pre-1974 (Control of pollution act) and would not contain any waste management engineering such as basal or side walls to control leachates (O'Shea *et al.*, 2018). Hence, historic landfills, potentially lead to an influx of waste polluting the Thames due to leachate or collapse, especially during storms or tidal surges that cause the shifting of sediments in the basin (Brand *et al.*, 2017). Other potential sources of pollution include its proximity to a major city (London), heavy shipping traffic, and receiving effluent from the catchment of the river with a population of over 15 million people (Environment Agency, 2019).

Although few studies have been conducted on plastics, many charities and initiatives have been set up to clean and monitor the river. The UK has committed to achieving "zero avoidable plastic waste by the end of 2042" using various methods ranging from taxes and policy implementation such as the 5p carrier bag tax, which could be increased to 10 p to cut further use of single use plastics (SUP) (Defra, 2018; GOV.UK, 2019). The Port of London Authority (PLA) set up the Driftwood Service approximately 20 years ago to remove large pieces of rubbish and debris that may cause damage to boats which are used for shipping or recreational use of the river. The Service uses 16 passive driftwood collectors located in specific locations along the tidal part of the

Thames. These collectors remove 400 tonnes of floating debris annually, which is then recycled or disposed of (PLA, 2019). However, the service does not explicitly focus on plastics, and due to the structure of the collector, will only be able to collect macroplastics within the river. Thames 21 is a charity that organises river clean-ups and uses citizen scientists to monitor and remove plastic pollution from the Thames and get local communities to improve the health of UK rivers (Thames 21, 2019). In their annual 2016 review (Thames 21, 2019), the charity found that 59% of all foreshores (the area of the riverbed exposed at low tide) had pieces of macroplastic from Teddington to the estuary and found a total of 35,000 pieces. Another initiative by the One Less Bottle campaign also aims to reduce plastic pollution in London by providing water fountains and reduce plastic bottles and SUP from sporting events and festivals (OneLessBottle, 2019).

A study on the Thames Estuary found that 28% of the fish had ingested MPs, showing that the river and its inhabitants had been affected (McGoran *et al.*, 2017). The most common polymers in these studies were PA and PES, used extensively in the textile industry and can enter the water via sewers or drainage systems. Polyester, a component of wet wipes, is one of the most common items recovered by Thames 21 in one month. This is similar to McCoy *et al.* (2020) who found 1/3 of plastics found within the Asian clam (*Corbicula fluminea*) in the river Thames were toiletry items including wet wipes. Over 5,000 pieces of plastic were recovered in 2016, with over 60% identified as SUP's (Thames21, 2019). The Seabin project has also been set up in Royal Victoria Dock and St Katherines Dock (near Tower Bridge) on the river Thames to collect floating rubbish, including plastic, down to 2 mm in size and then pump the clean water back into the Thames (Bottinelli, 2019).

2.7 Methodology variation

Plastic research, especially on micro-, nano- and picoplastic, is still in its infancy, and hence establishing standardised protocols and methods is still needed. Many studies concerning MP highlight the issue of having different size classifications for plastics. However, because these classifications are not uniform and standardised, the ability to compare between studies is compromised. There are no standard sampling techniques, especially for sediment or water samples. Various sampling techniques have been used ranging in ease of sampling, analyses and cost. Moreover, many studies do not report the methodology they have used in its entirety. This can lead to discrepancies in understanding of the data generated (Supplementary Table 1). As plastic is found worldwide, there is a need for practical, low-cost, and simple methods (Miller *et al.*, 2017), which compliments the identification of a suitable method for easy detection and monitoring within different environments.

2.7.1 Sample collection

Due to water samples being collected for many years including pre-plastic studies have resulted in sampling methods evolving and interest around plastic pollution growing. The sampling methods for pollution studies have been adapted to fit the highly variable physiographic setting for the various studies (rivers/ oceans, surface/ sediment and water, etc.). Sampling methods fall into three categories (Liu *et al.* 2020): 1) bulk water sampling, 2) net sampling, and 3) submersible pumps or in-situ sampling.

The collection methods vary depending on factors such as collection depth, water volume required, and if a boat or other floatation device is used. The primary method for water samples is a neuston net adapted from plankton sampling (Miller *et al.*, 2017). The net allows large volumes of water to be sampled quickly. However, a wide range

of net mesh sizes has been found in the literature, affecting the amount and size of particles found (Barrows *et al.*, 2017; Song *et al.*, 2015). Other devices used include, but are not limited to, manta trawl, sieves (Lusher *et al.*, 2014), water samplers (Ding *et al.*, 2019) and pumps (Bordos *et al.*, 2019).

2.7.2 Sample processing

Several procedures are used to prepare the sample for analysis, including chemical digestion and density separation (Prata *et al.*, 2019). Many studies have a stage that removes or reduces organic matter in the water samples. The main methods of removal are oxidative, acidic, alkaline or enzymatic digestion (Wu *et al.*, 2020) (Supplementary Table 1), using acidic or alkaline solutions such as sodium hydroxide, potassium hydroxide, hydrochloric acid and nitric acid. However, reports have suggested these may lead to the degradation of MPs, especially PET and PVC polymers (Hurley *et al.*, 2018; Karami *et al.*, 2017). Sodium hydroxide has also been reported to affect PET and PC (Dehaut *et al.*, 2016; Hurley *et al.*, 2018), whilst hydrochloric acid and nitric acid have been reported to affect PE and PP (Dehaut *et al.*, 2017; Karami *et al.*, 2017). While these methods make it easier to quantify the amount of MP abundance in a sample by removing the organic matter, there are potential implications for evaluating MP quantity and quality and increasing costs.

Density separation (Supplementary Table 1) is used extensively for sediment or freshwater samples to separate heavier, non-plastic material from plastic material. The most used chemicals are zinc chloride, zinc bromide and calcium chloride, but these have cost implications, and a reported inefficiency in separating different polymer types or damaging polymers or the environment (Maes *et al.*, 2017; Chang, 2015).

Filtration process follows the digestion and/ or density separation of samples, (Supplementary Table 1), Various filter types and pore sizes have been used in different studies. Filters include glass fibres, stainless steel, cellulose, nylon, polycarbonate and anodisc (Lu *et al.*, 2021) and pore sizes vary from 0.2 to 380 μm (Lu *et al.*, 2021). The type and size of filters could affect the retention of MPs in samples and affect abundance and shape.

2.7.3 Characterisation and quantification

After filtration, further analysis usually requires a visual inspection to identify particles into groups based on size, shape, morphology, and polymer type. Most studies use a microscope to sort and quantify MP. However, this visual identification can cause standard errors and bias, e.g., one study may identify a white fibre, and another may recognise the same fibre as grey or transparent. However, the type of microscope (stereo, digital, fluorescence, electron, light or compound) used varies depending on the equipment available, size of particles, and amount of time available to process. During microscopy, particles are usually grouped into different categories (i.e., type, size, colour).

Whilst the colour of microplastics is recorded during studies, it is well known that biofouling and photoaging from UV radiation, mechanical abrasion, wind and wave stress, thermal oxidation and biodegradation can cause changes in the colour of the plastic polymer (Zhao *et al.*, 2022). Previously this visual identification was used to identify potential sources, for example, transparent fragments identified as potentially originating from packaging (Marti *et al.*, 2020). The colour has also previously been used to investigate if marine species are more attracted to and likely to consume

specific colours. However, recent studies have identified the potential to use colour to explore the exposure time of the plastic product (Zhao *et al.*, 2022).

These particles then need further investigation to confirm they are polymers, or else, it can lead to the misidentification of plastics and overestimating MP abundances. Raman or scanning electron microscope (SEM) has been used to determine the polymer type, however Fourier Transform-Infra-Red (FTIR) spectroscopy is the most used method. These techniques allow the identification of polymer type and any other substance that may have been adsorbed by the particle being examined. The resulting spectra from FTIR can be run through a spectra library. FTIR is popular because it does not destroy the sample. However, the equipment is expensive and time-consuming, and an extensive, reliable polymer library is needed. The equipment limits the sample size as it cannot scan anything smaller than 10 μm (Xu *et al.*, 2019). Other techniques have also been developed, such as pyrolysis gas chromatography mass spectroscopy (GC/MS) which can detect organic additives and polymers; however, it is destructive, and further analysis cannot be carried out on the sample.

A mixture of microscopy and spectroscopy is needed for the data gathered to be accurate and reliable. The techniques used to analyse MP depend on the sampling methodology and the aims and objectives of the study.

2.8 Summary

This chapter showed that since the first study into MPs (1970s), considerable work has been done to advance the knowledge on MP contamination in the environment. It shows how the studies explore many topics within the broader scope of plastic pollution.

Many studies currently focus on the marine environment, although the limited number of studies in freshwater environment are also increasingly showing the impacts of plastic pollution from various and potential sources. An understanding of these sources are imperative. Plastic pollution in freshwater systems such as rivers, and especially estuaries remain primarily understudied. They should be investigated more due to their role as a transport system for land-based sources into oceans, and estuaries in particular as they are the merging point of rivers and oceans; rivers are exposed to multiple MP sources along their length.

Even though plastic pollution, including MP studies, has been carried out since the 1970s, their small size and expanding technical knowledge and equipment have led to the development of several methods to analyse and assess it. Many protocols have been developed to analyse and quantify MPs. Although several studies have shown the ubiquity of plastic in various aquatic environments, lack of standardisation and uniformity in sampling, analyses, and reporting data and knowledge gained through the studies, makes comparison difficult. Understanding land-based sources and the transport methods used by plastics, mainly MPs, may be imperative to find potential solutions to reduce the ongoing continual cycle of plastic pollution entering the environment. Careful monitoring will also be needed to assess the sources and impact of plastic pollution on the environment and the growing cost. There is a growing need for in-depth knowledge on the causes of MP abundance fluctuation within a system, as they are remarkably diverse and constantly changing, such as rivers. Discrepancies within study methods and quantification need to be amended and standardised to assess MP, which, can influence and contribute to implementing vital policies and control measures.

Chapter 3. Methodology

Abstract

Protocols for sample collection and analysis in microplastic (MP) research vary depending on the researcher, environment studied and the country where it is carried out. The most common protocols summarised in previous MP studies (Devereux *et al.*, 2021; Devereux *et al.*, 2022; Marine and Environmental Research Institute, 2020; Razeghi *et al.*, 2021) (Supplementary Table 1) are discussed in the literature review. Methods for this study were taken from the broad range of studies, and a suitable generalised protocol was developed and adapted for the study's specific objectives. This chapter provides a general description of the protocols, followed by further relevant details in the following chapters (4, 5, 6 and 7) to ease reading and reduce repetition.

3.1. Study sites

The site examined in this study was the river Thames, London, UK, which is one of the major rivers in Europe, with a total length of 346 km (Table 3.1) and can be split into two parts: non-tidal and tidal. For this study, a total of eight sampling points were located within the length of the tidal section of the river (Figure. 3.1; Table 3. 2), as well as two sites (Box Park and Three Mills Island) located within the river Lea tributary (which feeds into the river Thames) and one site at Limehouse Harbour (Chapter 4). Some of these sites changed location slightly due to the Covid-19 pandemic, but the replacement sites were in the general vicinity of the original site, and utmost care was taken to ensure they were still exposed to the same suspected sources of MP.

Table 3.1 Key parameters of the tidal estuary (river Thames)

Parameter	Thames Estuary	Source
Total length (km ²)	346	Thames Estuary Growth Commission, 2018
Population (mill)	1.25 residents	Thames Estuary Growth Commission, 2018
Intertidal area (ha)	13,510	Port of London, 2014
Mouth width (m)	2,100	Port of London, 2014
Marsh area (ha)	0	Port of London, 2014
Shoreline (km)	232	Port of London, 2014
Mean river flow (m ³)	92.5	Port of London, 2014
Maximum river flow (m ³)	572.7	Port of London, 2014
Tide type	Macrotidal	Port of London, 2014
Mean high tide (m)	Sheerness 5.2 (2003) Tilbury 5.9 (2003) London bridge 6.6 (2003)	Port of London, 2014
Drainage catchment (km ²)	14,000	Trimmer <i>et al.</i> , 2000
Average discharge (m ³ s ⁻¹)	65.8	Tye, Rushton and Vane, 2018

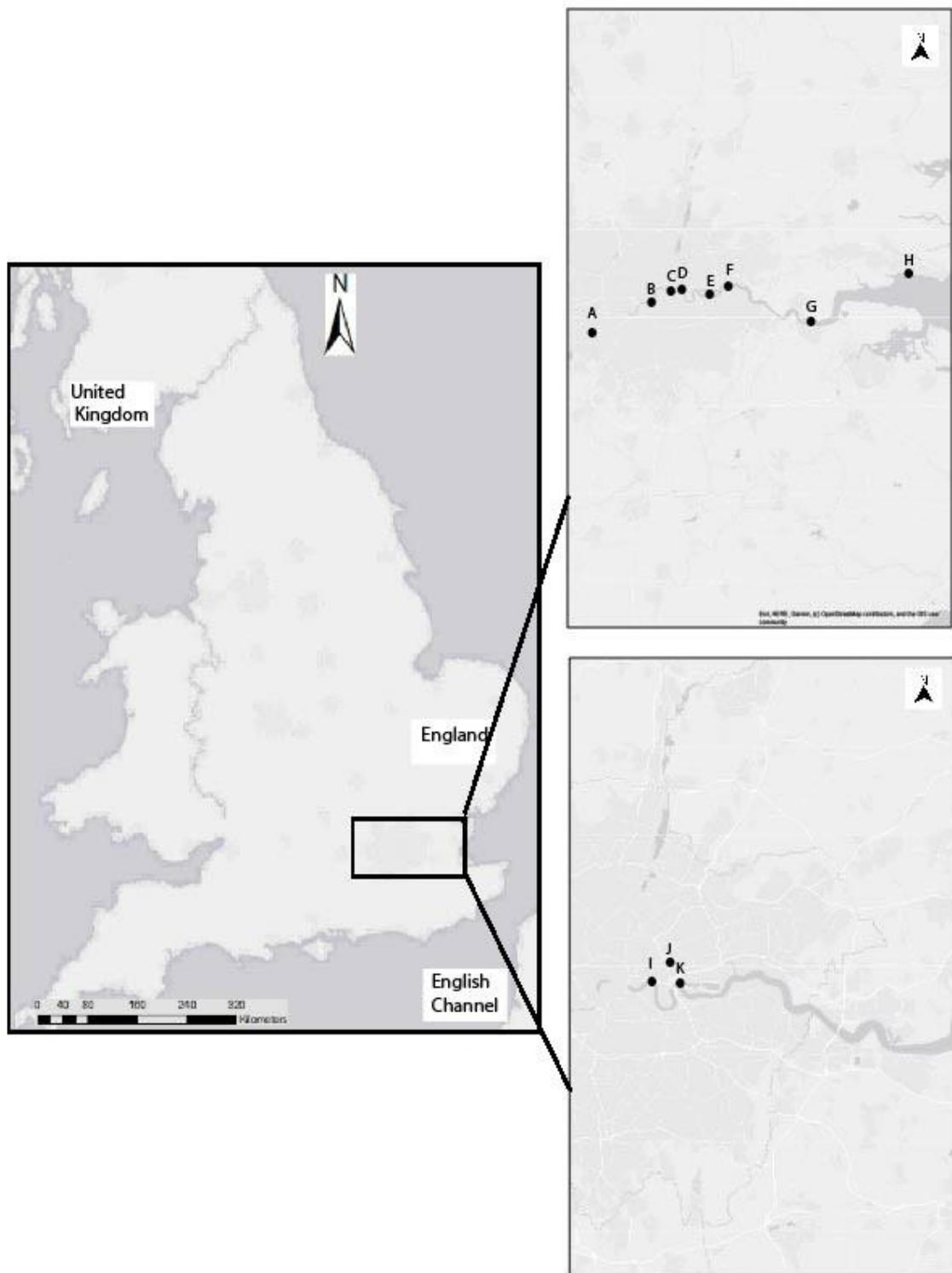


Figure 3.1 Water sampling areas along the river Thames; A) Teddington B) Westminster C) St Katherine's Pier D) Limehouse E) North Woolwich F) Barking

Riverside G) Tilbury Fort H) Southend-on-Sea on Sea I) Limehouse Harbour J) 3

Mills Island - River Lea K) Box Park- River Lea

Table 3.2 Water sample site locations along the Thames Estuary Pre- Covid-19 pandemic (May 2019 – February 2020) and sites during and post-Covid-19 pandemic (March 2020- May 2021)

Covid-19status / Date	Collection site	Address	Location Coordinates	Width (km)	Depth (ft)
Pre -Covid-19 Pandemic May 2019 – February 2020	Teddington Lock	Teddington Lock Footbridge, London Borough of Richmond upon the Thames, England, United Kingdom	N 51° 25' 47.856" W 0° 19' 20.24"	0.06	7.5
	Westminster boating base	Westminster Boating Base, 136 Grosvenor Road, London SW1V 3JY, United Kingdom	N 51° 29' 6.579" W 0° 8' 4.182"	0.14	6.56

	St Katherines pier	River Thames, Shad Thames, London SE1 2NJ, United Kingdom	N 51° 30' 22.504" W 0° 4' 24.324"	0.27	6.65 - 16.40
	Limehouse (Near the Narrow)	Ratcliff Cross Stairs, Jardine Road, London E1W 3WB, United Kingdom (Thames footpath)	N 51° 30' 34.589" W 0° 2' 17.732"	0.23	6.6 - 16.4
	Tate and Lyle (Sugar factory)	Factory Rd, Royal Docks, London E16 2EW	51°29'58.7"N 0°02'57.3"E	0.44	6.56ft - 16.40
	Barking Riverside	Dagenham Sunday Market, River Road, London IG11 0TD, United Kingdom	51°30'51.1"N 0°06'31.7"E	0.64	6.56 - 16.40

	Tilbury Fort	The World's End, Fort Road, Tilbury RM18 7NR, United Kingdom	N 51° 27' 6.276" E 0° 22' 13.364"	0.79	32.81 - 49.21
	Southend-on-Sea Pier	Lifeboat Station, Southend-Pier, Southend-on-Sea, SS1 2EL, United Kingdom	N 51° 30' 54.705" E 0° 43' 18.069"	6.83	32.81 - 49.21
	River Lea Tributary – 3 Mills Island	3 Mill Lane, Poplar, London E3 3AF	51°31'37.4"N 0°00'29.5"W		
	River Lea Tributary - Box Park	Trinity Buoy Wharf, Orchard Place, London, E14 0JW	51°30'27.2"N 0°00'28.7"E		

	Limehouse Harbour	Limehouse Marina British Waterways VHF.80, London E14 8EQ	51°30'35.5"N 0°02'13.3"W		
During and post – Covid- 19 pandemic March 2020 – May 2021	Teddington Lock	Teddington Lock Footbridge, London Borough of Richmond upon the Thames, England, United Kingdom	N 51° 25' 47.856" W 0° 19' 20.24"	0.06	7.5
	Westminster	The Queens Walk, Westminster, London, United Kingdom, SE1 7PB	51°30'05.3"N 0°07'11.6"W	0.14	6.56

	St Katherines Pier	River Thames, Shad Thames, London SE1 2NJ, United Kingdom	N 51° 30' 22.504" W 0° 4' 24.324"	0.27	6.65-16.40
	Limehouse (Near the Narrow)	Ratcliff Cross Stairs, Jardine Road, London E1W 3WB, United Kingdom (Thames footpath)	N 51° 30' 34.589" W 0° 2' 17.732"	0.23	6.6-16.4
	Barge Road Slipway	The Old Bargehouse Drawdock and Causeway, Bargehouse Road, North Woolwich, E16 2NW	51°29'56.8"N 0°04'12.7"E	0.44	6.56ft - 16.40

	Barking Riverside	Dagenham Sunday Market, River Road, London IG11 0TD, United Kingdom	N 51° 30' 51.446" E 0° 6' 33.947"	0.64	6.56-16.40
	Tilbury Fort	The World's End, Fort Road, Tilbury RM18 7NR, United Kingdom	N 51° 27' 6.276" E 0° 22' 13.364"	0.79	32.81-49.21
	Southend-on- Sea Pier	Lifeboat Station, Southend- Pier, Southend-on-Sea, SS1 2EL, United Kingdom	N 51° 30' 54.705" E 0° 43' 18.069"	6.83	32.81-49.21

The river Thames increases salinity, from freshwater to brackish and to marine, as it flows from Teddington down towards the estuary ending in Southend-on-Sea. The total of eight sampling areas (Teddington Lock, Westminster, St Katherine's Pier, Limehouse, North Woolwich, Barking Riverside, Tilbury, and Southend-on-Sea) were chosen because they span the length of the estuary. They are subjected to various potential microplastic (MP) sources such as groundwater inputs, sewage systems and overflows, input from tributaries, and a wide range of anthropogenic activities such as recreation and littering. This study establishes the abundance of MPs making their way from the non-tidal upper area down to the tidal section of the Thames. Teddington was selected as a control as it is the start of the tidal section of the river. Southend-on-Sea is located at the end of the estuary and was selected to investigate how much MP has the potential to enter the North Sea. The site was also chosen to analyse how much MP is added to the river system throughout the tidal section of the river.

The tidal Thames is highly urbanised, and heavily subjected to anthropogenic impacts from the businesses, industries and recreational activities that run across the length of the river. Over 1.5 million people live in the Thames District or enter the area around the Thames to work or visit daily (Environment Agency, 2019). The Port of London, a vital port in the UK that serves 30% of the UK population, employs over 40,000 people full-time and generates £4 billion yearly for local communities (Port of London Authority, 2015). The river is also impacted by at least 36 major sewage treatment works (STW) within the London area, and approximately 60 municipal and commercial discharge points (DEFRA, 2015). These STW are under increased pressure due to outdated systems, population increase, and climate change. These pressures increase the chances of overflows and flooding from the river system, thus

introducing raw sewage and untreated water regularly into the Thames at multiple sites, which are known to increase MP abundance within the area. The location of sampling sites on the river selected for this study are considered to provide data on MP that will be informative on MP pollution in the river Thames.

3.2 Sample Collection

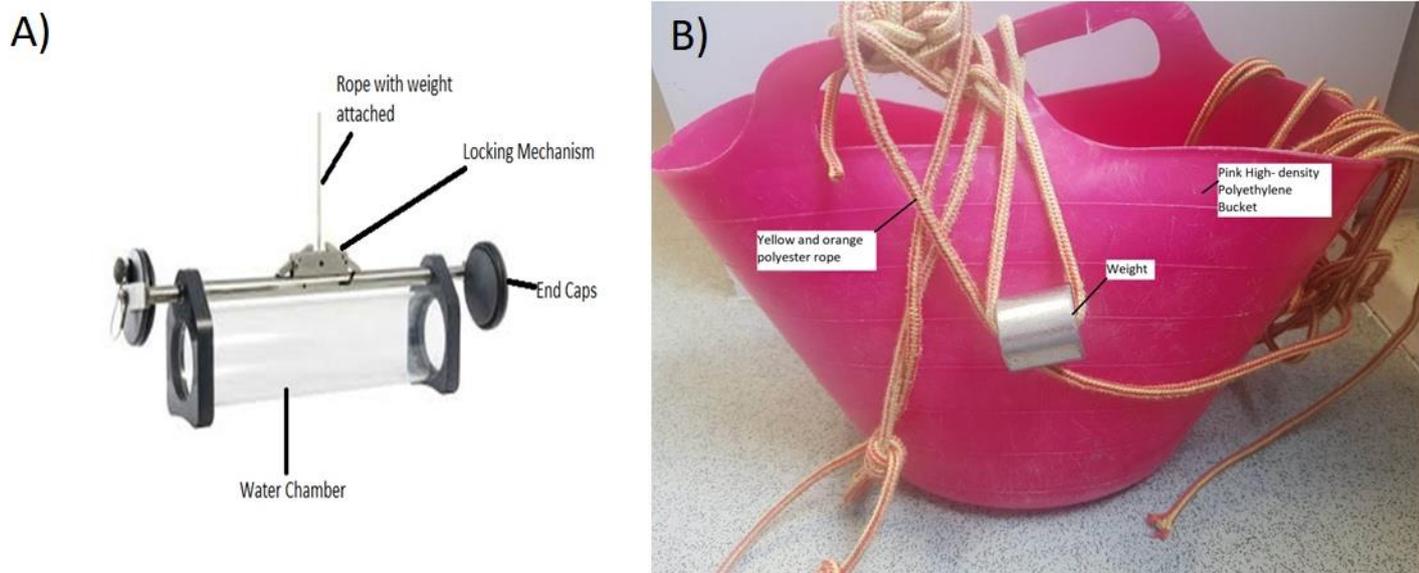


Figure 3.2 Water samplers used to collect water samples A) Lamotte horizontal water sampler and B) Pink high density bucket and rope

Water samples were collected from the eight sites along the river Thames over a two-year period from May 2019 to May 2021 (Table 3.1, Figure 3.1, Supplementary Table 2). Lamotte horizontal water sampler (Figure 3.2) was used to collect surface water samples within 0-50 (+/-10) cm depth between May - August 2019. However, the sampler could not cope with the pressure of the currents and the strenuous sample regime and for the rest of the sampling period, a pink high-density polyethylene (HD-PE) bucket with yellow and orange rope was used as an alternative sampler. As plastic equipment was used to gather the water samples the fibers from the rope could lead to shedding and potential contamination of the

samples, colours were chosen for the equipment that were less abundant in the water samples collected from the river Thames using the Lamotte water sampler. The colours pink, orange and yellow were chosen for the equipment as between May - August 2019; they were only observed 2, 7 and 15 times, respectively, considerably less than the other available colour options.

Due to this method adaptation for sample collection, control tests were carried out to check if MP abundance may be affected. These control tests were conducted by sampling 10 litres of water at two sites (Teddington and Barge Road, North Woolwich) with the bucket and the Lamotte water sampler and analysing the MP contents. These control tests showed no significant difference (ANOVA, $F_{1,14}=0.25$, $P=0.624$) (Figure 3.3) in the MP abundance of samples collected using the two sampling methods.

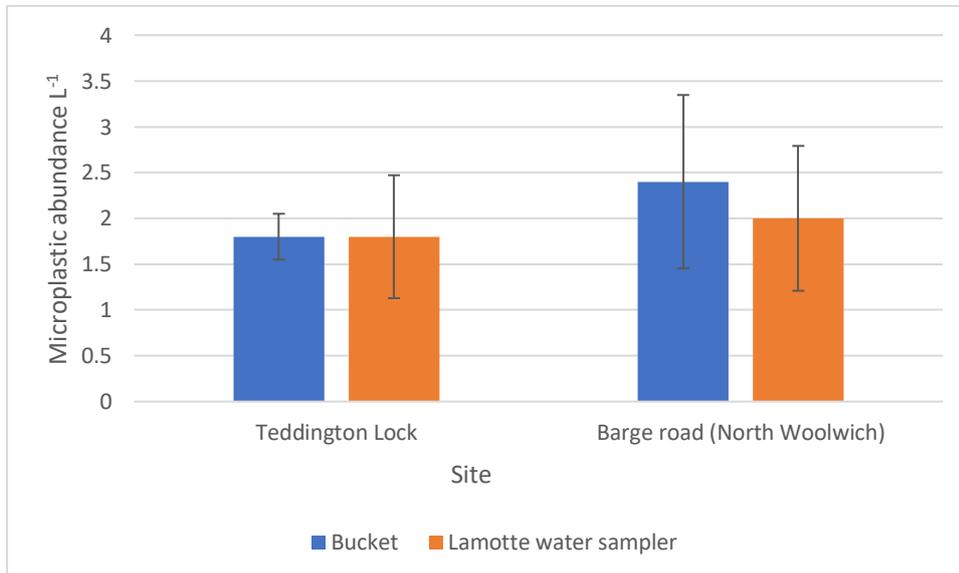


Figure 3.3. Average microplastic abundance L⁻¹ in 10 L of water collected at Teddington Lock and Barge Road (North Woolwich), using a HD-PE bucket and a Lamotte horizontal water sampler.

Due to the location and method of collection, samples could only be collected at high tide from the surface water at each site from land-based infrastructure. Water samples were immediately transferred into 2 L HD-PE double-lidded bottles and transported to the laboratory within 1-2 hours of sampling. Glass bottles were not used to transport water samples to the laboratory due to health and safety concerns and the possibility of the bottles breaking during transportation. Sampling across all eight locations was carried out within 3-5 days of the first sample being collected.

A total of 3.5 L of water sample was taken from each site once a month and transported to the laboratory at the Sustainability Research Institute at the University of East London, Docklands campus, to be kept at room temperature (20°C) until analysis. 500 mL of water from each sample was transferred into a Gosselin cornering HD-PE natural 500 mL round plastic bottle, which was sealed and kept in the dark cupboard in case further analysis was required. This was done as a precaution to minimise contamination and potential MP fragmentation due to exposure to heat, chemical and microbial action (Mammo *et al.*, 2020).

3.3 Sample filtration

An aliquot of 3 L water sample then filtered using a porcelain Buchner funnel with Whatman 1001-125 qualitative filter paper circles (11 µm, 10.5 s/100 mL flow rate, grade 1, 125 mm diameter).

Digestion methods used within MP studies vary from acidic, alkali, enzymatic or oxidative. However, although a digestion method is heavily recommended in studies, they are not widely applied due to polymers' possible degradation or destruction (for reasons stated in chapter 2- literature review) (Prata *et al.*, 2019). As a result, no digestion process was carried out during filtration or any other part of this study.

3.4. Microplastic characterisation

3.4.1. Light microscopy

For all samples, filter papers were examined under a light microscope to identify the presence of MPs; these were counted and measured. Visual sorting was carried out using a Keyence digital microscope VH-S30B with a VH-Z250R/W/T lens attachment and magnification ranging from 10x- 40x. MPs were then classified depending on the type, i.e., shape (fibre, fragment, bead, foam, pellet and other) and colour (transparent, blue, black, red, white, orange, yellow, brown, pink, green, purple and other). The width was also measured to confirm all suspected plastic fell into the microplastic categorisation. For this study, any piece of plastic with a larger width than 5 mm was discounted because they were classified as macroplastic, and the remaining material had its length recorded.

While visual identification is consistently used amongst MP studies, the categories materials are placed into may vary because of the diverse variety of MP shapes, sizes, and colours makes visual identification difficult. Due to these limitations, various sources were consulted to analyse MPs in this study. 'The Guide for Microplastic Identification' (Marine and Environmental Research Institute, 2020) as previously validated methods (Devereux *et al.*, 2021; Devereux *et al.*, 2022) were consulted to determine the category (fibre, fragment, bead, foam, pellet and other) of the microplastic observed (Table 3.3). While most plastic will be a homogenous colour, this is not always the case, as some material exhibits two or more colours. In this study, if two or more colours are present, the dominant colour was noted (Figure. 3.4), or if one of the colours was classified as transparent, the other colour was selected. For example, if a fibre was blue and transparent, the colour noted was blue as it was assumed the sample had discoloured due to the environment.



Figure 3.4 An example of a fragment that is yellow and red but would have been recorded as a yellow fragment in this study

Visual inspection and material classification are widely accepted and used in MP studies, and they can lead to the misidentification of polymers. As such, confirmation of suspected polymers can only be achieved through the second step in characterisation. This study used the chemical technique of Fourier-Transform Infrared Spectroscopy (FTIR) to confirm the presence and type of polymers and confirm visual observation.

Table 3.3 Classification of microplastic type identified by visual observation using light microscopy.

Plastic form	Characteristic	Picture
Fragment	<ul style="list-style-type: none"> • Rounded, subrounded, subangular or angular • Broken edges • Degraded, rough 	
Fibre	<ul style="list-style-type: none"> • Equal thickness throughout • Fraying/ splitting sometimes seen • No cellular or organic structures 	

<p>Bead</p>	<p>Spherical or similar</p>	 <p>Magnification: X500.0</p> <p>20.0µm</p>
<p>Foam</p>		 <p>Magnification: X1000</p> <p>100.0µm</p>
<p>Pellet</p>	<p>Cylindrical, disks, flat, ovoid, spherical</p>	 <p>Magnification: X50.0</p> <p>100.0µm</p>

<p>Glitter/ holographic</p>	<p>Holographic Reflective</p>	
<p>Biological i.e., shells, algae, salt crystals or sand</p>	<p>Cellular/ organic structures are present May break apart when probed with tweezers</p>	

3.4.2 Fourier-Transform Infrared Spectroscopy (FTIR)

MPs were selected randomly from filters gained within this study and included different shapes and colours. Ten pieces of MP were examined from each water sample collected throughout this study. If a sample did not have ten MPs, then all MPs were tested by FTIR. The selected MP were further investigated and identified using FTIR (manufacturer Bruker model Alpha fitted with a platinum ATR Model with Opus 8.2 software). FTIR uses infrared radiation (IR) that passes through a sample down to 10 µm in size. Due to the limitations of FTIR and to reduce the number of samples lost in the transition from the filter system to the FTIR, it was determined

that individual particles randomly selected were required to have a length greater than 200 μm . It is the most popular technique used to determine the chemical composition of the material and is used to identify polymers. FTIR provides data explicitly on specific chemical bonds within a particle, and the polymer spectrum library OpenSpecy (Cowger *et al.*, 2021) was used for this study.

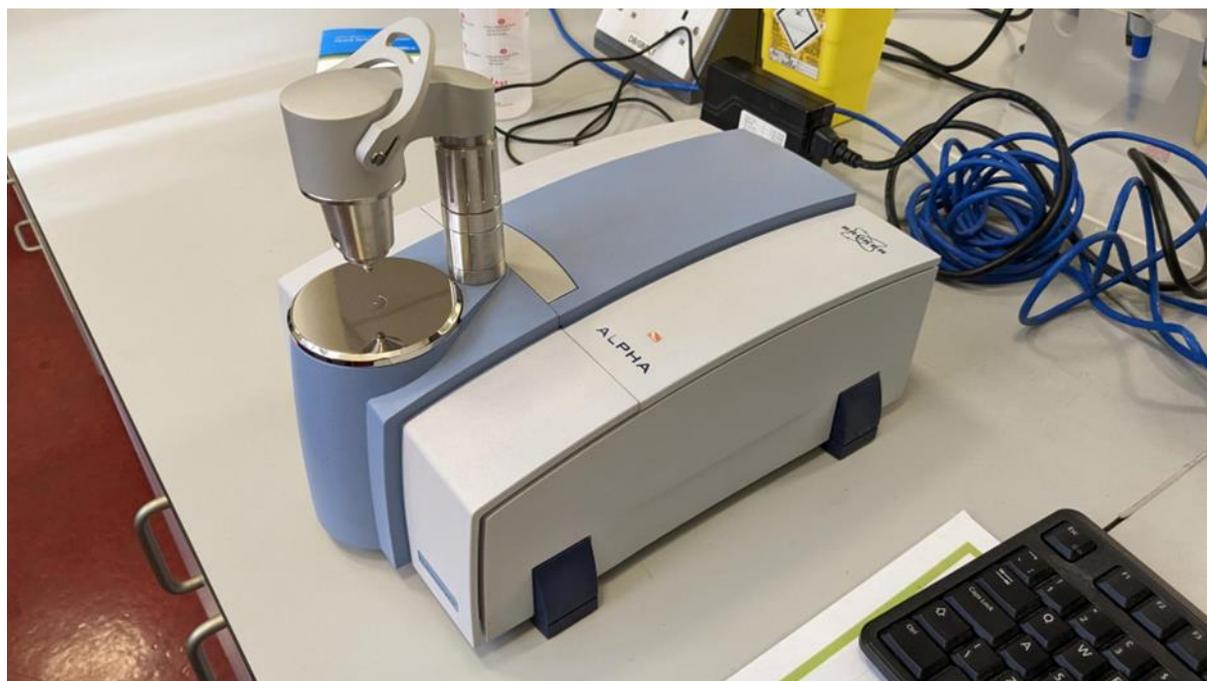


Figure 3. 5 Fourier-Transform Infrared Spectroscopy (FTIR) - Bruker model Alpha fitted with a platinum ATR Model with Opus 8.2 software

FTIR also identifies shells, biogenic waste, and anthropogenic fibres, which can be mistaken for MPs under simple microscopic observation, and it is a popular technique. However, it has limitations too which include loss of samples when moving them from filter to the FTIR as well as not being able to scan MPs smaller than 10 μm .

To reduce the number of samples lost in the transition from the filter system to the FTIR, only particles with a length greater than 200 μm were analysed by FTIR. The FTIR equipment and fine tweezers were cleaned with ethanol before and after use to

reduce the risk of potential contamination and false readings. A background scan was run 24 times before scanning the sample 24 times, resulting in a spectrum transmittance graph (Figure 3.6).

Due to the likelihood of MP being degraded due to exposure to the environment in MP studies, the “acceptable” range of what is a good match varies, and there appears to be no standardisation. For this study, spectra that had no defined peaks (i.e., <55%) were classified as “no-hit” or unknown. Particles that could be identified were classified by 1) polymer type (i.e., polystyrene, polyethylene), 2) natural (i.e., chitin or sand, or 3) anthropogenic microparticle or fibre (i.e., cotton, semi-synthetic cellulose - Rayon).

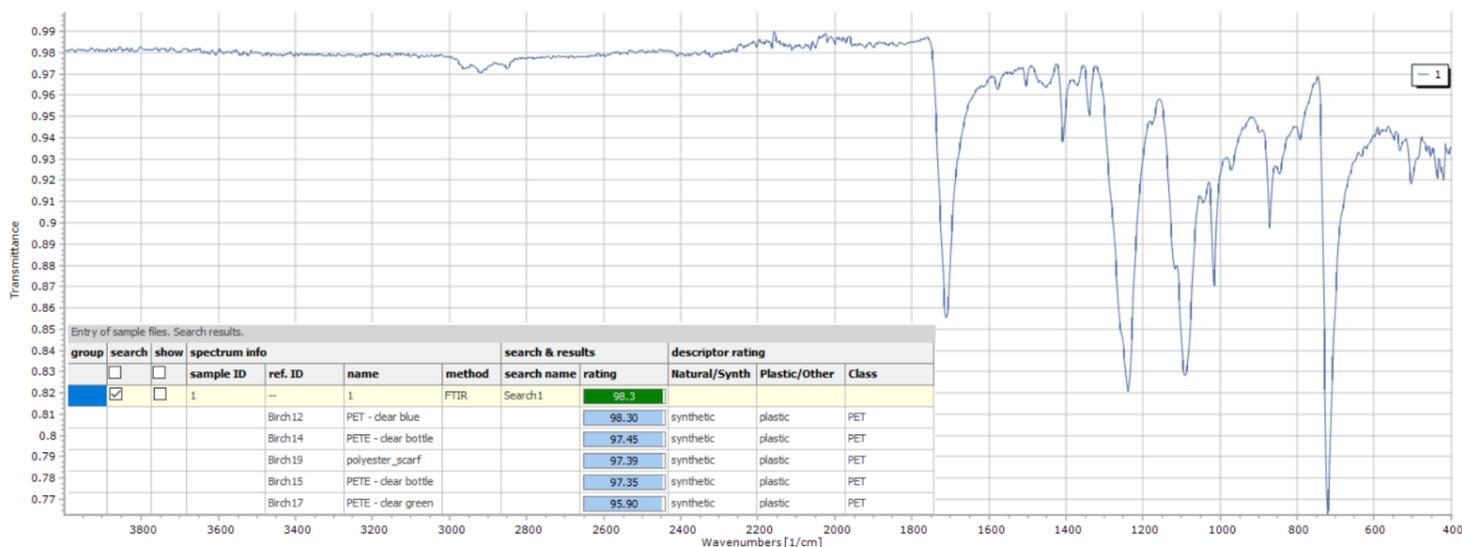


Figure 3.6 A representative example of a spectrum transmittance graph from a blue fibre found in samples from the river Thames at Teddington Lock (December 2019) identified as polyethylene terephthalate (PET).

3.5. Contamination controls

Due to the nature and small size of MPs, it is a common problem to have a form of contamination in these studies, especially concerning fibres which may be airborne.

Contamination can also result from using equipment with components of plastic during the sampling or in the laboratory. Due to this increased chance of contamination, many studies follow protocols to reduce the possibility of contamination, which were also considered, and appropriate protocols followed during this study.

Precautions were taken to prevent potential atmospheric contamination within a lab setting by 1) using adequate protection equipment (orange cotton lab coat and nitrile gloves), 2) reducing the amount of plastic equipment used, and 3) keeping filters always covered with a petri dish lid. Quality control tests were performed throughout all experiments. Atmospheric controls were created by placing one filter in an open petri dish soaked with distilled water on the workbench during filtration to capture airborne contamination (90 MP pieces) (Supplementary Table 3). The amount of time the filter was exposed to the atmosphere depended on how long filtration was carried out. If multiple samples were being filtered in a day, the filter (control) was prepared before starting sample filtration and the petri dish was sealed when the filtration for that day was completed. Out of 90 pieces of MP identified over 67 sampling dates, 61 pieces were investigated via FTIR. The majority (25 pieces) were identified as PVC (Figure. 3.7).

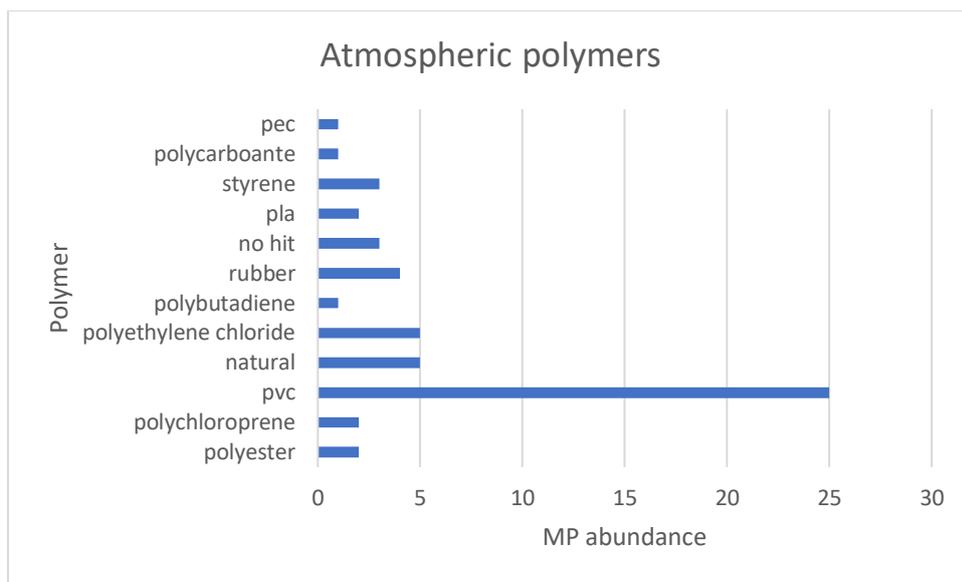


Figure 3.7 Microplastic polymers collected from desk-based filters used to test for atmospheric contamination from 2019 - 2021 identified via FTIR

A range of tests was also conducted to test for contamination during sampling and filtration. These included: 1) using distilled water to replicate the sampling process, 2) soaking the ropes used with the equipment, and 3) taking a small sample of material from the bucket and ropes used for visual and chemical characterisation, which aided the elimination of potential contamination (Supplementary Table 4). The material found in the water samples from the Thames was then cross matched with the material from the bucket and rope. If the colour and polymer type matched, they were disregarded from the count due to being potentially contaminated.

500 mL of each water sample was stored separately in case further analysis was needed. Due to these smaller samples being kept in 500 mL PE-HD bottles, these samples were held in the environment; three similar PE-HD 500ml bottles were chosen and filled with 500ml filter water and kept in the same conditions (dark and unopened) as the 500ml bottles of water kept after each collection. After two years

(2019 - 2021), the three controls with distilled water were filtered to test the water PE-HD for potential contamination and were found to contain zero MPs (Supplementary table 3).

Control tests for the Lamotte water sampler resulted in 4 MP pieces found when distilled water was used to replicate the filtering process; running distilled water over the rope resulted in nine MP pieces, and soaking the rope resulted in ten MP pieces. This is compared to the same controls run on the bucket, which resulted in 18 MP pieces replicating the filtering process, three MP pieces passing water over the rope and four MP pieces soaking the rope (Supplementary Table 3). During the controls with the bucket, the colours pink (4 pieces), orange (1 piece) and yellow (1 piece) were observed, which led to MPs of this colour being further tested by FTIR.

Section 3.6 Statistical analysis

In depth statistical and data analysis from the different studies that make up this thesis can be found in chapters 4, 5, 6 and 7.

Summary

The study sites and methodological framework are broadly described in this chapter. Further details for the techniques presented here are provided in the following chapters (4,5,6 and 7). The methods were adapted for each study according to the specific objects asked in the body of work. There was minimal contamination from atmospheric contamination compared to the 67 sampling dates.

4. River Thames "The great source" Microplastic abundance and characteristics along the river Thames



Marine Pollution Bulletin

Volume 189, April 2023, 114763



Impact of the Covid-19 pandemic on microplastic abundance along the River Thames

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Highlights

- 82.1% (3679 pieces) of microplastics were fibres.
- Covid-19 status significantly impacted microplastic abundance.
- Average microplastic abundance was highest during Lockdown 2 (27.1 piecesL⁻¹).
- Microplastic abundance decreased from pre Covid-19 (2019) to post Covid-19 (2021).
- The most commonly identified polymers were PVC, PS and PCP.

Part of this chapter was accepted and published in the Marine Pollution Bulletin in April 2023 (<https://www.sciencedirect.com/science/article/pii/S0025326X23001947?via%3Dihub>)

Abstract

This study focuses on quantifying the abundance of microplastics within the surface water of the river Thames, UK. Ten field sites covering eight areas were sampled within the tidal Thames, starting from Teddington and ending at Southend-on-Sea, as well as Limehouse Harbour and two sites in the river Lea (river Thames tributary). Three litres of water samples were collected monthly at high tide from land-based structures from each site from May 2019 to May 2021. Samples were filtered and underwent visual analysis for microplastics categorised based on type, colour and size. A selection of these suspected microplastics from each field site each month was then tested using Fourier transform spectroscopy to identify chemical composition and polymer type.

4.1 Introduction

The river Thames is the longest river in England, at 354km (Bowers, 2022). It flows through southern England, passing through London, and comprises two parts; 1) non-tidal: Gloucestershire to Teddington, and 2) tidal: Teddington to Southend-on-Sea. The river Thames has always been used to transport goods to the sea; in previous years, human and animal waste gave it the name "The great stink" in 1858 (Halliday and Hart-Davis, 2001). As a result, the river has been closely monitored for nitrates since the 1860s and has had its water quality closely monitored since the 1970s (Powers *et al.*, 2016; Wright *et al.*, 2002). However, the river Thames in recent studies has been noted as less polluted than in previous years for the pollutants currently investigated; however, these investigations did not consider more recent pollutants such as plastics or MPs, which are being transported down the river (ZSL, 2021). Microplastics have previously been reported in the river Thames (Table 2.4).

Dunn (2009) found 84.1 pieces of MP L⁻¹ at an unknown site in London, whilst Rowley (2020) found 24.8 pieces of MP m³ at Putney and 14.2 pieces m³ at Greenwich. Whitehead (2021) estimated that 100 tonnes of MP per year enter the Thames estuary. Whilst some studies have investigated MP abundances at individual sections of the river and its estuary, there is no study that has focused on the entire tidal section of the river to assess MP abundances and potential sources along the stretch of the river.

This study investigates MP's presence along the surface water of the tidal section of the river Thames, UK. The hypothesis is that MP's concentrations will be higher at Tilbury and Southend-on-Sea, where the Thames meets the North Sea. This is due to the potential influx of MP's along the Thames, the higher population density within the London area, and MP inflows from the North Sea. This study aimed to; 1) quantify the abundance of MP's along the tidal section of the river Thames, and 2) investigate the MP's morphology, colour, length and polymer type to identify their potential origin or source.

4.2 Methodology

4.2.1 Sampling sites

In total, there were ten sampling sites across eight areas chosen along the tidal section of the Thames River, UK, from Teddington (Freshwater) to Southend-on-Sea (Marine) (Figure. 3.1, Table 4.1). The eight areas chosen along the Thames were Teddington Lock, Westminster, St Katherine's Pier, Limehouse North Woolwich, Barking Riverside Tilbury Fort and Southend-on-Sea. These areas were sampled once a month (Supplementary Table 2). As well as the ten sampling sites along the Tidal Thames, a site at Limehouse harbour and two sites along the river Lea tributary

(Box Park, 3 Mills Island) (Figure 4.1). Limehouse harbour was sampled once on two consecutive days (5 - 6th November 2019) throughout the period, and the two sites in the river Lea tributary were sampled once in 2019 and once in 2020.

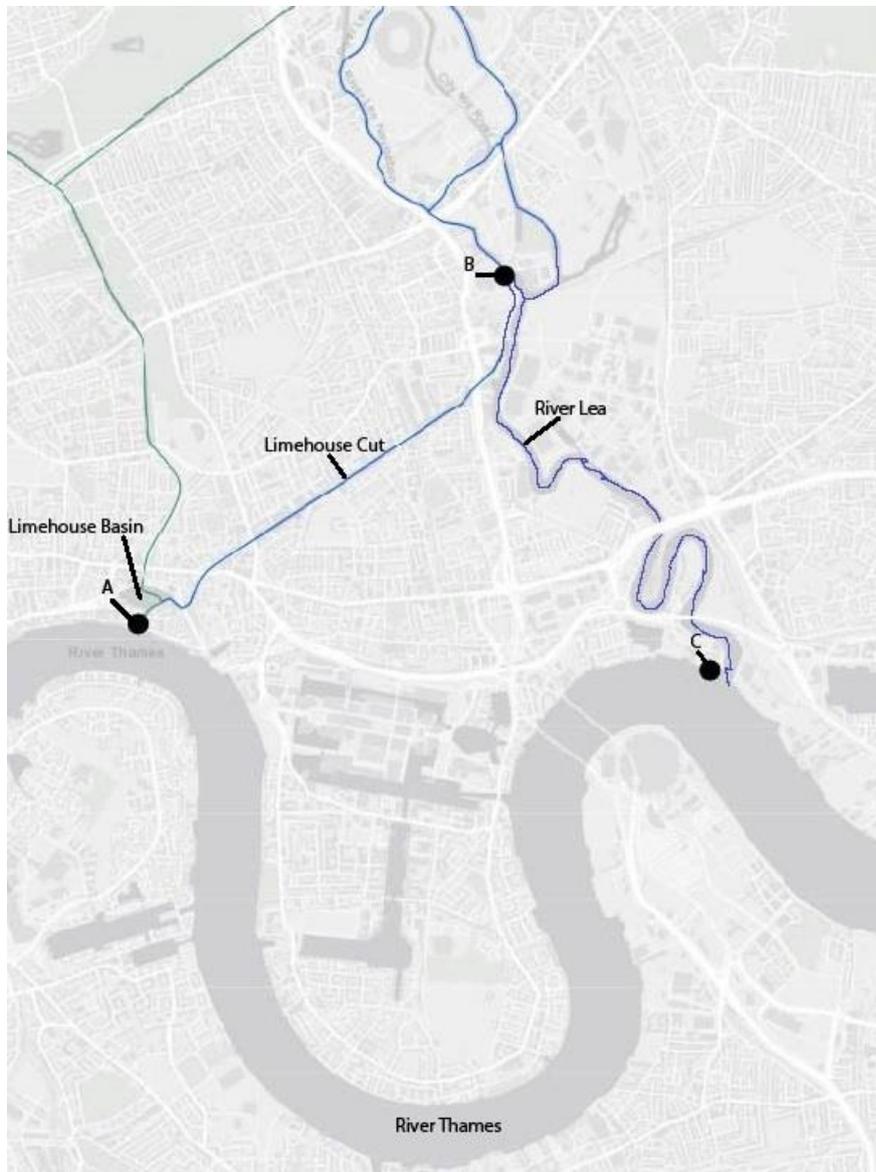


Figure 4.1 Location of sample sites A) Limehouse harbour, B) 3 Mills Island, and C) Box Park in relation to the river Thames and the river Lea

Due to the Covid-19 pandemic and subsequent lockdowns starting March 2020, some field sites (Westminster Boating Base (Westminster), Tate and Lyle (North

Woolwich) and Barking Riverside) that needed access to business sites to reach the river were closed (Table 4.1). As a result, other sites were sought to be close to the original sites. Westminster boating base was changed to Westminster (close to the Millennium eye). This site was found straight away, and as a result, no sampling from the Westminster area of the river Thames was missed. The site in North Woolwich, previously Tate and Lyle, was moved to Barge Road in North Woolwich. This site took longer to find as it needed to be on the same side of the river and the same side of the Thames barrier. As a result, sampling from this area from March 2020 stopped and resumed in August 2020 at Barge Road. The Barking Riverside site was harder to find an alternative location to sample that had access to the river 24 hours a day and was on the same side of the river and located within a short distance. As a result, no alternative could be found, so this site's data is missing during national lockdown months, i.e., April – June 2020, August - September 2020 and December 2020 – January 2021.

Table 4.1 Sampling areas and site locations along the River Thames and its tributary, the River Lea, for the collection of water samples between May 2019-May and 2021

Area	Site	Address	GPS coordinates	Sample dates
Teddington	Teddington Lock	Teddington Lock Footbridge, London Borough of Richmond upon the Thames	51° 25' 47.856" N 0° 19' 20.24" W	May 2019 - May 2021
Westminster	Westminster Boating Base	Westminster Boating Base, 136 Grosvenor Road, London SW1V 3JY	51° 29' 6.579" N 0° 8' 4.182" W	May 2019 - March 2020
	Westminster – Close to Millennium Eye	The Queens Walk, Westminster, London SE1 7PB	51°30'05.3"N 0°07'11.6"W	June 2020 - May 2021

London Bridge - St Katherines	St Katherines Pier	River Thames, Shad Thames, London SE1 2NJ	51° 30' 22.504" N 0° 4' 24.324" W	May 2019 - May 2021
Limehouse	Limehouse	Ratcliff Cross Stairs, Jardine Road, London E1W 3WB	51° 30' 34.589" N 0° 2' 17.732" W	May 2019 - May 2021
	Limehouse Harbour	Limehouse Marina British Waterways VHF.80, London E14 8EQ	51°30'35.5"N 0°02'13.3"W	5 - 6 th November 2019
North Woolwich	Tate and Lyle Sugar Factory	Factory Rd, Royal Docks, London E16 2EW	51°29'58.7" N 0°02'57.3" E	June 2019 - February 2020
	Barge Road - Slipway	The Old Bargehouse Drawdock and Causeway, Bargehouse	51°29'56.8" N 0°04'12.7" E	August 2020 - May 2021

		Road, North Woolwich, E16 2NW		
Barking Riverside	Barking Riverside	Dagenham Sunday Market, River Road, London IG11 0TD	51°30'51.1" N 0°06'31.7" E	June 2019 - May 2021 Excluding the following months: April – June 2020 August - September 2020 December 2020 - January 2021
Tilbury	Tilbury Fort	The World's End, Fort Road, Tilbury RM18 7NR	51° 27' 6.276" N 0° 22' 13.364" E	May 2019 - May 2021 Excluding: April 2020
Southend-on-Sea	Southend on Sea	Lifeboat Station, Southend Pier,	51° 30' 54.705" N 0° 43' 18.069" E	May 2019 - May 2021 Excluding: April 2020

		Southend-on-Sea SS1 2EL		
River Lea - River Thames Tributary	3 Mills Island	3 Mill Lane, Poplar, London E3 3AF	51°31'37.4" N 0°00'29.5" W	3 rd June 2020 17 th March 2021
	Box Park	Trinity Buoy Wharf, Orchard Place, London E14 0JW	51°30'27.2" N 0°00'28.7" E	3 rd June 2020 17 th March 2021

4.2.2 Sample collection

Water samples were taken from land-based infrastructure at all sites (except river Lea tributary and Limehouse Harbour) and collected monthly from May 2019 - May 2021 (Supplementary Table 2) at high tide throughout the sampling regime. Three sites were excluded from this monthly regime Limehouse harbour, which were sampled over two consecutive days (Table 4.1), and two sites in the river Lea (tributary) once in 2019 and again in 2020. Three one-litre bottles of surface water were collected at each site every month. Protocols established and discussed in Devereux *et al.* (2022) and chapter 3 were followed. Water was collected via a Lamotte horizontal water sampler from May – August 2019, after a Pink High-density Polyethylene (HD - PE) bucket was used. Water samples were transferred into 2l HD-PE double-lidded bottles for transport to the laboratory. Samples were filtered within one week after collection except for those taken during Covid - 19 lockdown months (March – June 2020; November - December 2020; January - February 2021); in these instances, filtration and analysis took considerably longer. However, filtering resumed once the lockdown was lifted, and the laboratory was opened. During the lockdown, samples were still taken at the site and collection bottles were kept in a cool, dark cupboard until they could be transported to the laboratory.

4.2.3 MP characterisation

Characterisation followed a 3-step process which started with visual sorting using a light microscope where suspected MPs were sorted into categories based on morphology (Figure 4.2) and then further grouped into colours. Each filter was then analysed using a Keyence digital microscope at X50 magnification to identify and quantify the size range of particles to ensure they fell within the MP size <5 mm. The

>5 mm categories were excluded from abundance totals as they are on the border of mesoplastic categorisation.

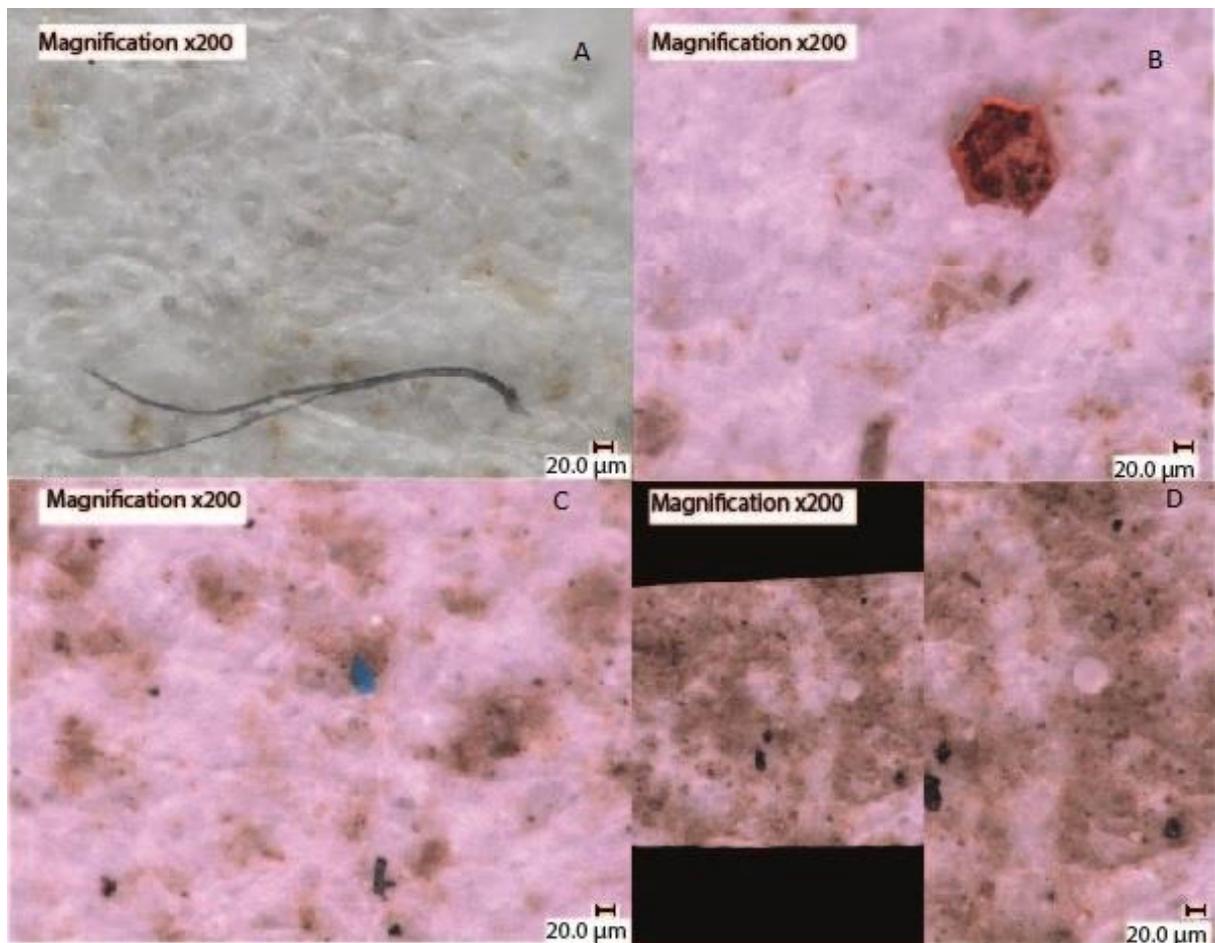


Figure 4.2 Microplastic categories at X200 magnification using a Keyence digital microscope A) Fibre, B) Glitter/ Holographic C) Fragment and D) Pellet

Due to the Covid - 19 pandemic and subsequent lockdowns, laboratory operating time was limited. As a result, only a subsection of suspected MP (10 pieces) on each filter was measured for length and analysis by Fourier-transform infrared spectroscopy (FTIR) to ensure enough time to analyse the particles.

A subsample of 1041 pieces of suspected MPs making up 15.64% of total MP abundance identified during visual identification was selected for polymer

composition confirmation by Fourier-transform infrared spectroscopy (FTIR).

OpenSpecy (Cowger *et al.*, 2021) is an open-access database that identifies spectra matches from FTIR analysis and was used during this study.

4.2.4 Contamination controls

This study used strict health and safety protocols during field sample collection.

Dependent on the site, some sites required more safety equipment than others. For example, Westminster Boating Base required a lifejacket to be worn whilst sampling; Tate and Lyle (North Woolwich) required a hard hat, steel toe boots and safety goggles but no lifejacket was needed. Due to these protocols, contamination controls, such as reducing plastic use, could not always be adhered to. Where possible, safety equipment, including lifejacket and hard hat, were pink in colour so that any potential contamination during sampling could be identified and considered.

Laboratory protocols included using personal protective equipment, including an orange lab coat, latex gloves and blue cotton face mask (during Covid - 19). Other protocols included covering filters when not in use to avoid atmospheric contamination. Used bottles were washed with distilled water, and equipment and surfaces were cleaned before and after use. Quality-control tests were carried out to test for potential plastic contamination. These included: 1) dampened filter paper placed on laboratory surfaces to monitor atmospheric contamination whilst filters were exposed and analysed daily (Supplementary Table 3), b) three HDPE bottles rinsed with distilled water and filtered (Supplementary Table 4), C) filtering blanks created using 3 x 3l of distilled water passed through the filtration setup (Supplementary Table 3) D) testing the sampling equipment used for water collection

(Supplementary Table 3). Visual counts were corrected by subtracting the corresponding procedural blanks to ensure contamination controls were considered.

4.2.5 Statistical analysis

Due to the Covid - 19 pandemic, two areas (Westminster and North Woolwich) had samples taken from two sites. The two sites that made up each area were compared using ANOVA. ANOVA was also used to check each area's MP abundance, size and colour significance. Two-way ANOVA was used to check for links between abundance, size and colour with the area, month and year.

4.3. Results

In this study, 6657 pieces of MP in 462 L of water in the river Thames were found across the eight study areas sampled monthly from May 2019 - May to 2021. This does not include the river Lea tributary sites with 73 pieces microplastic total (MPT) (Box Park = 41 pieces in 6L of water) and 3 Mills Island = 32 pieces in 6L of water) or Limehouse Harbour site samples with 138 MPT pieces in 6L of water.

An average of 12.27 pieces L⁻¹ were found in water samples at the eight areas along the tidal section of the river, compared to the river Lea 14.3 pieces L⁻¹ made up of Box Park (6.83 pieces L⁻¹) and 3 Mills Island (6.83 pieces L⁻¹). The highest MP average (46 pieces L⁻¹) was located at Limehouse harbour (Figure 4.3).

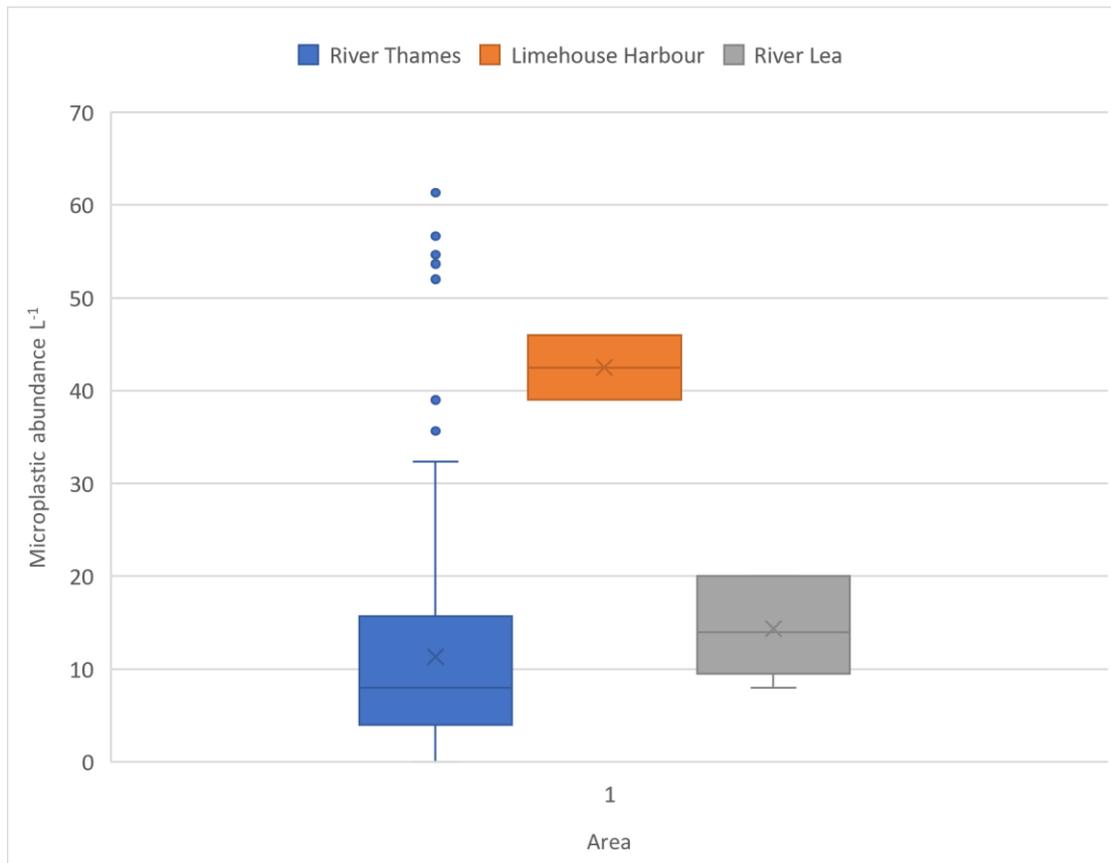


Figure 4.3 Average microplastic abundance L^{-1} along the river Thames 2019 - 2021 compared to the River Lea and Limehouse Harbour.

The two sites that made up the Westminster area were compared to ensure no difference between MP abundance and types, sizes, or polymer. The only significance between sites was between colour, due to the colour red being observed in a higher abundance at Westminster Millennium Eye (50 pieces) compared to Westminster boating base (12 pieces) (ANOVA, $f_{1,24}=5.13$, $P=0.033$)

There was no difference between sites located in the North Woolwich area (Tate and Lyle and Barge Road) for types, sizes, and polymer except for the MPT abundance of brown coloured plastic, which was only found at the Tate and Lyle site (5 pieces) (ANOVA, $f_{1,16}=6.404$, $P=0.023$).

4.3.1 Microplastic abundance along the river

The highest monthly MPT abundance was observed at Tilbury Fort in May 2019 (127.33 pieces L⁻¹), whilst the lowest abundance was observed at Limehouse in June 2020 (0.33 pieces L⁻¹). There was no significant difference between MPT abundance (ANOVA, $f_{7,181}=1.188$, $P=0.312$) or microplastic fibres (MPF) (ANOVA, $f_{7,181}=2.025$, $P=0.054$) between any area of the river Thames. However, there was a significant difference between fragment abundance (ANOVA, $f_{7,181}=2.838$, $P=0.008$) among areas along the river (Figure. 4.3). Post-hoc tests showed significant change in abundances between Southend-on-Sea and Teddington, Westminster, St Katherine's, Limehouse and Tilbury. Possibly because Southend-on-Sea had the highest abundance of MP fragments compared to any other area (253 pieces) (Figure. 4.4). There was no significant difference in MP sizes between all study areas (ANOVA, $f_{7,180}=0.735$, $P=0.643$).

Although there seemed to be a significance between MPT abundance and against study months, this was not the case (ANOVA, $f_{1,11}=1.656$, $P=0.097$). There was also no significance between area*month on MPT abundance (ANOVA, $f_{1,75}=0.571$, $P=0.993$). However, when comparing MP types, fibre and abundance, month appeared significant (ANOVA, $f_{1,11}=1.934$, $P=0.045$). Post-hoc tests showed a notable difference of MPF abundances between April and November MPF abundances, with fibres found in higher concentrations in November (3390 pieces) than in April (1611 pieces). This becomes insignificant once year*month is considered (ANOVA, $F_{1,12}=2.443$, $P=0.466$).

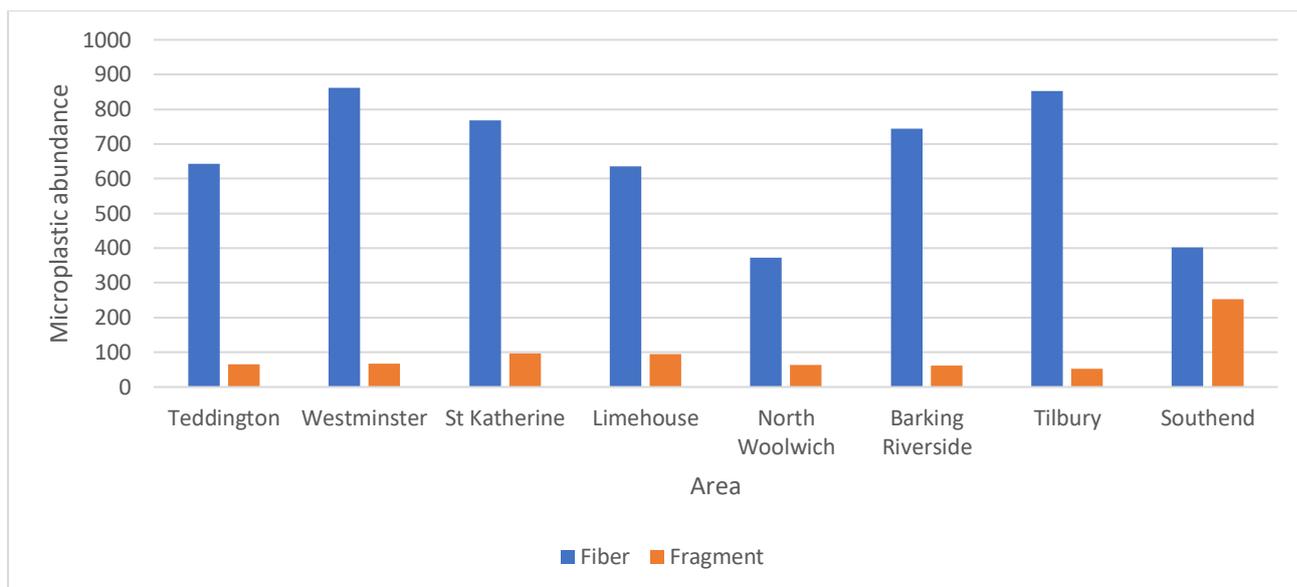


Figure 4.4 Microplastic fibres and fragment abundances found within water samples at sites along the river Thames from May 2019 to May 2021

4.3.2 Inter-annual trends

There appeared to be a significant variation in MPT abundance within each area over the sample period 2019 - 2021. The average MPT L^{-1} decreased per year within most areas studied, excluding St Katherine (12.71 pieces L^{-1} – 14.5 pieces L^{-1}) and North Woolwich (12.67 pieces L^{-1} - 14.89 pieces L^{-1}), which both increased from 2019 - 2020. The average MPT abundance along the length of the Thames through this study was 12.27 pieces L^{-1} , however, in 2019, the average MPT was 16.52 pieces L^{-1} , and by 2021 it was 5.92 pieces L^{-1} (Table 4.2). There appears to be a significance difference between MPT concentrations and year ($f_{1,2}=14.295$, $P=0.000$) but no significance between area and year ($f_{1,14}=0.664$, $P=0.806$). Post-hoc tests showed a considerable difference between every year, but the largest difference was found between 2021 and 2019 - 2020, this is possibly due to 2021 only having 5 sample months for each area.

Table 4.2 Average microplastic total (MPT) per litre (L⁻¹) of water collected in the 8 sampling areas along the river Thames during the study period (2019 - 2021).

Areas	Average MPT (L⁻¹) 2019 - 2021 (± stderr /SE)	Average MPT (L⁻¹) 2019 (± stderr /SE)	Average MPT (L⁻¹) 2020 (± stderr /SE)	Average MPT (L⁻¹) 2021 (± stderr /SE)
Teddington	10.01 (3.78)	15.13 (3.73)	8.1 (3.71)	6.4 (4.05)
Westminster	13.17 (5.09)	15.67 (4.92)	13.36 (5.68)	8.73 (3.93)
St Katherine	11.85 (4.42)	12.71 (4.11)	14.5 (5.43)	6 (2.48)
Limehouse	10.15 (3.86)	14.3 (5.22)	9.83 (3.66)	4.2 (2.18)
North Woolwich	11.14 (5.49)	12.67 (5.78)	14.89 (6.04)	4.8 (1.82)
Barking Riverside	18.82 (5.39)	29.56 (5.74)	19 (5.38)	7 (3.86)
Tilbury	12.75	17.21	12.94	5.2

	(5.35)	(7.61)	(4.64)	(2.86)
Southend- on-Sea	10.25 (2.93)	14.88 (4.60)	9 (2.65)	5.13 (0.85)

Microplastics were classified into six shape types (fibre, fragment, bead, foam, pellet and other) (Figure. 4.5). The most common shape across all areas was found to be fibre, which comprised 93.27% of all MPs within the river Thames. Southend-on-Sea had the lowest abundance of microplastic fibres (MPF) (55%, 402 pieces) compared to Tilbury (92.81%, 852 pieces), which had the highest value. Fragments (11.87%, 790 pieces) were the second most common and were found across all sites but mostly at Southend-on-Sea, where they made up 34.56% (253 pieces) of the sample compared to Tilbury, which had the lowest with 5.77% (53 pieces). All types of MPs were found at all study sites sampled except beads which were not found at Westminster, St Katherine or Southend-on-Sea. Beads were also the least type of MP found, making up 0.18% of all types (Figure. 4.4).

All MPs were further categorised by colour (Figure. 4.4). In total, 12 different colours were observed (blue, black, red, white, orange, yellow, transparent, brown, pink, green, purple and gold). The most observed colour at all sites was black (66.68%, 4439 pieces), followed by blue except for St Katherines (red, 79 pieces) and Southend-on-Sea (white, 84 pieces). The least common colour observed was Gold (0.06%, four pieces), which was only found at Westminster (1 piece) and Limehouse (3 pieces).

In total, 29% (1982 pieces) of all MPs found were measured for its length; the majority (40.53%, 1095 pieces) fell within the 0 – 1 mm category, followed by the 1 – 2 mm category (22.65%, 449 pieces). The 4 - 5 mm category (2.42%, 48 pieces) was the least abundant (Figure. 4. 5).

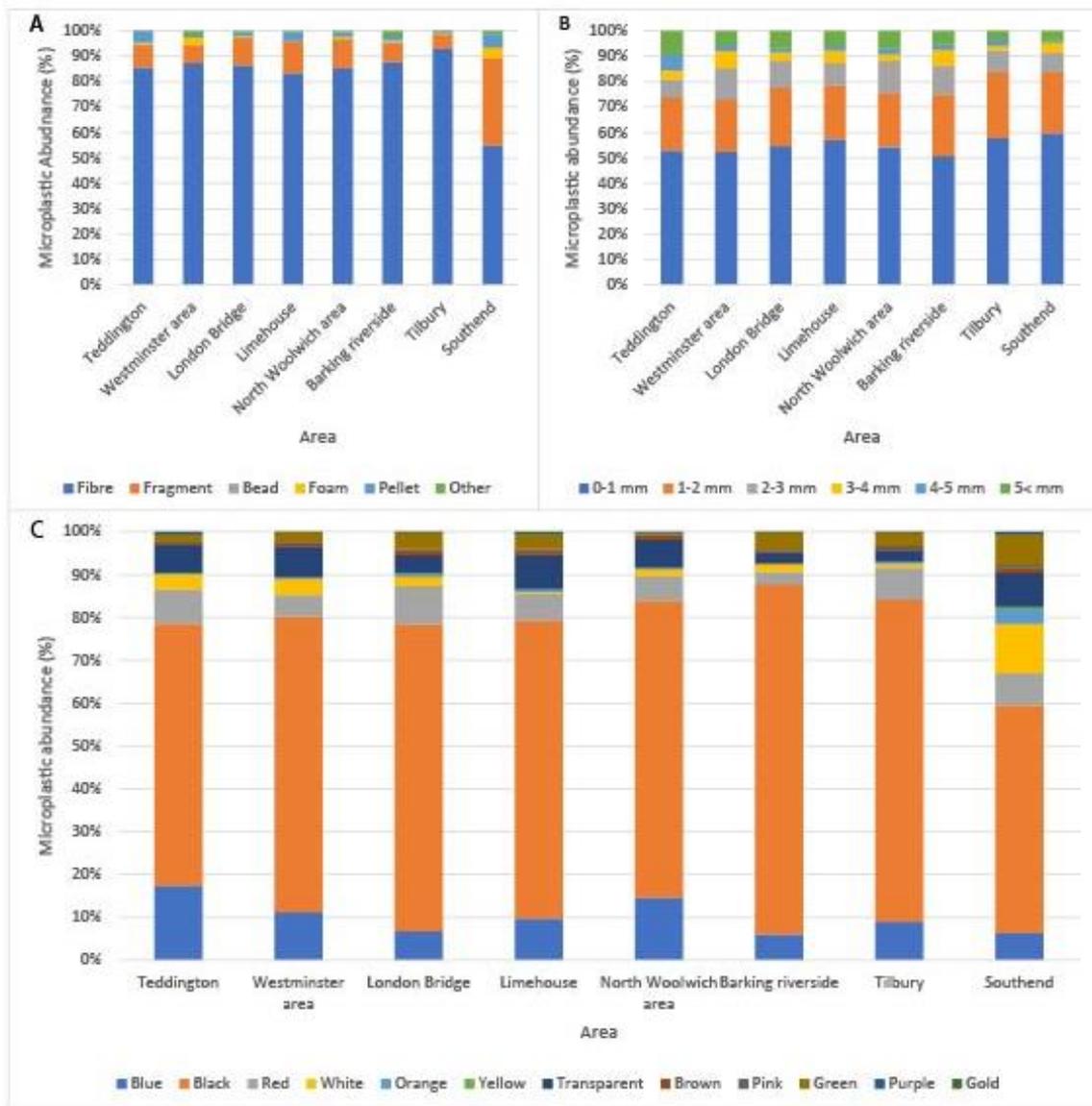


Figure 4.5 Microplastic abundances (%) found within water samples at the eight areas sampled along the river Thames during 2019 - 2021 A) MP type, B) Size, and C) Colour

4.3.3 Polymer types

A total of 1041 pieces (15.64%) were analysed via FTIR, which included “No hit” (176 pieces) and natural (7 pieces) (Supplementary Table 5). The natural material was located at Teddington, Westminster and London Bridge. The material placed in the natural category had the appearance of fibres of varying colours; however, once scanned was identified as Chitin (identified September 2020 and April 2021).

Anthropogenic microfibers/particles (31 pieces) were also found consisting of wool, cotton, flax, nylon, silk and silicone.

As a result, 827 pieces (79.44%) were identified as 40 distinct types of polymers. The most commonly found polymers in the river Thames were Polyvinyl Chloride (PVC) (255 pieces), Polystyrene (PS) (102 pieces), Polychloroprene (PCP) (80 pieces), and Polyethylene Chlorinated (PEC) (56 pieces) and Polypropylene (35 pieces). Polymers such as rubber and Acrylonitrile Butadiene Styrene (ABS) were also found. These are considered as tire wear particles (TWP) at Westminster, London Bridge and Limehouse. Biopolymers such as Zein purified (1 piece, London Bridge) and Alginic acid (4 pieces, Southend-on-Sea, London bridge and Teddington) were found only in samples from 2021.

4.3.4 River Lea Tributary

There was no significant difference between MPT abundance and sites sampled along the river Lea (ANOVA, $F_{1,11}=1.202$, $P=0.299$). Box Park had 82 pieces of MPT in the samples of 2020 and 2021 compared to 3 Mills Island, which had 99 pieces (Figure. 4.6). There was a significant difference between the locations depending on the year (ANOVA, $F_{1,1}=6.259$, $P=0.037$) as well as a significant difference depending

on the Year *Site (ANOVA, $F_{1,1}=10.704$, $P=0.011$). No post-hoc tests could be performed as there were fewer than three groups.

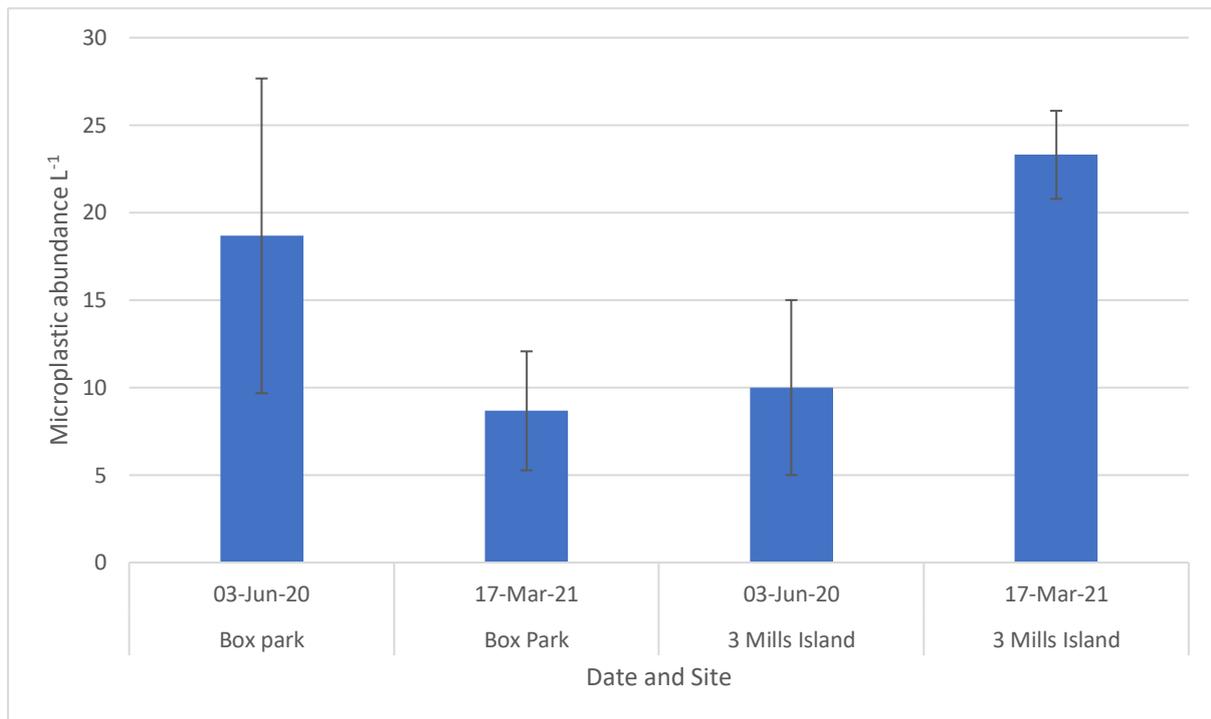


Figure 4.6 Microplastic abundance L⁻¹ of water sample from the two locations from the river Lea – Box Park and 3 Mills Island taken on the 3rd June 2020 and the 17th March 2021

Microplastics were found of every size; however, the size ranges 0 - 1mm and 1 - 2 mm were the most abundant at every location in both years. Polyvinyl Chloride was the most commonly identified polymer at both sites (Box park - 3 pieces, 3 mills

island – 5 pieces) (Figure. 4.7).

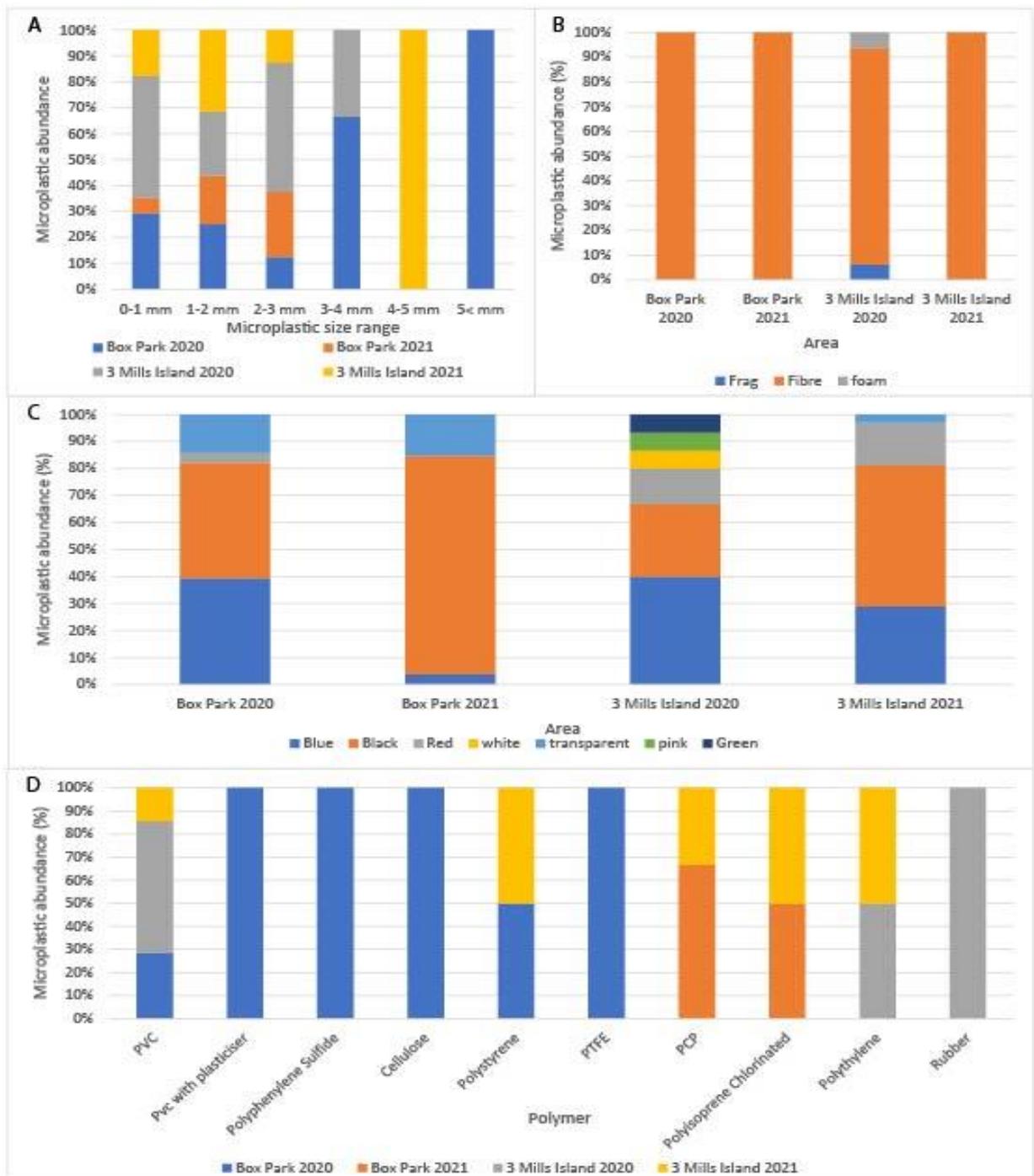


Figure 4.7 Microplastic characteristics of the water samples taken from the river Lea Tributary sites 3 Mills Island and Box Park taken on the 3rd June 2020 and 17th March 2021 A) Size range, B) Microplastic type, C) Microplastic colours, and D) Polymer

4.3.5 Limehouse Harbour

Microplastic abundances at Limehouse harbour were higher on the 6th November 2019 (46 pieces L⁻¹ ± 4) compared to the 5th November 2019 (39 pieces L⁻¹ ± 3). Fibres (T-test, 0.009) were the most abundant on both sample days, although fragments were found in higher abundance on the 6th November. Black-coloured microplastics were also the most abundant on both days (T-test, P=0.027).

Microplastics fell within the 0 – 1 mm, 1 – 2 mm, 4 – 5 mm, and 5 < mm categories.

The 5 < mm categories were excluded from abundance totals as they are on the border of mesoplastic categorisation. Once the 5 < category is excluded, the sample collected on the 5th November 2019 only contained microplastics in the 0 – 1 mm and 1 - 2 mm regions. On both sample days, no MP was found in the 2 - 3 mm or 3 - 4 mm region. Polystyrene was the most abundant type of polymer, followed by PVC, polycarbonate (PC), and PCP, which were also found in high amounts in the river Thames samples (Figure. 4.8).

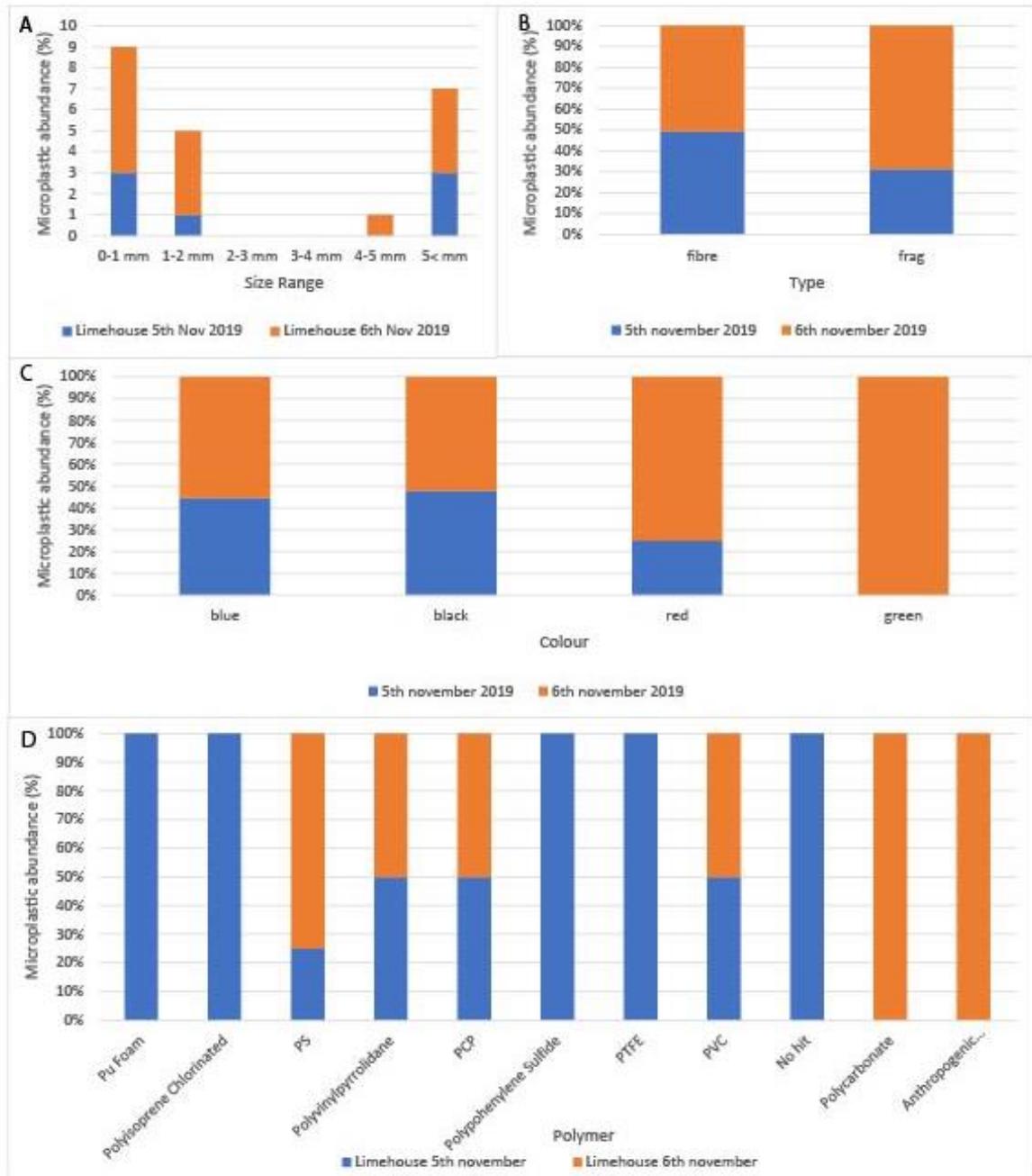


Figure 4.8 Microplastic characteristics of the water samples taken from Limehouse Harbour on the river Thames taken on the 5 - 6th November 2019 A) Size range, B) Microplastic type, C) Microplastic colours, and D) Polymer

4.3.6 Macroplastic presence

Whilst macroplastics were not the focus of this study; they were found or observed at sample sites and within water samples. Macroplastics, mainly plastic water bottles, were present in high quantities at Limehouse harbour, especially at high tide (Figure. 4.8). They were also found in water samples collected from the eight areas of the river Thames 2019 – 2021 (Figure. 4.9). A selection of these were identified via FTIR the top three polymers identified were PCP, PVC, and PP (Figure 4.10).



Figure 4.9 Macroplastic observed between the opening on Limehouse harbour and the river Thames at high tide on multiple occasions A) 2nd November 2019 various plastics including a large water bottle and B) 6th November 2019 multiple water bottles

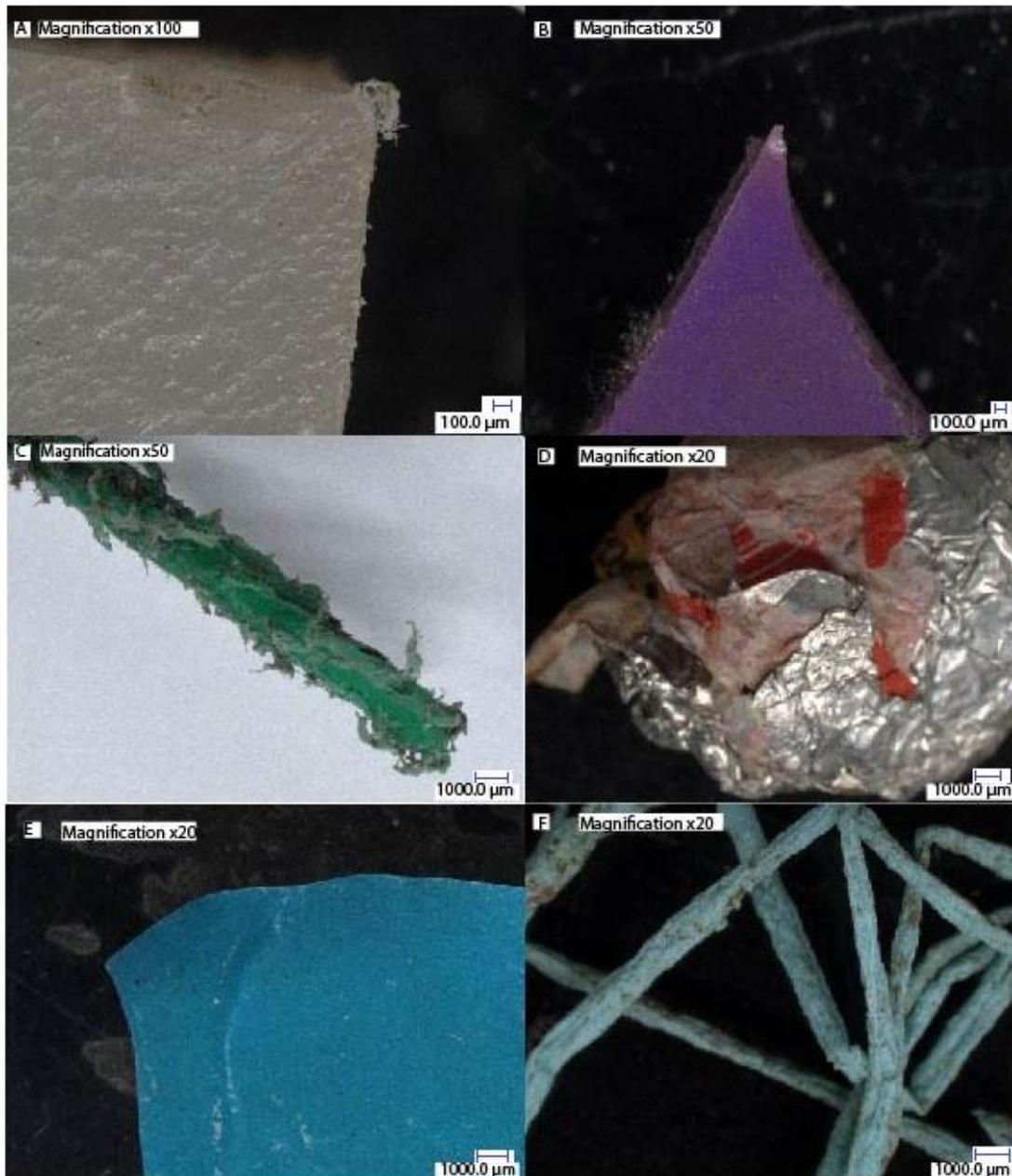


Figure 4.10 Examples of Macroplastics found in water samples taken from the river Thames between 2019 - 2021; A) White fragment in Limehouse, October 2019 - Polypropylene, B) Purple fragment in St Katherine's, October 2019 - Polyethylene chlorinated, C) Green rope in Teddington, August 2020 - Polyvinyl chloride, D) KitKat wrapper in Southend-on-Sea, May 2021 - Polyvinyl chloride, E) Blue fragment in Teddington, September 2020 – PU Foam, and F) Blue fibres (silly string) in St Katherine's, December 2020 - Polychloroprene.

4.4. Discussion

Rivers are widely reported as one of the central transport systems of MPs entering oceans from land-based sources (Ding *et al.*, 2019; Lebreton *et al.*, 2017; Mishra *et al.*, 2019). However, there is a lack of studies that focus on rivers. As a result, the number of MPs transported through rivers is unknown. When combining river dynamics (i.e., hydrology and tides) with the sinking and resuspension of MPs within a river system, the total abundance of MPs within a specific time and area becomes unpredictable.

4.4.1 Trend of Microplastic abundance along the river

As shown in this study and previous studies, MP quantity varies between and within the study sites across the river Thames over the sampling period. The highest concentration was found at Westminster and the lowest at North Woolwich. The lowest abundance at North Woolwich could be explained by the amount of sampling missed due to the Covid-19 pandemic and having to find another site within proximity. What is evident from this study is that the hypothesis that MP abundance increases as the river reaches the estuary mouth or, in this case, joins the North Sea was not supported, as this never happened in any of the monthly samples.

Microplastic monthly abundance at sites along the river Thames varied from 0.33 - 127.33 L⁻¹, however, in 2019 - 2021, the areas averaged 10.01 - 18.83 L⁻¹. Previous studies on the river Thames shows a range in MPT abundances from; 508 pieces L⁻¹ (Devereux *et al.*, 2022) (Chapter 7), 84.1 pieces L⁻¹ (Dunn and Friends of the Earth, 2019), 24.8 m⁻³ (Putney) and 14.2 m⁻³ (Greenwich) (Rowley *et al.*, 2020) and 8 - 36.7 particles m⁻³ (Rowley *et al.*, 2020). The results gained from this study fall within MP ranges obtained from previous studies on the river.

In comparison with rivers worldwide, the results obtained from this study appear to be higher than studies conducted on the Yangtze River, China, which had 0.5 - 10.2 particles of L⁻¹ (Zhao *et al.*, 2014), river Rhine, Germany, 0.05 - 8.3 particles m⁻³ (Mani *et al.*, 2019), and the Hudson River, USA 0.98 particles L⁻¹ (Miller *et al.*, 2017). However, MP abundances were lower than the river Marne, France, with 398 particles L⁻¹ (Dris *et al.*, 2015).

4.4.2. River Lea Tributary

The confirmation of MPs at sites along the river Lea is not surprising. The river is tidal to Bow Locks (Bromley by Bow), and watercraft can travel from the river through Limehouse cut into the Limehouse basin/ Limehouse harbour (Read, 2017). The river's connection allows MP to travel from one river to the other with water flow. Aswell as receiving wastewater from multiple sewage treatment works (STW) or combined sewage overflows (CSOs) such as Abbey Mills, which receives 40% of sewage discharge in London and Deephams STW (Water technology, 2022). These MPs will eventually enter the river Thames.

4.4.3. Limehouse harbour

Elevated levels of MPs were present at all sites, particularly Limehouse harbour, which is also supported by Classens (*et al.*, 2011). This can be explained by Massel (1999) that areas of low flow can lead to an increased sediment deposition due to the transportation of debris by the incoming current. Microplastics act as sediment, thus suggesting this may be the reason higher abundances can be found within Limehouse harbour compared to the river at Limehouse. Limehouse harbour was necessary to sample. Microplastics were present within the higher scale end of MP size range going into the mesoplastic category and the lower end of the MP size

range, however, there was no evidence of the middle range of MPs. This may be because there were only two days of sampling. Polymers such as PVC and PCP were heavily present within the river Thames samples were also present within the water samples taken from Limehouse harbour samples. As water samples were taken at high tide from this side, more samples at various times of the tidal cycle as well as from other areas of the harbour. To investigate if the harbour is possibly a source as well as a place that should be explored as a possible solution for MP pollution. At high tide, a large amount of macroplastic tended to accumulate by the harbour gates that separated the harbour from the river Thames and tended to be water bottles or litter. This could be due to the river dynamics where the current is slow in this area, and similar to sediment, the plastic accumulates there (Massel, 1999). The site is heavily populated as it falls within the London area. As well as housing a dock and marina, it receives water from the Limehouse cut and river Lea. However, more research would be needed to see if this were the case for the increase in plastic within this area. What is evident from the two days of sampling carried out during this study is that plastic seems to accumulate within this area.

4.4.4 Microplastic characteristics

Secondary MPs, particularly MPFs, are the most dominant form of MP found in all aquatic environments (Gago *et al.*, 2018; Rebelein *et al.*, 2021; Woods *et al.*, 2018). This is especially the case when looking at MPF abundance within river systems, with some studies showing that 99% of MPs found within rivers are fibres (Kiss *et al.*, 2021; Napper *et al.*, 2021). This was the case with this study, with fibres accounting for 93.27% of MPs. Fragments were second highest and most commonly found at Southend-on-Sea. This may be due to their polymer density and, as such, being found lower in the water column or, as shown in Horton (*et al.*, 2017), these types

may be lower than fibres due to sinking and being found in higher amounts in sediments of the river Thames. Compared to the sites along the river where samples contained mostly fibers Southend-on-Sea had a blending of fragments and fibers representative of the plastic soup found within oceans (Suaria *et al.*, 2016).

Total MPF concentrations are reportedly higher closer to shores than offshore (Lusher *et al.*, 2014; Nel and Froneman, 2015), which has been linked to wastewater from washing machines or laundry water, WWTP and Sewage Treatment Works (STW), (Browne *et al.*, 2011; Galvao *et al.*, 2020; Ramasamy and Subramanian, 2021; Yang *et al.*, 2019). This may explain why the Southend-on-Sea fibre content was the lowest compared to MPs. However, it is also possible that the constant wave action and turbidity at Southend-on-Sea resuspends fragments and fibres, so there is a more mixed MP concentration. It is also possible that the high MP abundances found at Tilbury and Barking Riverside, and this may be due to their proximity to sewage treatment plants or outlets. Barking Riverside is close to Beckton STW, the largest STW in Europe, serving 4 million people in north and east London (Grassly, 2022). In 2021 it discharged 12 times for a total of 26.6 hours, according to Thames Water (2022), whilst the Tideway CSO, which is in the same area, spilled 13 times for 81 hours (France, 2021). Tilbury has 3 points on the same side of the river, two discharge points and one CSO; however, all 3, as of 2021, are not monitored. On the opposite side of the river, there are 6 points, including Gravesend WWTP; in 2021, it spilled 60 times for a total of 235 hours, the Empress Rd CSO overspilled 25 times for 75 hours, High Street Gravesend CSO spilled eight times for 8 hours, Crowley Court CSO spilled 41 times for 72 hours whilst Tower pier CSO spilled 51 times for 100 hours (France, 2021). Whilst this data is readily available, the dates of the overspill are not. As a result, this data cannot be used to correlate MP abundances

with possible releases other than a possible reason for a change in yearly MPT abundances.

However, the distribution of plastic pollution can vary due to environmental factors such as wind, river depth, flow speed, salinity and vegetation, as well as the plastics size, shape and buoyancy, so whilst sewage treatment plants may be one explanation, a combination of factors may still be the cause.

Black was the most dominant colour; this is supported by other studies conducted within the river Thames. For example, McGoran (*et al.*, 2017), found black fibres were the most dominant type found in European flounder and European smelt found within the river Thames.

4.4.5 Polymer types

The abundance and nature (colour, types, sizes) of fibres and fragments within this study are secondary MPs from the fragmentation of consumer-based products such as textiles and packaging. This hypothesis is supported by the FTIR analysis carried out during this study which found that the highest polymer abundances were identified as PVC, PS, PCP, PEC and PP. However, these were expected as they are the most commonly produced polymers worldwide. Other types of polymers identified were acrylonitrile, butadiene and styrene (ABS), which are consistent with the composition of tires (Kole *et al.*, 2017), found at Westminster, London Bridge and Limehouse. Thus, some plastic within the river Thames has come from tires, particularly within London, where the study site is close to the main roads. One Swedish report (Verschoor *et al.*, 2016) estimated that 500 tons of TWP directly enter surface water, whilst 1,300 tons can enter via sewage systems from road runoff. More information is needed regarding preventative measures as it is not

sustainable or realistic to ban cars and remove all asphalt roads. Instead, it may be more practical to improve sewage systems and their ability to remove microplastics from these systems.

As well as polymers, anthropogenic material was also identified during this study. Although they were not the focus of this study, it is still important to investigate and record these materials as they can still pose a risk to the environmental and biological health of the waterways they are found within. Anthropogenic materials can still pose a risk due to the dyes and chemicals used in the textiles and manufacturing industry to prolong their life (Bikker *et al.*, 2020; Dris *et al.*, 2018; Remy *et al.*, 2015).

Materials placed in the natural category were all identified as Chitin, found in the exoskeletons of insects, fungi, invertebrates, and fish (Elieh-Ali-Komi and Hamblin, 2016). However, upon further investigation, Chitin is also used as a biopolymer with or without other materials such as silk, alginate, poly-lactic acid or collagen (Salaberria *et al.*, 2015). Chitin appears to be used in wound management, drug delivery and cosmetics (Singh *et al.*, 2017). However, it has also been used to make a plastic film for packaging similar to PET (Material District, 2018; Yu *et al.*, 2020). Chitin appears to be a new and upcoming polymer used within packaging within the UK. However, a closer examination of the material found in the Thames is needed to explore if this was the case.

Biopolymers were also found in water samples, such as alginic acid, which can be used in food packaging (Khalil *et al.*, 2017), and Zein purified, which can be used in paper coating and food packaging (Jones *et al.*, 2020; Patnode *et al.*, 2022).

Many studies (Browne *et al.*, 2011; Devereux *et al.*, 2021; Devereux *et al.*, 2022; Lusher *et al.*, 2020) have expressed the numerous possibilities of contamination whilst all possible precautions were taken to limit the exposure of sample contamination it is not possible to rule out.

4.5. Conclusions

These findings correlate with other studies on the MP abundance in rivers, including previous studies on the Thames. Microplastics were found at all sites within every sample that was collected and did not increase in abundance along the river. The results in this study can be used as a baseline for the presence of MP pollution within the tidal river Thames and be used to examine MP transport from rivers to the sea. This study also records MP pollution at these sites and potential sources, notably sewage – laundry, road particulates, and litter degradation. The majority of MP found in this study can be attributed to secondary MPs, and sources such as PVC, PS and PE used for packaging, textiles and within the building industry.

This study also shows a reduction in MP pollution from 2019 to 2021, except for two sites (St Katherine and North Woolwich) in 2020. Whilst this may be due to the samples collection in 2021 completing in May 2021, and as a result, seven months of sampling were not done. The impact of Covid-19 in 2020 must also be considered as a cause for reducing abundance. As a result, further studies would be needed to investigate if this is an anomaly or a trend due to the awareness of plastic pollution and the steps to reduce it. However, it must be considered that rivers are dynamic systems, and flow and depth can affect MPs presence, abundance, and behaviour from one location to another. Further studies are suggested to consider the effect of tides on MPs and vertical suspension of MPs, including sampling sediment from

these areas to investigate the sinking and resuspension of MPs within the river. This will further enhance our understanding of the presence and abundance of MPs and the potential environmental impacts within this riverine system

Chapter 5: Seasonal and rainfall microplastic abundance – The great river Thames washout

Abstract

This study focused on the seasonal impacts, including the effect of rainfall, on microplastic abundance within the surface water of the river Thames. Ten sites in eight areas were sampled along the tidal section of the river, starting at Teddington and ending in Southend-on-Sea. Three litres of surface water were collected monthly at high tide from land-based infrastructure from May 2019 - May 2021. A total of 6657 pieces were identified and recorded throughout this study, although there was no significant variation between seasons and microplastic abundance (ANOVA, $F_{3,178}=0.77$, $P=0.508$). However, there was a significant difference between MP abundance observed between consecutive seasons in the years 2019-2021 (ANOVA, $F_{3,178}=22.64$, $P=0.00$). There was a significant difference between fibres, the most abundant throughout, making up 77.1 - 85.96% of samples taken in all four seasons. A total of 1041 pieces of suspected microplastic were analysed via Fourier transform IR (Infrared Radiation) spectroscopy, of which 176 pieces were not identified. The most commonly identified polymers were PVC (24.5%), PS (9.8%) and PCP (7.69%). This study demonstrates a yearly variation in seasonal microplastic abundance with less MP observed in the 2020 year.

5.1 Introduction

Studies on MP within river environments tend to vary even along the same stretch of river (Devereux *et al.*, 2022; Dunn and Friends of the Earth, 2019; Rowley *et al.*, 2020). This is often due to differences in seasonality, methodology or sampling and

environmental factors. Several studies now consider seasonality, with many assessing the impact of rainfall or run-off at a particular site or along a stretch of river. Many studies only look at a short period of time of the same season to carry out a detailed analysis of how seasonality and rainfall subsequently affect MP abundance over a multi-season timeframe is scarce. Studies focusing on seasonality note that seasonal variations of MPs occur on the surface water of the river as well as impact MP abundance (Horton and Dixon, 2018). These are due to multiple inter-linked factors whilst understanding sources and anthropogenic factors that contribute to microplastic such as wastewater treatment plants (WWTP), urban areas, and industrial areas. These factors are essential to understanding the hydrological effect of a river and need to be considered as they influence river flux downstream and MP behaviour within the water column further adding to the complexity of MP behaviour with a constantly changing body of water (Zhao *et al.*, 2020).

In the UK, there are four seasons, spring (March - May), summer (June - August), autumn (September - November) and winter (December - February). Summer is the driest season compared to the other seasons, especially winter (Murphy *et al.*, 2020). As a result of low rainfall, many river water levels dip, so MPs may be concentrated (Govender *et al.*, 2020; Xia *et al.*, 2021). In the autumn and winter months, rainfall is high. This leads to water runoff, bringing in land-based MPs such as litter (Chen *et al.*, 2020; Fan *et al.*, 2022; He *et al.*, 2020). Heavy rainfall subsequently leads to more water within the sewers or wastewater/sewage treatment works, which are currently undergoing infrastructure changes. The current London sewers were built in the 19th century (Garrett, 2016) and had a maximum capacity of 4 million people (Thames Tideway, 2022). The system was designed to release into the river Thames during wet weather when the sewers reach capacity

(Stovin *et al.*, 2013). The old pipes often lead to an overflow of water that needs to be released from the system (France, 2021), and this leads to an influx of water and MPs entering rivers which may increase abundance. Studies have found that rainfall can increase abundance within rivers and decrease MP abundance. This results from the high levels of water entering the river and thus increasing the flow, so more MP is added, but more MP is potentially pushed out to the open sea quicker. Therefore, seasonality and subsequent rainfall, especially significant rainfall such as storms and torrential rain, must be considered when looking at MP abundance.

The river Thames has over 100 sewer storm overflows along it from Teddington to Southend-on-Sea, excluding overflows in tributaries that flow into the river (France, 2021). This is combined with 350 sewage treatment works across London and the Thames Valley (Water Projects, 2022). Wastewater treatment plants currently do not remove the majority of MPs, resulting in MPs being released into rivers or adding to agricultural land within sewage sludge (Mahon *et al.*, 2017). This often is because of household fibres being released in vast quantities and thus being the most abundant MP morphology noted in riverine studies. Arguably, more fibres enter the environment through WWTPs during winter months (Ben-David *et al.*, 2021) from households as people wear more clothes due to cold weather (Jiang *et al.*, 2020).

This study investigates the impact of seasonality, rainfall and WWTPs on MP abundance, morphology and polymer at sites along the river Thames. The hypothesis is that MPs would be higher in the autumn and winter months, and this is due to higher rainfall events and that sites closer to WWTPs will have a higher abundance of MP in these seasons. This study aimed to 1) investigate the variation in MP abundances and morphology at different seasons along the river Thames, 2)

investigate the impact on rainfall during these seasons, and 3) investigate if there is a relationship between rainfall, sites and MP abundances or morphology.

5.2 Methodology

5.2.1. Study sites and sampling

The tidal section of the river Thames was the focus of this study. Eight areas (Teddington, Westminster, St Katherine, Limehouse, North Woolwich, Barking Riverside, Tilbury and Southend-on-Sea) were selected along this stretch of the river from Teddington Lock to Southend-on-Sea (Figure. 5.1). Due to the Covid-19 pandemic, these eight locations were made up of ten sites with two sites at Westminster (Westminster Boating Base and Westminster – Millennium eye) and North Woolwich (Tate and Lyle – Sugar Factory and Barge Road) due to the inaccessibility of sites during national lockdowns.

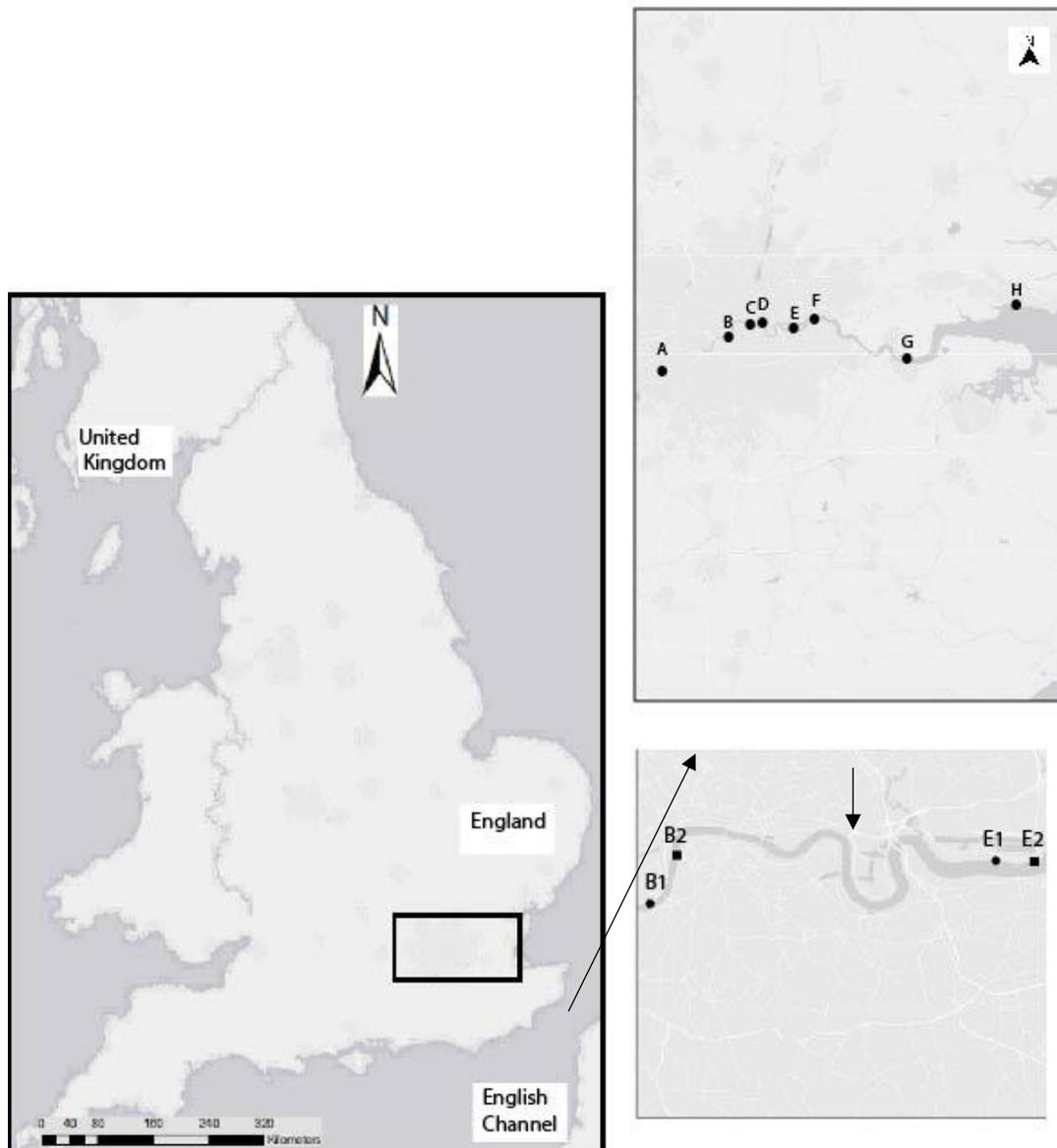


Figure 5.1 Water sampling areas along the river Thames; A) Teddington, B) Westminster, C) St Katherine's Pier, D) Limehouse, E) North Woolwich, F) Barking Riverside, G) Tilbury Fort and H) Southend-on-Sea. Due to the Covid - 19 pandemic, the Westminster area is made up of two sites: B1) Westminster Boating Base (pre-Covid-19) and B2) Westminster – Millennium eye (during and post- Covid-19). The North Woolwich area was also made up of two sites: E1) Tate and Lyle – Sugar factory (pre-Covid-19) and E2) Barge Road (During and post-Covid-19).

Three samples of 1 L surface water were collected from each area at high tide from a land-based structure every month from May 2019 - June 2021 (Supplementary Table 2). Sampling took place within three to five days of the 15th of the month. Sampling was initially carried out by a Lamotte horizontal water sampler from May to August 2019. However, it could not cope with the regime, so it was swapped for a pink plastic bucket with yellow and orange rope. Once the water was collected, 2L high-density polyethylene (HD-PE) double-lidded bottles were submerged in the bucket to collect a subsample of water that was transported back to the University of East London docklands campus for filtration and analysis as explained in Chapter 3.

During the Covid-19 pandemic, non-essential buildings, including university laboratories, were closed down. As a result, samples collected during this period (March – June 2020; November - December 2020; January - February 2021) were not transported back to the laboratory until the lockdown had lifted or the laboratory opened. These samples were kept in the dark, cool cupboard and not opened to prevent contamination and reduce the amount of plastic degradation within the samples.

Microplastic extraction, analysis and contamination controls were the same as discussed in chapter 3.

5.2.2 Statistical analysis

To compare seasonal abundances, the following months were included in the corresponding month; Spring is March - May, Summer is June – August, Autumn is September – November, and Winter is December – February as per the UK seasons. One-way and Two-way ANOVA were used to investigate microplastic total

(MPT) abundances season*rainfall, season*area and season*rainfall*area. Post hoc tests Tukey were used to investigate further the results obtained from the ANOVA.

Due to the reliance of high tides during this study, sample time varied, resulting in some samples being taken from midday to late evening. As a result, MP abundance was compared to rainfall from the previous day. This is because it may have resulted in comparing rainfall data that may have occurred after the sample had been taken and thus did not affect MP abundance. Linear regression was used to investigate MP L^{-1} and rainfall (mm).

5.3 Results

Microplastics were observed in all water sample sites. In total, 6657 pieces of MP were identified throughout this study. Whilst no significance difference was observed between MP type and seasons ($P < 0.05$) (Figure 5.2), some colours and seasons (Figure. 5.3) were significant. For example, the colours blue ($P = 0.000$), transparent ($P = 0.012$) and pink ($P = 0.023$) were the most abundant in spring than any other season, especially autumn, which had the lowest abundance of these colours. There

was also a significance between MP in the 0 - 1 mm size range and season (P=0.000), with summer containing the most MPs of this size range.

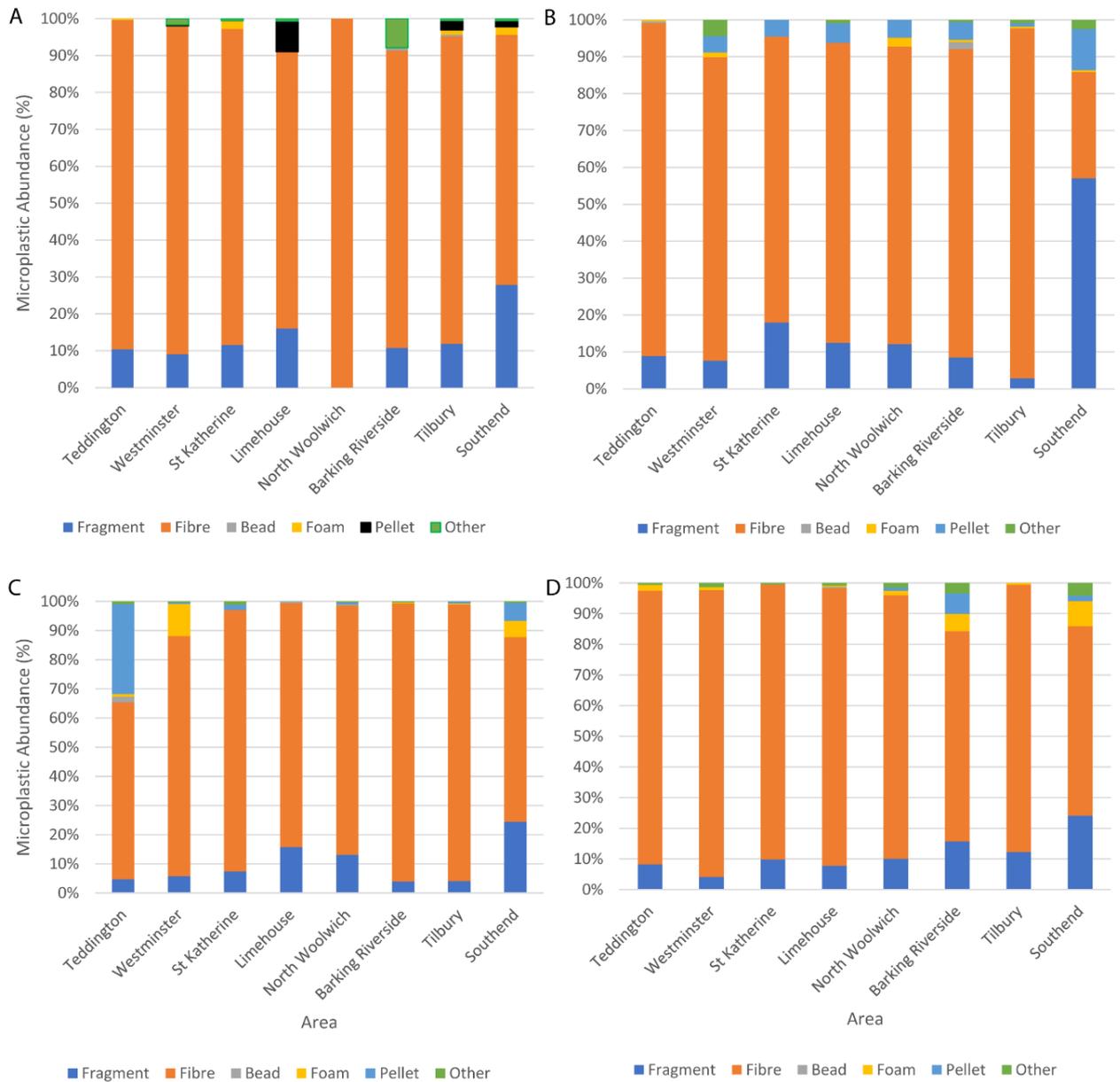


Figure 5.2 Types of Microplastic identified from water samples at areas along the river Thames seasonally from 2019 - 2021; A) Spring, B) Summer, C) Autumn, and D) Winter

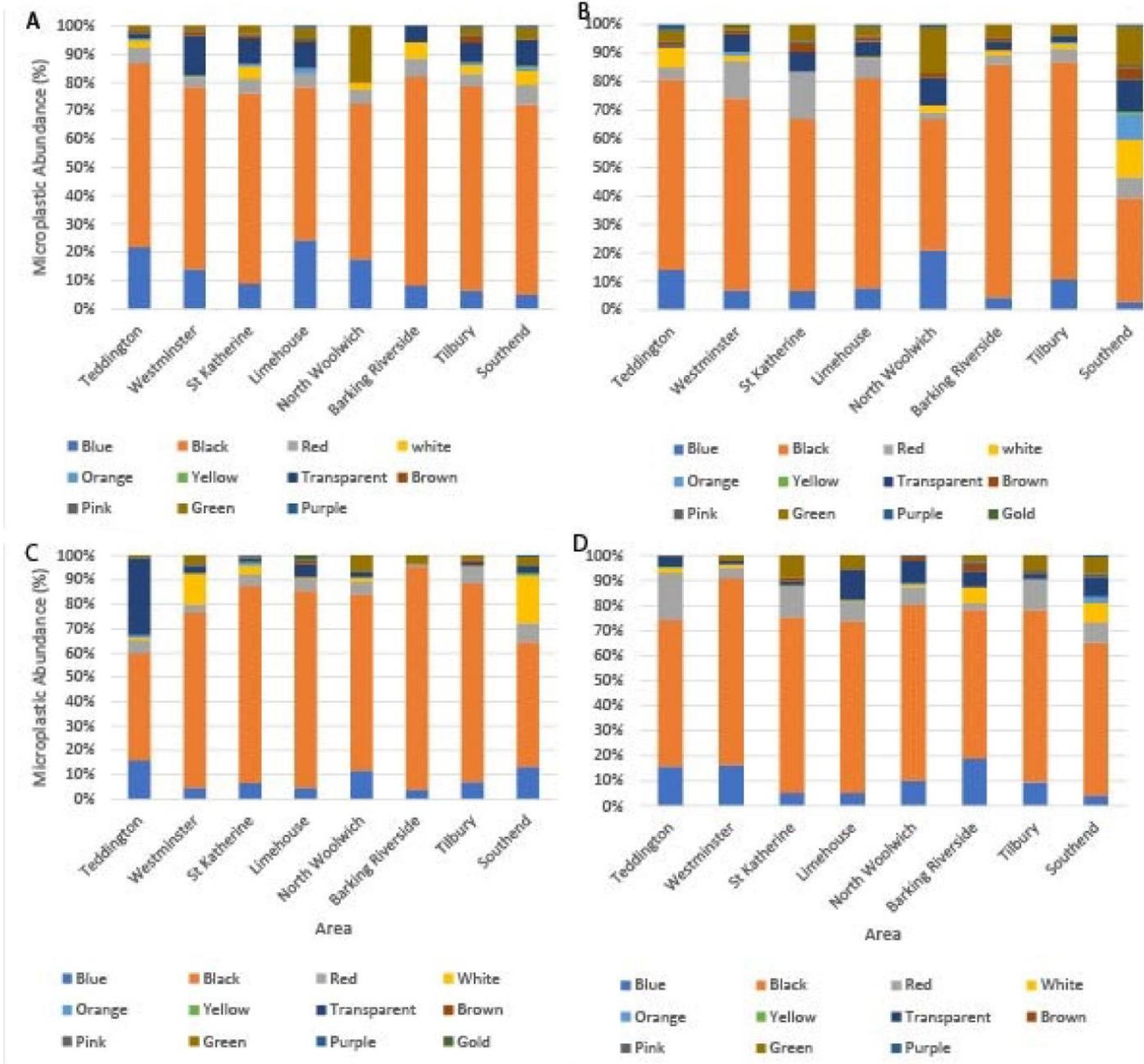


Figure 5.3 Microplastic colours identified from water samples at different areas along the river Thames seasonally from 2019 - 2021; A) Spring, B) Summer, C) Autumn and D) Winter

5.3.1 Seasonal abundances

During the spring season (2019 - 2021), 1724 pieces (25.9%) of MP were identified, and the abundance of MPT ranged from 1 - 68 pieces L⁻¹ with a mean value of 10.29 ± 4.34 L⁻¹ along the river (Figure. 5.4). The maximum and minimum values were found at North Woolwich and Tilbury, respectively. In Summer, 1467 pieces (22.04%) were identified with abundance ranging from 0.33 (Limehouse) – 35.67 pieces L⁻¹ (Southend-on-Sea), with a mean value of 12.14 ± 2.84 L⁻¹. Autumn's 1994 pieces (29.95%) ranged from 1.67 to 61.3 pieces L⁻¹ from Teddington and St Katherine, respectively. Microplastic abundance had a mean of 14.83 ± 7.49 L⁻¹. Winter had 1472 pieces (22.11%) ranging from 0.7 – 25 pieces L⁻¹ from Southend-on-Sea and Tilbury, respectively. Microplastic abundance had a mean of 10.83 ± 1.7 L⁻¹. Whilst there were variations between abundances and ranges each season, there was no significant difference between MPT between seasons*site (ANOVA, F_{3,178}=0.77, P=0.508).

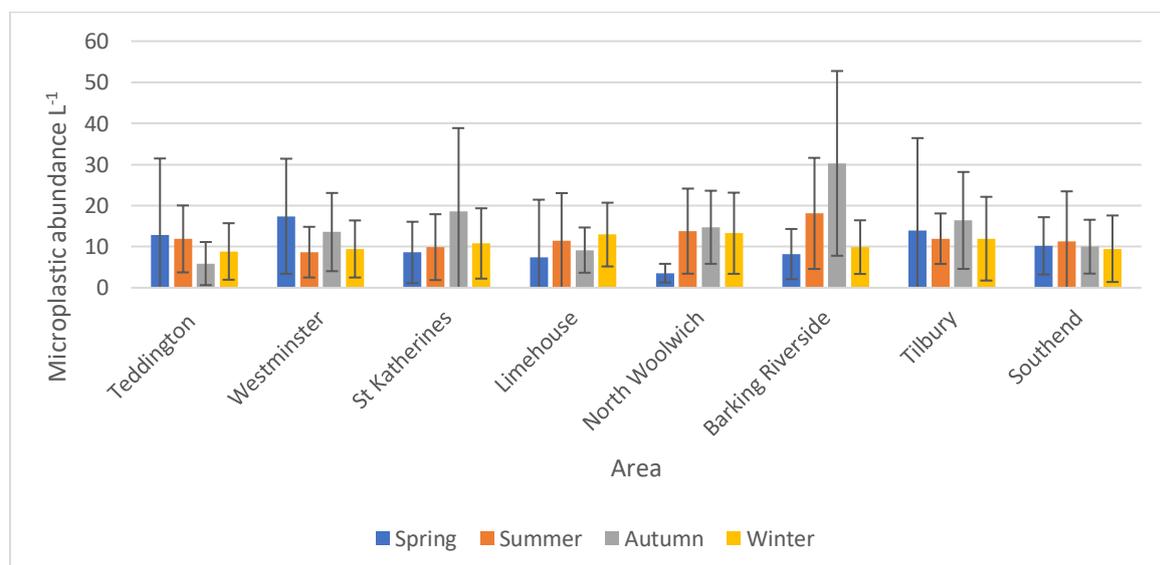


Figure 5.4 Total microplastic abundance L⁻¹ from water samples collected at the eight areas along the river Thames during each season from 2019 - 2020.

5.3.2 Seasonal Abundances variation by year

There was a significant yearly variation of MPT abundances seasonally (ANOVA, $F_{3,178}=22.64$, $P=0.00$) with a significance between seasons in 2019 and 2020 (ANOVA, $P=0.02$); 2019 and 2021 (ANOVA, $P=0.00$); 2020 and 2021 (ANOVA, $P=0.002$) (Figure. 5.5).

In spring 2019, with the exclusion of North Woolwich and Barking Riverside, where no samples were taken, abundances ranged from 20.67 - 67.67 L⁻¹ from Southend-on-Sea and Tilbury, respectively. In 2020, MPT ranged from 3.89 - 23.3 L⁻¹ from Limehouse and Barking Riverside; in 2021, they had an MPT range from 3.1 - 7.67 L⁻¹. Mean abundances also varied from 39.16 ± 12.97 L⁻¹ in 2019, when it was at its highest, to 2021, when MPT was 5.22 ± 4.05 L⁻¹.

In 2019 summer had an MPT of 8.89 - 25.5 L⁻¹ from St Katherines and Barking Riverside, respectively, compared to 2020, which ranged from 3.3 - 15.3 L⁻¹ from barking Riverside and North Woolwich. The MPT in 2019 - 2020 decreased from 13.51 ± 9.17 L⁻¹ to 9.92 ± 6.57 L⁻¹.

Autumn ranged from 8.56 – 29.56 L⁻¹ from Teddington and Barking Riverside, respectively, in 2019. Whereas 2020 ranged from 3.2 – 31.3 L⁻¹ from Teddington and Barking Riverside, respectively. The average MPT decreased from 2019 (14.71 ± 9.24 L⁻¹) to 2020 (14.99 ± 12.31 L⁻¹).

Winter 2019 ranged from 7.56 – 20 L⁻¹ from Teddington and Tilbury, respectively. MPT in 2020 ranged from 3.89 – 10.11 L⁻¹ from Tilbury and Teddington, respectively. The average MPT decreased from 2019 (14.74 ± 7.89 L⁻¹) to 2020 (7.02 ± 4.54 L⁻¹).

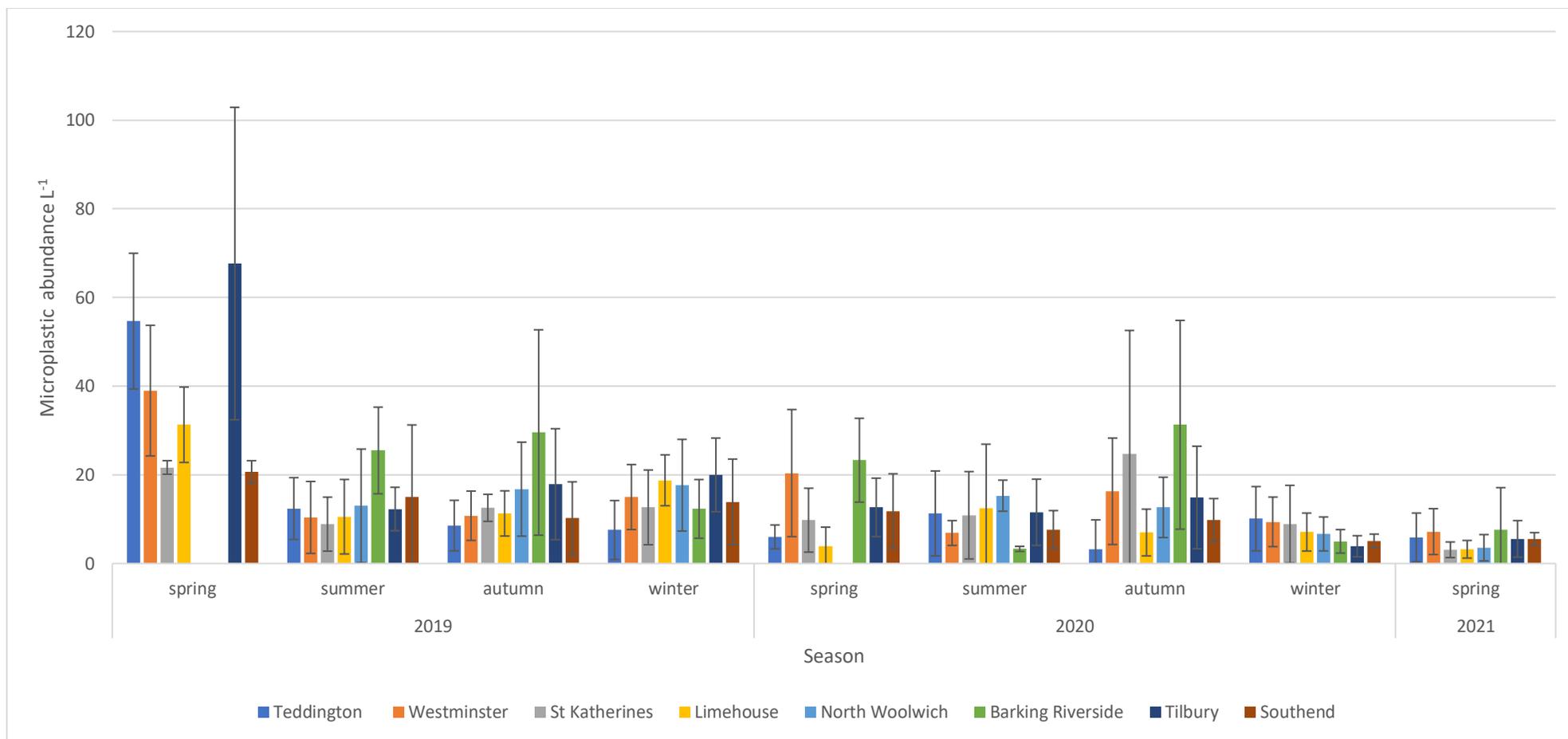


Figure 5.5 Microplastic abundance L⁻¹ from the eight areas where water samples were collected along the tidal river Thames seasonally from 2019 - 2021

5.3.3 Morphology

5.3.3.1 Spring

All categories of MP type (fibres, fragments, foam, pellet, bead and others) were found throughout the samples (Figure. 5.6), with fibres (1438 pieces, 83.41%) being the most commonly identified type of MP, followed by fragments (220 pieces, 12.76%). Fibres were most abundant at Tilbury (330 pieces) compared to North Woolwich (32 pieces). There is no significant difference between fragments or fibres (ANOVA, $P > 0.5$) between sites. Beads (3 pieces) were the least abundant morphology observed, however there was a significant difference at Barking Riverside (ANOVA, $P = 0.000$) and Tilbury (ANOVA, $P = 0.001$) which were the only sites beads were observed. The foam was only found at Teddington, St Katherine's, Tilbury and Southend-on-Sea, whilst pellets were only found at Westminster, Limehouse, Tilbury and Southend-on-Sea.

All category abundances decreased from spring 2019 to spring 2021 (Figure. 5.6). The largest percentage decrease was observed in fragments which decreased from 108 pieces in 2019 to 23 pieces in 2021. Microplastic fibre abundance also decreased from 2019 (631 pieces) to 2021 (344 pieces); however, there was no significance ($F = 7.153$, $P = 0.279$). There was however a significance between beads ($F = 4304E+28$, $P = 0.000$), Foam ($F = 1.073E +28$, $P = 0.000$), Pellets ($F = 1.577E+28$, $P = 0.000$).

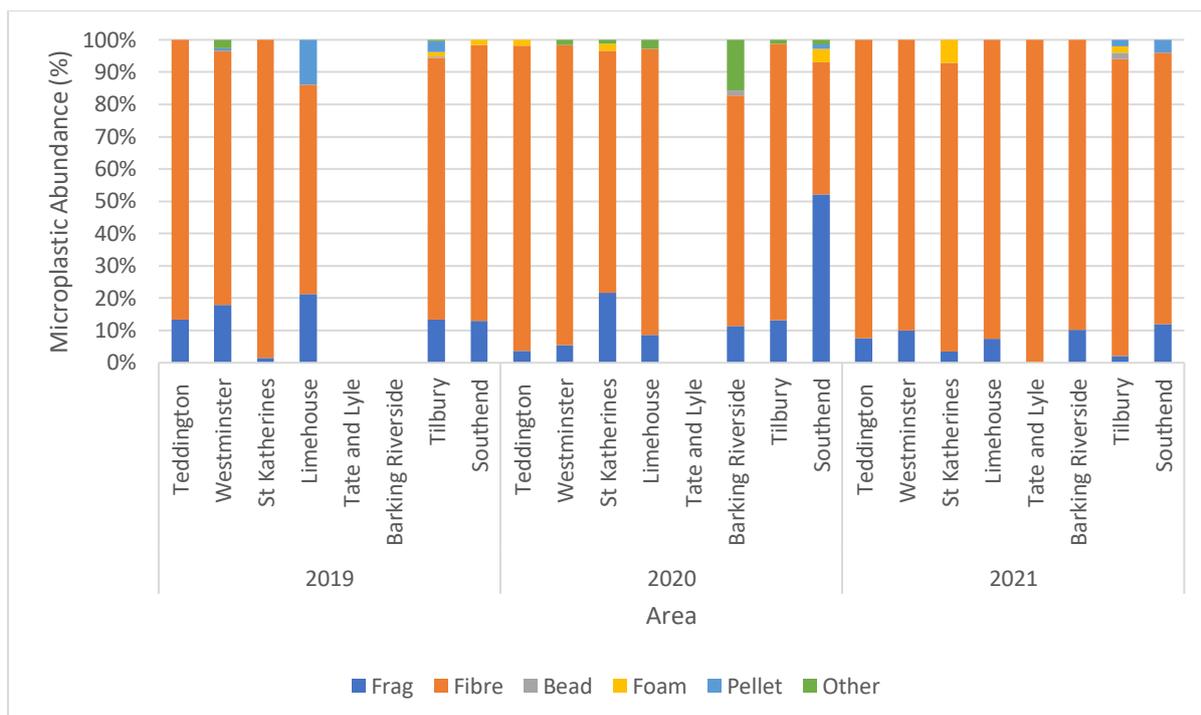


Figure 5.6 Types of Microplastic identified from spring water samples at areas along the river Thames in Spring 2019 - 2021

Eleven colours of MPs were observed during Spring season (Fig. 5.6), the most common being black (1140 pieces), the majority ranging from 22- 287 pieces from North Woolwich and Tilbury. Transparent (138 pieces) was the second common colour observed, ranging from 0 - 51 pieces from Westminster and North Woolwich. The least common colour was yellow (1 piece), only found at Southend-on-Sea in 2020. The only colour that was significant compared to all locations was blue ($P=8.671$, $P>0.000$), with a significant difference observed between Teddington (59 pieces) and Southend-on-Sea (9 pieces).

There was yearly variation with a decrease in many of the colours (Figure. 5.7). For example, black ($P>0.000$) decreased from 528 to 268 pieces from 2019 - 2021, and blue ($P>0.000$) decreased from 113 to 44 pieces from 2019 - 2021. However, whilst colours like blue and black decreased across the three spring seasons samples,

some saw an increase in 2020 from 2019 and then reduced to abundances lower than what was observed in 2019 in 2021. An example of this is the transparent (P=0.023) MPs which in 2019 had 48 pieces; observed this increased in 2020 (80 pieces) and then decreased red (P=0.05) and white (P=0.017) MPs also followed the same pattern by having the highest abundance in 2020 compared to 2019.

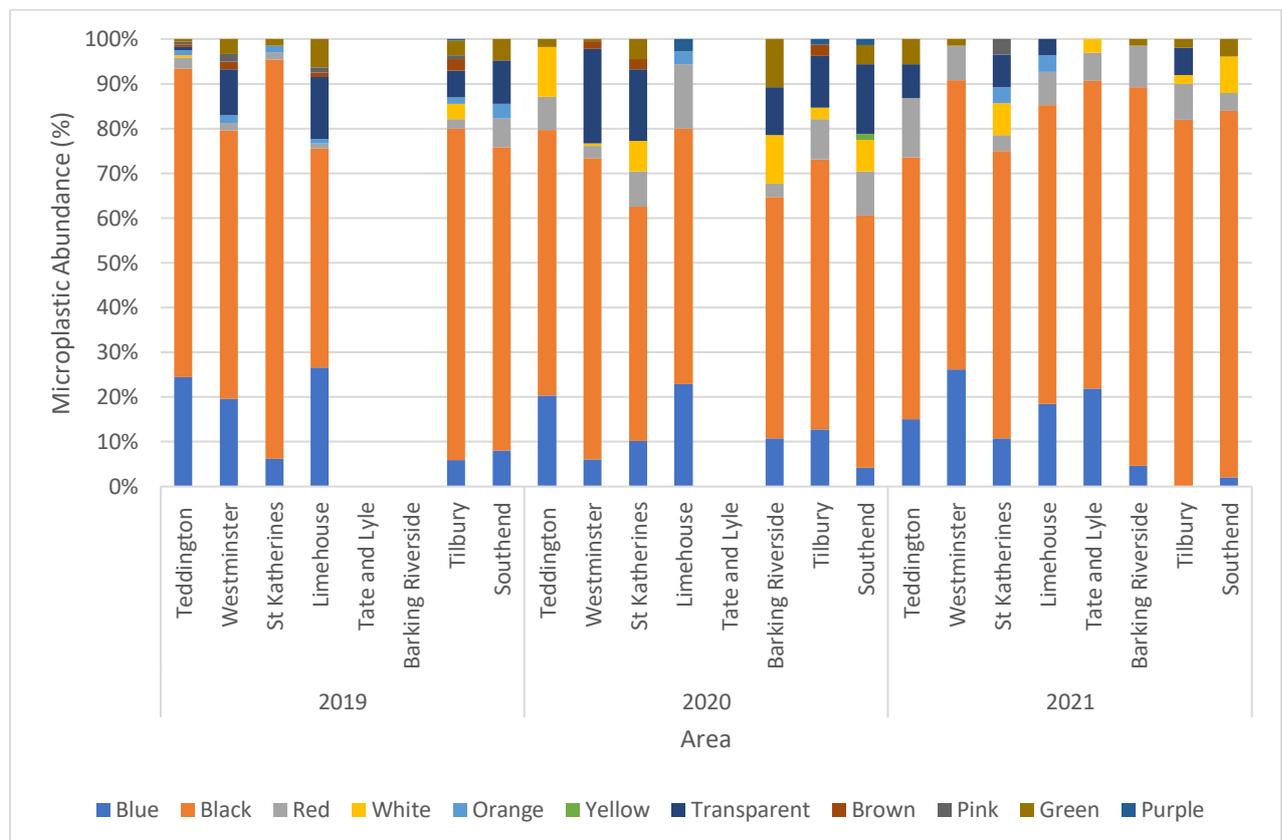


Figure 5.7 Microplastic colours identified from water samples at different areas along the river Thames in Spring 2019 - 2021

5.3.3.2 Summer

All types of MP were identified, with fibres (1131 pieces, 77.1%) and fragments (241 pieces, 16.43%) being the most abundant (Figure. 5.8). Fibres ranged from 59 to 204

pieces at Southend-on-Sea and Tilbury; however, there were no significant differences ($F=0.75$, $P=0.633$). The least observed type was beads ($F=0.996$, $P=0.457$) which were only found at Teddington (1 piece) and Barking Riverside (3 pieces), which were only found in 2019. The number of beads observed decreased from 2019 (60 pieces) to 2020 (5 pieces). Beads were observed at every site in 2019 except Tilbury in 2020; they were only observed at Westminster (1 piece) and Barking Riverside (4 pieces). In all areas except Southend-on-Sea, fibres were more abundant than fragments. Fragments (117 pieces) ($F=1.663$, $P=0.164$) were more abundant in Southend-on-Sea in 2019 than fibres (59 pieces). In 2020, fragments (33 pieces) were still higher, but there was not as much of a difference compared to fibres (31 pieces).

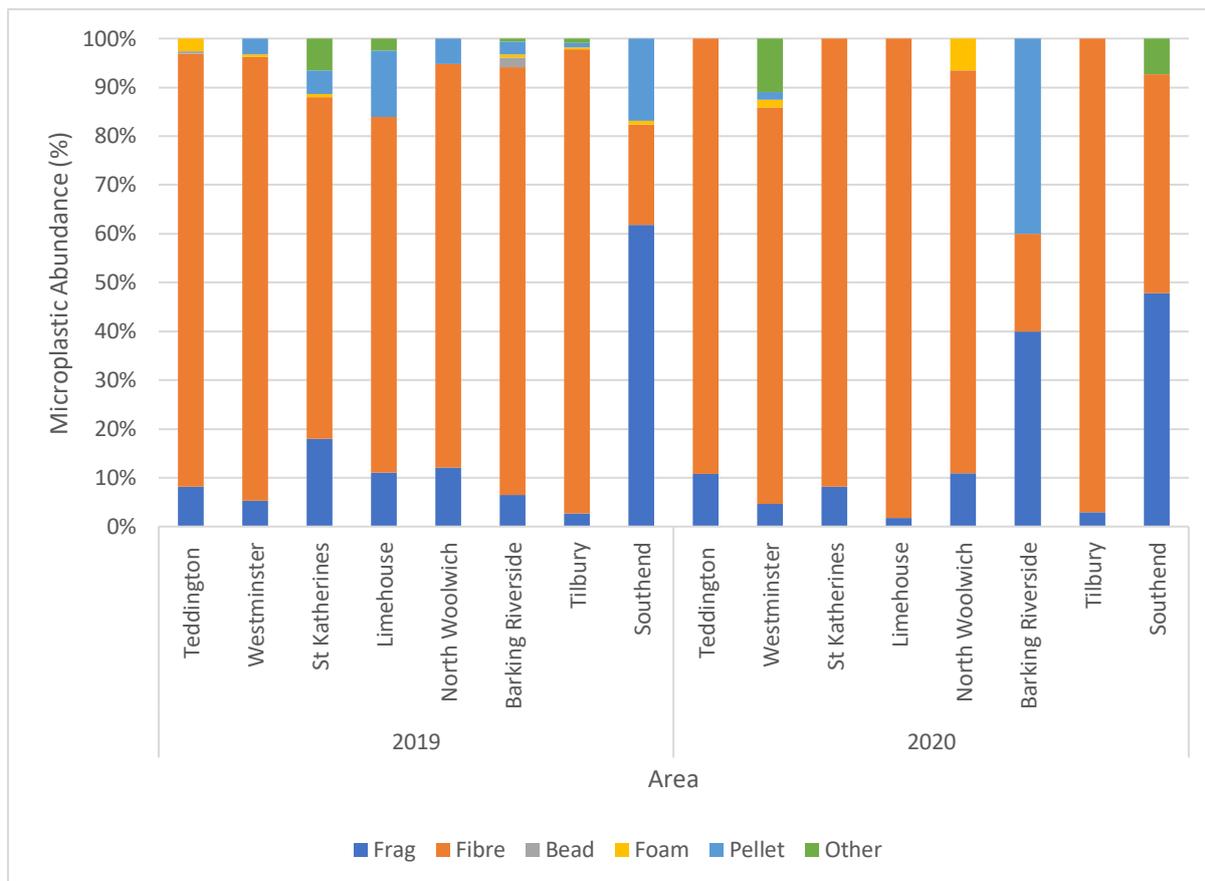


Figure 5.8 Types of Microplastic identified from water samples at areas along the river Thames in Summer 2019 and 2020

Twelve different colours (Figure. 5.9) were observed from MPs collected from samples in the summer seasons. The most common were black (933 pieces) ($F=0.517$, $P=0.813$) and blue (131 pieces) ($F=1.571$, $P=0.19$) compared to the least common gold (1 piece) ($F=0.767$, $P=0.62$) and yellow (2 pieces) which were only found at Westminster (1 gold piece, 2019) ($F=0.754$, $P=0.63$) and Southend-on-Sea (2 yellow pieces, 2020). Microplastics identified as orange (35 pieces) were only found in 2019 and mostly within Southend-on-Sea (26 pieces) samples. In 2019, the

most common colours were black (569 pieces) and blue (86 pieces), compared to 2020, which was black (364 pieces) and red (75 pieces).

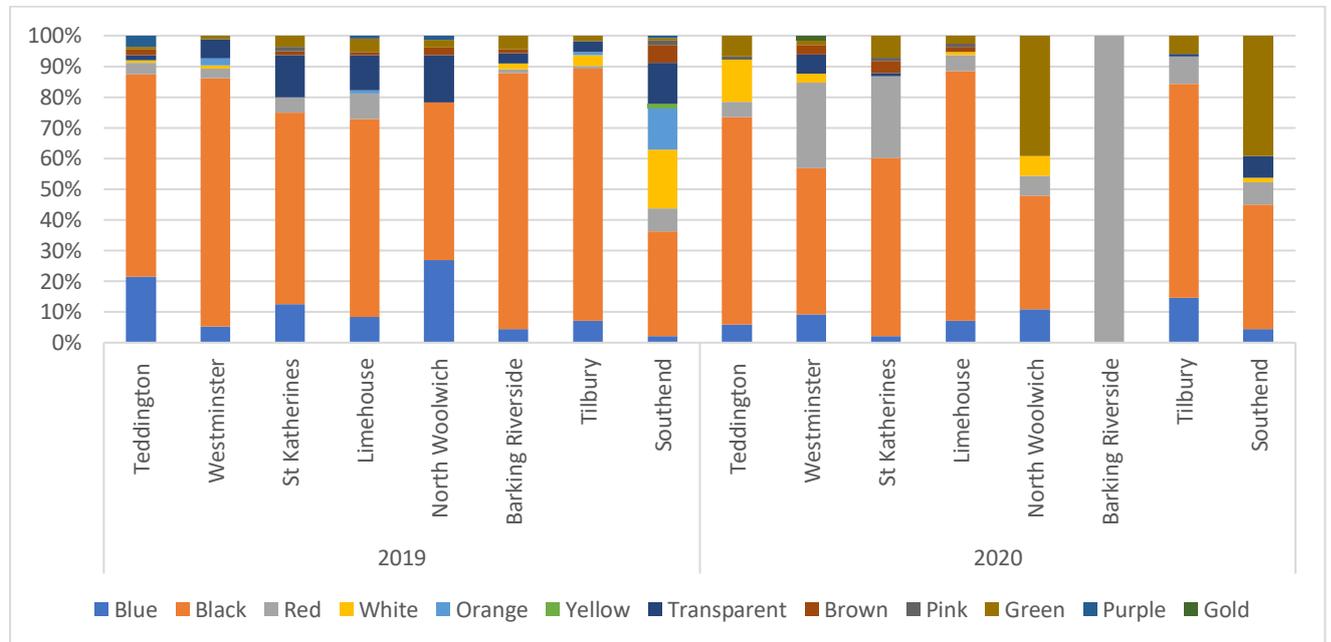


Figure 5.9 Microplastic colours identified from water samples at different areas along the river Thames in Summer 2019 and 2020

5.3.3.3 Autumn

A total of 1994 pieces of MP were found throughout water samples taken in autumn. All six types of MP were found, with fibres being the most abundant (1714 pieces, 85.96%) and beads (4 pieces, 0.2%) being the least abundant (Figure 5.10). Fibres ranged from 65 - 433 pieces from Teddington and Barking Riverside. However, there was no significant difference between areas ($F=1.866$, $P=0.112$). Beads were only found at Teddington (2 pieces), Limehouse (1 piece) and North Woolwich (1 piece), excluding the one bead found at Limehouse in 2019. The other three beads were observed in samples in 2020. Beads and all other types of MP were also not

significantly different at any location in autumn samples ($F=0.782$, $P=0.607$). There was a decrease in four categories (fragment, foam, pellet and other) from 2019 to 2020, with the most significant drop being observed in MP classified as foam which had 40 pieces in 2019 but no pieces observed in 2020 (Figure 5.10). Pellets dropped from 53 pieces (2019) to 1 piece (Westminster) observed in 2020. Fragments were the only MP type with a significant difference in yearly autumn samples ($F=16.358$, $P>0.000$). Post-hoc tests could not be performed because there was fewer than 3 group. There was no significance between MP type*location*year ($F=1.798$, $P=0.134$).

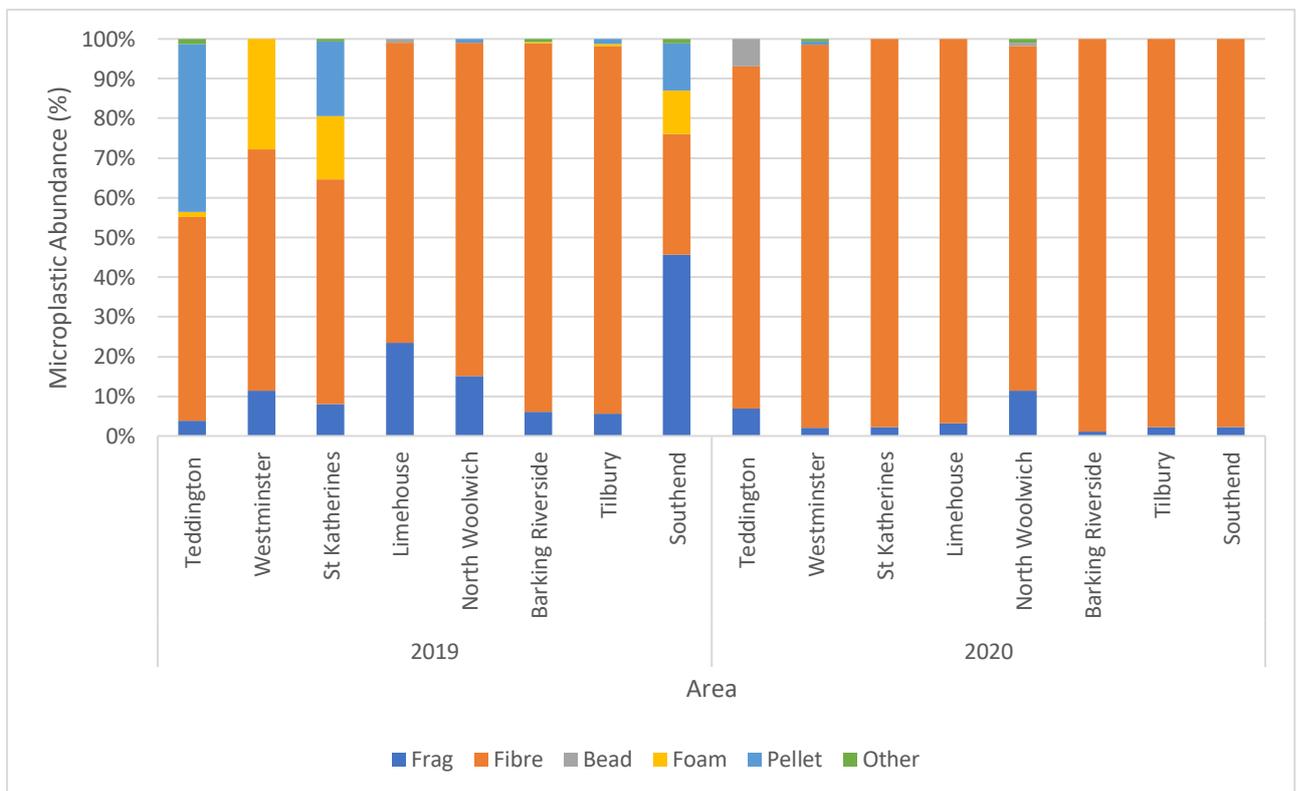


Figure 5.10 Types of Microplastic identified from water samples at areas along the river Thames in Autumn 2019 and 2020

Microplastics were observed in 12 colours, the most common being black (1517 pieces) and the least common being purple (2 pieces) (Figure 5.11). Black microplastics ranged from 47-406 at Teddington and Barking Riverside. The second most common colour was blue (145 pieces), ranging from 8-25 at Limehouse and North Woolwich. The least common colour, purple, was only observed at St Katherine (1 piece) and Southend-on-Sea (1 piece) in 2019.

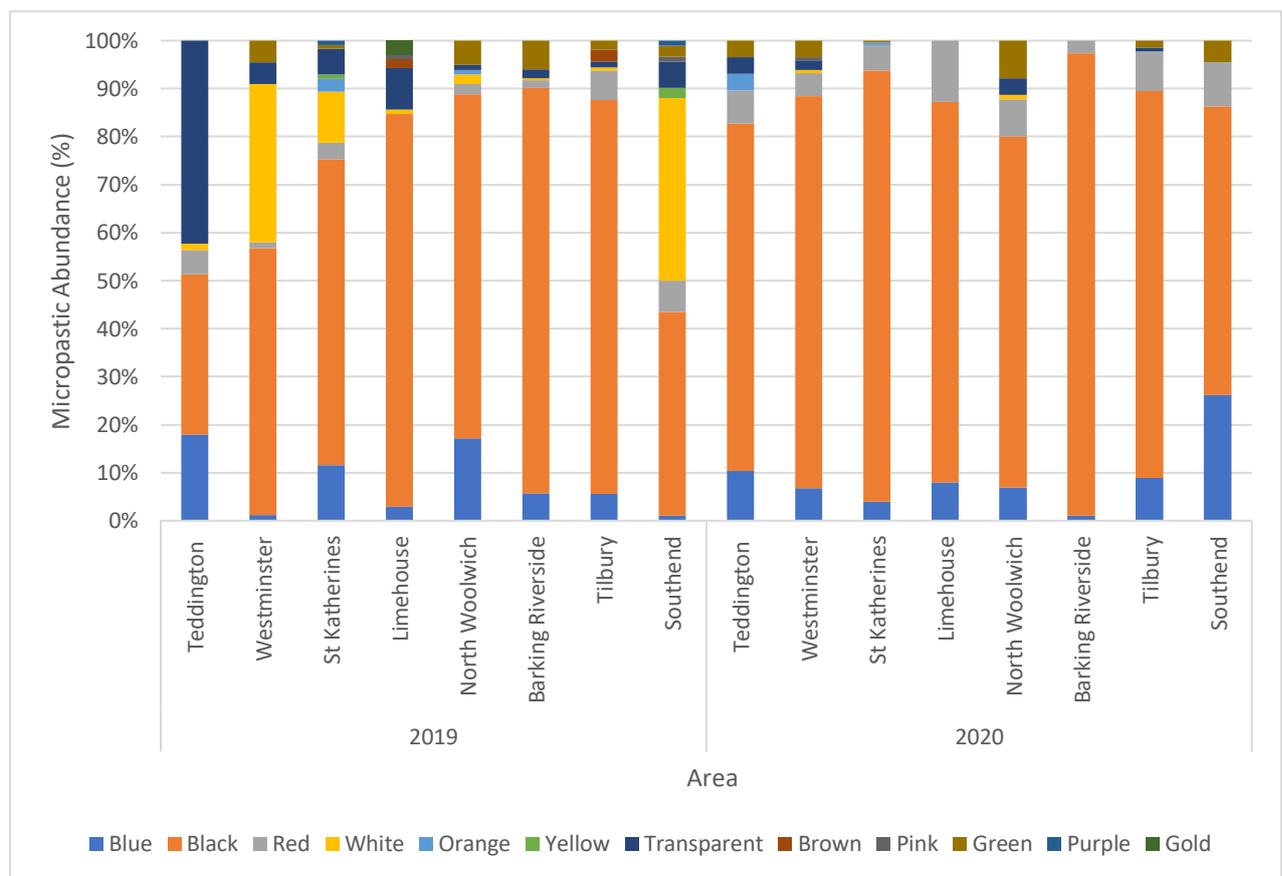


Figure 5.11 Microplastic colours identified from water samples at different areas along the river Thames in Autumn 2019 and 2020

All 12 colours were observed in the 2019 autumn samples compared to the eight colours in the water samples of 2020 (Figure 5.11). The colours yellow, brown, purple and gold were not observed in the 2020 samples. The most common colours in 2019 were black (700 pieces) and White (82 pieces). In 2020, the most common

colours were black (812 pieces) and blue (72 pieces). The only colour significantly different for the area was orange ($F=2.794$, $P=0.024$). Only one white MP was observed in 2020 samples at North Woolwich, whereas in 2019, samples ranged from 1 white MP, which was observed at Teddington, Limehouse, Barking Riverside and Tilbury, compared to the 35 pieces observed at Southend-on-Sea. White MPs was the only colour with a significant difference between white MPs*year ($F=5.866$, $P=0.022$). No Post-hoc test could be performed. Similarly, transparent MPs dropped from 65 pieces (range: 1-33 pieces at North Woolwich and Teddington) in 2019 to 9 pieces in 2020. There was no significance between transparent MPs*year ($F=2.863$, $P=0.101$). There was no significance between MP colour*location*year ($F=1.984$, $P=0.101$).

5.3.3.4 Winter

During winter water samples, 1443 pieces of MP were observed. All six types of MP were observed, with fibres (1226 pieces, 84.96%) being the most abundant type and beads (1 piece, 0.07%) being the least abundant (Figure. 5.12). Fibres ranged from 61- 211 pieces at Barking Riverside and Limehouse, and beads were only found at Limehouse in 2019. All types of MP (except pellets) decreased from 2019-2020. For example, foams decreased from 28 pieces, the most abundant being Southend-on-Sea (14 pieces), to only one piece being found in 2020 at North Woolwich. There was no significant difference between MP type*area ($F=0.298$, $P=0.947$). There was no significant difference between MP type*year except for fibres ($F=8.103$, $P=0.002$). No post hoc test could be performed. There was no significant difference between MP type*area*year ($F=0.339$, $P=0.972$).

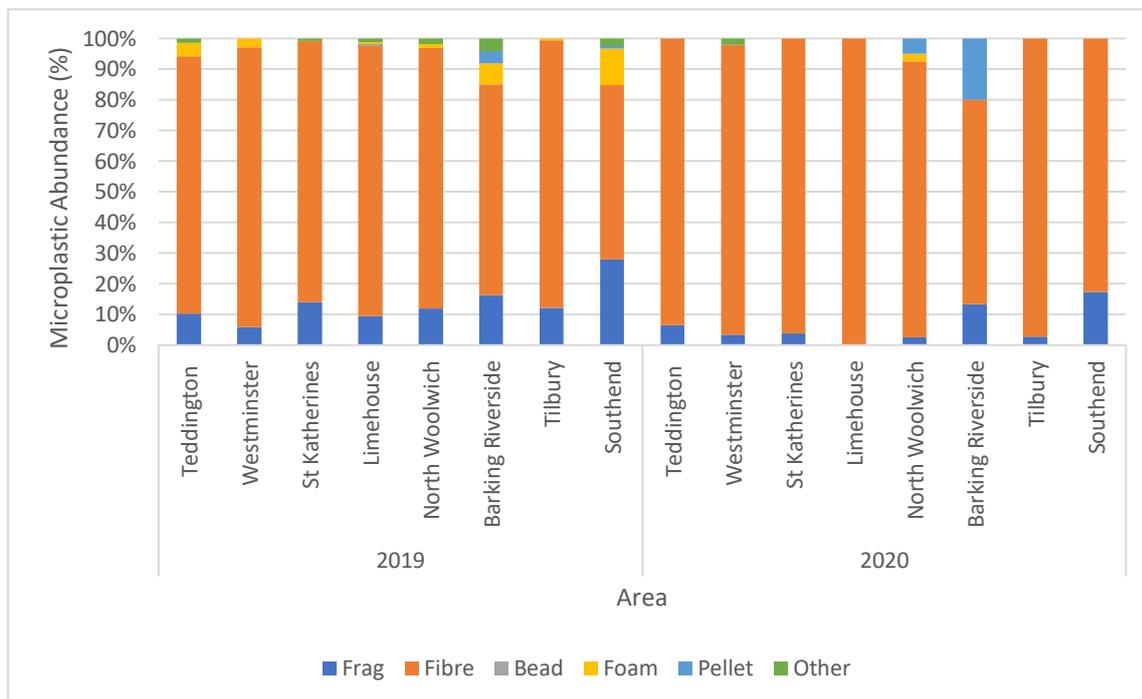


Figure 5.12 Types of Microplastic identified from water samples at areas along the river Thames in Winter 2019 and 2020

A total of eleven colours were observed, the majority of MP being identified as black (990 pieces), the least abundant being purple (1 piece) found at Southend-on-Sea (Figure. 5.13). Black MPs ranged from 47 - 171 pieces from Barking Riverside to Westminster. The second most abundant colour was blue (146 pieces), which ranged from 7 - 37 pieces from Southend-on-Sea and Westminster.

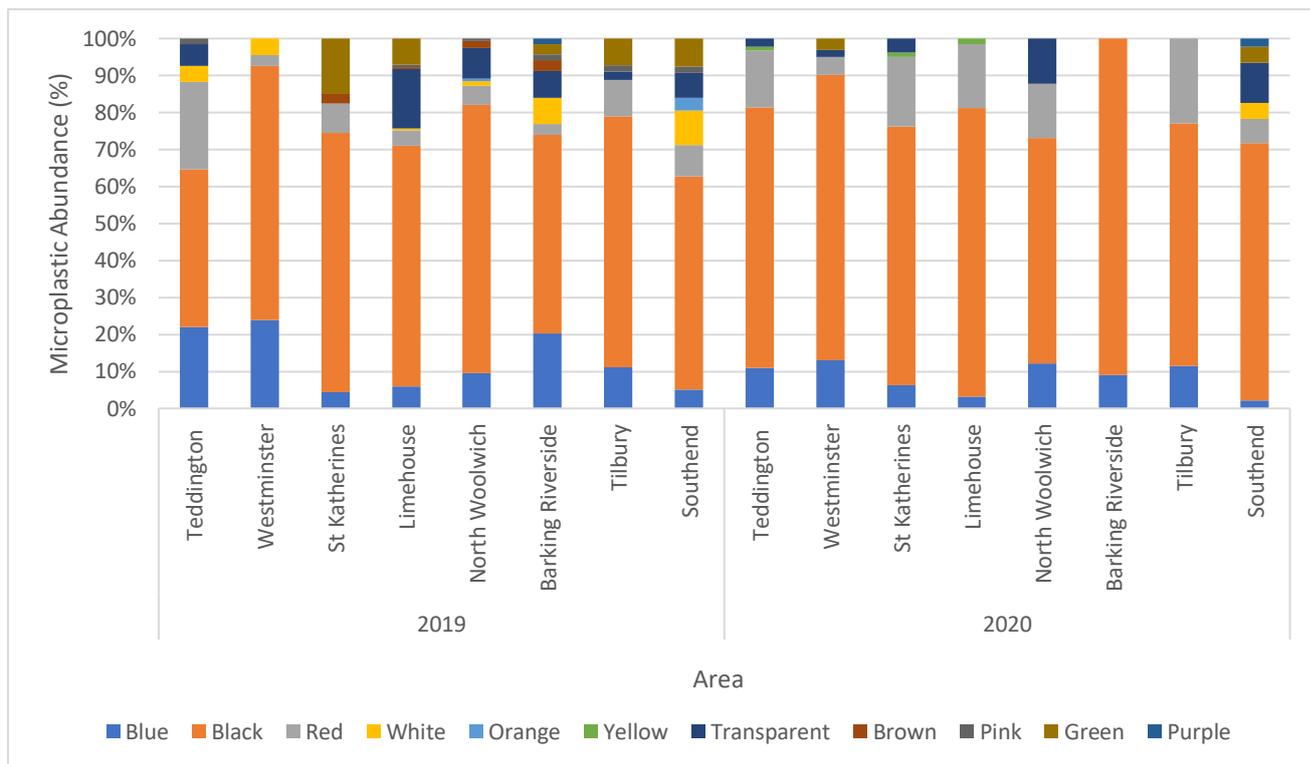


Figure 5.13 Microplastic colours identified from water samples at different areas along the river Thames in Winter 2019 and 2020

In 2019 a total of nine colours (Blue, black, red, white, orange, transparent, brown, pink and green) were observed in 958 pieces of MP (Figure 5.13). The most observed colour was black (619 pieces), ranging from 29 – 122 pieces from Teddington to Tilbury. The second most abundant colour was blue, ranging from 5 - 20 pieces from St Katherine, with Westminster and Tilbury having 20 blue MP each. The least abundant colour was orange (5 pieces), which ranged from 1 - 4 pieces at North Woolwich and Southend-on-Sea, which had a significant difference depending on location ($F=3.289$, $P=0.014$). Post-hoc tests confirmed that North Woolwich and Southend-on-Sea differed significantly from the other areas. Other than orange, the only colour with a significant difference depending on location was green ($F=2.553$,

P=0.042). Post-hoc tests showed significance between the different areas and North Woolwich and Teddington Lock.

In 2020, there were eight colours (Blue, black, red, white, yellow, transparent, green and purple) found in 511 pieces of MP (Figure 5.13). The most abundant colour was black (371 pieces), ranging from 10-111 pieces from Barking Riverside and Westminster. The second most abundant colour was red (64 pieces), found in all areas except Barking Riverside and ranged from 3-15 pieces at Southend-on-Sea and St Katherine. The least abundant colour was purple, with one piece found at Southend-on-Sea. There were some colour differences between 2019 and 2020. For example, purple (1 piece) and yellow (3 pieces) were only found in 2020, whilst orange (5 pieces), brown (9 pieces), and pink (9 pieces) were only discovered in 2019. There was a significant difference between blue ($F=8.837$, $P=0.001$), Black ($F=6.814$, $P=0.005$) and green ($F=13.861$, $P>0.000$) between years. No post-hoc test could be performed. There was no significance, however, between MP colour*location*year ($F=0.605$, $P=0.816$).

5.3.4 Length

5.3.4.1 Spring

A total of 457 pieces of MP observed during sampling in the spring season was measured. Microplastics mainly fell within the 0-1 mm category (277 pieces) (Figure 5.14). St Katherine's, Limehouse and Southend-on-Sea all had the highest amounts (43 pieces) within this category, with North Woolwich containing the least (17 pieces). The 4-5 mm category was the least abundant category (6 pieces). There was no significant difference between location and size ($F=1.513$, $P=0.205$) or location * size * year ($F=1.2$, $P=0.179$).

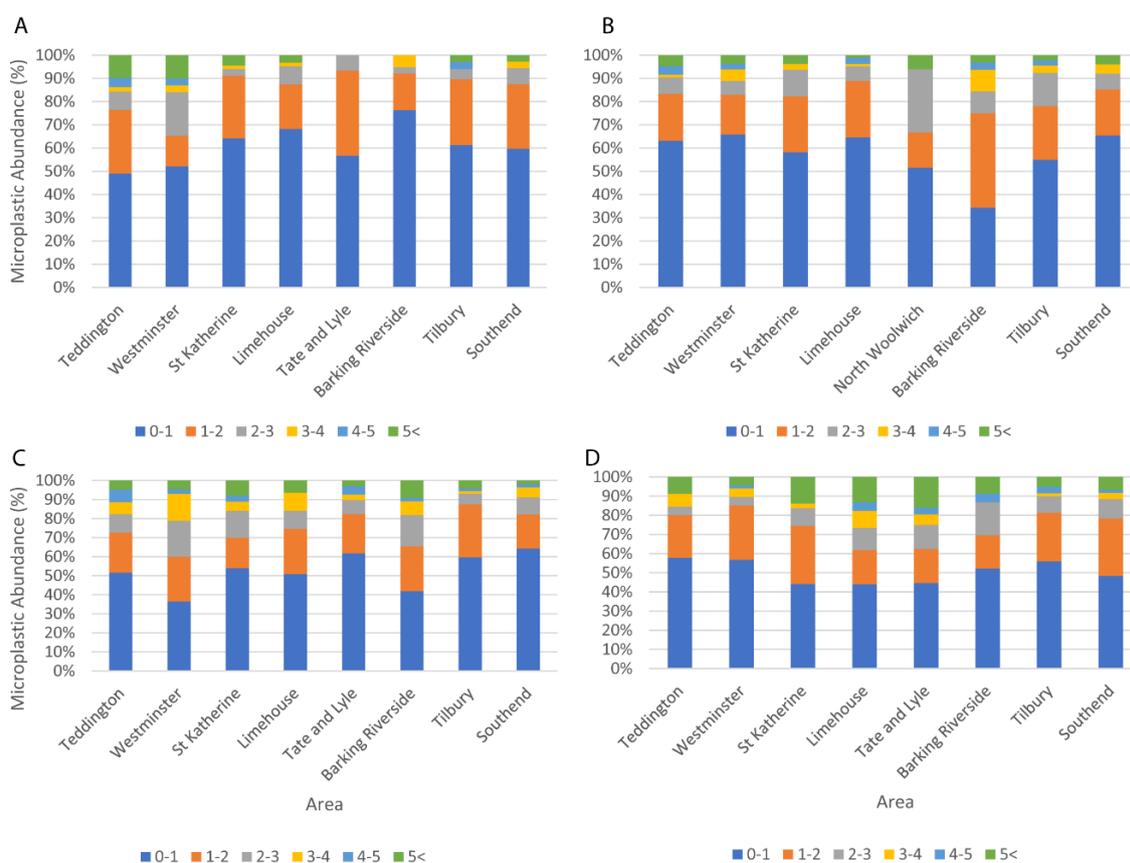


Figure 5.14 Microplastic lengths identified from water samples at different areas along the river Thames each season from 2019-2021; A) Spring, B) Summer, C) Autumn, and D) Winter

5.3.4.2 Summer

A total of 558 pieces of MP were observed during summer water samples. The most abundant category was 0 - 1 mm (333 pieces) (Figure 5.14). This size category ranged from 54 pieces at Westminster to 11 pieces at Barking Riverside. However, there was no significant difference between the 0 - 1 mm size category and location ($F=0.621$, $P=0.733$). The smallest category abundance was found in the 4-5 mm (10 pieces), mostly at Teddington (3 pieces). 19 pieces in the 5< category do not count as MPs. There was no significant difference between size and location during

summer for any category except for 2 - 3 mm ($F=4.82$, $P=0.002$). A post-hoc test could not be performed because North Woolwich only had one sample taken during the summer months.

5.3.4.3 Autumn

A total of 524 pieces of MP for length measurements were observed during autumn season (Figure 5. 14). Most MP fell within the 0 - 1 mm category (273 pieces), ranging from 23 - 43 pieces at Barking Riverside to Tilbury. The least abundant category was 4 - 5 mm (14 pieces), most of which were found at Teddington (4 pieces). A total of 27 pieces were $5 < \text{mm}$, making them macroplastics, not MPs. There was a significant difference between length*year for 0 - 1 mm ($F=5.951$, $P=0.021$), 2 - 3 mm ($F=7.011$, $P=0.013$) and $5 < \text{mm}$ ($F=4.496$, $P=0.043$), Post-hoc tests could not be performed. There was no significant difference between length*area ($F=0.470$, $P=0.848$) or between length*area*year ($F=1.068$, $P=0.404$).

5.3.4.4 Winter

A total of 421 pieces of MP for length measurements were observed during water samples in winter season. (Figure 5.14). Most MP fell within the 0 - 1 mm range (212 pieces), ranging from 12 - 38 pieces from Barking Riverside to Westminster. The least abundant category was the 4 - 5mm (10 pieces). The majority were found at Limehouse (3 pieces). A total of 40 pieces fell into the $5 < \text{mm}$ range and, as such, were not counted as MPs. Most of these were observed at Limehouse (9 pieces) and North Woolwich (9 pieces). There was no significant difference between length*area ($F=0.641$, $P=0.717$), length*year ($F=1.592$, $P=0.226$). There was no significant difference between the length*location*year except for the 2 - 3 mm category ($F=3.697$, $P=0.005$). No post-hoc test could be performed.

5.3.5 Rainfall

Rainfall throughout this study ranged from a monthly average of 8.9 - 162.2 mm at Teddington (May 2020) and Tilbury Fort (December 2020) (Figure. 5.15). There were several named storms in the UK during the 2019 - 2021 water sampling period, which led to heavy rainfall during some months (Table 5.1). However, there was a significance between storms and MP abundance (ANOVA, $F_{1,177}=4.673$, $P=0.032$) but not a significance between storm*area ($F_{,0.501}$, $P=0.833$), storm*season*area ($F=0.231$, $P=0.949$). Post-hoc tests could not be performed.

Table 5.1 Dates of storms that hit the UK from May 2019 - May 2021, with a comparison of average rainfall (mm) and Average Microplastic total (MPT) (L^{-1}) along the length of the river Thames

Name	Date of impact	Average rainfall along the river Thames (mm)	Average MPT (L^{-1})
Atiyah	8 - 9 December 2019	116.64	17.62
Brendan	13 - 14 January 2020	66.43	15.58
Ciara	8 - 9 February 2020	83.81	11.29
Dennis	15 - 16 February 2020	83.81	11.29
Jorge	28 February - 1 March 2020	83.81	11.29

Ellen	19 - 20 August 2020	99.59	7.1
Francis	24 August 2020	99.59	7.1
Alex	2 - 4 October 2020	127.2	8.13
Barbara	21 October 2020	127.2	8.13
Aiden	31 October 2020	127.2	8.13
Bella	26 - 27 December 2020	59.79	9.28
Cristoph	19 - 22 January 2021	135.29	6.71
Darcy	6 - 8 February 2021	76.51	6.21

The monthly rainfall average had no significant impact on MP L⁻¹ at any site (ANOVA, $F_{1,139}=0.845$, $P=0.760$) (Figure. 5.15). The seasonal average rainfall along the sample area ranged from 36.83 (± 19.28) to 98.44 (± 28.12) mm in spring 2020 and autumn 2019 (Table 5.2). Spring 2021 had the lowest MP abundance (4.94 ± 3.71 L⁻¹), whilst spring 2019 had the largest (94.83 ± 13.35 L⁻¹). As a result, seasons impacted MPT in the river Thames ($F_{1,3}=4.858$, $P=0.003$), and so did season*rainfall ($F_{1,3}=18.218$, $P=0.000$). Post-hoc tests confirmed spring rainfall was the most significant to any other season due to a combined average seasonal rainfall over the three years of 43.45 mm compared to summer (75.26 mm), autumn (84.53 mm), and winter (89.96 mm). However, only one month (May) of Spring was sampled in 2019, with the highest average MP L⁻¹. Season*Year also affected MPT ($F_{1,4}=0.712$,

P=0.003) (Figure. 5.15).; however, only one sample for the spring 2019 post-hoc test could not be performed. Season*area*year did not significantly differ in MPT ($F_{1,24}=0.712$, $P=0.829$), although post-hoc tests showed that the average MPT at Barking was 55 L^{-1} whilst the other sites had a mean MPT range of $30.92\text{-}39.44 \text{ L}^{-1}$.

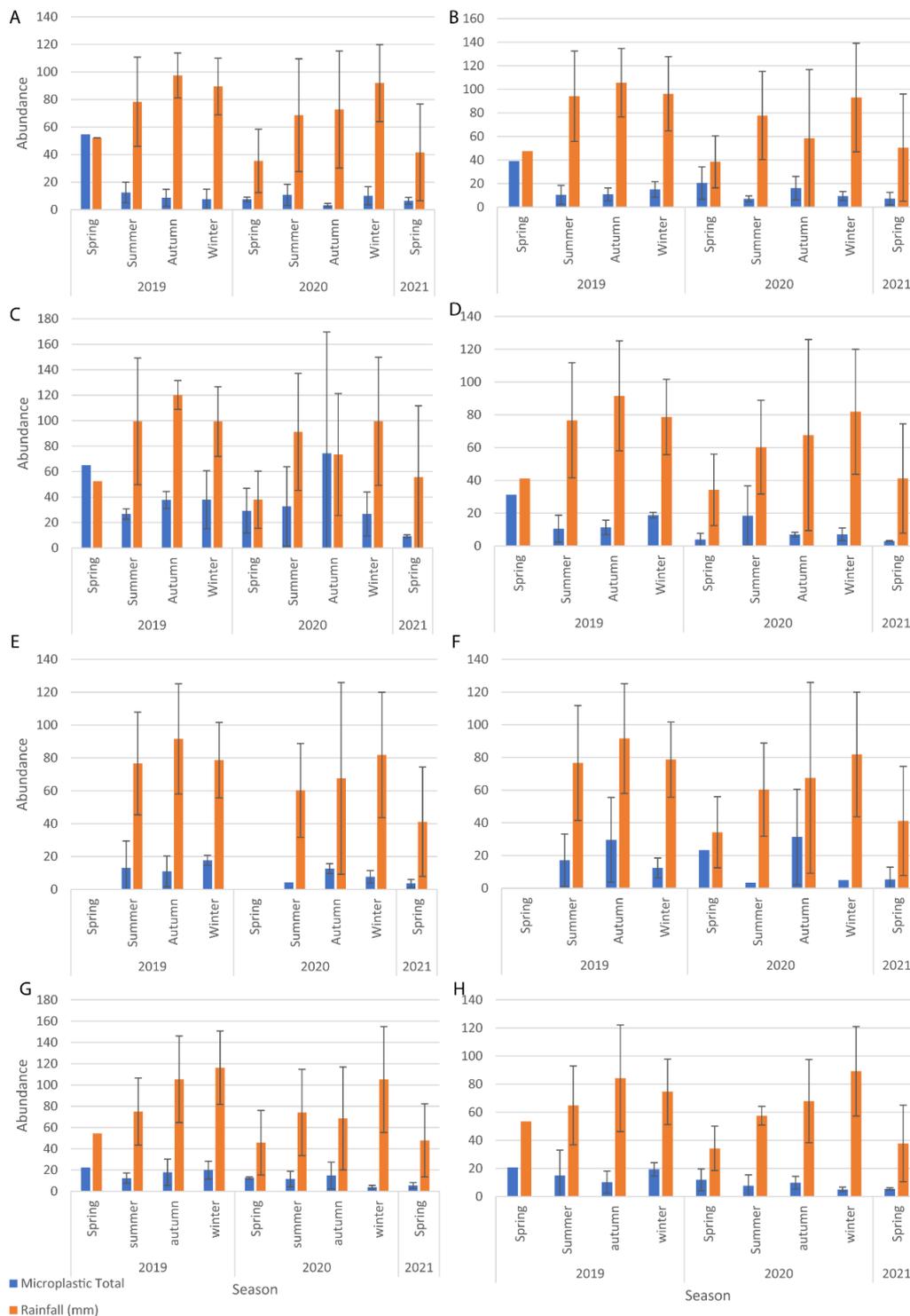


Figure 5.15 Seasonal variations of rainfall and microplastic abundances from 2019 - 2021 at the eight areas sampled along the river Thames: A) Teddington, B) Westminster, C) St Katherine's, D) Limehouse, E) North Woolwich, F) Barking Riverside, G) Tilbury and H) Southend-on-Sea.

Table 5.2 Seasonal microplastic L⁻¹ abundance from 2019 - 2021 and average seasonal rainfall (mm)

Year	Season	Microplastic L⁻¹ (± stderr /SE)	Rainfall (mm) (± stderr /SE)
2019	Spring	94.83 (13.35)	47.86 (6.02)
	Summer	12.45 (9.56)	80.22 (32.01)
	Autumn	14 (11.65)	98.44 (28.12)
	Winter	14.71 (7.17)	88.96 (25.74)
2020	Spring	11.85 (8.69)	36.83 (19.28)
	Summer	9.93 (7.79)	68.77 (30.58)
	Autumn	14.26 (15.02)	68.46 (43.43)
	Winter	7.35 (4.08)	90.53 (34.98)
2021	Spring	4.94 (3.71)	44.62 (31.42)

5.3.6 Plastic Polymers

A total of 1041 (15.64%) pieces were further identified; out of these, 176 pieces (16.91%) were not identified through FTIR, 31 pieces (2.98%) were identified as anthropogenic microfibrils/ particles (cotton, nylon, silk, wool or flax) and seven pieces (0.67%) identified as natural (salt or chitin).

In total, 41 different polymers were identified. The most commonly identified polymers overall were Polyvinyl chloride (PVC) (255 pieces, 24.5%), Polystyrene (PS) (102 pieces), Polychloroprene (PCP) (80 pieces, 7.69%), Polyethylene chloride (PEC) (56 pieces, 5.38%) and Polypropylene (PP) (35 pieces, 3.36%). The only polymer that was significantly different seasonally was PCP (ANOVA, $F_{3,90} = 4.626$, $P=0.005$), post-hoc tests identified the spring season (5 pieces) having the lowest abundance of PCP compared to winter (20 pieces), autumn (34 pieces) and summer seasons (21 pieces).

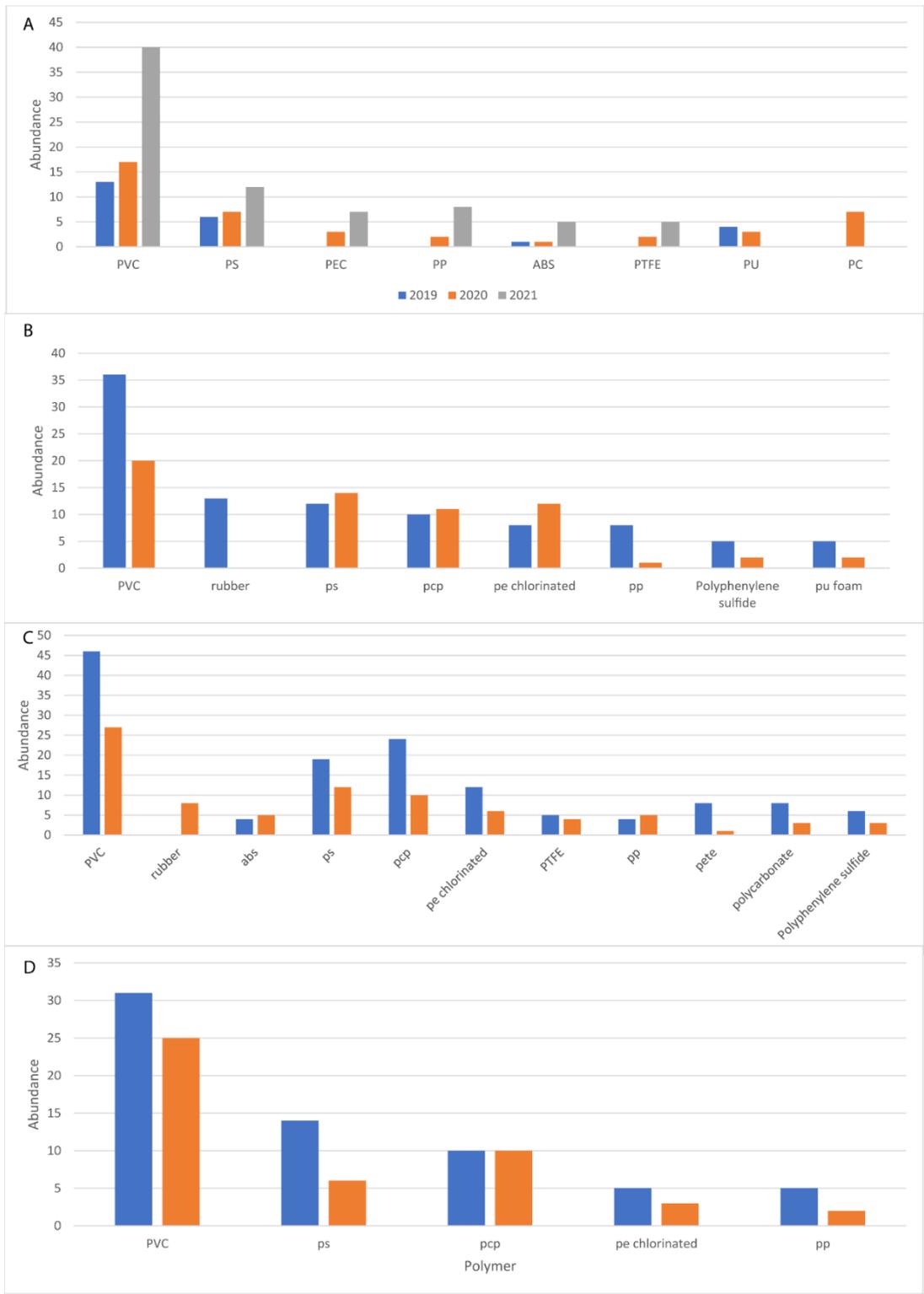


Figure 5.16 Comparison of Polymers identified from water samples collected along the river Thames during; A) Spring, B) Summer, C) Autumn, and D) Winter

A total of 237 pieces (22.77%) with 26 types of polymers identified through FTIR analysis were found in water samples collected in the spring season. However, 33 pieces were “no hits”, and as a result, the polymer was not recognised.

Anthropogenic microfibers/particles had 11 pieces, mostly made of cotton or nylon (6 pieces found in 2021) and natural material was also found in the form of Chitin (4 pieces). The majority of polymers identified were PVC (70 pieces), PS (25 pieces, 10.55%), PEC (10 pieces, 4.22%), PP (10 pieces, 4.22%), ABS (7 pieces, 2.95%), PTFE (7 pieces, 2.95%), Polyurethane (7 pieces, 2.95%) and Polycarbonate (7 pieces, 2.95%).

A total of 274 pieces with 30 different polymers were identified via FTIR collected in the summer season samples. There were 56 no-hits and 12 anthropogenic fibres/particles (silk, cotton, wool and flax). The majority of polymers were identified as PVC (56 pieces), PS (26 pieces), PCP (21), PEC (20), Rubber (13), PP (9), Polyphenylene (7), and PU foam (7).

In total, 319 pieces were identified through FTIR in samples of the autumn season. A total of 47 pieces were not identified and, as a result, recorded as “no - hit” anthropogenic microfiber/particle (wool, cotton and silicone) had five pieces with two natural pieces (chitin). A total of 32 polymers were identified. The majority of MP was identified as PVC (73), PCP (34), PS (31), PEC (18), PC (11), Polyphenylene (9), PP (9), PETE (9), PTFT (9), ABS (9) and rubber (8).

In total, 210 pieces from water samples collected in the winter season were analysed via FTIR, with 26 polymers identified. A total of 40 particles were “no - hits”, with three particles identified as anthropogenic microfibers/particles with one particle

identified as natural. The majority of MP was identified as PVC (56), PS (20), PCP (20), PEC (8), and PP (7).

5.4 Discussion

5.4.1 Seasonal variation in MP abundance

Microplastics were recorded throughout this study, and whilst there was variation in MP abundances between seasons, it was not significant. Many studies recorded higher MP abundances in wet seasons compared to dry seasons due to flash floods and monsoons, which cause resuspension of sediments and MPs (Chen *et al.*, 2021; James *et al.*, 2009). This study shows a slight increase in mean MP abundance in spring, summer and autumn; however, winter's mean MP is on par with spring's mean MP abundance, which is very surprising. One reason for the difference in results from this study and others may be how the results are reported. Many studies split seasons into dry and wet (Chen *et al.*, 2021; James *et al.*, 2009; Xia *et al.*, 2021), whereas the UK gets four seasons. There was also no significance between MP abundance for location and season.

Previous studies have found that global riverine input is higher from May to October when >74% of annual MP load is discharged into oceans, whilst Europe's peak is from November to May (Lebreton *et al.*, 2017). There were peak MP abundances observed in November (61.3 L⁻¹), October (56.67 L⁻¹) and May (54.67 L⁻¹). Although two of the highest MP abundances were observed during Europe's peak MP load discharge months, overall, the average mean MP abundance was lowest in winter and spring, December - May. Overall, MP abundance not being significantly different seasonally suggests that MP abundance may be more impacted by riverine discharge regimes rather than seasonal differences.

There was yearly variation with seasonality and MP abundances. This may be due to a few reasons; 1) study design: water sampling started in May 2019 and finished in May 2021. As a result, spring samples in 2019 did not include the data for two months from the eight sites, 2) Covid-19 pandemic: whilst the impacts of Covid-19 are not investigated explicitly during this study, the pandemic did affect some sample sites and resulted in missing samples for some months. The pandemic also affected anthropogenic impacts as human activity and behaviour changed during the pandemic.

5.4.2 Variation in MPs due to Rainfall

This study showed seasonal rainfall impacted MP abundances and affected MP abundance variation seasonally. Spring was identified during this study because spring 2019 had an extremely high mean MP abundance (31.61L^{-1}) compared to any other season whilst also having the lowest seasonal rainfall value. The high MP and low rainfall may have resulted in less river flow. However, this cannot be confirmed as spring 2021 (44.62 mm) had a similar rainfall to 2019 (47.86 mm) but considerably lower MP abundance.

Higher rainfall is usually correlated with autumn and winter, with high inputs of rainfall due to storms which are common in these months and a significant contributor to MP abundance (Hitchcock, 2020). Storms have been recorded as increasing MP abundance up to 5 days after the event, with Hitchcock (2020) recording MP abundance increasing from 400 particles m^3 before a storm to 17,383 m^3 after the storm in water samples from Cooks River estuary, Australia. These high rainfall periods may wash MPs off the shoreline into the river (Eerkes-Medrano *et al.*, 2015). Rainfall events can increase MP abundance due to urban run-off and

flooding, and increase turbidity within the river, thus resuspending sediment and MPs (Buwono *et al.*, 2021; Cheung *et al.*, 2019; Roscher *et al.*, 2022). Hurley (*et al.*, 2018) found that 70% of MP stored in sediment is transported downstream during flooding events along the Mersey and Irwell rivers, UK.

London's historic sewage system is currently being updated with the Thames Tidal Project. The outdated sewage system was made to cope with a population of 4 million, not the current population of nine million (Defra, 2015; Thomas and Crawford, 2011). As a result, during significant rainfall events, the system will overflow and result in combined sewage outflows, resulting in the input of sewage water containing MPs into the river (Horton *et al.*, 2017; Rowley *et al.*, 2020; Whitehead *et al.*, 2021). From 2011-2015, the combined sewage systems (CSOs) occurred 50-60 times with a spill volume of 39 million cubic tonnes annually (Ofwat, 2022; Thomas and Crawford, 2011). Thames Water, one of the leading water companies along the tidal Thames, had reported 325, 292 and 271 spills in 2019, 2020 and 2021 respectively into the river Thames (Environment Agency, 2022).

Whilst data on spills from CSOs along the river Thames obtained information was only given as an annual spill volume. As a result, there is not enough data to determine if WWTP and CSO impact on seasonal variation of MPs. Although this study shows there appears to be no link between location and MP abundance during any season, it may have explained why storms affected MP abundance. Barking Riverside, the site closest to the Becton sewage treatment plant, did have the highest MPT mean across all areas. Becton sewage treatment plant is the largest WWTP in London (Tideway, 2022).

5.4.3 Morphology

5.4.3.1 Observation of seasonal MP types

Fibres were the most abundant MP type found in water samples. Microplastics especially fibre abundance increased in winter seasons, possibly due to higher usage of washing machines and surface run-off (Browne *et al.*, 2011). Whilst efforts are underway to improve the outdated sewers in and around London by adding more pipes and increasing the amount of wastewater they can hold (Tideway., 2022). However, this will not be completed until 2024. Until then, MPs, particularly fibres from wastewater, will still accumulate in the river Thames.

The presence of fibres may also be due to the use of ropes in the fishing and shipping industry, resulting in 18% of all fibres (Andrady, 2011). The river Thames is used for recreational boating and partially for shipping, particularly Tilbury docks. The river also contains many marinas, docks and boatyards.

Pellets were mainly abundant in summer and autumn months and least abundant in winter season in 2019, whilst pellets in autumn, spring and summer in 2020 were considerably less. It is possible that Covid-19 and subsequent lockdowns had an impact on pellets. There appear to be many plastic fabricators' businesses along the Thames that use pellets as a raw plastic material which may have been shut down or working with limited human resources, thus decreasing the number of pellets that may have been released into the environment, including the river Thames. The main factories that use raw plastic materials can be found between Barking Riverside and Tilbury. However, these sites did not contain the highest abundance of Pellets. The fibres and fragments confirm the presence of secondary MPs within the river Thames, mostly likely caused by sewage and WWTPs along the river Thames.

5.4.3.2 Observation of seasonal MP colours

There was minor variation of MP colours amongst the seasons with black, blue and transparent as the most abundant across all sites and seasons. The lack of variation of colours between seasons appears to be common amongst studies (Dalu *et al.*, 2021; Veerasingham *et al.*, 2016) Black was predominantly the most common colour observed across all seasons. The colour of MPs originate from the parent plastic items that have fragmented if the MP is a secondary MP. Colours of MPs may change due to photodegradation or due to contamination, from the time spent in the environment. Previous studies (Ding *et al.*, 2019; Gallagher *et al.*, 2016) have attempted to link MP colour to the source.

Transparent MPs are highly present due to being a commonly used colour in items such as plastic bottles, bags, sanitary items, and wet wipes (Campanale *et al.*, 2020; Hidalgo-Ruz *et al.*, 2012). Wagner and Lambert (2018) also found high abundances of white or transparent MP in surface water due to discolouration by UV light.

Transparent fibers were the most abundant spring 2020 which is possibly due to the emergence of the Covid-19 pandemic and the UK lockdown.

Previous studies on the river Thames have found high abundances of black, blue, clear, and red MP, with fibres mostly reported as black (McGoran *et al.*, 2017). The high abundance of black fibres within the river Thames is supported by this study.

The presence of historic landfills that are now releasing their contents into the Thames River may explain why microplastics of varying colours and sizes are present within the river.

5.4.3.3 Observation of seasonal MP Length

Most of the particles detected in the river Thames were confirmed to be MPs, the majority measuring between 0 – 1 mm. There was no variation seasonally except for

the 2 – 3 mm range in the summer. It is possibly due to the high percentage of this range found in North Woolwich compared to the other sampling sites. The North Woolwich site in summer is interesting as there is a high presence of MPs 2 – 3 mm in length but no MPs in the 3-4mm and 4-5mm categories although there were MPs 5<mm. At the same site in spring there were no MPs over 2 - 3 mm found. As a result, the high presence of MPs in the 2 – 3 mm range could not be explained by the assumption that MPs from spring had broken down and caused the increase in summer. One possible explanation for the high abundance within the 2 – 3 mm category is that larger plastic broke down in the river Lea causing an increase at this site. Another point to consider is that North Woolwich in summer only had one sample carried out due to the impacts of the Covid-19 pandemic which may have skewed the data.

Due to many studies not recording length or differences in methodology (different mesh sizes) and size ranges, comparing data is challenging as plastic fragments down into smaller parts through degradation higher abundances of smaller MP can be found within the environment (Gebhardt and Forster, 2018). The high abundance of smaller MP may increase the risk of bioavailability and may therefore increase the ecological risk within the river Thames.

5.4.4 Observation of seasonal MP Polymer

This study showed a wide range of different polymers, the most common being PVC, PS, PCP, PEC and PP. The presence of PP is not surprising as it is largely manufactured and used worldwide in the packaging and textiles industries. These polymers, as well as being used worldwide, are also low-density polymers and, as a result, are often found within surface water samples. Previous studies have shown

that PP, Polyethylene, PVC, Polyester and PS are located within the river Thames tributary sediments (Rowley *et al.*, 2020) and within the river Thames.

Particles originating from tyres were recorded. However, they are not often recorded as being detected at high concentrations within studies, possibly due to technical issues or discrepancies (Hidalgo-Ruz *et al.*, 2012).

As well as polymers, cellulosic and animal fibres were also identified. Cellulose, cotton, wool and silk are just examples of the materials that were found and classified as anthropogenic microfibers/particles. These materials are normally under-reported in MP studies as they are not technically polymers. Because they are produced in significantly lower amounts compared to polymers they are not often taken into consideration. For example, cotton fibres in 2020 had a production volume of 26.2 million tonnes compared to polyester, which had a production volume of 57 million tonnes (52% global fibre market) in 2020 (Textile Exchange, 2021). Wool's global fibre production only reached 1 million tonnes in 2020 (Textile Exchange, 2021). Whilst these materials may not classify as polymers, very little is known about the degradation within freshwater and marine environments. These materials have also had dyes and other chemicals used on plastics to make them more beneficial. Whilst materials such as wool and cotton have previously been considered as biodegradable with processes to help extend their lives. These materials may now act as plastic polymers. However, further studies would be needed to confirm this finding and explore their impacts on the environment and biota, especially as these “natural” fibres are being suggested to reduce MPs input into the atmosphere.

5.4.5 Further research

Further studies need to be conducted especially with regard to the effect WWTPs and seasonality affect MP abundance. However, whilst WWTPs and CSOs are all supposed to be monitored for release events this does not appear to be the case. For this study, storms had some effect on MP abundance, however a specific reason for this impact can not be identified with the current data. Data were obtained from some combined sewage outflow (CSO's) releasing along the river Thames; however, the data provided on request was only given as a yearly figure, so it was impossible to see if the storms had an impact on seasonal variability due to this release of sewage water into the river system. Many studies reported that MP settles on riverbeds during periods of low rainfall events. As a result, this study could be expanded by testing sediment sampling, and water samples gathered from the river Thames seasonally; however, that was beyond the scope of this investigation.

5.5 Conclusions

This study aimed to investigate the seasonal impacts including rainfall on MP abundance at sites along the river Thames. Microplastics were present in every sample over the course of this study. This study showed that yearly MP abundance and seasonal MP abundances were not significantly different especially when considering the impact of rainfall. The yearly seasonal differences across the study period (2019 - 2021) suggest other factors such as Covid-19 have a stronger impact on MP abundance than environmental factors. Whilst rainfall was investigated due to the nature of sampling (once a month) in order to get a better representation of the impact of rainfall on seasonal MP abundance more samples would need to be taken around periods of high rainfall especially around CSO's and seasonal storms. This will further the knowledge on how environmental fluctuations seasonally may cause

an influx in MPs along rivers within a short period of time.

6. Impact of the Covid-19 pandemic on microplastic abundance along the River Thames



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Impact of the Covid-19 pandemic on microplastic abundance along the River Thames

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Highlights

- 82.1% (3679 pieces) of microplastics were fibres.
- Covid-19 status significantly impacted microplastic abundance.
- Average microplastic abundance was highest during Lockdown 2 (27.1 piecesL⁻¹).
- Microplastic abundance decreased from pre Covid-19 (2019) to post Covid-19 (2021).

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Abstract

In April 2020, the Covid-19 pandemic changed the human behaviour worldwide, creating an increased demand for plastic, especially single-use plastic in the form of personal protective equipment. The pandemic also provided a unique situation for plastic pollution studies, especially microplastic studies. This study looks at the impact of the Covid-19 pandemic and three national lockdowns on microplastic abundance at five sites along the river Thames, UK, compared to pre-Covid-19 levels. This study took place from May 2019 - May 2021, with 3-litre water samples collected monthly from each site starting at Teddington and ending at Southend-on-Sea. A total of 4480 pieces, the majority of fibres (82.1%), were counted using light microscopy. Lockdown 2 (November 2020) had the highest average MPT (27.1 L⁻¹). A total of 691 pieces were identified via Fourier Transform Infrared Spectroscopy (FTIR). Polyvinyl Chloride (36.19%) made up the most microplastics identified. This study documents changes in microplastic abundance before, during and after the Covid-19 pandemic, an unprecedented event.

6.1. Introduction

In December 2019, Covid-19 was detected in China; the World Health Organisation (WHO) declared it a Worldwide pandemic in the following months. To curb infection rates and flatten the infection curve, governments worldwide implemented preventive measures, including social distancing, lockdown and personal protective equipment (PPE) such as gloves, masks and hand sanitiser. The health crisis caused social, economic as well as environmental threats.

The use of PPE was originally only mandatory for frontline healthcare workers; however, during the pandemic, these became compulsory for the general public, especially face coverings. Over 50 countries required face coverings in public places and transport systems, including Austria, Morocco, Italy, Spain, Portugal, Cuba and the UK. The World Health Organisation (WHO) requested a 40% increase in disposable PPE protection due to the pandemic (Adyel, 2020). The estimation is that monthly PPE for healthcare workers alone would require 89 million masks, 76 million gloves, and 1.6 million goggles (Adyel, 2020; Prata *et al.*, 2020). Once countries required the general public to wear PPE, WHO estimated that the global population would monthly need 129 billion masks and 65 billion gloves if everyone wore one disposable standard face mask daily (Adyel, 2020). The UK alone has 66.7 million inhabitants. If every person used one mask daily, this would generate 60,000 tonnes of contaminated plastic waste (Allison *et al.*, 2020).

This increased demand for PPE led to an increase in production. China, for example, increased face mask production by 450% in a month, increasing output from 20 million to 110 million in February 2020 (OECD, 2022; Prata *et al.*, 2020). Health and social care services in England received 2 billion PPE items, including aprons, gowns, gloves, eye protection and face masks, between 25th February and the 30th June 2020, before Covid-19, 2.43 billion items were distributed from 1st January - 31st December 2019 (GOV.UK, 2022). PPE included face coverings, gloves and aprons, the most commonly used face coverings. These face coverings or masks are made of non-woven material, often a mixture of polypropylene (PP), polyethylene terephthalate (PET), polyethylene (PE), Polyurethane or polyacrylonitrile fibres (Ajmeri and Joshi Ajmeri, 2011; Martínez Silva and Nanny, 2020; Prata *et al.*, 2020). However, they used reusable masks made of cotton or other anthropogenic

materials besides plastics. Gloves also often are made or incorporated with PE, PP and PET (Ajmeri and Joshi Ajmeri, 2011; Martínez Silva and Nanny, 2020; Prata *et al.*, 2020). Multiple studies have found PPE especially face masks are prone to release microfibers (Aragaw, 2020; Fadare and Okoffo, 2020).

Protective equipment in a health or social care setting was also considered contaminated waste. As a result, it was incinerated, whereas the general public was encouraged to wear reusable and washable face coverings to limit the amount of waste generated. Once washed (recommended every two days), if reusable or disposed of, these masks will eventually shred, releasing polymer fibres into the environment, and contributing to plastic pollution (Prata *et al.*, 2020). The improper disposal of 1% of face masks would equate to an extra 10 million items entering the environment weighing 30,000 – 40,000 kg (Adyel, 2020), which would lead to an exponential increase in plastic pollution within the environment. As well as Macroplastics in the form of PPE, each mask could potentially release 2230 MPs (<5 mm) (Ma *et al.*, 2021).

Plastic use and consumption increased throughout the Covid-19 pandemic, especially single-use plastics (SUP), which resulted in abnormally high demand on plastic suppliers, e.g., China and the US, due to lifestyle changes. In addition, the price of petroleum oil fell dramatically due to the decrease in water, land and air transport (Patrício Silva *et al.*, 2020). The lower oil prices made the manufacture of virgin plastic from plastic fuels less expensive, with some estimating that making drinks bottles from recycled plastic became 83 - 93% more costly than new bottle-grade plastic. As a result, policies and ways to combat plastic pollution were delayed, paused or reversed (Adyel, 2020).

The shift in consumer behaviour was driven mainly by hygiene concerns and panic buying, leading to the shelves needing to be restocked quickly to cope with demand. This led to high sales of plastic packaged items such as groceries, i.e., pasta, wet wipes, hand soaps, sanitisers, toilet rolls and cleaning products (Jribi *et al.*, 2020). Home-delivered groceries, as well as takeaway meals, are being delivered increased worldwide. For example, during Singapore's 8 - week lockdown (April-June 2020), this contributed to an additional 1400 tons of plastic waste (Adyel.,2020).

After the lockdown, the business sector, whilst restarting after the pandemic, also heavily relied on SUPs to reopen. This includes but is not limited to the use of 1) microfibre wet wipes for cleaning surfaces, 2) face masks or shields, especially in healthcare clinics and within the beauty industry, 3) protective plastic for chairs or payment machines, and 4) Perspex plastic shields which is placed between checkout counters in supermarkets as well as around some desks in offices to prevent potential contamination by air droplets by customers or staff. Perspex saw a 300% increase in the production of its plastic screens since the start of the pandemic (Perspex., 2020).

Before Covid-19, plastic pollution had led to the development of international directives and national and regional initiatives; these ranged from fees, environmental taxes or legislative bans on certain items such as plastic bags and microbeads. However, these initiatives were impacted due to Covid-19 and lifestyle changes. As a result, policy such as the UK cotton bud ban was postponed (Patricio Silva *et al.*, 2020). In addition, concerns over cross-contamination caused by reusable containers and bags led to withdrawals or postponements of SUP bans and fees, as well as banning refilling items such as plastic takeaway cups in coffee shops (Schnurr *et al.*, 2018). These concerns over cross-contamination of reusable plastic

have been raised before Covid-19 by the plastic industry. The postponements of bans in 2020 were supported by plastic industry lobbyists (Schnurr *et al.*, 2018). The deposit return schemes for plastic bottles and crisp wrappers were also postponed. Scotland's deposit return scheme was delayed to July 2020; however, it is expected to start in 2023 (Scottish Government, 2022). In the UK, the ban on cotton buds, plastic stirrers and straws was scheduled to come into effect in April 2020. This law was delayed until October 2020 (UK government, 2022). Supermarkets could also remove the 5p bag tax until autumn 2020 to reduce the use of reusable bags. In March 2020, the UK announced it planned to introduce a tax on plastic packaging that contained more than 30% recycled plastic (Creech, 2020). The plastic packaging tax consultation period was supposed to end on 20th May 2020 but was extended to 20th August 2020 and eventually came into effect on April 2022 (Creech, 2020; HM Revenue and Customs, 2020; UK Government, 2022).

At first glance, the pandemic seemed to be a good thing for the environment, with a decrease in greenhouse gas emissions, air pollution, and noise pollution (Dutheil *et al.*, 2020; Muhammad *et al.*, 2020; Tobías *et al.*, 2020). However, increased medical waste and PPE usage combined with waste management practices worldwide, such as the reduction in recycling and growth in incineration and landfilling, led to a rise in plastic waste potentially entering the environment (Abu-Qdais *et al.*, 2020; Zambrano-Monserrate *et al.*, 2020). Environmental threats have seemingly been pushed aside during the pandemic to focus on public health. While the positive indirect ecological impacts of Covid-19 may be short-term, the adverse effects may have long-term consequences. The increased use of plastic, in particular, is concerning due to the implications on the environment and public health in the long run (Patrício Silva *et al.*, 2020).

This study investigates the impact of the Covid-19 pandemic and the mismanaged plastic waste that entered the environment, specifically microplastics within the river Thames. The hypothesis is that there would be no impact on microplastic abundances during lockdowns compared to before Covid-19. This is due to most, if not all, plastic entering the environment being macroplastics, i.e., masks and gloves, and as a result, not being counted or investigated during this study. This study aimed to; 1) investigate differences in MP abundances along the river Thames comparing pre-pandemic to during and post-pandemic, 2) investigate if lockdowns had an impact on microplastic abundances and morphology, 3) investigate if changes in microplastic abundances and morphology could be due to another factor such as rainfall.

6.2. Material and methods

6.2.1. Study site and sampling

Five sites (Teddington Lock, Tower bridge, Limehouse, Tilbury and Southend-on-Sea) along the tidal section of the river Thames were sampled pre-pandemic (May 2019- February 2020), during the Covid-19 pandemic 2020 (March 2020) and the month after the last Lockdown (May 2021) (Figure 6.1, Table 6.1)

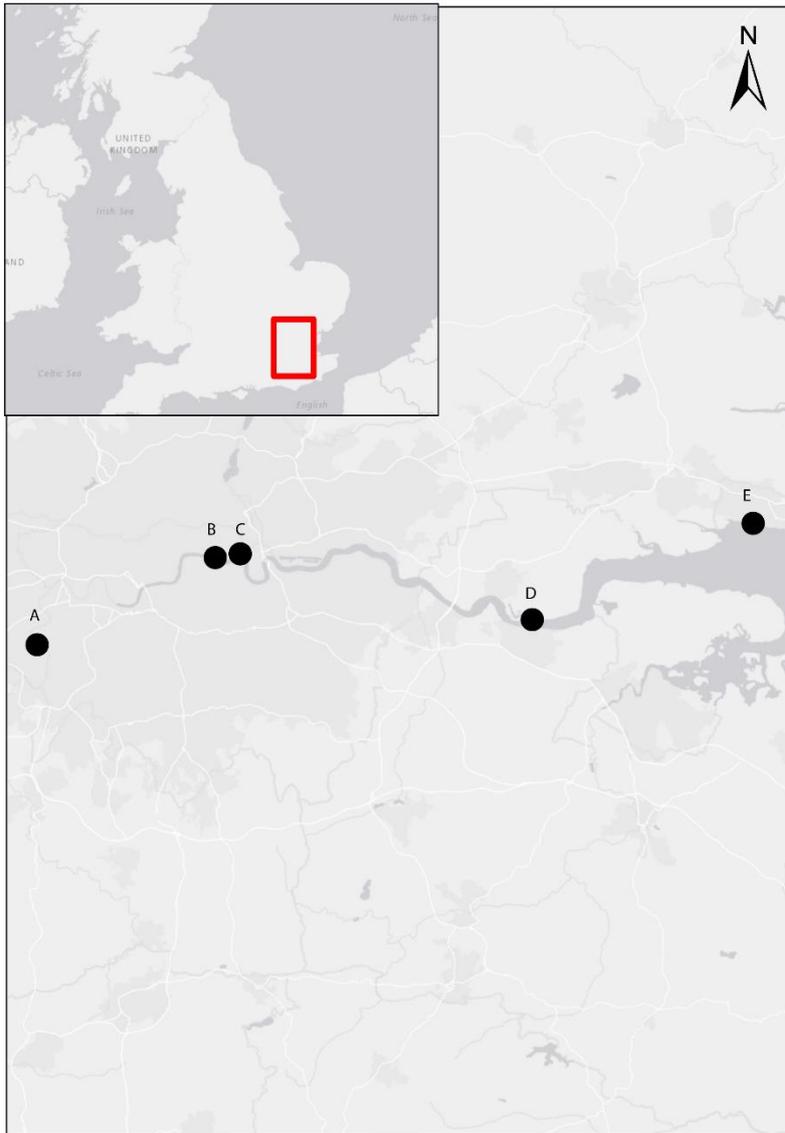


Figure 6.1 Water sampling sites along the River Thames May 2019 - May 2021; A) Teddington, B) St Katherine's, C) Limehouse, D) Tilbury and E) Southend-on-Sea

Whilst the utmost care was taken to sample each month continuously. Southend-on-Sea and Tilbury were an exception to this April 2020 due to self-isolating and the Teddington location changing from the island in the middle of the river to the side near a slipway. This was due to screening and barriers to prevent access to the usual sampling location on the island by the council and metropolitan police to

prevent the public from getting access to the river from the "beaches" on the island as members of the public were using these to gain access to the river and were swimming near the lock (Richmond Gov, 2020).

Table 6.1 Water Sampling site locations along the Thames Estuary

Collection Site	Address	Location Coordinates	Width (km)	Depth (ft)
Teddington Lock	Teddington Lock Footbridge, London Borough of Richmond upon the Thames, England, United Kingdom	N 51° 25' 47.856" W 0° 19' 20.24"	0.06	7.5
St Katherine	River Thames, Shad Thames, London SE1 2NJ, United Kingdom	N 51° 30' 22.504" W 0° 4' 24.324"	0.27	6.65-16.40
Limehouse	Ratcliff Cross Stairs, Jardine Road, London E1W 3WB, United Kingdom (Thames footpath)	N 51° 30' 34.589" W 0° 2' 17.732"	0.23	6.6-16.4
Tilbury Fort	The World's End, Fort Road, Tilbury RM18 7NR, United Kingdom	N 51° 27' 6.276" E 0° 22' 13.364"	0.79	32.81-49.21
Southend-on-Sea pier	Lifeboat Station, Southend Pier, Southend-on-Sea SS1 2EL, United Kingdom	N 51° 30' 54.705" E 0° 43' 18.069"	6.83	32.81-49.21

6.2.2 Sample collection

Water samples were collected monthly around the 15th of each month starting from May 2019 – June 2021 at high tide from land-based infrastructure at the site. Three 1L surface water samples were collected following protocols established by Devereux *et al.* (2022) and as described in chapter 3. Samples were filtered within a week of the collection; however, due to the pandemic and subsequent lockdowns, there were some occasions (March – June 2020; November - December 2020; January - February 2021) when this was not possible due to the University being inaccessible. As a result, samples taken during these months were taken as soon as possible once the lockdown was lifted. However, it meant that some samples, such as March 2020, did not get filtered for up to 4 months after collection. During these periods, samples were kept in a cool, dark cupboard to prevent degradation of MP, and samples were not placed in a freezer due to insufficient space.

Upon the reopening of the laboratory, samples were filtered as soon as possible using a porcelain Buchner funnel and Whatman 1001 - 125 qualitative filter paper circles (11 μm , 10.5 s/100 mL flow rate, grade 1, 125 mm diameter).

6.2.3. Microplastic characterisation

Microplastic characterisation is the same as discussed in Chapter 3. However, due to the Covid-19 pandemic and lockdowns, a limited timeframe was left for laboratory work. Only ten suspected MPs per filter were randomly selected to be measured.

In total, 691 pieces of suspected MPs were identified by Fourier-transform infrared spectroscopy (FTIR), which was used to determine the composition of the alleged MPs to confirm they were plastics. OpenSpecy (Cowger *et al.*, 2021) is an open-access database that identifies spectra matches from FTIR analysis.

Contamination controls used as the same as discussed in Chapter 3.

6.2.4 Statistical analysis

The following dates were used to classify samples; pre -Covid-19 (before March 2020), Lockdown 1 (April – June 2020), Lockdown 2 (5th November – 2nd December 2020), Lockdown 3 (5th January – April 2021) and post- Covid-19 (May 2021). If a lockdown occurred after a sample had been taken, the corresponding month was not included in that lockdown. For example, the first national lockdown started on the 23rd of March 2020 and ended on the 24th of June 2020. As a result, march samples were taken before the 23rd, so they are included in the pre-Covid-19 data. The June 2020 samples were taken during the first lockdown (before the 24th of June, when the lockdown was lifted), so they are included in the Lockdown 1 data and statistics. Any sample taken after June 2020 but not included in the lockdowns was classified as during Covid-19 but not included in specific lockdown data.

ANOVA was used to test for significance between Covid-19 statuses and Covid-19 status vs site, then Covid-19 status vs site vs rainfall. Post-hoc Tukey tests were used.

6.3. Results

A total of 4480 microplastics (MPs) were recorded across all five sites during all lockdown statuses. The highest MP abundance was recorded at Tilbury (1121 pieces) (Table. 6.2). The majority of MPs were recorded as fibres (3679 pieces, 82,1 %) and black (3003 pieces, 67,03%) (Figure 6.2).

Lockdown 2 (November 2020) had a higher average pieces L⁻¹ across all sites except at Teddington (5.5 pieces L⁻¹) than at any other point (Figure 6.2). The average microplastic total (MPT) abundance of L⁻¹ along the river Thames during

Lockdown 2 (27.1 pieces L⁻¹) was higher than at any other point; pre Covid-19 (15.34 pieces L⁻¹), Lockdown 1 (10.19 pieces L⁻¹), Lockdown 3 (5.87 pieces L⁻¹), Covid-19 but no lockdown (8.12 pieces L⁻¹) and post-Covid-19 (5.27 pieces L⁻¹) (Figure 6.2).

Table 6.2 Total microplastic abundance (MPT) and average MPT L⁻¹ during the different stage of the Covid-19 pandemic across five sites (Teddington, Tower Bridge, Limehouse, Tilbury and Southend-on-Sea) located within the tidal river Thames. The different stages of the Covid-19 pandemic are defined as pre-Covid-19 (Before March 23rd, 2020), Lockdown 1 (April - June 2020), Lockdown 2 (5th November – 2nd December 2020), Lockdown 3 (5th January – April 2021), post- Covid-19 (May 2021). Months where samples were taken from April 2020 – April 2021 but where a national UK lockdown was not in place are classified as During Covid-19 no Lockdown (July - September 2020, October – November 2020).

Site	Total Microplastic abundance	Average MPT L-1 pre-Covid-19 (± stderr/SE)	Average MPT L-1 Lockdown 1 (± stderr/SE)	Average MPT L-1 Lockdown 2 (± stderr/SE)	Average MPT L-1 Lockdown 3 (± stderr/SE)	Average MPT L-1 During Covid-19-no lockdown (± stderr/SE)	Average MPT L-1 Post Covid-19 (± stderr/SE)
Teddington	751	12.5 (14.52)	5.5 (4.48)	4 (0)	5.75 (3.78)	10.68 (7.54)	9 (0)
St Katherine	987	17 (10.3)	7 (2.17)	27 (0)	9 (4.43)	8 (3.49)	6 (0)

Limehouse	889	12.11 (5.18)	15.3 (7.3)	61.3 (0)	4.5 (1.5)	7.67 (4.39)	2.67 (0)
Tilbury	1121	21.17 (16.49)	15.83 (5.42)	29.3 (0)	4.83 (2.08)	7.4 (1.38)	2.33 (0)
Southend- on-Sea	732	13.94 (10.61)	7.33 (1.41)	14.3 (0)	5.25 (1.52)	6.87 (3.64)	6.33 (0)

Microplastic abundance was significantly different between Covid-19 status (ANOVA, $F_{1,5}=6.41$, $P>0.001$). A Post-hoc test indicated the following were significantly different; pre-Covid-19 and Lockdown 3, Pre Covid-19 and Covid-19 no lockdown and Lockdown 2 compared to every other Covid-19 status except pre-Covid-19. There was no significance between Site*Covid-19 status and MPT abundance (2-way ANOVA, $F_{1,20}=1.87$, $P=0.122$).

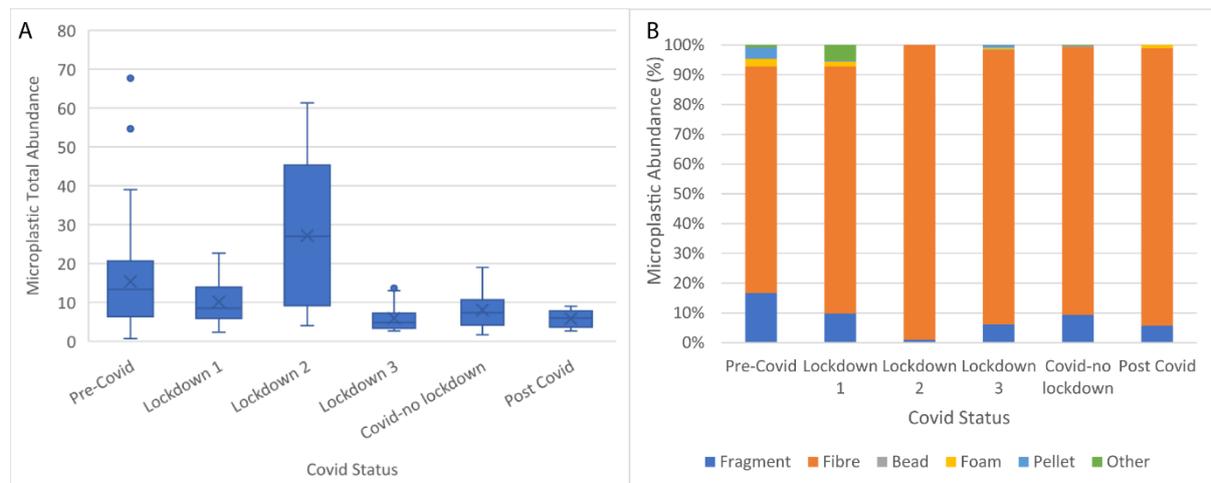


Figure 6.2 Microplastic A) Abundance L⁻¹ and B) Type found in water samples along the river Thames during the different stages of the Covid-19 pandemic.

6.3.1 Teddington

Teddington's average MPT abundance was 10.01 pieces L⁻¹ from 2019-2021. Pre-Covid-19 MPT average was 12.5 pieces L⁻¹ during the 1st national lockdown; this decreased by 44% to 5.5 pieces L⁻¹ (Figure 6.3). The average MPT abundance between lockdown 1, 2 and 3 (5.08 pieces L⁻¹) was almost half that of pre-Covid-19, Covid-19 with no lockdown and post-Covid-19 abundance (10.72 pieces L⁻¹). The highest MPT was observed pre-Covid-19 in May 2019 (54.67 pieces L⁻¹), whereas the lowest MPT abundance was observed in October 2020 (1.67 pieces L⁻¹) during

Covid-19 (Figure 6.3). However, the UK was not in a national lockdown at the time. Microplastic abundance, however, did not significantly differ between the UK Covid-19 statuses (ANOVA, $F_{5,19}=0.331$, $P=0.88$). Even with the removal of May 2019 data which appears to be an anomaly with a microplastic abundance of 54.67 pieces L^{-1} , there is still no significant difference between microplastic abundance and Covid-19 status in Teddington. (ANOVA, $F_{5,18}=0.482$, $P=0.785$).

In total, 724 pieces of MP were identified and sorted from water samples collected at this site. All morphologies (fibre, fragment, bead, foam, pellet and other) of plastics were observed at this site. Fibres (84.49%) were the most observed morphology, followed by fragments (8.66%) (Figure 6.4). Fibres ranged from 10.19 pieces L^{-1} (pre-Covid-19) to 3.67 pieces L^{-1} (Lockdown 2). However, there was no significant difference between fibres (ANOVA, $F_{5,19}=0.253$, $p=0.943$) or fragments (ANOVA, $F_{5,19}=0.234$, $P=0.943$) and Covid-19 status.

The colour black was the most predominant (62.12%), followed by blue (17.44%) and red (7.99%). The colour black, on average, was higher during Covid-19 but not in a lockdown (7.4 pieces L^{-1}); however, there was no significant difference (ANOVA, $F_{1,19}=0.208$, $P=0.955$). Blue had the highest abundance pre-Covid-19 (2.64 pieces L^{-1}) and was observed during every Covid-19 status except lockdown 2.



Figure 6.3 Microplastic abundances across water sample sites along the river Thames during the different stages of the Covid-19 Pandemic; A) Teddington, B) St Katherine's, C) Limehouse, D) Tilbury and E) Southend-on-Sea



Figure 6.4 Colours of Microplastics found within water samples at sites along the river Thames during the different stages of the Covid-19 Pandemic; A) Teddington, B) St Katherine's, C) Limehouse, D) Tilbury and E) Southend-on-Sea

6.3.2. St Katherine's

St Katherine's had an average MPT abundance of 13.17 pieces L⁻¹ (2019-2021). The highest MPT abundance on average was observed in Lockdown 2 (November 2020) water sample (27 pieces L⁻¹), whilst the lowest on average was observed post-Covid-19 (6 pieces L⁻¹) (Figure 6.3). There was an increase in MPT abundance between samples not in lockdown (10.39 L⁻¹) compared to those taken in Lockdown (14.39 pieces L⁻¹). However, there was no significant difference between all Covid-19 statuses and MP abundance (ANOVA, $F_{5,19}=1.83$, $P=0.15$).

In total, 987 pieces of MP were collected with fragments, fibres, foam, pellets and other morphologies (Figure 6.4). No beads were found at this site. Fibres (87.35%) were the most identified, followed by fragments (6.89%). There was a drop in fibre average between pre-Covid-19 (14.25 pieces L⁻¹) to lockdown 1 (4.17 pieces L⁻¹). However, there was no significant difference between fibres (ANOVA, $F_{5,19}=2.12$, $P=0.118$) or fragments (ANOVA, $F_{5,19}=1.016$, $P=0.42$) between the different Covid-19 statuses.

The majority of MP was classified as the colour black (69.2%), followed by blue (11.15%) and transparent (7.19%). Although there was a drop in black MP from Pre-Covid-19 (11.44 L⁻¹) to lockdown 1 (2.17 L⁻¹), there was no significance between Covid-19 statuses (ANOVA, $F_{5,19}=2.34$, $P=0.09$). There was also no significance in blue MP abundances (ANOVA, $F_{5,9}=0.56$, $P=0.7$).

6.3.3. Limehouse

Limehouse had an average MPT abundance of 10.15 pieces L⁻¹. The highest average MPT abundance was observed during Lockdown 2 (61.3 pieces L⁻¹) with only one sample (November 2020) (Figure 6.3). The lowest MPT abundance was observed post-Lockdown (2.67 pieces L⁻¹). There was a significant difference

between MPT abundance during the different Covid-19 statuses (ANOVA, $F_{5,9}=20.33$, $P>0.001$).

In total, 889 pieces of MP were collected, of which the majority were fibres (86.39%), followed by fragments (10.91%), foam, pellets and others (Figure 6.4). No beads were found during water samples. There was a significant difference between fibre abundance during the Covid-19 status (ANOVA, $F_{5,19}=21.66$, $P>0.001$), with the highest abundance being found during Lockdown. There was no significant difference between fragment abundance and Covid-19 status (ANOVA, $F_{5,19}=1.7$, $P=0.18$).

A total of 11 colours were observed, with black (637 pieces, 71.65%) being the most predominant, followed by red (79 pieces, 8.89%) and blue (60 pieces, 6.75%). Most black MP was found during lockdown 2 (58.3 pieces L^{-1}). As a result, there was a significant difference between black and Covid-19 status (ANOVA, $F_{5,19}=27.66$, $P>0.001$)

6.3.4 Tilbury

The average MPT abundance for Tilbury was 10.01 pieces L^{-1} between 2019 - 2021. The highest MPT was found during Lockdown 2 (29.3 pieces L^{-1}), and the lowest was found post-Covid-19 (2.3 pieces L^{-1}) (Figure 6.3). There was an increase in MPT abundance during lockdowns (16.67 pieces L^{-1}) compared to samples taken when not in a national lockdown (10.3 pieces L^{-1}). However, there was no significant difference between MP abundance and Covid-19 status (ANOVA, $F_{5,19} = 1.87$, $P=0.148$).

In total, 1121 pieces of MP were counted and classified as fragments, fibres, beads, pellets, foam or other. Most MP was identified as fibres (89.66%) and fragments

(7.85%) (Figure 6.4). On average, samples collected during lockdowns (16.31 pieces L⁻¹) contained more fibres than samples taken at any other time except pre-Covid-19 (18.31 pieces L⁻¹), but this was not significant (ANOVA, $F_{5,19}=2.395$, $P=0.076$).

Black (74.49%), blue (8.47%) and red (6.6%) were the most commonly identified colours. Whilst the average of black MP was higher during lockdowns (36.83 pieces L⁻¹) compared to when not in lockdowns (22.49 pieces L⁻¹), there was no significance (ANOVA, $F_{5,19}=2.055$, $P=0.116$).

6.3.5 Southend-on-Sea

The average MPT abundance for Southend-on-Sea 2019 - 2021 was 10.01 pieces L⁻¹. The highest average MPT abundance was observed in June 2019 (35.67 pieces L⁻¹), pre-Covid-19 (Figure 6.3). The lowest abundance was also pre-pandemic in February 2020 (0.67 pieces L⁻¹). Lockdown 2 had the highest average MPT (14.3 pieces L⁻¹), followed by pre-Covid-19 (13.94 pieces L⁻¹). There was no significant difference between no lockdown (9.05 pieces L⁻¹) compared to lockdown (8.96 pieces L⁻¹) samples (ANOVA, $F_{5,18}=1.079$, $P=0.405$).

A total of 732 pieces of MP were counted from Southend-on-Sea water samples, including fragments, fibres, foam, pellets and others. Fibres (54.92%) and fragments (34.56%) were the most common (Figure 6.4). The abundance of microfibres during the three lockdowns (7.67 pieces L⁻¹) was higher than samples not taken during a lockdown (5.34 pieces L⁻¹), but there was no significant difference between Covid-19 statuses and fibres (ANOVA, $F_{5,18}=0.67$, $P=0.651$) or fragments (ANOVA, $F_{5,18}=1.079$, $P=0.405$)

Black (53.14%) was the most commonly identified colour, followed by white (11.48%) and transparent (7.92%). Although blue microplastic was not one of the most

frequently identified MP colours, it was significantly different (ANOVA, $F_{5,18} = 12.573$, $P > 0.001$) between Covid-19 statuses. Lockdown 2 had the highest blue MPT average (15 pieces L^{-1}). The second highest blue MP average was found during the COVID-19 but not lockdown samples (2.2 pieces L^{-1}).

6.3.5 Polymer type

In total, 691 pieces (15.42%) of plastic were identified across all sites, whilst there was variation between the sites some polymers were more prevalent throughout the river. The highest polymers found across the river Thames were PVC (181 pieces, 36.19%), PS (70 pieces, 10.13%) and PCP (52 pieces, 7.53%) (Figure 6.5, Figure 6.6). As well as polymers, there were 122 'no hits' (17.66%) as well as anthropogenic microfibres/particles identified, such as cotton, wool, silk, nylon, and silicon (17 pieces, 2.46%).

When comparing polymer abundances across all sites, PVC was the most identified polymer during the various Covid-19 statuses, except during Lockdown 2, where rubber (average two pieces) polymers were the most abundant (Figure 6.5).

Polyvinyl chloride saw a 50.94% drop from pre-Covid-19 samples (average 1.963 pieces) to Lockdown 1 (average 1 piece), after which it gradually increased throughout the lockdowns and was more abundant on average post-Covid-19 (average 3 pieces), with the most pieces being found at Tilbury (33.33%) during this time.

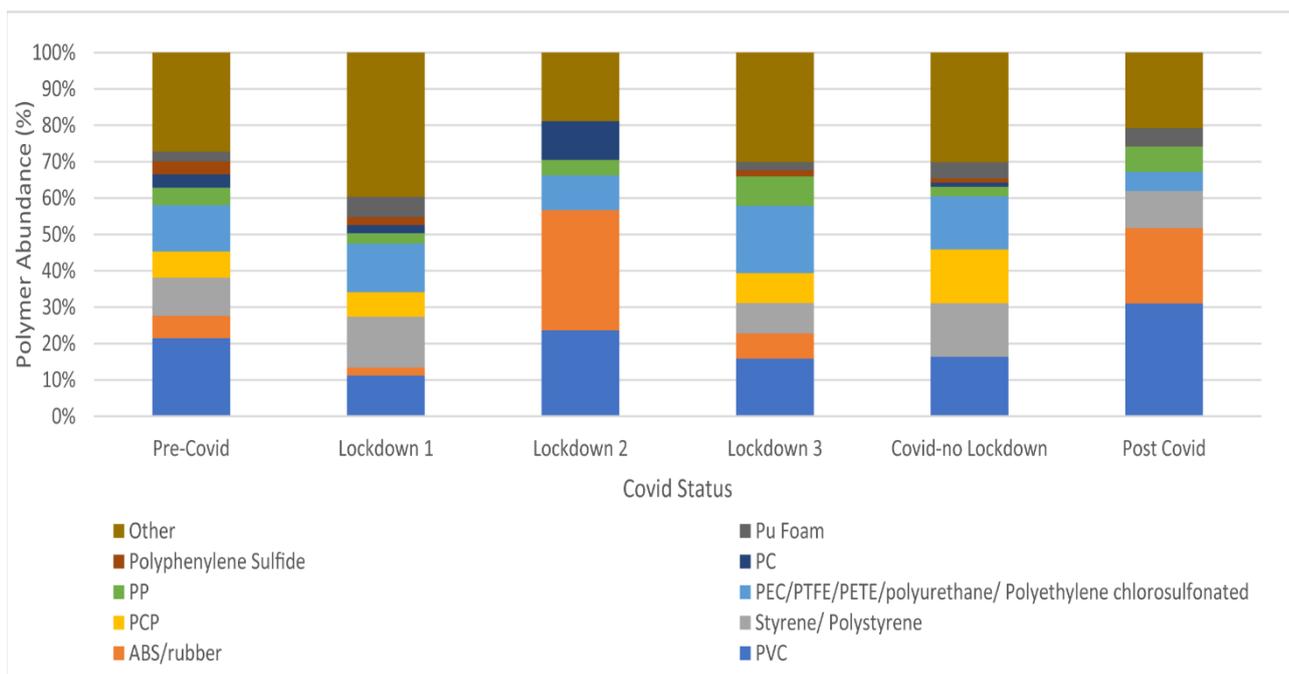


Figure 6.5 Overall polymer abundances (%) of microplastics found in water samples along the River Thames May 2019 - May 2021 during different stages of the Covid-19 pandemic.

Polymers identified via FTIR varied between sites as well as throughout the Covid-19 pandemic (Figure 6.6). Teddington's most abundant polymer was PVC (32 pieces, 28.32%) with Lockdown 3 having only having a total of 10 pieces compared to the lowest abundance found during Covid-19 with no lockdown (4 pieces) (Figure 6.6). Acrylonitrile Butadiene Styrene (ABS) was only observed post Covid-19 with a total of 2 pieces observed, whilst polyethylene chlorinated (PEC), Polyethylene terephthalate (PETE), Polycarbonate (PC) and polyphenylene sulphide (PES) were only observed pre-Covid-19.

St Katherines and Limehouse also had PVC (28 pieces, 24.78% and 39 pieces, 34.2%) as the most abundant polymer, followed by Polystyrene (PS) (16 pieces,

14.16% and 13 pieces, 11.4%) (Figure 6.6). However, unlike Teddington, St Katherine and Limehouse had fewer polymers present in post-Covid-19 water samples, with only PVC (7 pieces, 6.2% and 3 pieces, 2.65%) and PP (3 pieces, 2.65% and 1 piece, 0.89%) identified at both sites.

Tilbury followed a similar pattern with PVC (39 pieces) and PP (21 pieces) being the most identified (Figure 6.6). Unlike the other sites ABS was the only polymer identified in Lockdown 2 and PVC was the only polymer identified post-Covid-19.

Southend-on-Sea had 29 polymers identified throughout this study the highest variation at any other site (Figure 6.6). Whilst PVC was still the most abundant this was followed by Polychloroprene (PCP).

- Alkyd Varnish, Resin-dispersion, Vinylidene Chloride, Polyamide, Polyvinyl Alcohol, Polylactic Acid, Polyvinyl Fluoride, Polybutadiene and Zein Purified), D) Tilbury (Other – Alkyd Varnish, Vinylidene Chloride, Polyamide, Polylactic Acid, Polyvinyl Fluoride and Polyoxymethylene) and E) Southend-on-Sea (Other – Edterepolymer, Polyacetal, Alginic Acid, Alkyd Varnish, Resin – dispersion, Polyvinyl Butyral, Polyisoprene Chlorinated, Vinylidene Chlorinated, Polyamide, Polyvinyl Fluoride, Poly (2,4,6 tribromostyrene), Poly acrylic Acid).

6.3.6 Rainfall

Rainfall at this time ranged from 8.9 mm (Teddington, May 2020) – 162.2 mm (Tilbury Fort, January 2021). Whilst there was a variation in rainfall from May 2019 - May 2021 there was no significance between rainfall and MPT during this study (ANOVA $F_{1,39}=0.418$, $P=0.996$) or MPT x rainfall x Covid-19 status (ANOVA, $F_{1,95}=3.148$, $P=0.087$). Post-hoc tests could not be carried out for rainfall because some groups had less than two factors.

6.4 Discussion

The increase in plastic production, usage of PPE and change in public behaviour during the Covid-19 pandemic will eventually lead to an increase in MPs resulting from the inadequate disposal of facemasks and other PPE worldwide. This research specifically looked at the short-term impact of the Covid-19 pandemic on MP abundance within the river Thames, and every water sample contained microplastics. A difference was not expected immediately in MP abundance within the river Thames upon the announcement and implementation of Lockdown 1 due to plastics taking many years to degrade (Aragaw, 2020, Fadare and Okoffo, 2020,

Saliu *et al.*, 2021). Saliu (*et al.*, 2021) suggested face masks could degrade into MPs within two years).

The data showed a slight decrease in MP abundances from pre- Covid-19 samples to Lockdown 1 samples; however, significant differences were not seen until Lockdown 2, approximately seven months after the start of the first lockdown. Except for Lockdown 2, MP abundances never reached pre-Covid-19 levels (15.34 pieces L⁻¹) or even post-Covid-19 (5.26 pieces L⁻¹). Whilst the river Thames average MP never reached pre-Covid-19 numbers. There were some site exceptions. Limehouse in Lockdown 1 had a higher MP abundance than pre-Covid-19 possibly because the area surrounding this site was the most residential (population 7817 in 0.409 km²) (City population, 2022) as well as being within proximity of Limehouse harbour and marina, which has 75 permanent residential moorings and 56 leisure moorings (Aquavista, 2022). Teddington also had a higher MP during Covid-19, with no lockdown compared to pre-Covid-19. This is possible because members of the public were using the river recreationally when the country was not in lockdown, which led to the island and beach being barricaded by the council and police. The decrease at Tilbury could be explained by the lack of cruises leaving the area, as the sampling area is close to Tilbury port. During the Covid-19 pandemic, cruises to or from this port were suspended (Richards and Ilozue, 2020). As a result, there would have been less grey water from cruises, which was high in MPs (Peng *et al.*, 2021).

The low MP abundance in the post-Covid-19 (May 2021) sampling may be due to only having one sample from each site or the fact that the UK had been in lockdown for four months before the samples were collected. However, MP was lower across the river Thames than at any other time, including Lockdown 3 (January – April 2021).

6.4.1 Rainfall

Whilst rainfall in this study did not impact MP abundance, other studies have found that rain has a significant impact (Hitchcock., 2020; Veerasingam *et al.*, 2016). This is due to rainfall putting pressure on sewage and stormwater systems and increasing MP abundance within these systems, especially tire wear particles (TWPs) and degraded litter (Muller *et al.*, 2019; Vogelslang *et al.*, 2019). This increased pressure can cause combined sewage outflows to open, resulting in the direct input of untreated wastewater into rivers (Fendall and Sewell, 2009). Whilst three named storms (Alex, Barbara and Aiden) occurred in October 2020, the last Storm Aiden (Met Office (a), 2020; Met Office (b), 2020; Met Office (C), 2020), occurred two weeks before sampling took place for the Lockdown 2 samples. It is possible that whilst rainfall in the 24 hours pre-sample did not impact MP abundance, it is possible that the storms the previous month did put pressure on sewers around the river Thames and caused the release of sewage water from CSOs. The average rainfall across the London area in October 2020 was 174.3 mm (double the moderate rain) (Met Office (b), 2020); because samples were taken in the middle of the month, the impact of monthly rainfall was not considered during this study. Whilst it was also not possible to find data on specific CSO releases to see if there was a correlation, there were six sewage alerts for the river Thames between October 21st and November 15th from Mogden (4 alerts) and Hammersmith (2 alerts) (River Thames CSO, 2022). This could have increased the MP abundance seen during Lockdown 2.

However, for this study, rainfall appeared not to impact Lockdown 2 or any other Covid-19 Status. As a result, a conclusion may be drawn that the increase in MP abundance may be down to multiple factors, including the three storms the month before and the lifting of lockdown for the four months between June and November.

6.4.2 Microplastic type

Generally, all types of plastic are lower in abundance from pre-Covid-19 samples through to post- Covid-19, excluding Lockdown 2. Although there was no significance between the type of MP or Covid-19 status, there was a decline from pre-Covid-19 samples to Lockdown 1 samples in fragments, fibres, beads, foam, pellets and others. Fragments, beads, foam, pellets and others may be lower because only “essential work” could be carried out. It may also be because members of the public were told to stay at home, so there was possibly less litter on the street in the usual forms (plastic bottles or wrappers). This was especially the case during Lockdown 1. It is possible that there was no significance between Covid-19 status and MP abundance because PPE, such as masks and gloves, take a long time to break down.

The most common colours observed were black, blue, red and transparent. These colours have previously been noted as the most abundant in the digestive tracts of European flounder and European smelt (McGoran *et al.*, 2016). Coloured microplastics are common in other studies, possibly because they originate from commonly used items that have fragmented, and much of the plastic used is coloured (Zhang *et al.*, 2015)

6.4.3 FTIR

The majority of Plastic polymers identified were PVC, PS, and PCP. The high presence of PVC, PS, and PCP among samples is not surprising as they are among the most commonly produced and used plastic polymers worldwide (Chia *et al.*, 2020). Polypropylene increased from pre-Covid-19 abundances during post-Covid-19 and Lockdown 3 samples, and Lockdown three had the majority of PP found. This

is possibly due to the use of PPE, especially masks. Masks are composed of various polymers such as PP, PS, PE, and Polyester (Aragaw, 2020). Polypropylene was higher post-Covid-19 and during Lockdown 3 than pre-Covid-19. Although it was lower post-Covid-19 with no MP identified, polystyrene was higher during Covid-19, with no lockdown, than pre-Covid-19. One mask can release 24,300 fibres per wash, whilst using one mask daily for a year will produce 66,000 tons of plastic waste (Shen *et al.*, 2021; Shetty *et al.*, 2020).

ABS is regularly referred to as tire wear particles. ABS did the opposite of what was expected due to everyone staying at home during lockdowns and using the roads less; however, it remained relatively constant pre-Covid-19 and through lockdowns. However, ABS was more abundant post-Covid-19 than pre-Covid-19. It is possible that it was due to everyone doing their daily business. It may also be because sampling coincided with stage 3 in the UK lockdown (17th May 2021), which involved opening pubs, restaurants, and hotels and allowing people to meet in groups of 30.

6.5. Conclusions

This study aimed to investigate the impact of the Covid-19 pandemic on microplastic abundance at sites along the river Thames. Microplastics were present in every sample conducted throughout this study. This study showed that MP abundance was linked to Covid-19 status, especially regarding pre-Covid-19 samples and Covid-19 samples taken not in a lockdown, especially in Lockdown 2. The increase in PP throughout this study could be attributed to the use, inefficient disposal and breakdown of face masks used throughout the pandemic. Rainfall was investigated as a potential explanation for the high MP abundances seen in Lockdown 2.

However, the previous 24 hours rainfall did not affect the abundances; however, whilst this study was not investigated, the three major storms in October 2020 may

have affected Lockdown 2 samples. Whilst the Covid-19 pandemic did affect some samples along the river Thames the true impact of the Covid-19 pandemic may not be seen for some years as the plastic items that had increased production, such as masks and gloves, degraded and cause an increase in MP release into the environment.

Chapter 7: Microplastic abundance in the Thames River during the New Year period

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Microplastic abundance in the Thames River during the New Year period

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ABSTRACT

Microplastic pollution is widely studied; however, research into the effects of large-scale firework displays and the impact on surrounding waterways appears to be lacking. This study is potentially the first to look at microplastic abundance in rivers after a major firework event. To assess the impact of the 2020 New Year's firework display in London, a 3 litre water sample was collected over nine consecutive days at Westminster on the River Thames. A total of 2760 pieces of microplastics (99% fibres) were counted using light microscopy, and further analysis was performed on representative plastic samples (354) using Fourier Transform Infrared Spectroscopy (FTIR). Whilst anthropogenic microfibres made up 11%, most microplastic identified (13.9%) were polychloroprene. This study demonstrates the occurrence of a short-term influx of microplastics in the River Thames following the New Year fireworks, which will have an additional detrimental impact on the ecology and aquaculture of the river and neighbouring waterways.

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Abstract

Microplastic pollution is widely studied; however, research into the effects of large-scale firework displays and the impact on surrounding waterways appears to be lacking. This study is potentially the first to look at microplastic abundance in rivers after a major firework event. To assess the impact of the 2020 New Year's firework display in London, a 3-litre water sample was collected over nine consecutive days at Westminster on the River Thames. A total of 2760 pieces of microplastics (99% fibres) were counted using light microscopy, and further analysis was performed on representative plastic samples (354) using Fourier Transform Infrared Spectroscopy (FTIR). Whilst anthropogenic microfibrils made up 11%, most microplastic identified (13.3%) were polychloroprene. This study demonstrates the occurrence of a short-term influx of microplastics in the river Thames following the New Year fireworks, which will have an additional detrimental impact on the ecology and aquaculture of the river and neighbouring waterways.

Keywords: Microplastics, River Thames, Microfibrils, New Year fireworks

7.1. Introduction

Plastic production and inefficient waste management schemes and policies have resulted in plastic particles being found in varying sizes (macroplastic (>5 mm), microplastic (MP) (<5 mm), nanoplastic (1-1000 nm)) in aquatic and terrestrial habitats (Da Costa *et al.*, 2016; Huang *et al.*, 2020; Hurley *et al.*, 2020; Law, 2017; Peng *et al.*, 2020). Microplastics with size <5 mm in particular is becoming ever increasingly abundant locally and globally, with their impact widely documented (Browne *et al.*, 2011; Zhao *et al.*, 2018). Microplastics can leach and sorb harmful

toxins from the surrounding environment. As a result, MPs can transfer pollutants into organisms and result in bioaccumulation and biomagnification within food chains (Farrell and Nelson, 2013; Miller *et al.*, 2020). Many previous studies have focused on the effect of MPs in the marine environment. However, the focus appears to be shifting to freshwater systems due to rivers being the major pathway of plastic pollution estimated at 1.15 to 2.41 million tonnes per annum worldwide, with 80% of plastic originating from the terrestrial environment (Horton *et al.*, 2017; Lebreton *et al.*, 2017; Meijer *et al.*, 2021).

Freshwater and estuarine ecosystems are essential resources fully utilised as a food and water source, a network for economic development, industry, and agriculture (Carpenter *et al.*, 2011). Due to their connectivity and population density being higher around water systems, rivers have become a significant contributor and pathway for introducing plastics to the sea and making it polluted (Claessens *et al.*, 2011; Willis *et al.*, 2017). A range of sources have been identified for plastic pollution in rivers via natural processes such as flooding and wind (Bruge *et al.*, 2018; Tramoy *et al.*, 2019), and anthropogenic sources such as wastewater treatment plants (WWTP's), human littering, building works and road run-off (Horton and Svendsen, 2017; Kay *et al.*, 2018; Lechner and Ramler, 2015; Seo and Park, 2020). Another less examined potential source is large-scale nationwide firework events that contribute to atmospheric, terrestrial, freshwater and marine pollution due to their explosive nature and use worldwide (Tandon *et al.*, 2008).

The amount of pollution released varies depending on the scale of the firework event. These events can range from small scale celebrations to larger nationwide events. The global Diwali festival, Independence Day in the USA (Seidel and Birnbaum, 2015), and Bonfire Night (gunpowder plot) in the UK are examples of

large-scale firework events. biggest celebrations worldwide are New Year, celebrated each year with huge firework displays. Research studies such as Moreno *et al.* (2010) and Greven *et al.* (2019) have already shown that setting off fireworks results in clouds of smoke which increase the amount of CO₂ and the atmospheric pollution within the immediate area in the short term (Ravindra *et al.*, 2003). These studies have documented that firework can on average cause a 42% increase in air pollutants, due to charcoal being the most commonly used fuel (Ravindra *et al.*, 2003; Seidel and Birnbaum, 2015). The amount of plastic varies depending on the type of firework involved. According to Toader *et al.* (2017), a pyrotechnic mixture like fireworks contains approximately 10% of a natural or artificial polymeric binder. These binders are typically made from either a natural material such as starch or Arabic gum, synthetic material such as shellac, novolac, or synthetic polymers such as nitrocellulose, polybutadiene, polyisobutylene, polyurethane or polyvinyl chloride (PVC) (Naik and Patil, 2015; Poulton and Kosanke, 1995). Rocket type fireworks that explode in the air also have a mortar and a tube sealed at the bottom end to help the firework get enough momentum to lift off the ground (Naik and Patil, 2015). These mortars are made from wrapped paper, high-density polyethylene (HDPE), or steel (Poulton and Kosanke, 1995). Rockets also have plastic cones at the top to aid flight (Naik and Patil, 2015).

Toxic substances, metals, plastics, cardboard, and many other materials and compounds have been found around firework display sites (Attri *et al.*, 2001; Baranyai *et al.*, 2014). The resulting particles of plastic, cardboard, smoke and airborne particulates or chemical pollutants tend to accumulate close to the fireworks display area (Azhagurajan and Selvakumar, 2014). Due to rain, surface run-off and subsurface drainage, these particles may reach rivers in these cities, and

subsequently impact water resources. The majority of the New Year firework displays take place in cities or are located over water, for example, in the UK (London, Westminster), Australia (Sydney Harbour), Brazil (Rio de Janeiro, Copacabana), Hong Kong (Victoria Harbour), Singapore (Marina Bay).

The 2020 firework display held at Westminster caused a level 4 (moderate) air pollution level, with an air quality index value of 105 (PM 2.5) in the surrounding area of Westminster (The World Quality Index Project, 2021). To compare, the Diwali festival of lights in Delhi in 2019 reached the maximum index value of a hazardous 500 (PM 2.5) for air quality due to the concentrations of airborne pollutants caused by the number of fireworks released (Central Pollution Control Board, 2020). Whilst these pollutants are airborne, they still pose risks to the aquatic environment.

Dutcher *et al.* (1999) and Perry (1999) found that the heavy metals used in pyrotechnic devices can travel 62 miles over two days. It is likely that plastic or MP could similarly cover the same distance once airborne, contributing to atmospheric pollution. These airborne particles eventually settle in and pollute waterways due to being washed down with rainfall. Hence it was expected that an increase in MP concentration in the atmosphere would lead to an increased concentration on nearby land or water after a firework event.

Our study aimed to investigate the impact of London's 2020 New Year firework celebrations on microplastics (MP). The objectives were 1) to quantify the

abundance of MP in the River Thames at Westminster where the fireworks were taking place, and 2) to classify MP by shape, colour and polymer.

7.2. Methodology

7.2.1 Study area

Water sampling took place on the River Thames at Westminster, London, close to the Millennium / London Eye on the river's south bank (Figure. 7.1). The sampling site was chosen due to its proximity to the firework detonation area, expected to have a relatively higher concentration of microplastic from the New Year celebrations. Westminster is a highly urbanised area of London located on the River Thames with a residential population of 254,375 in 2018 (Greater London Authority, 2021). As a result of the businesses and tourist attractions in the area, Westminster's daytime population increases to over a million people (Westminster City Council, 2019). The site is a low-lying stretch of the Thames, with Westminster having 4.7 km of River Thames frontage (Westminster City Council, 2008).

The New Year London firework celebrations attracted thousands of people to the area. A total of 86,265 tickets were scanned on the night; however, this does not include residents and businesses within the area who do not need to buy tickets. A total of 12,000 fireworks were set off in approximately 15-minute intervals with a cost of approximately £2 million (Phillips, 2020).

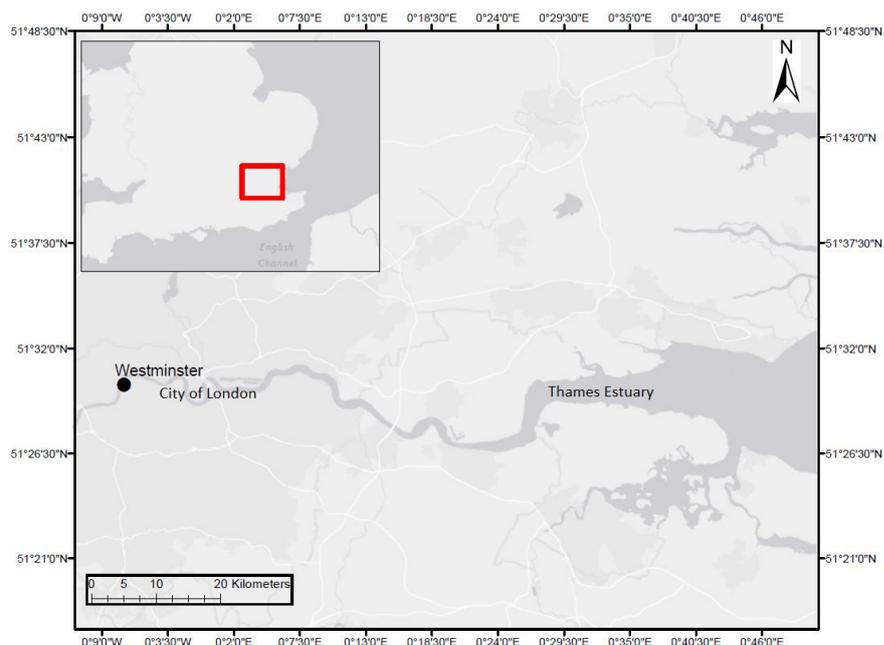


Figure 7.1 Location of water sampling site in the River Thames, Westminster, London.

7.2.2. Water sample collection

Nine samples were collected at high tide from a land-based infrastructure (Figure 7.1): 8 samples were collected on consecutive days from 29/10/19 to 5/01/20, covering pre-and post-New Year Day fireworks. One more sample was taken on 23/01/20 to check if the abundance of MPs had returned to levels observed in the area before the firework event. The New Year Day samples were taken almost 6 h after the firework displays. Surface water samples were collected from an individual location on the bank of the river, near the fireworks detonation site that would be most indicative of microplastics input from the fireworks. The surface water at the site of entry to the river could only be reached during high tide. Hence, sampling at the first high tide of the day leading to daily variation in sample collection times (between midnight and 8 AM, Table 7.1) was rational and the closest timeframe to

the New Year fireworks. On each sampling day, three 1 litre bottles of water were collected in Gosselin cornering high-density polypropylene (HDPE) natural rounded plastic bottles. The bottles were sealed on-site to be transported back to the University of East London's Docklands campus for filtering and analysis.

Concurrently, rainfall data was gathered using ainfall gauges at a meteorological station close to the site and downloaded from the weather monitoring system ORP (2020).

Table 7.1 A comparison of microplastics observed per litre of water sampled in the River Thames at Westminster between the period 29/12/19 – 5/01/20 and on 23/01/20.

Date	Time of sample collection	Average microplastic fibre (MPF) (\pm SD)	Average microplastic particles (MPP) (\pm SD)	Average length
29/12/2019	03:31	21 (0.82)	0.67 (0.94)	986 (3.2)
30/12/2019	04:11	36.67 (10.62)	0	1608.9 (4.98)
31/12/2019	04:40	44.3 (6.44)	0	892.45 (2.03)
01/01/2020	05:43	508.3 (40.45)	2 (1.41)	663.40 (1.6)
02/01/2020	05:45	43.67 (9.04)	2 (2.82)	1437.42 (6.38)
03/01/2020	06:30	52.33 (8.38)	2 (0.82)	1014.4 (4.65)
04/01/2020	07:15	43.67 (2.62)	1.3 (1.25)	1608.81 (9.67)

05/01/2020	08:28	37 (2.16)	0.33 (0.47)	1309.84 (6.65)
23/01/2020	00:29	121.67 (5.58)	2.67 (2.36)	1170.80 (3.29)

7.2.3 Filtering and contamination controls

The water samples were filtered using a Haldenwanger Porcelain Buchner funnel with Whatman 1001–125 qualitative filter paper circles (11 µm pore size, 10.5 s/100 ml flow rate, grade 1, 125 mm diameter). Strict health and safety protocols and precautions were used in the field during collection and in the laboratory to prevent contamination of samples. Field and laboratory safety protocols were adhered to, such as wearing cotton clothing, cotton lab coats and latex gloves. Cotton clothing was worn at all times except on one occasion when a purple polyester raincoat was used during sample collection. Due to potential contamination from the raincoat used, all purple particles and fibres were discounted if they were identified as polyester during FTIR protocols. Other protocols included covering the filter immediately after filtering to avoid airborne contamination, and reduce the time that samples were exposed to air. Used bottles were washed out with distilled water, and surfaces were cleaned before and after use. The use of plastic equipment was kept to a minimum, but this was not always practical. Hence, quality control tests were carried out for all experiments in this study to test for potential plastic contamination (Table 7.2): a) dampened filter paper placed on laboratory worktops to check for

airborne contamination whilst samples were exposed, which were analysed daily, b) three high density polyethylene (HDPE) bottles rinsed with distilled water and filtered, and c) filtering blanks created using 3 × 3 L of distilled water passed through the filtration setup.

Table 7.2 Cross contamination controls - microfibre count and type of colours present a) on desk filters (n=10) exposed to the atmosphere on a daily basis, b) in distilled water kept in HDPE bottles (3x3 L), and c) on filtering blanks where distilled water was run through the filtering set up. Routine observation showed only microfibre on the control sample filters.

Tested for cross- contamination	Microfibre colour				Fourier-Transfer Infrared (FTIR) tested
	Blue	Black	Red	Transparent	
Desk based filters (10) - atmospheric	3	3	2	0	2 black fibres: polyethylene terephthalate (PET)
Distilled water (3×3 L)	1	1	0	0	1 black fibre: polypropylene (PP)
Plastic bottles (3)	0	3	2	0	2 red fibres: high density - polypropylene (HDPE)

7.2.4 Classification of microplastics (MPs)

The filter papers were examined under a Keyence digital microscope VH-S3OB with a VH-Z250R/W/T lens attachment at 50× magnification, and observed MPs were classified and counted. Based on “The Guide for Microplastic Identification” (Marine and Environmental Research Institute, 2020), the type of MPs observed were classified into two main types: 1) shape: a) fibre, b) fragment including bead, foam, pellet, and other, and 2) colour (blue, black, red, white, orange, yellow, brown, pink,

green, purple, transparent, etc.). The width was also measured to confirm all suspected plastic fell into the microplastic categorisation. For this study, any piece of plastic with a larger width than 5 mm was discounted as they were classified as macroplastic, and length was recorded from the remaining plastic fraction.

A selection of particles was scanned using a Fourier-Transform Infrared Spectrometer (FTIR) (Bruker model Alpha), fitted with a platinum ATR Model with Opus 8.2 software. FTIR scans particles down to 10 µm in size, is used to determine the chemical composition, and it is a popular technique to identify polymers (Alfonso *et al.*, 2021; Uurasjärvi *et al.*, 2021). Due to the limitations of FTIR, and to reduce the number of samples lost in transition from filter system to the FTIR, it was determined that individual particles were required to have a length greater than 200 µm. The FTIR analysis was carried out on 354 particles and enabled identification of shell and biogenic waste that under simple observation can be mistaken as MPs. Spectra were analysed using OpenSpecy (Cowger *et al.*, 2021). Spectra that had no defined peaks (i.e., <55%) were classified as “no hit”; particles were classified by polymer type (i.e., polystyrene, polyethylene), or as 1) natural (i.e., chitin or sand), or 2) anthropogenic microparticle or fibre (i.e., cotton, semi-synthetic cellulose-Rayon). The FTIR equipment and fine tweezers were cleaned with ethanol before and after handling each sample to reduce the risk of contamination and false readings.

7.2.5 Statistical analysis

Statistical analysis was carried out on the data using IBM SPSS Statistics 26 (Statistical Product and service solutions) (IBM, 2021). Where microplastic total (MPT), microplastic particles (MPP) and microplastic fibres (MPF) quantities are stated, it refers to the mean value (+/-) of the triplicate samples taken on a given date. Data was standardised to MPs mL⁻¹ based on 1 L of water collected per

replicate. Analysis of Variance (ANOVA) was used to determine relationships between date and MP abundance, based on standardised microplastic (MP) concentrations. Due to a limited amount of rainfall (one event) during this study, it was impossible to conduct statistical analysis to determine the impact of rainfall on MP abundance on in this present study.

7.3. Results and Discussion

Microplastics were observed in all samples collected during this study, and a total of 2760 MP pieces were identified. There was variation in abundance (Figure. 7.2), ranging from the lowest concentration (MPT 22 pieces L⁻¹) observed on 29/12/19 (the first sampling day) to the highest concentration (MPT 510 pieces L⁻¹) observed on 01/01/20, following the fireworks display on New Year Eve. Within 24 h of this

peak, MP concentration returned to its pre-firework event range (MPT 34 pieces L⁻¹) observed in samples from 29th to 31st December 2019.

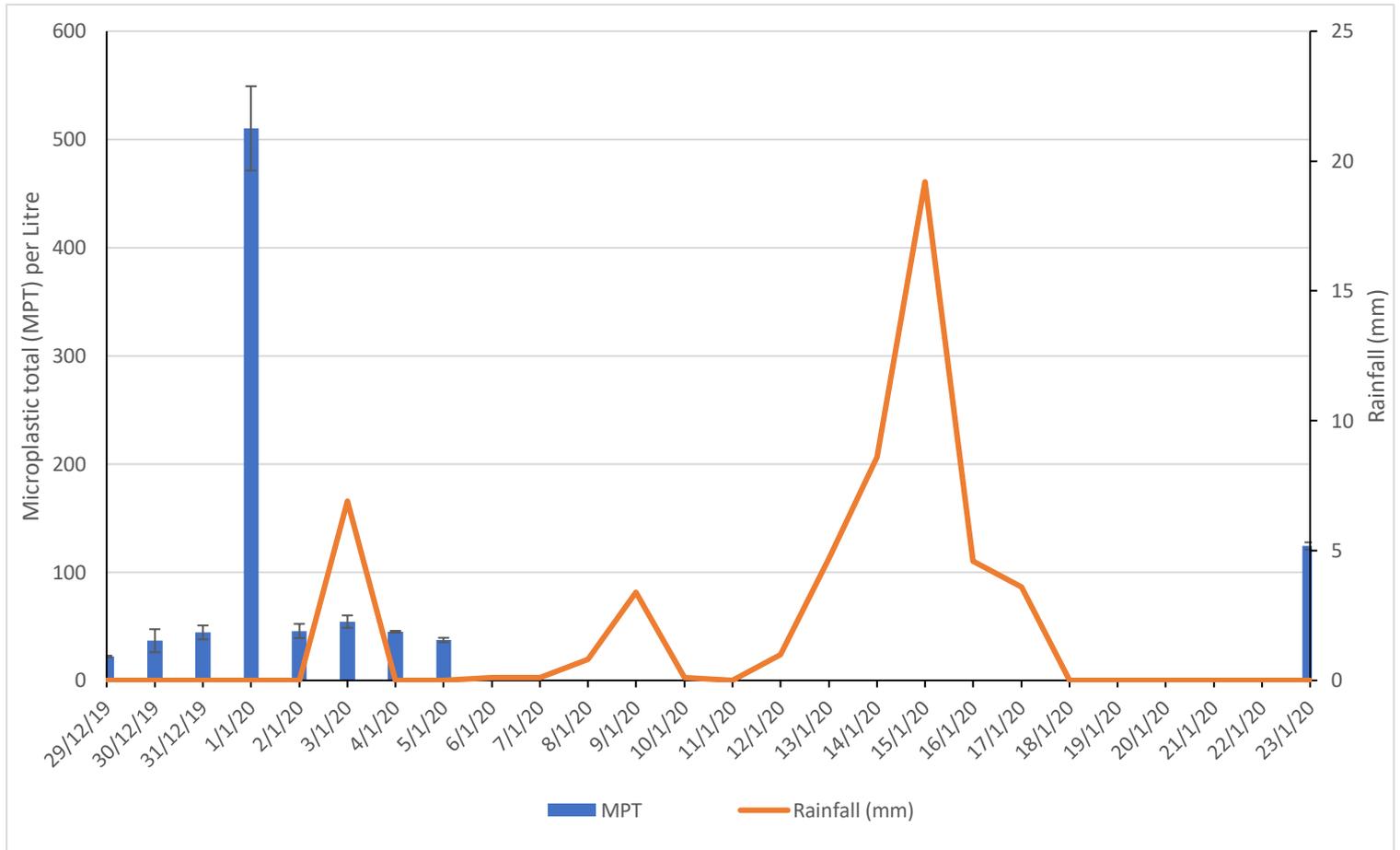


Figure 7.2 Mean (± stderr /SE) microplastic total abundance (MPT) per litre in water samples collected in the River Thames, Westminster, London on consecutive days at high tide from the 29/12/19 to 5/1/20 and on the 23/1/20 and rainfall (mm) records during the sampling period.

The average MPT abundance over the study period, excluding the 1st January 2020, was 51.2 pieces L⁻¹. The sample taken later in the month, on 23rd January, showed a spike (124.3 pieces L⁻¹) that is more than twice this average abundance value.

The presence of MPs in the River Thames before the New Year event suggests that there are sources and factors to increase the value other than fireworks, which is supported by previous studies on sources of MPs into the River Thames (Horton *et al.*, 2018; McGoran *et al.*, 2017; Rowley *et al.*, 2020). This study is part of a larger ongoing study where samples from 8 sites along the River Thames were collected monthly from May 2019 to May 2021. The maximum microplastics abundance (61 pieces L⁻¹) measured during the study period covering a larger stretch of the river, through all seasons, and at high and low tide, clearly shows that it is highly exceeded by abundance measured (maximum 508 pieces L⁻¹) in samples taken following the fireworks event on the river. Potential sources of MPs within the River could be the result of sewage systems (Browne *et al.*, 2011), personal care products (Rochmann *et al.*, 2016), anthropogenic activities such as swimming, boating, fishing, or littering (Zhang *et al.*, 2015) or tire wear particles (TWP) from road runoff (Goßmann *et al.*, 2021). Sewage system input can take approximately one month for the litter to make its way through the system and exit from the estuary into the sea, potentially explaining why microplastics are already present in the river system (Munro *et al.*, 2019). Rowley *et al.* (2020) found that microplastic abundance at Putney, a site located upstream of Westminster, increased when Hammersmith pumping station combined sewage overflow (CSO) released higher quantities of sewage into the River Thames. Given the site's central location and busy roads surrounding it, it is important to consider the possibility of TWP entering the river, thus adding to the MP pollution. Previous studies have accounted TWP for 28–45% of MPs in rivers or water sources near roads (IUCN, 2017; Royle *et al.*, 2019).

The hydrodynamics of the river may also explain the daily variation in microplastic abundance during this study. Rowley *et al.* (2020) also found that approximately 35

thousand MPs per second travel downstream at Putney, and 94 thousand MPs per second at Greenwich. This section of the river at Westminster is also reasonably straight compared to the section at Greenwich, which may mean that the flow is faster, leading to more MPs being dispersed to other areas of the river (Baldwin *et al.*, 2016). This leads to MPs being found throughout the river system and varying flow depths depending on the plastic type and size (Kooi *et al.*, 2017).

One study (Dunn and Friends of the Earth, 2019) reported 84.1 pieces L⁻¹ in a water sample taken from a site (not identified) along the River Thames. The study does not inform about the sampling date and the pre-sample conditions such as rainfall, seasonality or tide conditions, making it difficult to compare the data with the current study. Rowley *et al.* (2020) found an average of 24.8 pieces per m⁻³ at Putney and 14.2 plastics per m⁻³ at Greenwich. However, unlike the current study, the authors omitted microfibres in their MPs analysis, so their values may likely be underestimated. Differences could also be due to variations in sampling period, river location and other factors, including rainfall intensity and hydrology of the area.

7.3.1 Impact of New Year firework event

Mean MPT abundance was 51.2 pieces L⁻¹ on the dates immediately prior to the firework event. However, samples collected hours after the firework show a sharp increase in MPT to 510.3 pieces L⁻¹ (Figure 7.3) (One-way ANOVA, $f_{1,8} = 12.94$, $P < 0.001$,) with an MPF of 508.3 pieces L⁻¹ (Table 7.1), in comparison MPF 24 hours previously had been 44.3 pieces L⁻¹. Microplastic abundance within 24 hours had returned to baseline values whilst there was a slight variation 45.7 pieces L⁻¹ was deemed to be close enough to pre-firework levels seen on the 31st December 2019. This indicates that fireworks are a significant source of plastics and microplastic debris within the environment and may ultimately contribute to the pollution of rivers.

Such pollution after firework events is a known occurrence globally, with microplastics and substantial amounts of cardboard debris collected in large quantities. In 2016, the National Park Service in San Francisco removed four 50-gallon waste containers full of charred firework fuses, plastic and cardboard pieces after Super Bowl festivals (San Francisco Baykeeper, 2016). Microplastics were not explicitly collected, possibly due to their small size (Choksi-Chugh, 2016). In the same area, after a second firework show, over 30 lb of firework debris washed up at the Aquatic Park beach and continued to wash up for weeks after the event (Choksi-Chugh, 2016). It is possible that peak MP abundance in the River Thames was missed as a water sample was only collected once after the New Year show during our study instead of multiple times over the following 24 hours. Sijimol and Mohan (2014) reported that perchlorate concentrations spiked 14 hours after a firework show, reaching concentrations between 24-1028 times higher than the baseline value.

7.3.2 Effect of rainfall on microplastics

There was only one rainfall event recorded between 29/12/19- 05/01/20 however, there were multiple rainfall events between the 6th-23rd January (Figure 7.2). In total over the sampling period, there were 11 days of rain ranging from 0.1 - 19.2 mm rainfall, but a sampling day coincided with a rainfall event only on 3rd January when 6.9 mm rainfall was recorded (ORP, 2022). The highest amount of rainfall during the sampling period (19.2 mm) was recorded on 15th January. Relatively higher MP abundance (124.3 pieces L⁻¹) than found in all other samples except on 1st January was recorded in samples taken a week later, on 23rd January. This spike on the 23rd January may be attributed to the amount of rainfall that occurred between the 12th –

17th January. However, the absence of more samples taken closer to these dates makes it difficult to imply rainfall as a possible cause for the spike in MP abundance.

There was a 19% increase in MPT abundance from 2nd to 3rd January. However, on the 4th January, MP abundance had returned to its pre-rainfall value. Previous studies (Hitchcock and Mitrovic, 2019; Hitchcock, 2020; Zhao *et al.*, 2015) have found that rainfall is a significant factor for MPs abundance in rivers. Hitchcock (2020) found that MP abundance was 40 times higher after two days of heavy rainfall than before, increasing from 400 particles per m³ to a maximum abundance of 17,833 particles per m³ during the peak rainfall. Rainfall increases the turbulence of the water, thus increasing the energy within the river. As a result, MPs are resuspended and likely to be present in more significant numbers than times of no rainfall when MPs are likely to sink and are stored in the benthos (Horton and Dixon, 2018). Due to a single rainfall event during the study period, the effect of flow velocities on MP could not be analysed and a significant correlation between rainfall and microplastic abundance could not be observed.

7.3.3 Characteristics of microplastics

The shape, colour and length of MP observed were recorded during the present study. The intention was to classify MPs shape into six groups (fibres, fragments, bead, foam, pellet and other) (Figure 7.3 and 7.4). Fibres (MPF) (98.95%) were the most abundant throughout the study, whilst fragments (1%) and other (glitter) (0.5%) made up the rest; no beads, foam or pellets were recorded (Figure 7.4). Whilst fibres were found in every sample, fragments were not found on the 30th and the 31st December. Five pieces of glitter were recorded (4 pieces on the 1st January and one piece on the 3rd January 2020) and classified as “other”. Fibres being the most dominant is similar to other studies such as Salvador Cesa *et al.* (2017), who found

that fibres are predominant in all water bodies. They can enter rivers through multiple sources, but the most likely is through the clothes shedding fibres during the washing process and entering rivers via wastewater treatment plants. Browne (*et al.*, 2011) found that a single garment can produce >1900 fibres per wash. Fibres may also be in high abundance due to sampling close to the river Thames' edge, as this is where the sewage outflows or effluents are likely to discharge (Luo *et al.*, 2019).

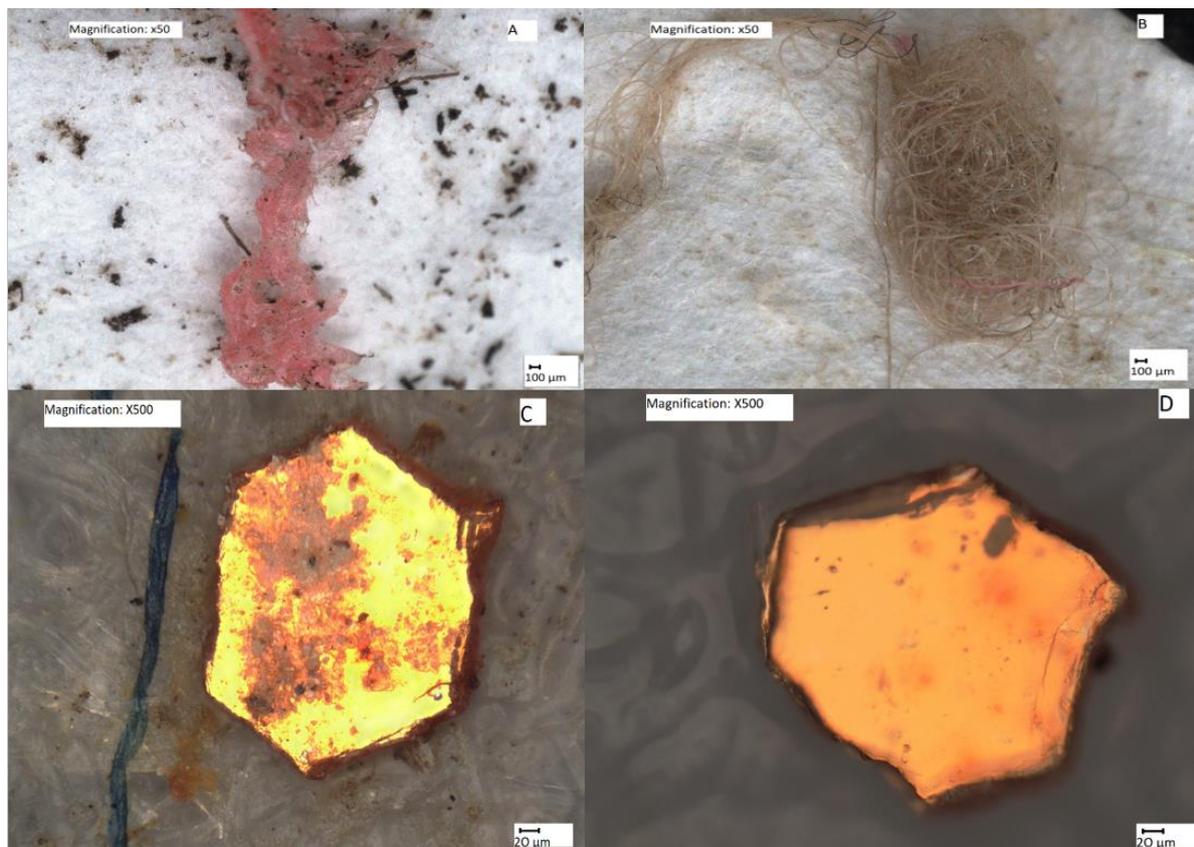


Figure 7.3 Types of microplastics observed in water samples collected from the River Thames, Westminster from 29/12/19 - 5/1/20 including 23/1/20: A) Fragment – has rough or uneven edges with irregular shape, B) Fibre – frayed ends, same width throughout, C) Fibre and “Glitter” – holographic, and D) Glitter.

In total, nine different plastic colours were recorded: blue, black, red, white and others. Black (93%, 2566 pieces) was the most abundant colour category, followed by red (3.4%, 94 pieces) and blue (2.3%, 64 pieces) throughout the study (Figure

7.4). Similar studies on estuaries also show a high abundance of coloured microplastics due to the intense human activities in the area and along the river (Zhang *et al.*, 2018; Zhao *et al.*, 2015).

The microplastics were put into five size categories: <0.5mm, 0.5-1mm, 1-2mm, 2-3mm, 3-4mm and 4-5mm. Smaller MPs (<0.5mm) were in high abundance throughout the study, making up to 50% at times during this study and 62% on the 1st January (Figure 7.4). The high presence of smaller MPs may result from fragmentation of larger pieces of plastic within an estuarine system from physical variables (salinity, light and temperature) and microbial degradation (Fernandino *et al.*, 2016). The increase in smaller MPs present on the 1st January may be due to fragmentation of firework casing. However, further studies would be needed to confirm this.

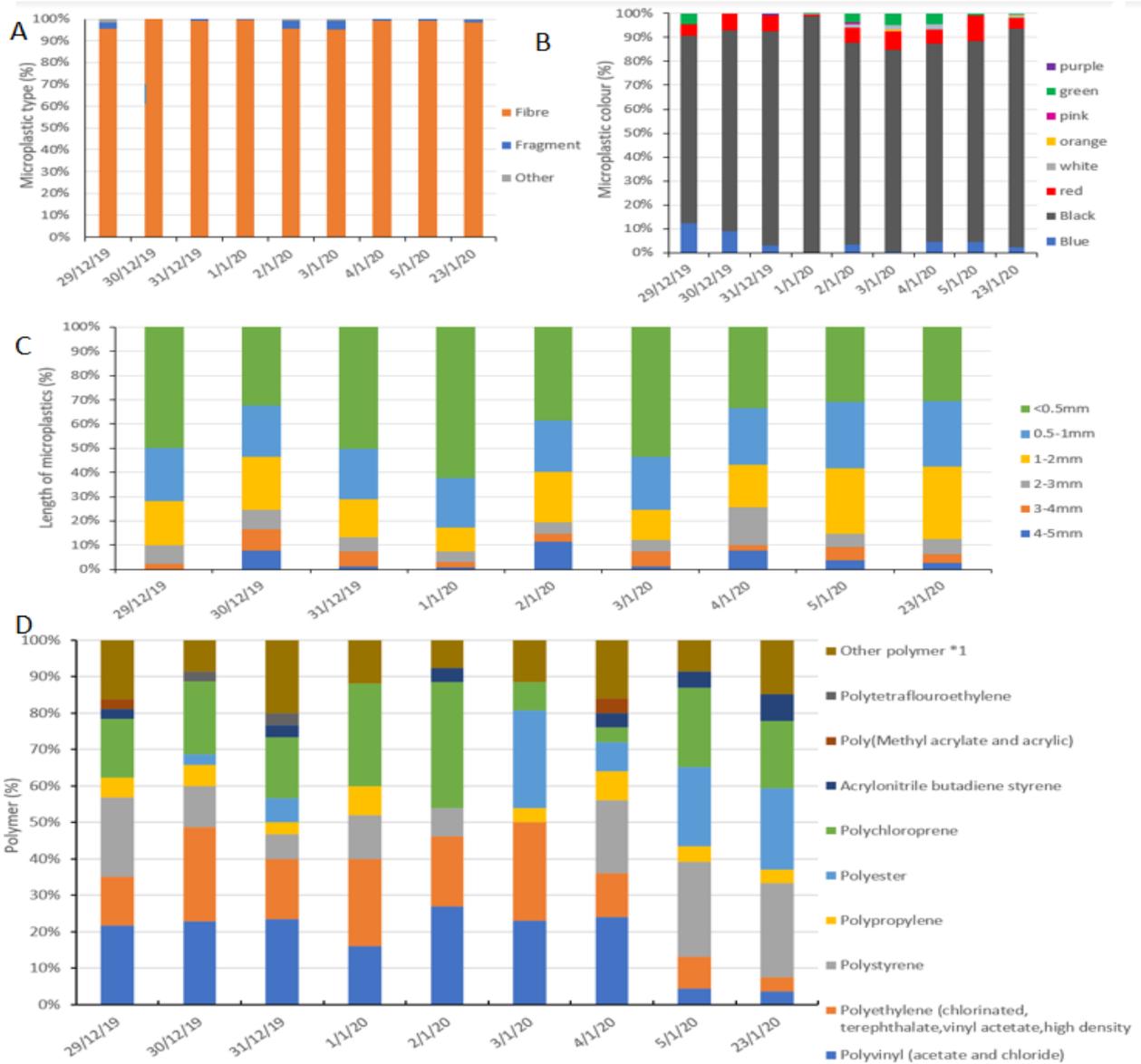


Figure 7.4 Measurements of MPs in water samples collected from the River Thames, Westminster from 29/12/19 - 5/1/20 including 23/1/20: A) Abundance of MP types, B) Range of colours, C) % composition of MP lengths, and D) % Polymer identified via FTIR.

A total of 354 pieces taken from the samples were identified using FTIR. As a result, 24 different polymers such as polystyrene, polyethylene and polychloroprene were identified, as well as natural material (i.e., sand and chitin) (22 pieces), anthropogenic microfibres (38 pieces) and no hit (41 pieces) (Figure 7.4). The most

dominant polymer where polychloroprene (e.g., rubber) (13.3%, 47 pieces), followed by polyvinyl chloride (PVC) (13%, 46 pieces) and polyethylene (PE) (12.15%, 43 pieces). These are the most common polymer types produced globally and used worldwide, mainly within the packaging industry (Andrady, 2015). They are commonly identified in aquatic environments, marine and freshwater, and the associated with sediment and organisms (Zhang *et al.*, 2017). Previous studies on the river support these results of fibres dominating counts as well as Polyethylene (PE) and polypropylene (PP) being found (Horton *et al.*, 2018; McGoran *et al.*, 2017; Rowley *et al.*, 2020). Styrene butadiene (2%, 7 pieces) was also identified, suggesting the presence of TWP in the River Thames (Krieder *et al.*, 2019). The presence of TWP is to be expected due to the location and proximity of the site of main roads to the river, especially within the London region. Boucher and Friot (2017) estimate TWP's contribute to 28% of primary microplastics in the ocean. However, due to the methodological limitations within microplastic studies TWP's are only mentioned in 1% of environmental studies (Kole *et al.*, 2017).

The types of plastic identified via FTIR may also be due to the plastic density as only the surface water was sampled. Natural material (6%, 22 pieces) and anthropogenic microfibrils (11%, 38 pieces) also made up a percentage of FTIR samples. In total, 11.6% (41 pieces) of samples could not be identified via FTIR.

On visual observation, the water sample on the 1st January 2020 was much darker than the water sample collected on any of the other sample days (Figure 7.5). After

the firework event, three pieces of gold glitter were recorded and later tested with FTIR, and these were identified as PET.



Figure 7.5 Observed colour differences of water samples taken from the River Thames, Westminster on the 31/12/19 (clear) and 1/1/20 (dark).

7.3.4 Cross-contamination

Potential cross-contamination sources were tested MP from plastic high-density polypropylene (HDPE) bottles used to hold and transport the environmental samples and distilled water used to irrigate the filtering system (Table 7.2). Three plastic bottles were rinsed with distilled water and then filtered through filter papers to adhere to the same experimental procedure. Filter papers were also used to check for atmospheric contamination in the laboratory. The contamination results were added to the statistics by removing the contamination found from each water sample.

Although cross-contamination controls were taken due to the size and abundance of microplastics, particularly microfibres, contamination cannot be ruled out.

Due to rinsing the equipment with distilled water, distilled water (3 bottles of 3l) was also tested and found a total of 2 fibres; 1 blue and 1 black (Table 7.1). Desk-based filters (10) did contain plastics (8 fibres; 3 blue, 3 black and 2 red) which were considered, as did the high-density polypropylene (HDPE) bottles (5 fibres; 3 black and 2 red). Some fibres from contamination controls were sampled using FTIR (Table 7.1) in total. Five randomly selected fibres were selected out of the 15 that were found in or on for the cross-contamination controls. Two black fibres were identified as polyethylene terephthalate (PET), one black fibre as polypropylene (PP) and two red fibres, high-density polypropylene (HDPE).

Although plastic laboratory equipment was used, it was limited, and glassware and porcelain equipment were used as much as possible. Due to practicality and safety issues with transporting large amounts of water, HDPE bottles were used instead of glass bottles. Contamination issues are common and reported among studies due to the nature and size of microplastics (Browne *et al.*, 2011; Dris *et al.*, 2016; Foekema *et al.*, 2013; Lusher *et al.*, 2017).

7.4. Conclusions

Microplastic pollution leads to a vast range of potential impacts on wildlife and humanity, with the leading source being human activities itself. Many studies have been conducted to examine the effects of human activity on MP abundance in the surrounding environments. A limited number of research studies look at fireworks as a source, and studies that mention fireworks as a source refer to plastic firework

casing classified as a macroplastic (Filella *et al.*, 2021; Ory., 2020). The results of this study show a clear indication that fireworks are a potential source of MP pollution influx within a short space of time in estuarine environments. A 1051% increase in MP abundance was observed between the 31st December 2019 to the 1st January 2020, increasing from 44.3 pieces per l to 510 pieces per l within 24 hours, with the only major event in the area being the New Year firework celebrations. Although, there is no clear link between the impact of rainfall and MP abundance in this study due to a lack of rainfall events, it cannot be ruled out as having an impact on MP abundance within the River Thames. Whilst this study focused on a single large event it could imply that many small personal at home displays would have the same effect. This study showed that fireworks can have short and long-term impacts on the environment, not just from an atmospheric pollution point of view but also plastic pollution that needs further exploration. As such, low pollution options or alternatives, i.e., drones, should be considered to prevent or lower the impacts these displays cause. Unfortunately, due to the Covid-19 pandemic and secrecy of the 2021 New Year celebration plans, the 2020 and 2021 displays could not be compared to see how the impact on MP abundance varied. However, these displays appear to result in an influx of pollution in one area within a short period, which has unknown consequences on the area's ecology and biodiversity.

Chapter 8: Summary and conclusions

This PhD thesis investigated microplastic (MP) abundance within the river Thames. Microplastic studies have been expanding for many years. There is a growing interest in the abundance and impacts on freshwater and river environments, which have lacked investigation compared to the marine environment. The river Thames is one of the most well-known rivers in the UK and is economically and commercially significant, with multiple potential MP sources. As sampling got underway, the Covid-19 pandemic made its presence known and, as a result, had worldwide consequences. The pandemic impacted the investigations undertaken during the process of sampling and carrying out this thesis. As a result, objective **3** has been expanded to include the influences and effects of the Covid-19 pandemic on changes in MP abundances.

8.1 Objective 1: Determine the extent of microplastic abundance along the tidal section of the Thames River and estuary;

The first objective of this thesis was to assess the amount of MP pollution present within the tidal section of the river Thames and its estuary. To address this, eight areas and ten sites of the river Thames from Teddington Lock to Southend-on-Sea were consecutively sampled monthly from May 2019 - May 2021. Microplastic abundance within the river Thames has previously been investigated; however, previous studies have investigated MP abundance in the tributaries of the river Thames, the non-tidal section of the river Thames, and sediment samples within the river Thames as well as organisms such as fish and MP concentrations. Before conducting this research, no studies specifically collected surface water and investigated MP abundances at multiple sites along the tidal section of the river

Thames. Whilst some studies looked at macroplastics carried out numerous times a year with the help of citizen science, there was not a baseline of continuous data for MP abundance in surface water specifically.

To fully answer this objective, MP abundance was put into two categories: 1) concentration – how much and where, and 2) what types – morphology such as fibres or particles as well as colour and polymer types.

8.1.1 Microplastic abundance

Microplastics were abundant throughout the river Thames. Every water sample taken had the presence of MPs, which is consistent with other studies. The mere presence of MPs shows that rivers, especially the river Thames, have a continuous input of MPs from various sources. Microplastic abundances fluctuated amongst the sites and samples, which is also supported by other studies. This is especially the case when comparing studies investigating the same rivers. This thesis consisted of multiple areas with eight central locations with three 1 litre replicates of water sampled every month for 24 months resulting in over 576 litres of water being sampled and above 9,460 pieces of MP being counted.

The average MP abundance of L^{-1} varied within this thesis. The largest abundance was observed during the New Year firework study (**Chapter 7**) on the 1st January 2020 (510 pieces L^{-1}) at Westminster, compared to Limehouse (**Chapter 4, 5 and 6**), which had the lowest observed abundance on 19th June 2020 (0.33 pieces L^{-1}). Overall excluding the data gathered for the experiment carried out in **Chapter 7**, Barking Riverside had the highest average (2019 - 2021) MP abundance with an average of 18.82 pieces L^{-1} . The lowest average abundance was observed at Teddington Lock (10.01 pieces L^{-1}). One hypothesis was that MP abundance would

increase downstream as more MPs would be added to the river as it made its way to open water; however, the average at Southend-on-Sea was 10.25 pieces L⁻¹, a 2.4% increase in abundance from Teddington (10.15 pieces L⁻¹) with the sites in between excluding Limehouse having a higher average abundance. Whilst the average MP abundance did not increase as much as expected from each end of the river Thames, this may be due to changes in river morphology such as depth, width and tidal flow, thus causing a difference in water volume at the sites.

It became apparent that differences in abundance at each site across the sampling years were significant. Whilst this may be due to many factors such as months sampled, seasonality, rainfall and the Coronavirus, which will be further explained in **objectives 2, 3 and 4**. Microplastic abundances decreased from 10.01 - 18.82 pieces L⁻¹ in 2019 to an average range of 4.2 - 8.73 pieces L⁻¹, which decreased by over 115 % from 2019 - 2021. Previous studies on the river Thames have shown an MP abundance ranging from 24.8 pieces m³ (Putney), 14.2 pieces m³ (Greenwich) (Rowley et al., 2020), to 84.1 pieces L⁻¹ (Dunn, 2019).

The results of this thesis and research support the hypothesis that MPs are present within the surface water of the river Thames. However, more data and further investigation will be needed to see if the apparent current downward MP abundance trend continues.

8.1.2 Microplastic types

Other than visual counting of MPs present within the water samples, they were categorised by size, colour, type and polymer. As this categorisation is required for MP studies, evidence of this data can be found throughout **chapters 4, 5, 6 and 7**.

Microplastics were found in various colours, sizes, types and polymer compositions. Fibres were the most dominant, compatible with similar MP abundance studies within rivers and other environments. As the majority of MPs fell within the fibres and fragments categories, it is consistent with the opinion that many of the MPs entering riverine environments are a result of the fragmentation of macroplastics, thus resulting in copious amounts of secondary MPs (Osorio *et al.*, 2021). The prevalence of fibres suggests that they are the result of shedding of clothing during the washing process and enter the river via WWTP's. Solutions to this problem have been suggested the most recent suggestion is the fitting of microfiber filters inside new washing machines. This suggestion is gaining traction with a new bill being introduced into parliament in January 2022 (*UK parliament, 2022*). However, with littering common especially white goods questions need to be raised on how these filters will be correctly disposed or recycled at the end of their life. In theory the use of filters appears to be a satisfactory solution to the issue however, more information is needed concerning the practicality (can the filters be easily replaced, cost implications on the household and how they will be disposed of etc.).

Over 40 distinct types of polymers were found during this thesis. The most commonly identified were PVC, PS, PCP, PP, and PEC. This is not surprising as these are the most widely produced and used polymers worldwide used for a variety of material such as packaging and textiles industry. Rubber and Acrylonitrile butadiene styrene (ABS) or more commonly identified as Tire wear particles (TWP), were also observed at sites within close proximity to major roads such as

Westminster, London Bridge and Limehouse. These sites were in the heart of London, Westminster and London Bridge sites also have bridges within very close proximity that have a lot of road traffic.

One piece of Zein purified and four pieces of alginic acid were identified from samples taken from 2021. These appear to be classified as biopolymers. However, this is something that would need to be studied and investigated further.

8.2 Objective 2: Determine potential microplastic sources along the Thames and the effect they may have on the abundance.

Fibres were the most dominant type of MP within the river Thames. Fibres have been linked to WWTP, specifically the use of washing machines or laundry water (Browne *et al.*, 2011). Fragments were the second most abundant. The presence of Fibres and Fragment particles shows that most MP is from secondary sources and the fragmentation of macroplastics. Macroplastics were observed throughout this study, although it was not included in the data (**Chapter 4**).

Macroplastics in the form of plastic drink bottles and wrappers (**Chapter 4**) were observed, especially within Limehouse harbour. Whilst Limehouse harbour may be a collection zone due to low flow or barriers, in this case, locks to keep the water height constant within the harbour, the presence of moorings and the site being located within a highly populated area may be a potential source of littering. However, data gained from this thesis concludes that harbours are a source of macroplastic and thus result in microplastics, which cannot be obtained due to a lack of data gathered on littering in this area.

The presence of plastic bottles and wrappers in the form of macroplastic confirms the presence of litter within the river, high levels of MPs identified as PVC, PS and

PE, which are commonly used polymers within the packaging, textiles, and building industries also support this observation (**Chapters 4, 5, 6 and 7**). Transparent MPs were found during this study (**Chapters 4, 5 and 6**). This, coupled with the presence of polymers commonly found within the packaging, supports the suggestion that littering, or the incorrect disposal of the packaging is contributing to MPs within the river Thames as transparent plastic is common within plastic food containers, plastic bags and plastic bottles as well as other packaging as it keeps costs lower due to not having to add dyes to the plastic (Su *et al.*, 2016).

Pellets and nurdles were observed in MP types along the river Thames, suggesting using raw plastic material entering the river (**Chapters 4 and 5**). There are multiple potential sources of this along the river, with numerous businesses or factories that use this type of material that run alongside the river, particularly at Barking Riverside and Tilbury. However, these sites did not have the highest abundance of these types of MP.

Polymer identification allows for the potential of other sources of MPs within the river. This thesis (**Chapters 4 and 7**) shows the presence of ABS or Tire wear particles as MPs. Tire wear particles were identified at most sites but were highest at Westminster, London Bridge and Limehouse. These particles have been found within other rivers that run alongside roads; however, they are not often recorded or detected due to technical issues or discrepancies.

The river Lea tributary is a potential source of MPs into the river Thames, although it could equally be argued that tributaries are not a source of MPs but a transport system (**Chapter 4**). Like much of the tidal river Thames, the river Lea is subjected to watercrafts such as houseboats and pleasure crafts, which can be a source of

MPs. The river Lea is also highly affected by pollution from domestic water and industrial processes that can result in MPs entering the system.

Wastewater and sewage treatment systems have been noted as sources of MPs within rivers, and this is also supported by data gathered from this study. As previously mentioned, high fibres are shown to result from WWTPs. Barking Riverside had the highest abundance of MPs (18.82 pieces L⁻¹) compared to any other site from 2019 - 2021 and is within proximity to Becton sewage works which is the largest STW in Europe (Grassly, 2022) (**Chapter 4**).

Chapter 7 discussed the potential source of MP from fireworks, whilst macroplastics have been identified as originating from firework events with packaging and cones from the top of fireworks being found scattered on the ground. This thesis identifies fireworks as a source of MPs within the environment, a novel idea that needs further investigation at the time the paper was published.

8.3 Objective 3 Changes in plastic pollution quantities depending on site or influences such as rainfall and seasonal effects as well as through the Covid-19 pandemic

During this thesis, no sample contained the same MP quantity as other sites during the same month or season (**Chapter 5**). Whilst there was yearly variation between MP abundance and seasonality, there may be many contributing factors, such as the Covid-19 pandemic (**Chapter 6**) or rainfall (**Chapters 5 and 6**). Rainfall coupled with season did impact MP abundance, with spring 2019 the lowest rainfall having the highest MP abundance. This can be explained by MPs collecting within the river for longer than possible due to a low river flow. However, that is beyond the scope of

this study as flow was not investigated. Whilst storm events impacted MP abundance (**Chapter 5**), specific reasoning for this could be linked to CSOs, river flow or multiple other factors; that have not been determined due to having insufficient data (**Chapter 5**).

The Covid-19 pandemic (**Chapter 6**) provided a unique sampling opportunity due to the increase in plastic production coupled with the public order to remain home, reducing the potential to litter whilst increasing the amount of household plastic due to deliveries of groceries and fast food. The effect of this was a decrease in MP abundances from pre-Covid-19 samples to samples taken during lockdown 1. However, Lockdown 2 had a higher MP abundance than at any other point of the Covid-19 pandemic. There were no significant differences between any site and MP abundance during the Covid-19 Pandemic. Pellets, however, did decrease in abundance during the Covid-19 pandemic, possibly due to only essential workers being required to go to work and businesses working from home or with limited staff. As a result, plastic fabricators or businesses requiring pellets may have decreased, but this is beyond the scope of this study as data has not been released concerning this explanation to date.

What is evident from this thesis is that MP abundance fluctuates with multiple factors contributing to abundance especially as human activity/ behaviour and environmental factors can both impact MP abundance at the same time thus blurring the ability to investigate factors separately.

8.4 Objective 4: Determine potential sources of microplastics in the Thames and use this information to highlight similar issues and preventative measures to stop the flow of plastic pollution into rivers, from wastewater treatment plants and industrial sectors

This thesis confirms the presence and potential sources of microplastics present within the surface water of the river Thames, UK (**Chapters 4, 5,6 and 7**). This is not unique, as microplastics have been found in all environments and within rivers worldwide, with many rivers facing the same issues and sources shown within this thesis. Whilst an urgent preventative measure is needed to ensure the efficient and correct plastic end-of-life practices, whether it is from collection, recycling or disposal methods to form a circular plastics economy due to the complex nature and minuscule size of the plastic, this may reduce but not entirely prevent the introduction of plastic into the environment. An example of where it may not benefit is within plastic production itself and the use of nurdles or raw plastic material used by industries of plastic output, which were observed within this study (**Chapters 4, 5 and 6**).

Previous studies noted Wastewater systems (**Chapter 4, 5 and 6**) as a primary contributor of microplastic into rivers, especially microfibers. Multiple preventative measures have been patented, funded, used or investigated worldwide. Some examples include the GoJelly Project funded by the European Union, which uses jellyfish mucus to capture nanoplastic from wastewater; laundry balls to capture microfibers in laundry machines or filters attached to washing machines to capture. As well as reducing the number of microfibers that can enter wastewater treatment systems works are currently being carried out to update the historic sewage systems in London (Thames Tideway, 2022) to reduce the amount of sewage entering the river, especially during periods of heavy rainfall.

Limehouse harbour (**Chapter 4**) was observed to have high microplastic abundances and appears to be a plastic collection zone, although the further investigation will be needed. This is supported by other studies with similar findings

due to reduced flow rates due to obstructing structures that increase microplastic deposition (Ballent *et al.*, 2016). Similar structures, including dams, weirs, and reservoirs, have also been identified via studies. Mr Trash Wheel (MrTrashWheel,2022), a harbour water wheel, is currently used in a Baltimore harbour to collect and remove macroplastic. Seabins are a similar idea that works by filtering water to contain any floating material. There are currently over 800 Seabins in over 50 countries. There are presently seabins within the river Thames at St Katherine Docks (3 Seabins) and London Docklands (1 Seabin).

The presence of tire wear particles (TWP) (**Chapter 4**) is common, especially in waterways in cities or heavily populated areas or close to highways due to high traffic.

Firework displays (**Chapter 7**) have been identified as a potential source of microplastics, whilst macro material has been identified to be from fireworks, such as rocket cones in previous marine studies, microplastics have not (Naik and Patil, 2015; Seidel and Birnbaum, 2015) as fireworks are released worldwide for multiple reasons from small gatherings on family occasions to large events such as Diwali and New Year. Many of these large-scale events occur via water. Whilst fireworks are popular alternatives, such as light shows using lasers or drones can be used to prevent plastic pollution from the potential source identified during this study.

The presence of biodegradable or anthropogenic material (**Chapters 4, 5 and 6**), whilst interesting as it may signal further investigations are needed, is also concerning as whilst it shows public perceptions are changing, the development of biodegradable plastic products needs to be investigated further as they still contain chemicals that give them abilities to act like plastic whilst at the same time allowing

them to fragment into smaller pieces that may last the same amount of time as plastic within the environment.

Whilst preventative measures are needed, there must be a worldwide effort to stop the flow of plastic pollution effectively. However, with extreme weather events becoming more common such as hurricanes, cyclones and flooding and plastic being such a common item within society, it will always make its way into the environment. The only effective preventative measure is to stop producing and using plastic, which is unrealistic today.

8.5 Challenges and Limitations

The majority, if not all, of MP studies mention the impact of having an underdetermined standard whilst sampling, processing and analysing MPs. During this study and **chapters 4, 5, 6 and 7**, the methodology involved light microscopy to visually identify and categorise MPs and further verify this identification through Fourier Transform infrared spectroscopy (FTIR). However, as mentioned in **Chapter 3 and Supplementary Table 1**, methodologies and reporting of MP vary, which hinder the ability to compare data and results between studies.

The reliance on visual inspections when categorising the shape and colours of MPs causes concern. There is a high chance of human error when counting samples, especially when abundances enter the hundreds. There is also no standard classification for MPs as of yet. There is still no definitive definition of the size range of MPs whilst it is widely accepted as <5mm. There is still variation, making comparisons hard. There is also no standard for types of plastics whilst it is commonly accepted that fibres are long and the same width whilst fragments have uneven edges, phrases a definitive definition of the difference between bead and

pellets are not clear. However, shapes such as sphere/ bead, irregular, fragmented and granules have also been reported. This distinction of characteristics makes it difficult to compare between studies, especially as shape may be subjective to the person's choice.

An ongoing issue with microplastic studies is the particle's size. There is a high chance of potential loss, especially when transferring the piece to the FTIR or cross-contamination. Whilst many methodologies involve visual identification and further identification through FTIR. However, due to the size limitations of FTIR, suspected MPs under 500µm cannot be processed by FTIR. It is possible in theory to scan MPs under 500µm in practicality, but it is not possible due to the minuscule sizes. The possibility of losing the sample during transfer is massive. As a result, there is an underestimation of the smaller size categories of microplastic due to the inability to analyse pieces in detail once they reach a specific size. In this thesis, MPs were required to have a length greater than 200 µm to reduce the chance of losses during transfer; however, this was not 100% effective, and some samples were lost.

An issue that presented itself very early on within this study was how much water to sample from each site each month. There is no agreed standard; the sample size varies from 500ml to 200 L (Supplementary Table 1) among freshwater and marine water studies. Whilst substantial sampling may be possible for short-term studies, this study encompassed monthly samples over 24 months across eight locations. Even without the time constraints that Covid-19 presented, it was evident early on that 3 Litres made up of three 1 litre replicates of water for each site in a month was still 24 Litres of water and would be very time-consuming to process and analyse each month. A larger sample was not practical. There was not enough time, and as there was no standard guideline on sampling and replicates, an appropriate sample

and replicate regime was designed from various studies and adapted to work within this study.

The decision to only investigate microplastic abundance in the tidal section of the river Thames was decided due to previous and continuous studies undertaken by the Centre of Ecology and Hydrology, which investigate microplastics in water and sediment samples in the non-tidal section of the river. Due to limited studies on the tidal section and time constraints, the decision to focus solely on this section of the river was taken. To investigate how much microplastic abundance changed within the river water, samples were taken at Teddington, where the river becomes tidal.

One unprecedented impact on this study was the outbreak of Covid-19 (April 2020). The outbreak of Covid-19 and subsequent lockdowns, whilst providing a unique sampling and data analysis, also limited the study. Like many, once lockdowns were announced, people were required to stay at home unless essential this resulted in a few weeks of not knowing if sampling was going to take place or not. Luckily permission was granted, and sampling could continue except for business-based sites such as Westminster Boating Base, Tate and Lyle – North Woolwich and Barking Riverside. A decision then had to be made on whether to stop sampling at these locations and what was assumed at the time missing the month of May 2020. Whilst changing the Westminster Boating Base site was easy, an area near the Millennium eye had been used in December 2019, was appropriate, and safe. Once it became clear that the Lockdown lasted longer than expected, alternative sampling locations were investigated. As sampling had been taking place at these sites for almost a year, by this point, decisions were made to try and find alternative sampling sites within the proximity of the original site. Whilst this was not possible with the Barking Riverside location, a site was located close to the original North Woolwich

(Tate and Lyle) site. The alternative site for Tate and Lyle was on the same side of the river, and the same side of the Thames barrier, whilst the site conditions were not the exact sampling here, allowing sampling within the North Woolwich area of the River Thames to continue.

Covid-19 also caused further challenges as laboratories were closed. This meant monthly site samples were kept at the family home for months. Whilst samples were kept in the dark, cool place, they were left and unfiltered this led to some samples growing bacteria on the bottles in which they were stored. Whilst it has been documented that MPs can break down from bacteria, only ten were identified during research. Most needed extreme heat or cold made the likelihood of this bacteria being found in the river Thames unlikely. However, it also posed the question of whether to investigate these bacteria to see if it would affect MP presence within the sample; ultimately, due to time constraints due to the pandemic and subsequent lockdowns, bacteria analysis was impossible. The time constraints also resulted in less FTIR and length analysis occurring than what would have been preferred.

The Covid-19 pandemic also resulted in the shortening of a study conducted for this research. The impact of the firework display on MP abundances within the river Thames (**Chapter 7**) was cut short due to the announcements that the government were cancelling the New Year London firework displays. Although this eventually took place, members of the public were not told, which meant whilst this study managed to gather some data (2019-2020), further planned data gathering and analyses were not achieved, leaving many answers unsolved.

8.6 Contribution to wider research

Whilst MPs are a growing topic and public interest, research into rivers compared to the marine environment is still limited. As a result, many rivers worldwide have not been investigated to see how much plastic, mainly MP is present within their water. As plastic, including MPs, the main transport system from land to the sea is by rivers, as much data as possible is needed to understand the best way to prevent or reduce the influx of MPs into oceans and to know how MPs act within this environment. Therefore, this research contributed to understanding the role of MPs within rivers, particularly the river Thames, as a transport system by measuring MP abundances along the river Thames tidal section at eight locations. It has established a baseline of monthly data at these locations over approximately 24 months, May 2019 - May, 2021. As well as identify potential sources of MPs based on polymer type, morphology and size. This research focused on gathering data on MP abundances within the river Thames, its sources and factors that may affect these abundances as research on MPs within rivers, especially the river Thames, are scarce, with only a few studies investigating the river over the last few years. Currently the only investigations known to this author concerning plastic pollution within the River are from Thames 21 (tidal section) and Centre of Ecology and Hydrology who currently investigate plastic pollution in the non-tidal section of the river.

This thesis was conducted during the Covid-19 pandemic. The Covid-19 pandemic saw many unprecedented events, from national lockdowns and the use of personal protective equipment (masks, gloves and hand sanitisers) by millions worldwide. This led to an increase in plastic production to cope with demand. Data for this thesis started six months before cases of Covid-19 were first reported and carried on during lockdowns and one month after the last Lockdown in April 2021. This provided a unique opportunity to investigate the impact of the pandemic and subsequent

lockdowns on MP pollution within the river. As a result, this research can be used to investigate the Covid-19 pandemic in the short term and as part of a more extensive study to investigate the long-term impacts of the pandemic.

This thesis investigated sources of MPs. Through this, a potential uninvestigated source in the form of fireworks was identified. Previous research concerning macroplastics has identified firework cases as a source of plastic pollution. However, when conducting and submitting **chapter 7**, "Microplastic abundance in the Thames River during the New Year period", for peer review, there had been no mention of fireworks as a source of MP pollution or in-depth study on the impact of large firework displays on MP abundance. Although investigations into the effects of large firework displays were limited during this thesis, it has identified a potential area of interest for future work.

8.7 Future work

Due to the growing nature of MP studies, this thesis highlights and recognises areas that could be expanded on in future studies to further expand on knowledge gained or questions left unanswered from this study;

1. Seasonality should be further investigated to assess the short-term and long-term impacts of fluctuations from extreme weather such as storms and heat waves.
2. This study only collected water from one edge of the river, which should be expanded by investigating both edges and the middle of the river. Thus,

investigating how MP abundance can vary within the same section of a river and potential factors that may influence this.

3. This study did not investigate MPs at different depths. This should be investigated to understand other spatial differences and how MP density contributes to the microplastic abundance to varying depths within a river.
4. As some MP sink, MPs within sediment should be investigated to explore the differences between MPs with sediment and water within the river. This could be further expanded to investigate hydrology's effects on the sedimentation of MPs within waterways.
5. This thesis identified a potential source of MPs in the environment in the form of fireworks. This study did aim to investigate this source further; however, the Covid-19 and cancellation of NewYears' eve fireworks in 2020 and 2021 prevented this. As a result, fireworks need to be investigated further to see if the data gained during this thesis is correct or if an unexplored factor contributed to the high levels of MPs identified after the New Year display. Further work could investigate hourly changes of MP abundances before and after the firework displays for 24 hours to see when MP abundance peaks, as well as looking at a site downstream and upstream of the site to compare MP abundance.
6. Whilst MP abundance may not have had a significant difference before, during or in the month after the last Covid-19 Lockdown, plastic production increased dramatically. Future work needs to analyse the long-term impacts of the Covid-19 pandemic on MP pollution. As plastic produced to cope with the demands of a pandemic will take years to break down, macroplastics such

as masks are evident now, and the actual impacts of Covid-19 may not be apparent for many years.

Conclusion

This thesis reports findings that contribute significantly to knowledge of MP pollution abundances within the tidal River Thames and its estuary. This research showed a potential source (fireworks) of MPs in the previously unexplored environment and needs further investigation. In addition, this work has highlighted key areas that need to be investigated in future work to further our understanding of a critical transport mechanism of microplastic movement from land to oceans. The results obtained during this research can provide a baseline of MP abundance along the river Thames, which can be used by stakeholders such as the Environment Agency, Thames Water and non-profit organisations to help remove plastic waste from the river.

Supplementary Material

Supplementary Table 1. Methods for collection, analysis and identification of Microplastics in Microplastic studies

Reference	Location	Source	Sampling method	Water depth	Analysis method	Identification method
Abayomi <i>et al.</i> , 2017	East coast of Qatar	Sea	<ul style="list-style-type: none"> • Surface neuston net (SeaGear 9450, 0.5 × 1 M), 300 µm mesh 	Surface	<ul style="list-style-type: none"> • Digestion protocol (1 M Sodium hydroxide (NaOH), 10 M NaOH, and 16 M nitric acid (HNO₃)) • filtration 	<ul style="list-style-type: none"> • FTIR

<p>Abayomi <i>et al.</i>, 2017</p>	<p>Qatar</p>	<p>Coast</p>	<ul style="list-style-type: none"> • Surface neuston net from side of the boat 	<p>Surface</p>	<ul style="list-style-type: none"> • Sieved through a 20 µm mesh with ultrapure water to remove the salt. • Digestion protocol -Proteinase-K enzyme 	<ul style="list-style-type: none"> • Stereomicroscopy • FTIR/ near-infrared (FT-NIR)
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<p>Aliabad <i>et al.</i>, 2019</p>	<p>Chabahar Bay, Gulf of Oman</p>	<p>Bay</p>	<ul style="list-style-type: none"> • Neuston net (0 × 120 cm² rectangular opening, 250 cm long and 333 μm mesh size) equipped with a Hydro-Bios sample collector • Samples were collected 2 hours after low tide. • Samples were fixed with 2.5% formalin 	<p>Surface water</p>	<ul style="list-style-type: none"> • Wet sieving -5mm and 50μm stainless steel sieve. • Digestion protocol - 25ml of 30% hydrogen peroxide (H₂O₂) • Density separation protocol - sodium chloride (NaCl) powders • Filter protocol- 5.5cm 1.2 μm glass fibre papers (Whatman Glass Microfiber filter (Grade GF/C) by vacuum pump 	<ul style="list-style-type: none"> • Stereomicroscopy • ATR-FTIR
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					<ul style="list-style-type: none">• Further steps- rinsed with 20 mL of 0.5 M hydrochloric acid (HCl) and 50 mL distilled water and dried overnight.	
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Anderson <i>et al.</i> , 2017	Lake Winnipeg, Canada	lake	<ul style="list-style-type: none"> • Manta trawl; 333 mm mesh • Preserved in 70% ethanol 	Unknown	<ul style="list-style-type: none"> • Samples rinsed and large objects removed • Wet peroxide oxidation (WPO) treatment with Fe (II), heated to 75 °C 	<ul style="list-style-type: none"> • Visual inspection • Scanning electron microscope (SEM) • Energy dispersive X-ray • Spectroscopy
Atwood <i>et al.</i> , 2019	Po River	River	<ul style="list-style-type: none"> • mini-manta trawl (300 µm mesh) • collected in glass jars 	Unknown	<ul style="list-style-type: none"> • Fractionated – no description • Digestion protocol - enzymatic purification and WPO • Filter: glass-fibre filters grade MN 85/90 BF 	<ul style="list-style-type: none"> • ATR- FTIR

<p>Aytan <i>et al.</i>, 2016</p>	<p>Black sea</p>	<p>Sea</p>	<ul style="list-style-type: none"> • cylindro-conical WP2 net with 57 cm mouth diameter (0.25 m²), 260 cm long and 200 µm mesh 	<p>surface</p>	<ul style="list-style-type: none"> • Put in a Glass bottle and preserved in 4% borax-buffered formaldehyde • Separation protocol - gravity method (no further details) 	<ul style="list-style-type: none"> • Binocular microscope • No information on polymer identification
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<p>Bagaev, Khatmullina and Chubarenko, 2018</p>	<p>Baltic sea</p>	<p>sea</p>	<ul style="list-style-type: none"> • individual lowering of the 10-litre Niskin sampling bottles • Water from the surface was collected with black plastic (polyethylene) bucket • MultiWater Sampler SlimLine 12 at different depths 	<p>Water column – surface water and multiple depths (depths unknown)</p>	<ul style="list-style-type: none"> • Filter - 174 μm filters 	<ul style="list-style-type: none"> • optical microscopy • No information on polymer identification
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<ul style="list-style-type: none"> Bailey et al., 2021. 	<p>Hudson-Raritan Estuary, Staten Island, New York</p>	<p>River and estuary</p>	<ul style="list-style-type: none"> six sites were sampled in duplicate on July 26th, 2018, April 11, 2019, and April 16, 2019. collected by an R/V Rutgers boat 20.3cm diameter plankton nets (mesh size 80 or 150 μm). 	<p>Unknown</p>	<ul style="list-style-type: none"> wet sieving using soil sieves (2000, 500, 250 μm size). Organic digestion protocol -Fenton's reagent was added and heated to 75 °C Density separation protocol – NaCl left overnight 	<ul style="list-style-type: none"> ATR-FTIR
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<p>Baldwin <i>et al.</i>, 2016</p>	<p>29 Great Lakes tributaries in six states</p>	<p>lake</p>	<ul style="list-style-type: none"> • Neuston net -net mesh size was 333 μm 	<p>Surface and upper 20-35 cm</p>	<ul style="list-style-type: none"> • Put in a glass jar, preserved with isopropyl alcohol. • Sieving through 4.75, 1.00- and 0.355-mm mesh. • Organic digestion - WPO with Fe (II) catalyst at 75°C). WPO solution sieved through 125 μm 	<ul style="list-style-type: none"> • No information on polymer identification
<p>Barrows <i>et al.</i>, 2018</p>	<p>Gallatin watershed/ river</p>	<p>river</p>	<ol style="list-style-type: none"> 1. 1-1.3L of water collected with stainless steel sample bottles 2. wading, sample poles, kayaks or standing on ice 	<p>surface</p>	<ul style="list-style-type: none"> • Filtering protocol- Vaccum filtration using Whatman mixed cellulose nitrate 0.45 μm filter, 	<ul style="list-style-type: none"> • Stereomicroscopy • Micro FTIR

Browne <i>et al.</i> , 2011	West Hornsby and Hornsby Heights, New South Wales, Australia,	Wastewater treatment plant (WWTP) - effluent	Pre-cleaned glass bottles (750 mL) with metal caps	Unknown	<ul style="list-style-type: none"> • Density separation - NaCl • Filtering protocol - no information given 	<ul style="list-style-type: none"> • FTIR
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<p>Campanale, <i>et al.</i>, 2020.</p>	<p>Ofanto River</p>	<p>River</p>	<ul style="list-style-type: none"> • collected in February, April, October and December 2017 and May 2018 from one location • 3 plankton nets (2.5 m long, mesh size 333 µm and opening of 55 × 55 cm). • six replicates on the sampling day and a total of 30 samples throughout the whole sample regime 	<p>Surface water (45cm)</p>	<ul style="list-style-type: none"> • Wet sieved- 300 µm and a 5 mm stainless steel sieve. • weighed • Digestion protocol - 30% H₂O₂ in the presence of an iron (II) catalyst. • Density separation protocol - NaCl solution. • Filter - 1.2 µm glass microfiber filter. 	<ul style="list-style-type: none"> • 40X digital microscope (Keyence VH-Z 100 UR) • Pyrolysis–gas chromatography/mass spectrometry (Py–GC/MS)
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<p>Castillo <i>et al.</i>, 2016.</p>	<p>Quatars EEZ</p>	<p>Marine</p>	<ul style="list-style-type: none"> • Plankton tow nets (0.5 m diameter mouth, 2 m length, mesh size and cod end of 120 µm) • Transferred to a 250ml glass container 	<p>0.25m beneath the sea surface</p>	<ul style="list-style-type: none"> • Digestion protocol - 1 M NaOH, 10 M NaOH, and 16 M HNO₃ • Filtration protocol – no information given 	<ul style="list-style-type: none"> • Stereomicroscopy <ul style="list-style-type: none"> • FTIR • ATR- FTIR
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<p>Chinfak <i>et al.</i>, 2021</p>	<p>Bandon Bay and Tapi - Phumduang River</p>	<p>Bay and river</p>	<ul style="list-style-type: none"> • Samples were collected from 15 sites diurnally at 6- hour intervals and 2 low tides and 3 high tide periods at one location. • Collected via boat in triplicates of 5L 	<p>Surface water - 10cm</p>	<ul style="list-style-type: none"> • Filtering protocol - Samples were filtered using a vacuum pump using a vacuum pump, 47-mm diameter PALL® Ultipor N66 nylon membrane (5 µm pore size). 	<ul style="list-style-type: none"> • Stereomicroscope • Hot needle test <ul style="list-style-type: none"> • FTIR
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<p>Deng <i>et al.</i>, 2020.</p>	<p>Zhejiang Providence, China</p>	<p>Small bodies of water</p>	<ul style="list-style-type: none"> • Eleven sites were sampled from July- October 2018. Three replicates of 5L were collected at each site • collection method unknown. 	<p>Surface water 0-5cm</p>	<ul style="list-style-type: none"> • Filtering protocol - 20 µm nylon mesh filter (Millipore Nylon NY 2004700). • Organic digestion protocol -150 mL of H₂O₂ and using shaking incubator at 65 °C and 80 rpm for three days. • Filtered again - 5 µm nylon filter (PALL Nylon NCG047100). • Other protocols - filters baked at 450°C for 8 hours. 	<ul style="list-style-type: none"> • Stereomicroscope • µ-FTIR
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<p>Donoso and Rios-Touma, 2020</p>	<p>Rivers from the Upper Guayllabamb a river basin</p>	<p>Rivers</p>	<ul style="list-style-type: none"> • Four samples were taken from each of the five sampling points between March-June 2018. • Collected via a 250 µm mesh drift net composed of 4 sub-nets with dimensions of 35cm in height and 17cm in width each. • Samples were taken for a total of 20 minutes at each point. 	<p>Surface water</p>	<ul style="list-style-type: none"> • Stacked sieves 5 mm, 1.1 mm and 0.3 mm. • Organic digestion protocol -20 ml of 30% H₂O₂ and 20 mL of 0.05 M Fe (II), heated at 75 °C. • Density separation protocol - 5 mL of 5M NaCl solution, stirred and left overnight • Filter- Whatman glass fibre filters of 0.7 µm and 47 mm. 	<ul style="list-style-type: none"> • Olympus microscope • Tweezer test (If squeezer by tweezers and it does not break, it was classed as a plastic)
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<p>Eriksen <i>et al.</i>, 2013</p>	<p>Laurentian Great Lakes</p>	<p>lake</p>	<ul style="list-style-type: none"> • 333 µm mesh manta trawl 	<p>Unknown</p>	<ul style="list-style-type: none"> • Sieved into three size classes: 0.355–0.999 mm, 1.00–4.749 mm, >4.75 mm. 	<ul style="list-style-type: none"> • Scanning electron microscope <ul style="list-style-type: none"> • (SEM) • Energy-dispersive X-ray spectroscopy (EDS)
<p>Estahbanati and Fahrenfeld, 2016</p>	<p>Raritan River, central New Jersey, US</p>	<p>River</p>	<ul style="list-style-type: none"> • plankton nets (0.2 m diameter, 0.51 m long) with 153 µm mesh size 	<p>Unknown</p>	<ul style="list-style-type: none"> • Seived (4000, 2000, 500-, 250-, 125-, and 63-mm aperture size). • Organic digestion protocol -hydrogen peroxide then heated • Density separation protocol - NaCl 	<ul style="list-style-type: none"> • No information on polymer identification

<p>Fan <i>et al.</i>, 2022.</p>	<p>WangYu River Network</p>	<p>Rivers and lakes</p>	<ul style="list-style-type: none"> • Seventeen sites were sampled in December 2018 and March, June and September 2019 (spring, summer, autumn and winter). • 2L of water was collected from the surface and bottom of every site • Collection method - Rutter water sampler and transfer to glass bottles. 	<p>Surface and bottom (unknown depths)</p>	<ul style="list-style-type: none"> • 500ml sample was covered loosely with aluminium foil and placed in a drying oven at 50 °C for 48 hours. • Organic digestion protocol- Fenton reagent (20ml iron solution and 20ml 30% H₂O₂), left for 96h • Density separation protocol – Zinc chloride (ZnCl₂) solution. • Filtering protocol - using a vacuum pump with a polycarbonate filter 	<ul style="list-style-type: none"> • Stereomicroscope, • LDIR automatic chemical imaging system
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			<ul style="list-style-type: none">• No information on if replicates were carried out.		(5 μm , \O 47 mm, Millipore).	
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<p>Hayes <i>et al.</i>, 2021.</p>	<p>Four branch rivers (Xiangjiang River, Zishui River, Yuangjian River and Lishui River) flowing into Dongting Lake</p>	<p>Rivers</p>	<ul style="list-style-type: none"> • Samples collected - April 2018 • Collection method - using a Nylon plankton net (0.65 m in diameter, 1.55 m in length and 0.333 mm in mesh size, 0.333 mm is a fixed value) for 10-20 minutes 	<p>Unknown</p>	<ul style="list-style-type: none"> • Filtered protocol - membrane (47 mm diameter, aperture 0.45 µm, Millipore TMTP polycarbonate filter). • Organic digestion protocol - H₂O₂ at room temperature for 72 hours. • Filtered again - 0.45 µm membrane via vacuum pumping. 	<ul style="list-style-type: none"> • Zeiss metallurgical microscope (Axiovert 200 MAT, Germany) <ul style="list-style-type: none"> • FTIR
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He <i>et al.</i> , 2021	Yangtze River	River and Estuary	<ul style="list-style-type: none"> • Ten sites in July 2019 • Collection method-Trawling with a modified manta trawl - three triplicated 40 L surface water at each sampling point. • 40L was collected by a stainless-steel bucket and filtered through a 48 µm stainless steel mesh. • All samples preserved with 	0-30cm	<ul style="list-style-type: none"> • Sieved down to 300 µm. • Organic digestion protocol - 30% H₂O₂ for a week. • Density separation protocol - saturated NaCl solution. • Filter protocol - gridded 0.7 µm GF/F filters 	<ul style="list-style-type: none"> • Stereoscopic microscope • FTIR • ATR-FTIR
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			5% methyl aldehyde.			
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<p>Hossain <i>et al.</i>, 2022</p>	<p>Karnafully River</p>	<p>River</p>	<ul style="list-style-type: none"> • Nine sites • Samples were collected in March 2020 • Collection method - 10L bulk containers filtered through a plankton net (mesh size: 20 μm). • Reduced volume to 500ml, which was placed in glass jars. 	<p>10cm below the surface</p>	<ul style="list-style-type: none"> • Filtering protocol - using a vacuum pump, 20 μm nylon membranes with a diameter of 47 mm (Millipore, NY2004700). 	<ul style="list-style-type: none"> • Stereomicroscope <ul style="list-style-type: none"> • μ-FTIR
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<p>Huang <i>et al.</i>, 2021.</p>	<p>West River Zhaoping headstream to Gaoming river inlet</p>	<p>River</p>	<ul style="list-style-type: none"> • Twenty sample points during the summer of 2019 • 30-litre water samples • Collection method - via stainless steel drums. • Six replicates were collected at each site. 	<p>Surface water</p>	<ul style="list-style-type: none"> • Filter protocols- stainless steel screen (75 µm). • Organic digestion protocol - 30% H₂O₂ at 65°C and 100 rpm for 12 h • Further filtering - 0.45 µm filter paper by a vacuum pump and dried for 24 hours at 50 °C. 	<ul style="list-style-type: none"> • Metallographic microscope (MV5000(R/TR)) • ATR-FTIR
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<p>Jiang <i>et al.</i>, 2019.</p>	<p>Six Rivers in the Tibet Plateau</p>	<p>Rivers</p>	<ul style="list-style-type: none"> • Collected 9-12 July 2018. • 30 litres • Collection method - large flow sampler (KLL-S4, SEBA, Germany). • Three replicates at each sampling site 	<p>surface water</p>	<ul style="list-style-type: none"> • Filtering protocol - with a 0.045mm stainless steel mesh. • Organic digestion protocol – WPO • Density separation protocol - ZnCl₂. • Filtered again - 0.22 µm pore size GF/C filter. 	<ul style="list-style-type: none"> • Stereomicroscope <ul style="list-style-type: none"> • Ramen spectroscopy
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<p>Kay <i>et al.</i>, 2018.</p>	<p>WWTP in North England</p>	<p>WWTP- effluent</p>	<ul style="list-style-type: none"> • Samples were collected via a 300-μm mesh net attached to a wooden pole. • The net was submerged for 15 minutes against the river's bed facing upstream. • The sample dates are unknown • five replicate samples were collected over six weeks. 	<p>Specific depth is unknown, but the net was placed on the riverbed</p>	<ul style="list-style-type: none"> • Samples were refrigerated at four $^{\circ}$C for 48 hours to prevent bacteria growth. • Steel stacked sieves (mesh size: 5.6 mm, 4 mm, 2 mm, 1 mm, 500 μm, and 250 μm). 	<ul style="list-style-type: none"> • Stereomicroscope, • Tweezer test
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<p>Kittner <i>et al.</i>, 2022.</p>	<p>Danube River</p>	<p>River</p>	<ul style="list-style-type: none"> • Twenty-two samples were taken from 18 sites from late June to mid-december 2019 • Collection method - sedimentation box. Placed for 14 days to collect 50L of water and sediment into stainless steel drums. 	<p>Surface water 0.5m</p>	<ul style="list-style-type: none"> • Filtering protocol - Stainless steel sieves with pore sizes (1000 and 500 μm). • 5L was removed from the <500 μm and suspended in 45 L of tap water to prevent clogging of the sieves. Solution was then passed through a 100 μm stainless steel sieve, and 5L was taken and air dried. • Organic digestion protocol -Samples with high organic 	<ul style="list-style-type: none"> • Thermogravimetric analysis • TED-GC/MS, gas chromatography
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					matter had a NaCl solution added.	
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<p>Kor and Mehdinia, 2020</p>	<p>Persian Gulf</p>	<p>Unknown</p>	<ul style="list-style-type: none"> • Neuston net (300-μm mesh size and 130 \times 30 -cm rectangular opening equipped) • Preserved in 70% ethanol. 	<p>surface water</p>	<ul style="list-style-type: none"> • Wet sieve (5 mm and 50 μm mesh stainless steel). • Density separation protocol - Zinc salt-saturated solution • Filter protocol- 5.5 cm of 1.2 μm glass fibre papers (Whatman, Grade GF/C) and rinsed with 25 mL of 0.4 M HCl. 	<ul style="list-style-type: none"> • Stereomicroscopy • Hot needle test <ul style="list-style-type: none"> • ATR
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<p>Laermanns <i>et al.</i>, 2021.</p>	<p>Elbe River</p>	<p>River</p>	<ul style="list-style-type: none"> • January 2020, seven water samples • Collection methods – 1) The filter cascade was connected to a pump with mesh sizes 100 and 50 µm. Sample size varied between 530-680L. • 2) 3 samples - Apstein plankton net (opening: 0.022 m², diameter 17 cm, length 110 cm) with two 	<p>Surface water - 30cm</p>	<ul style="list-style-type: none"> • Filter protocols – 1) Vacuum filtered with stainless steel sieves mesh sizes of 50 and 100 µm for the samples of the filter cascade, 2) mesh sizes of 150, 300 and 500 µm for the samples of the nets. • Organic digestion protocol - H₂O₂ • Filter - glass microfibre filter 	<ul style="list-style-type: none"> • Digital microscope • Pyr-GC-MS Analysis
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			<p>connected nets of 150 and 300 μm mesh size.</p> <ul style="list-style-type: none"> • Samples were stored in glass jars. 			
Lam <i>et al.</i> , 2020	Pearl River Estuary, Southern China	Estuary	<ul style="list-style-type: none"> • Eleven sites sampled on February 4th and 6th, 2018 • Collection method - manta nets (0.87 \times 0.16 m² rectangular opening, a 333 μm Nitex mesh and a detachable cod-end). 	Surface water	<ul style="list-style-type: none"> • Organic digestion protocol - H₂O₂ • Five stainless steel sieves (0.355, 0.5, 0.71, 2.8 and 5 mm). • Density separation protocol - NaCl 	<ul style="list-style-type: none"> • ATR-FTIR

<p>Lestari <i>et al.</i>, 2020</p>	<p>Lower Brantas River (Wringinano m, Driyorejo, Bambe, Karang Pilang, Gunung Sari, Joyoboyo and Jagir)</p>	<p>River</p>	<ul style="list-style-type: none"> • Samples (replicates =2) • Rainy season from the end of February to early May 2019. • Sample Collection - manta trawl net with pore size 333 μm. • Cod ends containing the sample collection were soaked with 70% alcohol for preservation and placed in an aluminium foil zip lock. 	<p>Surface (0.16-0.30m), middle (1.2-8m) and bottom (1.7-15m)</p>	<ul style="list-style-type: none"> • Wet filtered using stainless steel sieves (5.6 mm and 0.3 mm pore sizes). • Organic digestion protocol -Samples were dried for 24 hours at 90 °C and oxidised using Fenton's reagent (20 mL Fe (II) and 20 mL 30% H₂O₂) to digest • Density separation protocol - 6 g NaCl per 20 mL sample. • Filter protocol - 0.3 mm filters. 	<ul style="list-style-type: none"> • Stereomicroscope • FTIR
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<p>Lisina <i>et al.</i>, 2021.</p>	<p>Volga River</p>	<p>River</p>	<ul style="list-style-type: none"> • Samples were collected using a trawl net or manta net at 34 sites. During sampling, an LEI-MANTA300 set with 300 µm bags for filtration and a 2m long net was towed behind the boat for 45-60 minutes. 	<p>depth unknown</p>	<ul style="list-style-type: none"> • Sieving protocols - stainless steel filters 5mm - 0.3mm. The samples in the 0.3-0.5mm sieves were transferred to a glass container • Preserved in 70% alcohol. • Organic digestion protocol - 30% NaCl 	<ul style="list-style-type: none"> • Stereomicroscope • FTIR
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<p>Liu <i>et al.</i>, 2022.</p>	<p>Xiantanwei mangrove wetland, Xiamen Bay, Fujian province</p>	<p>River</p>	<ul style="list-style-type: none"> • Nine 50 L water samples • 8th November 2019 • Collection method - unknown. 	<p>Surface water</p>	<ul style="list-style-type: none"> • Organic digestion protocol - 100ml 30% H₂O₂ solution, placed in a water bath at 60°C for 24-48 hours until the solution became clear. • Density separation protocol - 250ml of 1.5 g/cm³ ZnCl₂ for • After 12 hours, the top 3/4 of the liquid was filtered onto a 45 µm filter film. 	<ul style="list-style-type: none"> • Electron microscope • FTIR
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Lusher <i>et al.</i> , 2014	Northeast Atlantic Ocean	Ocean/sea water	<ul style="list-style-type: none"> • 2000L samples were taken from a continuous intake located on the vessel. 	Unknown	<ul style="list-style-type: none"> • Filter protocols – vacuum filtered onto a GF/C paper (Whatman™: 47 mm diameter, pore size: 1.2 μm). 	<ul style="list-style-type: none"> • dissecting microscope • Raman analysis
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Ma <i>et al.</i> , 2022	Songhua River - China	River	<ul style="list-style-type: none"> • Three surface water samples (50L) and one WWTP effluent (150L). • July and September 2019. • Collection method- pump with a flow meter. Samples were put through stainless steel sampling sieves (5 mm and 50 µm mesh size). Only the 50 µm sieve was saved and washed into 50 ml glass bottles. 	0.5m	<ul style="list-style-type: none"> • Samples were filtered through 2 µm cellulose nitrate filter. • Organic digestion protocol - 50 ml of 30% H₂O₂ • Density separation protocol - NaCl 	<ul style="list-style-type: none"> • Stereomicroscope • ATR-FTIR
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MacEachern <i>et al.</i> , 2019	Tampa Bay, Florida	Bays	<ul style="list-style-type: none"> • Collection method – 1) Discrete water sampling using a Van Dorn sampler 2) Plankton tows 330 μm plankton net with a 50 cm diameter • Stored in a 1 L HDPE collection bottle. 	1-2 meters below surface level	<ul style="list-style-type: none"> • Discrete samples: Vacuum filtered through a 1.2 μm pore size, 47 mm diameter, gridded cellulose nitrate filter paper. • Plankton tows: Enzymatic digestion -15.77 g Tris HCl, 4.38 g EDTA, 1.53 g NaCl, and 1.26 g SDS in 250 mL deionized water. 375 μL of Proteinase K (500 μg/mL) after incubation 5 mL of 5 M NaClO₄ 	<ul style="list-style-type: none"> • Dissecting microscope
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<p>Mani, T. and Burkhardt-Holm, P., 2020.</p>	<p>River Rhine</p>	<p>River</p>	<ul style="list-style-type: none"> • Manta trawl 0.3mm • Stored in Glass schott • Preserved ~40% ethanol 	<p>Unknown</p>	<ul style="list-style-type: none"> • Fractional filtration using sieves • Density separation protocol - castor oil 	<ul style="list-style-type: none"> • stereomicroscope <ul style="list-style-type: none"> • FTIR
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<p>Nan <i>et al.</i>, 2020</p>	<p>Greater Melbourn Area and Goulbourn River catchment</p>	<p>Streams and wetlands, and River catchment</p>	<ul style="list-style-type: none"> • Grab surface water samples - three 5L food-grade blue polypropylene jars 	<p>0-5cm</p>	<ul style="list-style-type: none"> • Filtering protocol - nylon membranes (Millipore NY2004700, pore size = 20 µm) using a vacuum pump in a fume hood separately 	<ul style="list-style-type: none"> • Leica M125 Stereo microscope attached with a Leica MC 170 HD digital camera <ul style="list-style-type: none"> • FTIR
<p>Napper <i>et al.</i>, 2021.</p>	<p>Ganges River (Bhola, Chandpur, Rajbari,</p>	<p>River</p>	<ul style="list-style-type: none"> • Ten sites in India and Bangladesh 	<p>0.5m below surface</p>	<ul style="list-style-type: none"> • Protocols - Unknown 	<ul style="list-style-type: none"> • Stereomicroscopy <ul style="list-style-type: none"> • FTIR

	<p>Sahibganj, Patna, Varanasi, Kannauj, Anupshahar, Rishikesh and Harsil)</p>		<p>along the length of the Ganges.</p> <ul style="list-style-type: none"> • Collection method - 30 L water pumped using a hand- operated bilge pump • filtered through a 330 µm nylon mesh placed across a polypropylene tube. • Filters were then wrapped in foil and put in separate PP bags. 			
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			<ul style="list-style-type: none">• Collection dates - pre-monsoon (May 2019-June 2019) and post-monsoon (October 2019-December 2019).• Samples were collected at three points at each location and replicated on two consecutive days.			
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<p>Ravit <i>et al.</i>, 2017.</p>	<p>New Jersey - Raritan and Passaic River watersheds</p>	<p>Rivers/ freshwater</p>	<ul style="list-style-type: none"> • 45 sites were sampled between May 12 and August 6, 2016. • Triplicate samples • Collection method - manta trawl (rectangular opening 16 cm high × 61 cm wide, attached to a 333 μm mesh collection net 3 m long and 30 × 10 cm²) under dry weather conditions on an outgoing tide. 	<p>Unknown</p>	<ul style="list-style-type: none"> • Organic digestion protocol -Fentons reagent (20 mL of 0.05 M iron sulfate and 20 mL 30% H₂O₂). 	<ul style="list-style-type: none"> • Microscope (type unknown), • Pyrolysis GC-MS, Gas chromatography/ion trap mass spectroscopy
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<p>Roscher <i>et al.</i>, 2021.</p>	<p>River Weser</p>	<p>River</p>	<ul style="list-style-type: none"> • Collection - April 2018 using an RV • 23 sampling sites. • Sampling occurred 30 minutes after high tide. • Triplicate water samples • Filtered on board RV's using glass fibre filters and frozen. 	<p>surface water - 1 m</p>	<ul style="list-style-type: none"> • Samples were purified by adding 10% sodium dodecyl sulfate in distilled, deionized water (SDS) solution and incubated for 24 h at 50 °C. • Seive protocol - 47 mm stainless-steel screens (mesh size: 18 µm). • Organic digestion protocol- H₂O₂ • Density separation protocol - ZnCl₂ 	<ul style="list-style-type: none"> • Stereomicroscope • FTIR
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<p>Scircle <i>et al.</i>, 2020.</p>	<p>Mississippi River</p>	<p>river</p>	<ul style="list-style-type: none"> • Collection method – 1) 360 litres <p>field filtered sampling using a pump, and 2) 1L grab sampling (Straight into a glass jar)</p>	<p>surface</p>	<ul style="list-style-type: none"> • Organic digestion protocol - WPO using Fenton reagent • Filtering protocol - 25mm diameter, 10 µm pore size, PC track-etched filter (PC filter) and a 25 mm diameter, ~30 µm pore size, 200 x 600 mesh Monel wire screen 	<ul style="list-style-type: none"> • Fluorescence microscopy with the use of Nile red • Micro FTIR
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<p>Shi <i>et al.</i>, 2022.</p>	<p>Cherry River, an outlet of washing machines in East China Normal University (Shanghai, China) and Hangzhou Bay of East China Sea</p>	<p>River and outlet</p>	<ul style="list-style-type: none"> • Samples were collected in May 2020 and July 2021. • 400ml of river water and 100ml of domestic sewage were collected in triplicates. • Collection method - Unknown 	<p>Unknown</p>	<ul style="list-style-type: none"> • Filtering protocol - 20 µm-pore size filter membrane (Merck Millipore). Magnetic 1.3 g·L⁻¹ nano-Fe₃O₄ were added to the samples, and magnetisation was set at 180 rpm at 25 °C for 150 min. Magnetised 	<ul style="list-style-type: none"> • Microscope (type unknown), <ul style="list-style-type: none"> • FTIR
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					microplastic s were then removed due to being attracted to the magnets.	
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<p>Singh <i>et al.</i>, 2021.</p>	<p>Ganga river (Ballia, Patna, Bhagalpur, Farakka and Diamond Harbour)</p>	<p>River</p>	<ul style="list-style-type: none"> • Collected during April 2019 • Three spots at each location in triplicate • Collection method- 300 µm mesh plankton net towed to a boat. 	<p>Unknown</p>	<ul style="list-style-type: none"> • Organic digestion protocol -Samples Fentons reagent (ferrous sulfate and 30% hydrogen peroxide solution) at 70°C • Density separation protocol -5 M NaCl and left overnight • Filtering protocol - Whatman™ GF/F glass filter of 47 mm diameter (pore size 1.2 µm). 	<ul style="list-style-type: none"> • Stereomicroscopy • FTIR
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<p>Tien <i>et al.</i>, 2020</p>	<p>Fengshan River</p>	<p>River</p>	<ul style="list-style-type: none"> • Six sampling sites • 5th September 2018 • 50 L of water • Collection method - middle of the river using a hemp sling with a hanging stainless steel bucket. 	<p>Surface water</p>	<ul style="list-style-type: none"> • Seiving protocol - 50 µm, 297 µm and 5000 µm). <ul style="list-style-type: none"> • Density separation- ZnCl₂ • Filter protocol - Advantec® grid filter membranes (47 mm diameter and 0.8 µm pore size). • Organic digestion protocol - 20 mL 35% H₂O₂ solution, stored at room temperature for seven days 	<ul style="list-style-type: none"> • Dissecting microscope • ATR-FTIR
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<p>Vermaire <i>et al.</i>, 2017</p>	<p>Ottawa River, Canada</p>	<p>River and tributaries</p>	<ul style="list-style-type: none"> • Summer 2016 samples were taken from 5 areas total number of sites unknown. 3 replicates were taken at each location. • Collection method – 1) manta trawl (~100 000 L), and 2) bottle sampling (100L). For the bottle sampling, 100L of water was sampled through 	<p>surface water - 0.5m</p>	<ul style="list-style-type: none"> • Organic digestion protocol - WPO (30%) heated at 80 °C for seven h • Filter protocol - 100 µm filter. 	<ul style="list-style-type: none"> • Stereomicroscope
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			a 100 μm nylon mesh.			
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<p>Vibhatabanand Srithogouth, 2022</p>	<p>Gulf of Thailand</p>	<p>River estuaries and coastal sea</p>	<ul style="list-style-type: none"> • 74 sites in the dry season (April to May 2018) and 70 in the wet season (July to August 2018). • Collection method - clean bucket and submersible pump • Samples were then transferred to PP bottles. 	<p>Surface water 0-50cm</p>	<ul style="list-style-type: none"> • Separation density protocol –NaCl₂ • Organic digestion protocol – WPO • Seive protocol - 1000–5000 μm, 100–300 and 300–1000 μm. 	<ul style="list-style-type: none"> • Stereomicroscope, <ul style="list-style-type: none"> • FTIR • Spectrophotometer <ul style="list-style-type: none"> • ATR
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<p>Warrier <i>et al.</i>, 2022</p>	<p>Lake Mannapalla - Southern Indian Lake</p>	<p>Lake</p>	<ul style="list-style-type: none"> • September 2019 (12 samples) and January 2020 (6 samples). • Collection method - 125 L was collected using a steel bucket (10L volume) filtered through a 0.3mm stainless steel sieve. 	<p>surface water</p>	<ul style="list-style-type: none"> • Sieve protocol - stack 5mm (top) to 0.3mm (bottom). • Organic digestion protocol - WPO (20 ml each of aqueous 0.05 M Fe (II) and 30% hydrogen peroxide (H₂O₂)) • Density separation protocol - ZnCl₂ 	<ul style="list-style-type: none"> • Stereo zoom microscope, • FTIR/ ATR-FTIR • Scanning electron microscope
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<p>Xiong et al., 2022.</p>	<p>Flathead Lake, Montana, USA</p>	<p>Lake</p>	<ul style="list-style-type: none"> • Twelve sites in summer 2018. • Collection method - 330-μm mesh panelled trawling net with a 45 cm \times 25 cm opening that was attached to a sample collection bucket in • At each site, a transect of ~500 m at a speed of <5 km/h to collect samples • The sample was transferred to a glass jar with a metal cap. 	<p>Surface water - 25cm</p>	<ul style="list-style-type: none"> • Seive protocol -two stainless steel mesh screens fitted with 2-mm and 100-μm mesh • Organic digestion protocol - 30% H₂O₂ at 60 °C for 72 hours. • Filtering protocol - Millipore S-Pak 1.2-μm mixed cellulose esters filter. 	<ul style="list-style-type: none"> • Stereomicroscope • Raman microscope
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<p>Zhang <i>et al.</i>, 2020</p>	<p>Qin River</p>	<p>River and estuary</p>	<ul style="list-style-type: none"> • 12 sites in October 2018 • Collection method - 30L of water with three replicates was collected using a 12-V DC Teflon pump. • Filtered on-site via a 25 µm mesh screen attached to the pump. 	<p>Surface water- 20cm</p>	<ul style="list-style-type: none"> • Filtering protocol - 0.45 µm filter membranes. • Organic digestion protocol - 200ml H₂O₂ (30%), kept at room temperature for 24 hours. • Density separation protocol - 800ml NaCl solution, kept at room temperature for a further 24 hours. 	<ul style="list-style-type: none"> • Visual screening with a magnifying glass • Optical microscope (SAIKEDIGITAL SK 2500H) • FTIR
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Supplementary Table 2. Months and years sampling occurred at sites along the River Thames

Year	Month	Sample taken (yes/no)									
		Teddington	Westminster		St Katherine	Limehouse	North Woolwich		Barking Riverside	Tilbury	Southend
			Westminster Boating Base	Westminster (the eye)			Tate and Lyle	Barge Road			
2019	May	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	June	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	July	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	August	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	September	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	October	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	November	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	December	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
2020	January	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	February	Yes	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes
	March	Yes	Yes	No	Yes	Yes	No	No	Yes	Yes	Yes
	April	Yes	No	Yes	Yes	Yes	No	No	No	No	No
	May	Yes	No	Yes	Yes	Yes	No	No	No	Yes	Yes
	June	Yes	No	Yes	Yes	Yes	No	No	No	Yes	Yes
	July	Yes	No	Yes	Yes	Yes	No	No	Yes	Yes	Yes
	August	Yes	No	Yes	Yes	Yes	No	Yes	No	Yes	Yes
	September	Yes	No	Yes	Yes	Yes	No	Yes	No	Yes	Yes

	October	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
	November	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
	December	Yes	No	Yes	Yes	Yes	No	Yes	No	Yes	Yes
2021	January	Yes	No	Yes	Yes	Yes	No	Yes	No	Yes	Yes
	February	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
	March	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
	April	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes
	May	Yes	No	Yes	Yes	Yes	No	Yes	Yes	Yes	Yes

Supplementary Table 3. Atmospheric control – Desk filters (Main study – monthly samples 2019-2021)

<u>Year</u>	<u>Date</u>	<u>Microplastic total (MPT)</u>
2019	20 th May	13 (3 blue, 9 black, 1 red)
	21 st May	8 (4 blue, 4 black)
	22 nd May	4 (1 blue, 3 black)
	3 rd June	3 (black)
	4 th June	0
	19 th June	6

		(black)
	20 th June	0
	24 th June	3 (1 black fragment, 2 black fibres)
	25 th June	0
	3 rd July	2 (1 black fragment, 1 black fibre)
	6 th august	6 (black fibres)
	15 th august	6 (2 red fibres, 4 black fibres)

	2 nd September	0
	25 th September	0
	26 th September	1 (black fibre)
	30 th September	3 (1 blue fibre, 1 black fibre, 1 red fibre)
	2 nd October	2 (1 blue fibre, 1 black fibre)
	24 th October	2 (1Red fibre, 1 black fibre)
	25 th October	5

		(2 red fibres, 3 black fibres)
	30 th October	0
	2 nd November	0
	4 th November	5 (4 black fibres, 1 red fibre)
	5 th November	7 (3 black fibres, 3 blue fibres, 1 red fibre)
	11 November	3 (1 red fibre, 1 blue fibre, 1 black fibre)
	21 st November	4 (3 black fibres, 1 red fibre)

	24 th November	0
	9 th December	2 (1 blue fibre, 1 red fibre)
	11 th December	6 (2 black fibres, 4 red fibres)
	19 th December	2 (black fibres)
2020	16 th January	0
	28 th January	9 (8 black frag, 1 black fibre)
	29 th January	0
	24 th February	0

	27 TH February	5 (4 black fibres, 1 red fibre)
	28th July	4 (2 black fibres, 2 blue fibres)
	29 th July	0
	30 th July	3 (2 black fibres, 1 blue fibre)
	3 rd August	0
	4 th August	0
	5 th August	1 (blue fibre)
	26 th August	4

		(2 blue fibres, 2 red fibres)
	27 th August	1 (black fibre)
	2 nd September	2 (black fibres)
	10 th September	0
	26 th October	5 (4 black fibres, 1 red fibre)
	27 October	1 (black fibre)
	3 rd November	4 (blue fibres)

	11 th November	1 (black fibre)
	18 th November	0
	1 st December	0
	2 nd December	2 (1 black fibre, 1 blue fibre)
2021	26 th April	16 (4 blue fibres, 8 black fibres, 1 black fragment, 3 red fibres)
	29 th April	2 (2 black fibres)
	5 th May	2

		(1 blue fibre, 1 red fibre)
	6 th May	1 (Black fragment)
	15 th June	2 (1 Black fibre, 1 red fibre)
	16 th June	4 (2 blue fibres, 2 red fibres)
	20 th June	1 (Black fibre)
	24 th June	2 (Black fibres)

	28 th June	6 (1 blue fibre, 5 black fibres)
	29 th June	4 (3 blue fibres, 1 red fibre)
	2 nd July	2 (1 blue fibre, 1 black fibre)
	6 th July	3 (1 Black fibre, 2 red fibres)
	7 th July	3 (2 black fibres, 1 blue fibre)
	8 th July	3

		(Black fibre, blue fibre, red fibre)
	12 th July	1 (Black fibre)
	14 th July	3 (2 Blue fibres, 1 black fibre)

Supplementary Table 4. Contamination controls conducted from 2019-2021, including distilled water kept in 500ml bottles, as well as controls to test for contamination via the sampling equipment (bucket and Lamotte horizontal water sampler).

Control	Microplastic per replicate	Mean MPT	Average length (mm)
Distilled water kept in 500mL bottles 21/11/19 – 14/6/21	0	0	-
	0		
	0		
500mL distilled water passed through the sampler	2 black fibres 1 black particle	1.3	1.57
	0		
	1 black fibre		
	3 blue fibres	3	2.89

500mL distilled water passed over the rope (sampler)	4 white fibres		
	2 blacks		
500mL distilled water rope soak (sampler)	1 black fibre	3.7	1.95
	1 blue fibre		
	1 red fibre		
	3 green fragments		
	3 white fibres		
	1 blue fibre		
500mL distilled water inside the bucket	7 black fibres	5.67	4.63
	2 blue fibres		
	2 pink fibres		

	1 green fibre		
	2 pink fibres		
	1 black fibre		
	2 blue fibres		
	1 white fragment		
	0		
500mL distilled water passed over the rope (Bucket)	0		
	1 black fibre	1	2
	1 orange fibre		
	1 yellow fibre		
0			
	1 blue fibre	1.67	1.28

500mL distilled water rope soak (Bucket)	1 black fragment		
	2 black fibres		
	1 transparent fibre		
	0		

Supplementary Table 5. FTIR results for the eight areas sampled along the river Thames. Westminster (Westminster Boating Base and Westminster close to the Millennium eye) and North Woolwich (Tate and Lyle and Barge Road) have been made up of both the respected sites in that area

FTIR result	Teddington	Westminster	St Katherines	Limehouse	North Woolwich	Barking Riverside	Tilbury	Southend- on-Sea
Abs	2	3	4	0	8	2	2	3
alginic acid- biopolymer	2	0	0	1	0	0	0	1
alkyd varnish	2	1	1	0	0	1	1	1
Anthropogenic microfiber/particle	5	3	2	7	1	6	7	0
edterepolymer	1	0	0	0	0	0	0	1
ethylene vinyl alcohol	0	0	0	2	1	0	0	0

HDPE	2	0	0	0	0	0	0	0
malaic acid	0	0	0	0	0	0	0	0
Natrual	3	1	3	0	0	0	0	0
No Hit	24	19	18	21	9	24	44	17
Pcp	14	8	7	11	10	7	10	13
Pe	1	1	1	2	0	0	0	2
pe chlorinated	2	9	8	14	9	6	2	6
Pete	2	1	2	2	1	5	1	4
Pla	0	1	1	3	0	1	0	0
Poly (2,4,6 tribromostyrene)	0	0	0	1	1	0	0	1
Poly acrylic acid	0	0	0	1	0	0	0	2

poly vinyl butyral	1	0	0	0	0	0	0	1
polyacetal	1	0	0	0	0	0	0	1
polyamide	0	1	1	1	0	1	0	2
polybutadiene	0	1	1	0	0	0	1	0
polycarbonate	2	4	3	4	3	2	4	2
polyester	1	2	2	3	1	1	0	0
Polyethylene chlorosulfonated	0	1	0	0	1	1	1	2
Polyhydroxyl butyric acid	1	0	0	0	0	0	0	0
polyisoprene chlorinated	1	1	0	1	3	1	0	1
polyoxymethylene	0	0	0	0	0	0	1	0

Polyphenylene sulfide	2	4	1	3	4	4	3	2
polysulfone	3	0	0	0	1	0	0	0
polyurethane	1	1	1	0	3	0	2	2
Polyvinyl flouride	0	1	1	0	0	0	1	3
PP	10	6	2	7	2	2	2	4
PS	12	16	13	12	11	9	21	8
PTFE	4	5	4	2	3	2	3	1
pu foam	2	3	2	1	2	3	4	4
Pva	0	1	2	0	0	0	1	0
PVC	33	28	39	24	31	19	39	42
resin-dispersion	1	3	4	2	4	2	0	3
Rubber	0	3	5	2	2	5	8	2

styrene acrylonitrile	1	0	0	1	0	0	0	0
styrene allyl alcohol	1	0	0	0	0	0	0	0
Styrene ethylene butadiene	0	1	1	1	0	0	0	0
Vinylidene chloride	0	3	2	2	0	4	0	1
Zein purified	0	0	1	0	0	0	0	0

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