Quantifying Microplastic Contamination in the Río Bermejo (Argentina) Compared to the River Wear, Durham (UK)

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Master of Science by Research

Department of Earth Sciences

Durham University

2024

Abstract

Microplastics are defined as plastic particles <5 mm, with the lower size limit defined as the pore size of the sieve used during sample preparation. There have been increasing concerns on the ecological effect of microplastics, and therefore understanding the microplastic assemblage and the sources of microplastics can help inform microplastic contamination policies. Limited studies have looked at changes in microplastic concentration along the course of a river, to assess how different factors can affect microplastic contamination. This study quantifies and compares microplastic contamination along two rivers, the Rio Bermejo, Argentina, and the River Wear, UK, which serve two different societies. This will help to address how wastewater treatment plants (WWTPs), population and anthropogenic activity can affect microplastic contamination. Sediment samples were obtained from 8 locations in the River Wear, and 6 in the Rio Bermejo. Microplastics abundances were recorded and characterized by shape, size, and colour. Microplastics were observed in all study sites across the Rio Bermejo and the River Wear. Microplastic contamination changes along the course of both the River Wear and Rio Bermejo, and is influenced by WWTPs, population and land use. The River Wear contained a higher abundance of microplastics overall (208 microplastics/100 g) than the Rio Bermejo (35 microplastics/100 g and 22 microplastics/100 g in suspended sediment and riverbank sediment respectively) due to higher urbanisation and population density. High abundances of microplastic fibres in the River Wear (93.7%) and the Rio Bermejo (100% and 76.9% in suspended sediment and riverbank sediment respectively) suggests that WWTPs are the dominant input source of microplastics in both locations. Although generally, microplastic abundances are higher in more urban areas than rural, hydrodynamic forces must be understood to better understand its effects. The microplastic assemblage observed in this study are significant when considering ecological impacts.

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Declaration

I declare that this thesis presented for the degree Master of Science by Research in Geological Sciences at Durham University has not been submitted by myself or for another individual for a degree in this or at any other institution. This thesis is a result of my own original research.

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Chapter 1: Introduction

1.1. Introduction to plastics

Plastics are synthetic, organic, polymeric materials with versatile properties, such as durability, lightness, and low price, which make them ideal for a range of applications (Andrady, 2011). Since the large-scale global production of plastic in the 1950s, the demand for plastic has exponentially increased (Andrady, 2011), with a worldwide production of 368 million tonnes in 2019 (PlasticEurope, 2020). Plastics are relatively inert, thereby resistant to degradation in natural environments, and have been proposed to be persistent in the environment for centuries (Bajt, 2021).

Processing plastic waste through safe disposal or recycling has become difficult to keep up with due to increasing demands and consumption of plastic items (Peng et al., 2021): resulting in mismanaged plastic waste (MMPW). In 2016, 12% of plastics were recycled globally (Hundertmark et al., 2018), and in 2018, only 32.5% of plastics were recycled in Europe (PlasticEurope, 2020). Low recycling rates may be attributed to the lack of necessary facilities, costs of collection, and low demands from processors for recycled plastic material (Lebreton & Andrady, 2019). Their high-volume consumption, subsequent rapid wastage, MMPW, and resistance to breakdown contributes to worldwide plastic pollution, a significant environmental issue and concern within the global scientific community (e.g. Andrady, 2011; Bajt, 2021; Woodall et al., 2014).

1.2. Plastic in the environment

Plastic has been reported in all major oceanic basins, coastlines of remote islands, within deep sea sediments (Barnes et al., 2009; Woodall et al., 2014), at high altitudes on Mount Everest (Napper et al., 2020), and the poles (Waller et al., 2017). 13 million tonnes of plastic enter the ocean globally (UNEP, 2018) as a result of MMPW (Boucher and Friot, 2017), with an estimated 1.15–2.41 million tonnes of plastic arriving from rivers (Lebreton et al., 2017). Other pathways from land-based plastic to marine environments include deliberate littering in seas and on beaches and wind transportation (GESAMP, 2016). Studies estimate that terrestrial sources account for 80% of all marine plastic pollution (Andrady, 2011). Marine litter causes economic effects, with clean-up costs of plastic waste in European coasts and beaches amounting to €630 million per year (UNEP, 2018). A schematic diagram representing potential source inputs of microplastics, and terrestrial dynamics is presented in Figure 1.

Globally, 20 rivers, mainly in Asia, represent 67% of the marine plastic waste input, representative of 21% of the world's population; and 86% of all riverine plastic input into oceans come from Asia (Lebreton et al., 2017). As the transport of riverine plastic debris to the ocean is driven by turbulent flows and flooding events, the relatively heavy rainfall events in Asia significantly contributes to the input, along with the relatively high population densities and vast amounts of mismanaged plastic waste produced (Lebreton et al., 2017). It has been estimated that 60–80% of oceanic debris is plastic, despite constituting approximately 10% of all municipal litter mass (Gregory and Ryan, 1997; Barnes et al 2009). Food and drink packaging, films and plastic bags, and fishing material are the most prevalent macroplastic items in marine litter (Barnes et al., 2002).

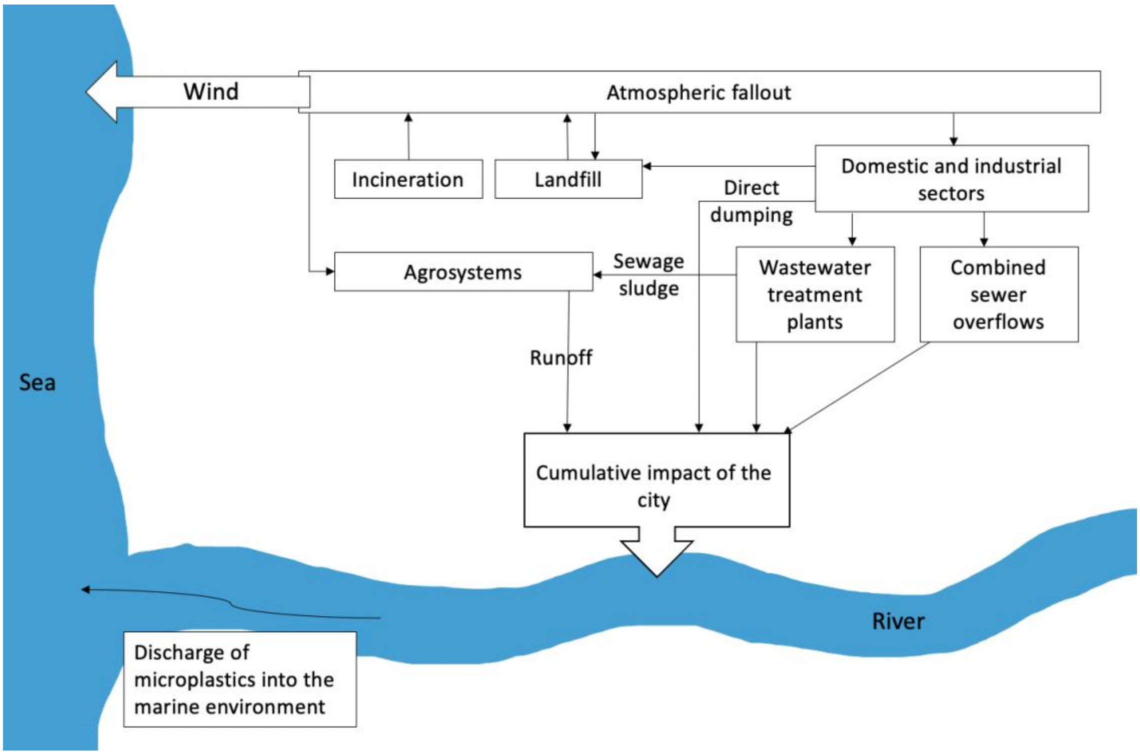


Figure 1. *Schematic diagram of potential sources and pathways of microplastics in an urban environment (modified from Dris et al., 2015).*

1.3. Degradation of plastic

It is difficult to accurately quantify the longevity of plastics in the natural environment, with estimates ranging from centuries to millennials, depending on the physical and chemical characteristics of the material (Barnes et al., 2009; Bajt, 2021). This is contrasted with the average lifetime use of plastic, before being disposed of, ranging from 1 year for packaging, to ~35 years for plastic use within construction and building (Geyer et al., 2017). Plastic degradation, to eventually form secondary microplastics (see Section 1.4), is assisted through a combination of oxygen, heat, moisture, and exposure to ultraviolet radiation through sunlight, with sunlight being the most important factor for degradation (Bajt, 2021). It was predicted that degradation rates would likely decrease in deep marine conditions with low light and oxygen availability (Barnes et al., 2009). However, due to differences in physical forces between freshwater and marine systems, plastic degradation rates may be different (Eerkes-Medrano et al., 2015). For example, microplastics in marine systems would be affected by storms and wave action, whereas freshwater microplastics may be influenced by turbulence and chemical degradation (Eerkes-Medrano et al., 2015). Therefore, differences in degradation between freshwater and marine secondary microplastics remain uncertain (Eerkes-Medrano et al., 2015).

1.4. Microplastics

Our understanding of microplastics and their environmental and ecological impacts is relatively new, with the first detailed study presented nearly 20 years ago (Thompson et al., 2004), although microplastics were first reported in the early 1970s (Carpenter et al., 1972). The European Marine Strategy Framework (Hanke, 2013) define microplastics as plastic materials <5 mm in their largest dimension, with the lower size limit defined as the pore size of the sieve used during sample preparation (Hanke, 2013; Arthur et al., 2008).

Microplastics can be subdivided into primary microplastics and secondary microplastics. Primary microplastics are purposely manufactured within these dimensions, for example beads used in cosmetics, and pellets used within the plastic production industry. Microplastic fibres released from textile and clothing laundering are considered primary microplastics (Boucher and Friot., 2017). Approximately 1.5 million tonnes of primary microplastics are released into the oceans each year (Horton et al., 2017). Most microplastics in the oceans (98%) are from land-based sources, particularly urban runoff (66%), wastewater treatment plants (WWTPs) (25%) (see Chapter 1.6.1), or wind (2%) (Figure 1) (Boucher and Friot, 2017). The remainder are released directly from marine-based sources (Boucher and Friot, 2017). Therefore, rivers can act a major source for microplastics to the marine environment (Horton et al., 2017). Secondary microplastics are a result of degradation and breakdown of macroplastics (Besley et al., 2017) (see Section 1.3) and are thought to be the main source of environmental microplastics (Yang et al., 2021).

1.4.1. Transport and fate of microplastics

The transportation of microplastics in freshwater environments and its fate is unknown due to limited research and the complex factors that affect it. A variety of factors can influence the fate of microplastics along a river course, such as whether they are transported along the river, or whether they settle in channel sediment (Horton et al., 2017). Factors include microplastics characteristics (e.g., size, shape and density), external riverine forces (e.g., flow regimes and velocities, storms, water depth, stream power), the properties of the river channel (e.g., channel substrate type, channel topography), biofouling, and anthropogenic activity such as release of sewage effluent (Horton et al., 2017; Meng et al., 2020; Nizzetto et al., 2016). However, factors such as flood events can remobilize deposited microplastics, and therefore channel bed sediment may only act like a temporary sink for microplastics (Hurley et al., 2018; Nizzetto et al., 2016).

Previous research on the deposition of microplastics in sediment have focussed chiefly on marine environments (Lobelle and Cunliffe, 2011; Andrady, 2011), with less studies on riverine systems (Nizzetto et al., 2016). The density of plastic particles (Table 1) is an important factor, dictating whether the particle will float or sink (Andrady, 2011). Microplastic particles deposited in sediment are likely to be polymers denser than the water medium than those that have a density lower than the water (Figure 1) (Andrady, 2011; Nizzetto et al., 2016). Previous studies have estimated that microplastics smaller than 200 μm, regardless of their density, are less likely to be retained in the channel bed sediment than larger particles and will eventually end up in the marine environment (Nizzetto et al., 2016). Biofouling on plastics can cause buoyant plastics that have been transported downstream to become negatively buoyant and hence sink (Andrady, 2011). The dynamics, abundances and spatial variations of microplastics in river systems is complex due to the number of factors involved, therefore, more research is required to better predict the fate of microplastics in riverine systems (Horton et al. 2017).

Polymer	Density (g cm^{-3})
PP	0.9−0.91
PE	0.92−0.97
PA	1.02−1.05
PS	1.04−1.1
Acrylic	1.09−1.20
PMA	1.17−1.20
PU	1.2
PVC	1.16−1.58
PVA	1.19−1.31
Alkyd	1.24−2.10
Polyester	1.24−2.3
PET	1.37−1.45
POM	1.41−1.61

Table 1. *Density ranges of different plastic types, and densities of different density solutions used within density separation. PE: polyethylene, PP: polypropylene, PS: polystyrene; PA: polyamide (nylon), POM: polyoxymethylene, PVA: polyvinyl alcohol, PVC: polyvinylchloride, PMA: poly methyl acrylate, PET: polyethylene terephthalate, PU: polyurethane (adapted from Prata et al., 2019b).*

The spatial distribution of microplastics along the course of the river can be understood by assessing the influence of factors, such as population size, and proximity to WWTPs. For example, no specific distribution or trend with microplastic abundances was observed in the Ciwalengke River, Indonesia, and was interpreted to be caused by a number of factors (Alam et al., 2019). Such factors include the proximity of the sampling site to industrialised areas, as well as differences in flow velocity along the course of the river (Alam et al., 2019). In the River Ems, Germany, no trend was also observed between microplastic abundances and how downstream of a river the sampling site was (Eibes et al., 2022). Eibes et al. (2022) suggested that weirs affected the deposition of microplastics, due to the lower river velocities they create. In the Nakdong River, South Korea, a trend of increasing microplastics from upstream to downstream was observed, but this was thought to be influenced by external factors (Eo et al., 2019). Further downstream, there is a higher population size, number of WWTPs, and a higher processing capacity of the WWTPs (Eo et al., 2019). Such factors therefore showed a positive correlation with microplastic abundance (Eo et al., 2019). Yonkos et al. (2014) also observed a correlation of microplastic abundance between population density and proximity to industrial areas. However, more research is required to fully understand the range of factors that affect microplastic abundances to enhance predictions in the future (Eerkes-Medrano et al., 2015).

1.5. Microplastic ecological impacts

Increasing concerns surrounding microplastic pollution in freshwater and marine environments within the scientific community has encouraged the research of impact of microplastics on ecological organisms (Andrady, 2011; Cole et al., 2011). The ubiquitous nature and low degradation rates of microplastics emphasises the need of understanding the potential ecological risks and impacts (Yang et al., 2021). Ecological impacts of microplastics have mostly been researched in marine systems, having first been studied in the 1970s (Carpenter et al., 1972), with fewer studies in freshwater environments (Eerkes-Medrano et al., 2015; Hurley et al., 2017).

1.5.1. Factors affecting microplastic bioavailability

Microplastics can affect ecological organisms indirectly or directly in aquatic systems (Yang et al., 2021). Direct effects may be through ingestion of microplastics, and indirect effects through the release of toxic chemicals adhered to the microplastics during ingestion (Yang et al., 2021). Other effects of ingesting microplastics on organisms in aquatic environments include blocking the digestive tract, changes in feeding, increased mortality rates, release of toxic chemicals (Zhang et al., 2018) and translocation of microplastics within the body (Browne et al., 2008).

The effects that microplastics may have on organisms can depend on differences in their chemical composition, shape, size (Yang et al., 2021) and colour (Carpenter et al., 1972). A greater abundance of microplastic particles also increases the bioavailability due to a greater likelihood that the organism will encounter a particle (Wright et al., 2013). The size of microplastics is a significant factor that contributes to bioavailability (Wright et al., 2013). As microplastics have similar size dimensions to sediment and some types of plankton, there is an increased risk of bioavailability to many organisms (Wright et al., 2013), hence may mistake microplastics as food. For example, smaller sized microplastics are more accessible to smaller sized organisms (Wright et al., 2013). Previous research observed that microplastics with a size dimension of <500 μm were ingested far more than greater size dimensions from certain detritovore and deposit feeders (Wright et al., 2013). Moreover, ingestion of microplastics with a diameter of 4000 μm was limited, potentially due to size restrictions from their mouth or difficulties of picking them up (Wright et al., 2013). In a previous study of tubifex worms in river bottom sediments, which are deposit feeders, it was observed that they had a size selectivity of <63 μm (Hurley et al., 2017). However, although many microplastic fibres and fragments are larger than 63 μm, their diameter is typically much smaller and therefore able to be ingested alongside fine-sediment particles and organic matter (Hurley et al., 2017). Previous studies also observe selectivity for microplastic shapes. Hurley et al. (2017) observed that *Tubifex* worms preferred certain microplastic shapes during ingestion. Of the ingested microplastics, 87% were fibres, 13% were fragments, and no beads, which typically have larger dimensions than fibres or fragments, were ingested (Hurley et al., 2017). Therefore, *Tubifex* worms do not ingest microplastic beads due to their typically larger size, but are not selective between microplastic fibres or fragments

(Hurley et al., 2017). Additionally, it has been suggested that some fish species may feed selectively on plastic spherules (Carpenter et al., 1972).

Density also affects the distribution of microplastics in the water column. For example, higher density microplastics such as PET and polyester (Table 1) are likely to sink and therefore be found in greater quantities in the benthic zone (Cole et al., 2011), whereas lower density microplastics such as polypropylene (Table 1) will more likely be found on the surface of the water (Eerkes-Medrano et al., 2015). Therefore, the type of microplastics bioavailable to different organisms will differ. Higher density microplastics will be more bioavailable to benthic suspension and deposit feeders, and detritovores, whereas lower density microplastics more bioavailable to suspension and filter feeders, and planktivores (Wright et al., 2013).

The colour of microplastics may also affect the possibility of ingestion, due to a similar colour resemblance to prey (Wright et al., 2013). Studies have indicated that some fish species may feed selectively depending on colour, ingesting only white-coloured plastic spherules (Carpenter et al., 1972). Therefore, understanding the colour distribution between locations can be used to help to understand the relationship between ecological organisms and microplastic particles. It is therefore important when researching microplastics to characterize microplastic particles by size, colour, and density, as these factors affect how bioavailable a microplastic particle is to organisms. This study will look at the size, shape and colour of observed microplastics, but due to equipment issues (see Section 3.5), the density of the microplastics recovered could not be investigated.

As organisms can feed selectively on colour (Carpenter et al., 1972) and can ingest microplastics (Wright et al., 2013), understanding the colour distribution between locations can be used to help to understand the relationship between ecological organisms and microplastic particles.

1.5.2. Effects of microplastic ingestion on freshwater organisms

There have been limited field studies of the effects of freshwater organisms ingesting microplastics, with the first article published in 2017 (Hurley et al., 2017), compared to marine organisms, such as seabirds (Wolfe, 1987). Hurley et al. (2017) identified microplastic particles in *Tubifex* worms, one of the most prevalent invertebrates in freshwater environments (Lagauzère et al., 2009). Additionally, Andrade et al. (2019) found ingested microplastics in freshwater fishes in the Amazon.

Microplastics, once ingested in organisms, have various transfer paths (Browne et al., 2008). Microplastics can be stored in the digestive gut, causing physical harm through blocking the digestive tract (Wright et al., 2013). Microplastics were found to be retained in the guts of *Tubifex* worms longer than other non-plastic ingested matter (Hurley et al., 2017). Persistence of microplastics in the digestive tract can also reduce the amount of food ingested due to satiation (Wright et al., 2013). Longer retention times in the gut also increases the risk of exposure to additives and contaminants adhered to microplastics in the organism, potentially causing toxic effects (Kirstein et al., 2016; Hurley et al., 2017; Mato et al., 2001). Microplastics can also be defecated out (Browne et al., 2008). Microplastics that are defecated out will be released as faecal matter into the aquatic environment (Hurley et al., 2017). This may result in the microplastics ending up the water column (Hurley et al., 2017) or settling in sediment (Wright et al., 2013). Microplastics can also be translocated from the gut into body tissues, within the circulatory system, which can persist for over 48 days (Browne et al., 2008).

1.5.3. Trophic level effects

Microplastics are able to move through the food web. It has been observed that higher trophic level predators ingested microplastic particles transported by lower trophic level organisms (Wright et al., 2013). For example, detritovores and suspension feeders can ingest defecated microplastics (Wright et al., 2013). Bioturbation of sediment by benthic organisms further provide availability of buried microplastics (Wright et al., 2013). *Tubifex* worms, one of the most widespread invertebrate species in freshwater environments (Lagauzère et al., 2009), and are at the base of the food chain, are ingested by salmon and trout (Dunbrack et al., 1988). As salmon and trout are commonly ingested by humans, this also presents a direct risk to human ingestion and transfer (Hurley et al., 2017). Benthic organisms such as molluscs are also commonly eaten by humans, posing a risk of ingestion (Wright and Kelly, 2017). This highlights the risk of microplastic transfer to higher trophic organisms and humans (Hurley et al., 2017).

1.5.4. Effects of microplastics on humans

There has been increasing concerns for the effects of microplastics on human health, which is still poorly understood (Yan et al., 2021). Microplastics are ubiquitous in the environment, in global freshwaters and drinking (treated tap and bottled) (Koelmans et al., 2019), suspended in air (Akhbarizadeh et al., 2021), and within food (Yan et al., 2021). Therefore, human ingestion of microplastics, through inhalation, drinking and ingestion, is inevitable (Yan et al., 2021). Similar to animals, humans ingest microplastics through the digestive tract, and can be defecated out (Yan et al., 2021). However, the abundance and movement of microplastics in the human body are difficult to determine and quantify due to inadequate models of detecting them and understanding the persistence of microplastics within the human body (Yan et al., 2021). Recent studies have identified microplastics in human blood (Leslie et al., 2022), human lung tissue

(Jenner et al., 2022), and human breast milk (Ragusa et al., 2022). This emphasises the need for future research to understand the impacts of microplastic particles on human health.

1.6. Input sources

Microplastic particles can enter freshwater systems through a variety of input sources and routes. Sources of inputs can include atmospheric fallout, wastewater treatment plants (WWTPs), terrestrial run off, and combined sewer overflows (Figure 1) (Dris et al., 2015; Horton et al., 2017). It is important to identify input sources to help mitigate reduce microplastics entering the freshwater system and its ecological effects in the future. Studies have identified that atmospheric fallout from rainwater can significantly contribute microplastic fibres into freshwater systems (Dris et al., 2015). A study in the Ciwalengke River, Indonesia, an area influenced by industrialisation and slums observed a dominance of microplastic fibres in river sediment samples (Table 2). This was interpreted that anthropogenic activities, such as textile washing or bathing in the river, influences the abundance of microplastic fibres (Alam et al., 2019). Therefore, the differences in anthropogenic activities between the Global North and the Global South may affect abundances in freshwater microplastic contamination.

The dominant source of microplastic particles may also be determined by the physical characteristics of the dominant microplastic observed in the sample location (Horton et al., 2017). The dominant shape of microplastic particle can allude to the dominant input source (Horton et al., 2017). A location with predominantly more secondary microplastic fragments than fibres would indicate a dominating input source that was locally derived, likely from terrestrial run off (Horton et al., 2017). As WWTPs in the UK do not effectively remove microplastic fibre shapes from the effluent (Woodward et al., 2021), a dominance of fibres suggests a dominating input source from WWTPs (Horton et al., 2017). For example, previous research in the Ciwalengke River, Indonesia observed a dominance of microplastic fibres in river sediment samples (91%) (Table 2) (Alam et al., 2019). This was indicative of domestic and industrial washing of clothes due to the influence of industrialization as well as slums in this area (Alam et al., 2019). Microplastic shapes can also be influenced by the urban nature of the site location (Horton et al., 2017). Large amounts of secondary microplastics such as fragments are typically indicative of an urban sampling site, from the degradation of macroplastics in landfill, litter, tyres and/or road paint, sourced from terrestrial runoff (Horton et al., 2017). This was also observed in McGuinness (2022), who observed a higher proportion of fragments with an increase in urbanisation and population density. Variations in proportions of microplastic shapes between sample sites could therefore allude to changes in the dominant influencing input source between sites (Hurley et al., 2018).

Colour is also an important characteristic that may provide additional information of the input source. However, in previous studies, microplastic particle colours are used solely to aid in identifying microplastics from natural biological material, but are not accounted for or discussed in their analyses (e.g. Hurley et al., 2018; Dris et al., 2015; Alam et al., 2019). Transparent microplastics are generally derived from single-use plastics with a short time of usage, such as disposable plastic bags and bottles (Yang et al., 2021). Coloured microplastics are thought to be associated with consumer products with a longer time of usage (Yang et al., 2021; Shruti et al., 2019). Detailed interpretations about the source of the microplastic can also be alluded to by colour (Horton et al., 2017). For example, in previous studies, red and yellow microplastic fragments observed in the Thames River were associated with polymeric road marking paint when further analysis took place, therefore also suggestive of terrestrial runoff (Horton et al., 2017). However, the colour of microplastic can change due to its impermanence, for example, bleaching or yellowing during organic matter digestion during sample processing (Prata et al., 2019b). Moreover, as the origins of microplastics are vast, particularly fibres (clothes, ropes, carpets) (Browne et al., 2011), interpreting the origins solely based on colour is ambiguous, and therefore using colour to predict the source of microplastics is out of this study's breadth. Therefore, caution should be taken when making assumptions based on colour. Only half of previous studies on microplastics in freshwater sediment have a description for microplastic colour (Yang et al., 2021), and thus, future studies should account for colour due to its significant nature of alluding to input sources.

1.6.1. Wastewater Treatment Plants

Wastewater treatment plants (WWTPs) are an important link to the distribution and transport of microplastics from domestic and industrial sources into the natural environment (Horton et al., 2017; Kay et al., 2018). Kay et al. (2018) observed that the abundance of riverine microplastics was greater downstream of WWTPs, suggesting that WWTPs are a significant source of microplastics. In the UK, 96% of the population are connected to a WWTP (DEFRA, 2012). 11 billion litres of treated wastewater are directly released into rivers, estuaries, the sea and inland waters daily in the UK (DEFRA, 2012), representing a point source input. Without treatment in the WWTP, microplastics can pass through and be released into the environment within the effluent or within sludge (Habib et al., 1996). It has been estimated that 37% of all microplastics entering the world's ocean are released from WWTPs (Boucher and Friot, 2017). Policies in the United Kingdom allow untreated wastewater to be released from WWTPs and combined sewer overflows into inland rivers and the sea during rainfall storm events (DEFRA, 2002). The high rates of rainwater in these releases will dilute contaminants and disperse them downstream (DEFRA, 2002). However, recent studies have identified that untreated wastewater containing microplastics is regularly released during periods of low flow, therefore unable to disperse them downstream (Woodward et al., 2021).

An important pathway for microplastics to enter the freshwater environment from the terrestrial environment is through the application of sewage sludge on agricultural land (Horton et al., 2017). In the UK, 80% of all sewage sludge produced is used in agricultural soil as fertilizer (DEFRA, 2012). From soils, microplastics can be transported into freshwater systems through terrestrial run off (Figure 1) (Horton et al., 2017). Terrestrial run off combined with direct release of wastewater effluent are also likely to release microplastic fibres (Browne et al., 2011). It has been estimated that 1kg of synthetic textiles can release millions of microplastic fibres during a standard domestic wash, with polyester textiles emitting the most (Vassilenko et al., 2019; De Falco et al., 2018). An estimated 25% of global ocean microplastics are thought to be released from WWTPs (Boucher and Friot, 2017).

Previous studies for assessing wastewater treatment plants in England found that WWTPs removed microplastic fragments and beads effectively from the wastewater, but not microfibres (Woodward et al., 2021). Therefore, treated water from WWTPs do not influence the inputs of microplastic fragments or beads found in the river channel (Woodward et al., 2021). However, untreated wastewater discharges from WWTPs and combined sewer overflows during rainfall storm events may discharge microplastic fragments and beads into the riverine system (Horton et al., 2017; Woodward et al., 2021). Microplastic beads released in WWTPs are typically from cosmetic and personal care products, and fibres are released from the degradation of textiles from washing machines (Tibbetts et al., 2018). Additionally, previous studies also suggest that a high abundance of microplastic fibres in freshwater sample locations indicate an influence from sewage effluent (Horton et al., 2017). It was also found that there was a there was a greater abundance of microplastics with a greater number of WWTPs in the proximity of the sampling area (Shruti et al., 2019). Additionally, a greater processing capacity, related to the population size served, is positively correlated to the amount of microplastics released (Eo et al., 2019). WWTPs are generally located downstream from the settlements served, and therefore, sample sites upstream of the WWTP may be a good indicator for the impact of terrestrial runoff and effluents from industrial activity (Kelly et al., 1996). However, due to difficulties accessing the river at certain locations (and hence health and safety restrictions), it was not possible to sample any sites located upstream of any WWTPs in this study, so all study sites sampled will be influenced by sewage effluent from a WWTP (Figure 2).

1.7. Microplastic investigations

Typically, research quantifying microplastics in freshwater systems in England, UK have focussed predominantly on standing bodies of water, such as within lakes (Vaughan et al., 2017; Turner et al., 2019), or single locations in rivers and its tributaries (Horton et al., 2017). Limited research has looked at changes of microplastic concentration along large sampling areas, such as the course of a river, from source to the estuary (Woodward et al., 2021; Alam et al., 2019). As of January 2023, no studies have looked at microplastic contamination in rivers in Argentina. There is also limited research on microplastic contamination in freshwater systems in the Global South (Hurley et al., 2018; Yang et al., 2021). Additionally, compared to research of microplastics in marine environments (Ivar do Sol et al., 2007; Claessens et al., 2011; Hidalgo-Ruz et al., 2012), there have been comparatively less studies on microplastics in freshwater environments, although research has now increased over recent years globally (Table 2) (e.g. Dris et al., 2015; Horton et al., 2017; Hurley et al., 2018; Alam et al., 2019). Differences exist between riverine and marine systems, including a closer location of input sources in rivers, the smaller size of riverine systems, and different physical forces (for example, flow regimes, velocities, storm events) affecting the spatial and temporal distribution of microplastics (Eerkes-Medrano et al., 2015). It is therefore important to research microplastics in riverine systems, to understand the interactions with marine systems.

Microplastics in the River Wear, UK, have been recently previously researched (McGuinness, 2022). McGuiness (2022) focussed on the quantification of microplastics in fine channel bed sediment, as well as characterizing their physical properties (Table 2). However, McGuiness (2022) focussed on microplastic contamination in 5 sample sites chiefly around the urban area of Durham City, rather than the complete course of the river, from source to mouth. To avoid confusion, the study and data by McGuinness (2022) will herein be referred to as River Wear (Durham City). McGuinness (2022) carried out a similar sampling method to this study (Chapter 3), and hence direct comparisons will be made during the discussion (see Chapter 5). McGuinness (2022) observed a higher abundance of microplastics at a study site that was directly downstream of a WWTP. This suggested that WWTPs are a significant source of microplastics in the River Wear.

A summary of results of global microplastic abundances and their physical characteristics found in sediments in freshwater environments from select studies is shown in Table 2. A study from an urban lake (Hampstead Pond, UK: Turner et al., 2019) is included in the summary of results to provide attention to other freshwater bodies. This may help future studies to understand differences in microplastic abundances in different freshwater systems. Lakes are lower velocity environments than rivers and therefore are areas of microplastic accumulation (Tibbetts et al., 2018). As of March 2023, of all global microplastic studies in freshwater environments, the River Tame, Greater Manchester, UK recorded the highest abundance of microplastics (2960 microplastics/100 g of sediment) (Woodward et al., 2021) (Table 2). Compared to other studies within the UK, the River Tame, Greater Manchester, has over 4 times the abundance than the Mersey/Irwell Rivers (Hurley et al., 2018) (Table 2), the second highest abundance of microplastics in the UK (635 microplastics per 100 g of sediment) (Table 2). However, the high microplastic abundances in the River Tame, Greater Manchester, have been attributed to untreated wastewater released during periods of low flows from WWTPs at proximal sources to the sampling areas (Woodward et al., 2021). These releases also resulted in a varying microplastic assemblage, dominant in microbeads (Woodward et al., 2021).

Tibbetts et al. (2018) recorded 16.5 microplastics per 100 g of sediment in the River Tame, Birmingham, UK, much lower than recorded in other UK studies (Table 2). The River Tame, Birmingham, represents the most urbanised river basin in the UK (Tibetts et al., 2018), and so it would be expected that it should have a high microplastic abundance. Differences in sampling methods may cause these differences, highlighting the importance of methodology standardization (Tibbetts et al., 2018).

Study area	Abundance (per 100 g of sediment)	Shape	Size	Colour	Reference
River Thames, UK	66	Fragment (49.5%), fiber (47.4%)	1–4 mm	N/A	Horton et al., 2017
Mersey/Irwell Rivers, UK	635 (baseflow)	Fragment (57%), bead (33%), fiber (9%), other (1%)	N/A	N/A	Hurley et al., 2018
7 rivers and 1 tidal flat in Shanghai, China	80.2	Pellet (89%)	<100 μm (31.19%); 100–500 μm (62.15%); 1000–5000 μm (2.8%)	White (90%)	Peng, G. et al., 2018
River Tame, Birmingham, UK	16.5	Fragment (49%), fiber (22%),	<1 mm dominant	N/A	Tibbetts et al., 2018
Ciwalengke River, Indonesia	3.0	Fiber (91%)	50–100 μm (34%); 300–500 (18%); 500–1000(18%)	N/A	Alam et al., 2019
Nakdong River, South Korea	197	Fragment (84%), fibers (15%), beads (1%)	<300 mm (81%)	N/A	Eo et al., 2019
River Tame, Greater Manchester, UK	2960	Bead dominant	N/A	N/A	Woodward et al., 2021
Hampstead Pond, Lake in UK	53.9	>80% fiber	500 μm to 1 mm dominant	Blue (25%), white (22%), red (17%)	Turner et al., 2019
River Wear (Durham City), UK	153.7	Fiber (55%), fragment (26%), beads (11%), other (8%)	N/A	Transparent (27%), brown (17%), black (14%)	McGuinness, 2022
Rio Bermejo, Argentina (suspended sediment)	35.0 ± 25.9	Fiber (100%)	67–500 μm (50%); 500–1000 μm (27.3%); 1000–1500 μm (9.1%); 1500–2000 μm (4.5%)	Black (61.9%), red (14.3%), blue (14.3%), grey (4.7%), indigo (4.8%)	This study
Rio Bermejo, Argentina (river bank sediment)	21.7 ± 18.3	Fiber (76.9%), film (15.4%), other (7.7%)	67–500 μm (47.1%); 500–1000 μm (23.5%); 1000–1500 μm (23.5%); 1500–2000 μm (5.9%)	Black (61.5%), blue (15.4%), red (7.7%), transparent (7.7%), green (7.7%)	This study
Durham, UK	208.4 ± 157.3	Fiber (93.7%), fragment (3%) film (1.2%), bead (1.5%), other (0.6%)	85.5–500 μm (35.5%); 500–1000 μm (34.4%); 1000–1500 μm (17.2%); 1500–2000 μm (4.1%)	Black (45%), blue (22%), indigo (12%), red (11%), transparent (6%), grey (2%), orange (1%), white (1%)	This study

Table 2. *Summary of results from selected previous studies in global freshwater sediments and this study showing mean average microplastic abundances per 100g of dry sediment, and microplastic physical characteristics. This study's results are included for later comparison in the discussion (Chapter 5). Note that the results from Hurley et al. (2018) are the pre-flooding (i.e. baseflow) sample results. There are also two rivers in the UK named the River Tame, one in Greater Manchester, and one in Birmingham, as noted in the table.*

There is a large variance between the proportion of microplastic shapes between studies (Table 2). For example, fibres make up 91% of the total microplastic assemblage in the Ciwalengke River, Indonesia (Alam et al., 2019), compared to the Mersey/Irwell Rivers, UK (9%) (Hurley et al., 2018) (Table 2). Differences in the proportions of microplastic shapes between river catchments in sediment and water samples between previous studies are likely representative of the dominance of different input sources (Kay et al., 2018; Horton et al., 2017) (see Chapter 1.6).

1.7.1. Population density

The correlation between population density and the abundance of microplastics in previous literature has been widely contended. Positive correlations have been observed globally in the Chesapeake Bay, USA (Yonkos et al., 2014) and the Nakdong River, South Korea (Eo et al., 2019). However, no correlation was identified in the Tame River, Birmingham (Tibbetts et al., 2018), or the Rhine and Main Rivers, Germany (Klein et al., 2015). Previous studies suggest that riverine hydrodynamic forces effect microplastic abundance more than population density (Alam et al., 2019).

1.8. Global regional differences

Global regional differences can also affect the abundances of microplastics. The economic development of a country has a significant impact on the amount of microplastics released into the environment (Boucher and Friot, 2017). The amount of microplastics released into the oceans regionally can be estimated (Boucher and Friot, 2017; Ehrlich and Holdren, 1971). This estimation, the IPAT formula, is based on the combination of population size, GDP per capita (the portfolio of activities to cause microplastic release), and the efficiency of technology to prevent microplastic release (Boucher and Friot, 2017; Ehrlich and Holdren, 1971). Technology efficiency is based on population size, the share of population connected to WWTPs, and processing capacity of the WWTPs (Boucher and Friot, 2017). Europe and Central Asia release significantly more microplastics (239 kilotons per year) than South America (136 kilotons per year) into the global oceans (Boucher and Friot, 2017). South America has a lower population and GDP per capita than Europe and Central Asia, therefore generally releasing less microplastics (Boucher and Friot, 2017). South America generally also releases proportionally lower microplastics from WWTPs and road runoff (tyres and road marking paint) than Europe and Central Asia (Boucher and Friot, 2017). Road runoff and WWTPs are the main contributor of microplastics into the oceans (Browne et al., 2011; Boucher and Friot, 2017). From this, it can be hypothesised that the Rio Bermejo will have a lower abundance of microplastics than the River Wear.

The type of microplastics released into the environment is also dependent on the economic development of the country (Boucher and Friot, 2017). The predominant amount of synthetic fibres (63%) are consumed mainly in developing countries due to more purchases of synthetic textiles (FAO/ICAC, 2011). Fibres are the main source of microplastics in Asia, Africa and the Middle East (Boucher and Friot, 2017). This is due to a greater consumption of synthetic textiles (FAO/ICAC, 2011) and a lower divide of the population connected to WWTPs compared to more economically developed countries (Boucher and Friot, 2017). Tyres and road wear are the main source in Americas, Europe and Central Asia due to a greater vehicle driving distance (ETRma, 2011) and higher proportion of the population connected to WWTPs (Boucher and Friot, 2017). From this, it should be expected that the Rio Bermejo would contain a higher proportion of primary microplastic fibres than in the River Wear.

1.9. Study aims

The aim of this study is to quantify the concentrations and assemblage types of microplastics along the course of the River Wear, northeast England, in comparison to the Rio Bermejo, Argentina. To understand the complete variance of microplastics along a greater course of the river, from near the source to the mouth, this study will look at quantifying and assessing the physical characteristics of microplastics along a longer distance of the River Wear. This will enable an understanding of how factors such as land use (i.e. rural vs urban), WWTPs, population and industrialization affect microplastic contamination.

This research will help to understand the changes in microplastic concentration between two very different societies and therefore help to understand the influences between population size, urbanization and industrialization. The study will be important within the scientific community to aid in filling a geographical gap within the UK and Argentina, as well as comparing differences in contamination levels between the Global North and the Global South. This study will characterize microplastics into abundances, size ranges, colours and shape of microplastics, which will help to understand the input source of the microplastic. This study will also help identify relationships between previous studies of microplastic quantification in other areas of the UK. Moreover, comparing concentrations within the UK and Argentina will aid in understanding the global differences between treatment of microplastic contamination, as well as differences in anthropogenic activity. Further, this will aid in informing stricter targets for microplastic contamination policies and compliance.

1.9. Geographical location

1.9.1. River Wear, Durham

This study focuses on microplastics within the River Wear, and two of its related tributaries, River Deerness (a tributary of River Browney), and River Browney (a tributary of the River Wear). The River Wear rises in the North Pennines, and flows for 107km long, beginning at Burnhope Seat, Wearhead, County Durham, Northeast England, UK, and drains into the North Sea in Wearmouth, City of Sunderland, Northeast England (Figure 2). The River Wear passes through several towns and 2 major cities, the

City of Durham and the City of Sunderland. The River Wear has a catchment area of 1080 km^2, serving 620,000 people, and is a single thread, meandering, gravel-bed river channel. The Pennines are a rural area with rough sheep grazing and a low population density, where it was the largest lead-zinc mining area in the world (Kelly, 2001). The River Wear then flows into the Durham Coalfield, 20 km from the source, an area with a higher population density, that was heavily mined until the 1980s (Kelly, 2001). The Durham Coalfield extends from Bishop Auckland to the mouth of the River Wear. Coal mining was the main industry in County Durham, with approximately 170,000 of the 500,000 population employed within coal mining in the early 1920s (HMSO, 1923). The most upstream wastewater treatment plant (WWTP) is located around 20 km from the source of the River Wear, near Wolsingham, where sewage effluent first enters the River Wear (Figure 2). Along the River Wear and the four associated tributaries in this study, there are 19 WWTPs from the source to the mouth. All sample site locations in this study are influenced by sewage effluent input from WWTPs.

All sample site locations are located on the River Wear, apart from two sites: Holliday Park and Deerness Valley Nursery, which are located on the River Browney and the River Deerness respectively (Figure 2). River Deerness is a tributary to the River Browney, and the River Browney is a tributary to the River Wear (Figure 2).

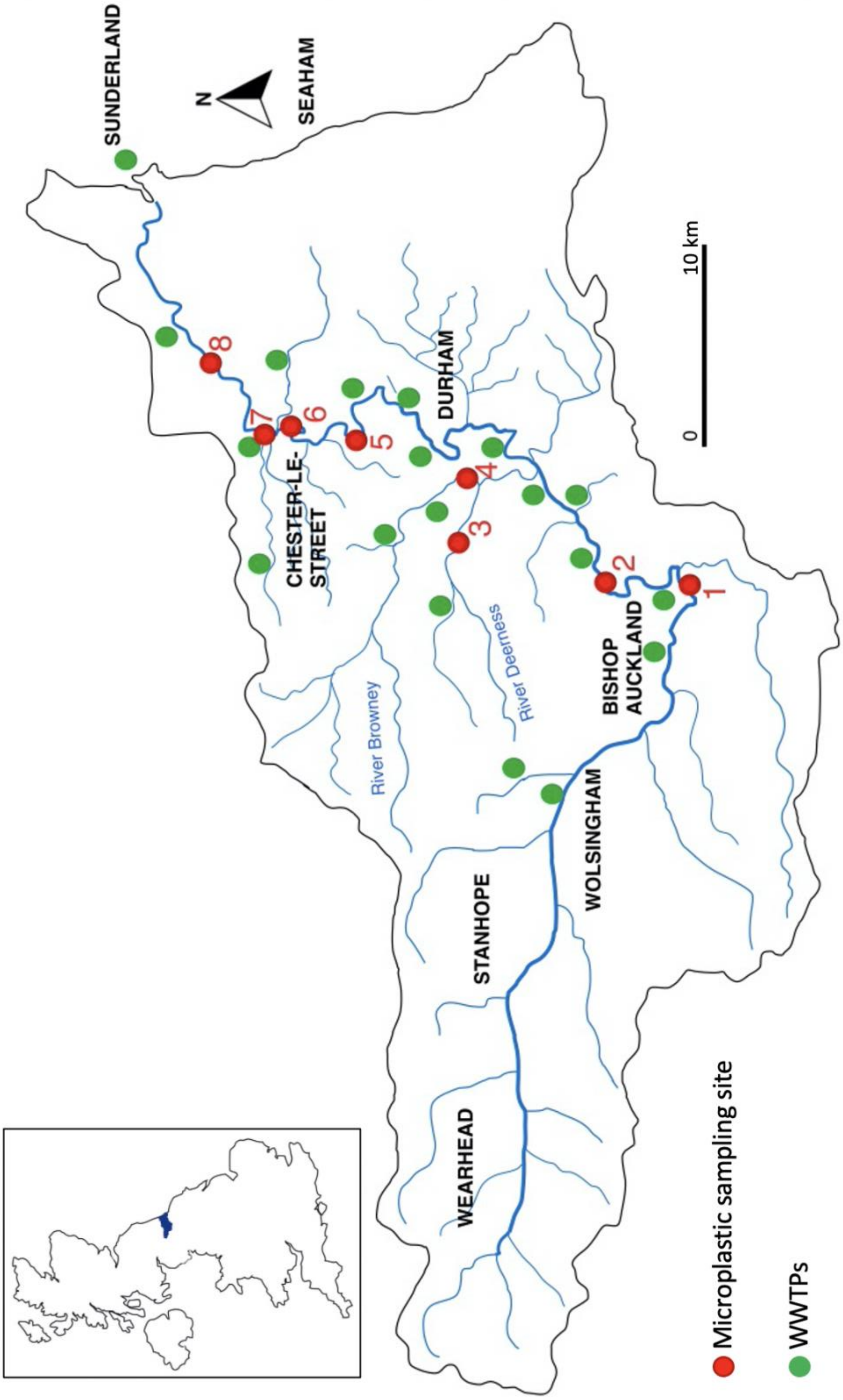


Figure 2. *Map showing the 8 microplastic sampling sites within the River Wear basin, shown in relation to the United Kingdom (shaded blue). Thicker blue line represents the River Wear and thinner lines represent its tributaries. Also shown are the 19 wastewater treatment plants (WWTPs) in the River Wear basin. Wastewater treatment plant data taken from* https://uwwtd.eu/United-Kingdom/*. 1: Batts Terrace; 2: Jubilee Nature Area; 3: Deerness Valley Nursery; 4: Holliday Park; 5: Cocken Road; 6: Riverside Wildlife Area; 7: Chester-le-Street Park; 8: Washington. For coordinates of sample sites, see Figure 5.*

1.9.2. Rio Bermejo, Argentina

The Rio Bermejo is a single thread, meandering river primarily in Argentina, South America, with no tributaries or distributaries, and is part of the Rio de la Plata basin. The upper reaches of the River begins in South Bolivia, and flows south-easterly for 1060 km before entering the Rio Paraguay (Figure 3). It has a drainage area of 123,162 km^2, and is primarily a silt-bed river. The Rio Bermejo has a relatively high overall sediment yield of 10×10^7 tonnes/year received from the Andes, and a high suspended sediment load of 98% (Orfeo et al., 2006; Iriondo & Orfeo, 2012). The last major tributary that transports water and sediment to the Rio Bermejo is the Rio San Francisco (Figure 3). Sediment load in the Rio Bermejo is either transported downstream or deposited in the riverbanks, and does not receive any tributary inputs, and therefore is a good location to understand spatial variations in sediment and microplastics without any external inputs (Repasch et al., 2021). The Rio Bermejo has high flow velocity and turbidity, and therefore minimal aquatic activity (Pedrozo et al., 1987).

The sampling site locations in the Rio Bermejo were selected based on the anthropogenic activities and to have a full understanding of microplastic pollution from upstream to downstream of a river. Sample locations were also selected based on accessibility of collecting sediment samples from the river, for example, having a bridge nearby to collect surface suspended sediment, as well as ease of accessibility of collecting riverbank sediment. A total of 6 locations were sampled (Figure 3). Surface suspended sediment and riverbank sediment were taken in the same locations on the same day.

The Rio Bermejo is estimated to serve 1.2 million people, of which many are rural workers and farmers, and indigenous populations. Compared to the River Wear, the Rio Bermejo has limited anthropogenic activity and a very low population density (see

Chapter 1.9.1) (Kelly, 2001; Pedrozo et al., 1987). The Rio Bermejo serves one major city, Orán, which has a population of 73,000 and is located between the confluence of Rio San Francisco and Rio Bermejo (Figure 3), but generally only smaller settlements are located along the Rio Bermejo (Pedrozo et al., 1987). Commercial and recreational fishing activities is common in upstream-midstream riverside locations within the Salta province, such as Embarcación, Orán, and in the study site Rio San Francisco (Figure 3), up until the Salta–Chaco province boundary, where an agrarian economy is more prominent in both the Chaco and Formosa provinces (Regidor, 2009; Miller et al., 2015). The Salta province has a population of 1,210,000 as of 2010, with an economy based on manufacturing and agriculture, whereas the Chaco and Formosa provinces have an agrarian economy based on growing commercial quebracho wood, cotton, cattle farming, and fruit cultivation (Miller et al., 2015), both with a relatively low population density, and a population of 1,050,000 and 530,000 respectively, as of 2010 (Regidor, 2009). The Rio Bermejo flows out from the Salta province and then marks the natural boundary between the Chaco and Formosa provinces, between the sample sites of San Francisco and Reserva Natural Formosa (Figure 3). Study area Embarcación is the most upstream site in the Rio Bermejo, located 10 km upstream from the confluence with the Rio San Francisco, and is the only study site that is not influenced by inputs from the Rio San Francisco. Between Rio San Francisco and the next downstream location, Reserva Natural Formation, the Rio Bermejo splits into the smaller Rio Bermejito, which later rejoins the Rio Bermejo near Villa Rio Bermejito, just upstream of the study location Puerto Lavalle (Figure 3).

Some hypotheses can be made based on the predominant land use and anthropogenic activity of the study sites in the Rio Bermejo. The upstream areas of Embarcación and Rio San Francisco, where commercial and recreational fishing takes place, is estimated to have a relatively greater amount of microplastics, compared to downstream locations in the Chaco and Formosa provinces, where there is less commercial fishing activity, a more predominant agrarian economy, and less population density. Additionally, study site Reserva Natural Formosa (Figure 3) is a large (91 km^2) protected nature reserve and therefore has a low population density and therefore relatively low anthropogenic activity. Periodic flooding is unprohibited and therefore has floodplains. It can therefore be estimated that there will be less microplastic particles found in this location due to the greater surface area for sediments and microplastics, received from upstream, to settle, and due to less microplastic inputs from nearby areas.

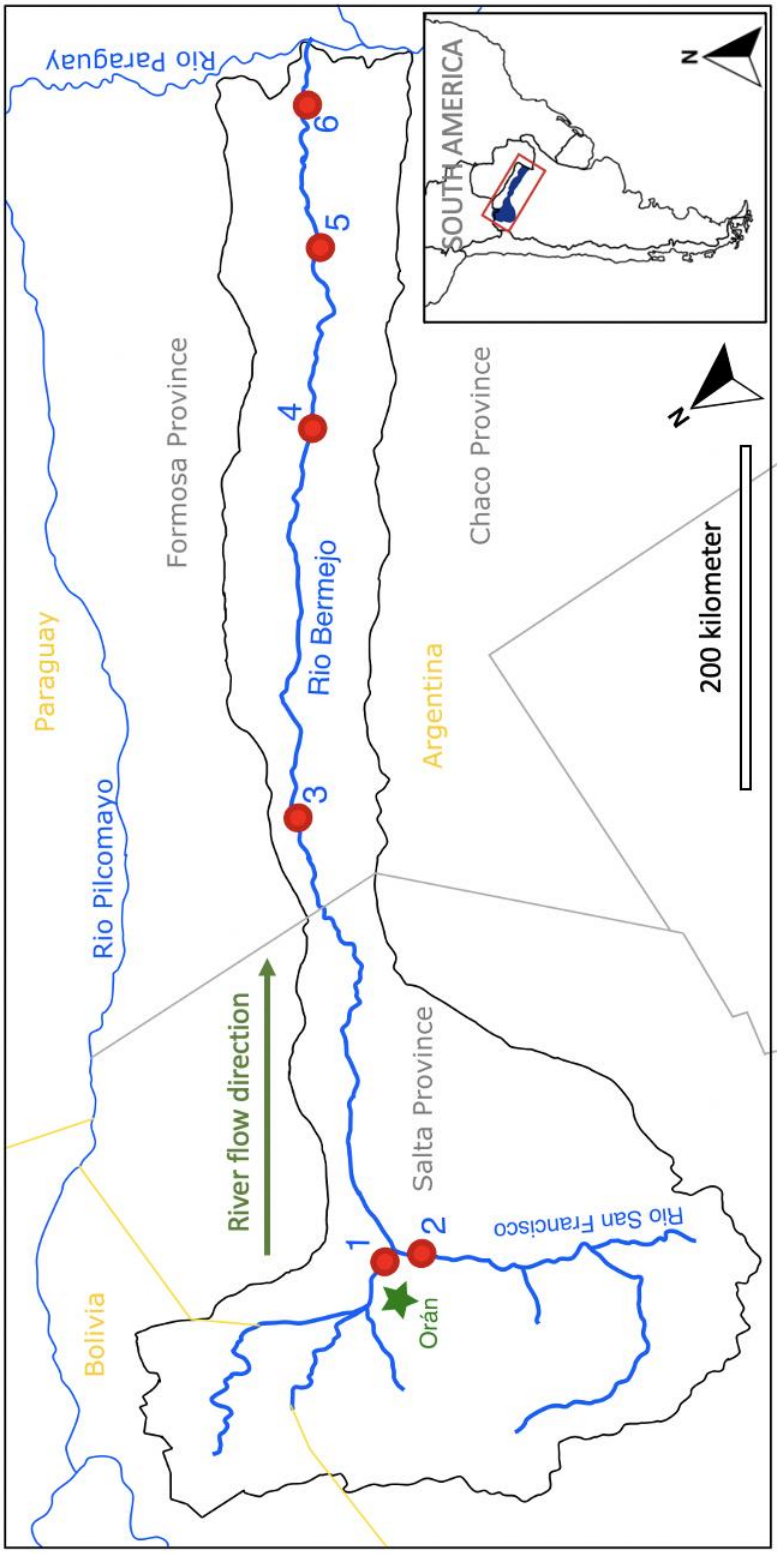


Figure 3. *Map of the Rio Bermejo basin in Argentina and its tributaries, shown within South America, with the basin shaded blue. Locations of sediment samples taken are shown as red dots. Green star, Orán, represents a major city. The direction of flow of the Rio Bermejo is shown. The Rio Bermejo marks a natural boundary between the Formosa and Chaco provinces. The Rio Pilcomayo also marks a natural boundary between Paraguay and Argentina. Surface suspended sediment and riverbank sediment were taken in the same locations. 1: Embarcación; 2: Rio San Francisco; 3: Reserva Natural Formosa; 4: Puerto Lavalle; 5: El Colorado; 6: General Mansilla. See Figure 4 for coordinates of sampling sites.*

Chapter 2: Methodology Review

2.1. Introduction to methodologies in literature

Although microplastic research in natural water bodies has been conducted since the 1970s (Carpenter et al., 1972), the methodologies for collecting samples, sample separation, pre-treatment and identification are not yet currently standardized (Yang et al., 2021; Prata et al., 2019b; Stock et al., 2015). A standardized method has been suggested for microplastics in beach sediments (Besley et al., 2017), which has similar applications to freshwater sediments during sample preparation. However, ambiguities remain about sample processing procedures in freshwater, for example the depth and type of field sampling (Stock et al., 2019; Yang et al., 2021) and use of organic digestion methods (Prata et al., 2019a). Further, the lack of standard net or sieve size during collection and laboratory filtration between studies results in a range of different microplastic sizes sampled (Prata et al., 2019b). This section will compare and review the different sampling procedures used in freshwater microplastic sampling methodologies, and the chosen method that will be used in this research paper.

2.2. Field sampling: sampling area

Methodologies for the specific environment area of sampling in a river has not been standardized. Measurement samples may be obtained from water samples from the water column or surface, or sediment samples along different areas of the river, such as in the channel and sand banks (Yang et al., 2021; Prata et al., 2019b). Water sampling, for example by using manta ray nets, are not representative of the entire microplastic assemblage (Woodward et al., 2020) as microbeads can only be sampled with a 100 μm mesh size (Lindeque et al., 2020). Additionally, microplastics that have a density greater than freshwater will sink and will not be observed in samples collected by neuston nets (Higaldo-Ruz et al., 2012).

Additionally, water sampling has issues with reproducibility as the distribution of microplastics in the water column is affected by geographical, temporal and meteorological factors (Prata et al., 2019b). In literature, manta trawl nets and neuston nets are interchangeable, the only difference being that neuston nets sample a greater surface depth (<50 cm) compared to manta trawl nets (15–25 cm). From herein, neuston nets will be grouped with manta trawl nets. Nets are able to sample a large volume of water to retain the volume-reduced samples quickly (Hidalgo-Ruz et al., 2012). The main difference between plankton nets and manta trawl is that the former is conical in shape, the latter rectangular pyramid. In previous studies, manta trawl nets with a mesh size of 300-390 μm are the most used equipment during water sampling (Lindeque et al., 2020), preferred over plankton nets (Hidalgo-Ruz et al., 2012). A greater mesh size allows to sample a greater volume of water hence being more representative of the sample location (Dris et al., 2015). However, a larger sized mesh allows smaller sized particles to pass through the mesh, underestimating the amount of microplastics in the water column by 2.5 times less when using a 333 μm mesh size compared to 100 μm (Lindeque et al., 2020). Additionally, previous studies observed that using a 333 μm mesh size during water sampling will not recover microbeads when compared to using a 100 μm mesh size (Lindeque et al., 2020). Therefore, the microplastic shape assemblages may not be fully represented when using a larger mesh size of the manta trawl net over a 100 μm mesh size.

Further, the density of the water in the environment affects the vertical distribution of microplastics, and the depth of water sampling must be adjusted according to location and salinity (Prata et al., 2019b). Generally, overbank floodplain sediments will underestimate microplastic concentrations that would otherwise be observed in the channel bed and should not be a sampling area (Woodward et al., 2021). Furthermore, studies have found that the concentration of microplastics in channel bed sediments were greater than in water samples or floodplain sediments at the same sampling site (Woodward et al., 2020; Eo et al., 2019), hence acting like a sink (Horton et al., 2017). Channel bed sediments also do not have a bias towards the accumulated type of microplastic unlike water sampling (Woodward et al., 2020), and therefore provide a more accurate representation of the microplastic assemblage and abundance in freshwater environments.

2.3. Field sampling: collection method

The general sampling collection method from the sampling environment (either sediment or water) is also not standardized and is described in Hidalgo-Ruz et al. (2012). Bulk sampling, which refers to collecting a known mass or volume of sediment/water in the field, is most appropriate when microplastics are difficult to identify by the naked eye due to low abundances, small sizes, or covered by sediments (Hidalgo-Ruz et al., 2012). Bulk sampling was used in the study by Hurley et al. (2018). Selective sampling refers to selectively extracting plastic particles visible to the naked eye (Hidalgo-Ruz et al., 2012), for example, used in the study by Corcoron et al. (2015). Selective sampling is not recommended due to the strong possibility of overlooking plastics, for example due to a similar colour to the sediments and due to plastics smaller than the naked eye (~<1 mm), and hence will be an underestimation (Stock et al., 2019; Yang et al., 2021). Volume-reduced sampling refers to remove the volume of the bulk samples during sampling to preserve the section of the sample that requires processing, for example by sieving sediments directly in the field, or using nets in surface water (e.g. Dris et al., 2015) (Hidalgo-Ruz et al., 2012). Volume-reduced sampling is advantageous in terms of only having to transport the samples needed for analysis but can be time-consuming and harder to mitigate contamination when sieving, such as washing the sieve between use, compared to carrying out filtration in the laboratory (Prata et al., 2019b).

Previous quantification of microplastics within rivers in England are limited (e.g. Woodward et al., 2021; Hurley et al., 2018), but employ the same methods. River channel beds are a recommended area to sample due to their role as an ecosystem for macroinvertebrates, with fine channel bed sediments providing sustenance, such as algae, for macroinvertebrates as well as fish and waterfowl (Woodward et al., 2020). Fine bed sediments contaminated with microplastics are an issue due to the increased bioavailability of microplastics (Wright et al., 2013) hence increasing the potential of microplastics entering the food chain through ecological ingestion (Hurley et al., 2017). Sampling fine bed sediments will therefore help to assess the concentration of microplastics and help understand the potential risks to aquatic ecology (Woodward et al., 2020) (Section 1.6).

The bulk sampling collection method is the most appropriate method for sample collection in the River Wear, Durham, in this study for the collection of samples, due to the collection of fine channel bed sediment and turbid water. Further, volume-reduced sampling, although would make transferring the samples easier into the laboratory, would require carrying more equipment (e.g. deionised water, sieve) into the field, and more processing, which would be more time consuming and laborious. However, volume-reduced sampling was carried out for the surface suspended sediments in the Rio Bermejo, due to the manta trawl net filtering out water during water sampling.

2.4. Field sampling: sampling depths

Sampling depths have also not been standardized and is recommended for comparison amongst datasets. Previous studies have found that the highest concentrations of microplastics during sediment sampling are found at a sampling depth of 1–5 cm, compared to the top 10 cm (Besley et al., 2017). Most previous studies collect samples from the top 2–3 cm or 5 cm, with some sampling the top 10 cm or deeper (Yang et al., 2021). A standardized sampling depth of 5 cm is therefore recommended by Besley et al. (2017). However, to help understand the interactions between the ecology and microplastics, it would be reasonable to suggest sampling the biotic zone, as in Hurley et al. (2018). The biotic zone in freshwater channel environments is the top 10–15 cm (U.S. EPA, 2015). Sampling the top 10 cm, used in this study for River Wear and Rio Bermejo riverbank sediments, would therefore be an optimal depth for representing the concentrations of microplastics whilst accounting for ecological interactions.

2.5. Laboratory processing: organic matter digestion

Organic matter is prevalent within freshwater samples and may increase misidentification of organic material for microplastics. Organic matter digestions method during pre-treatment have been used in previous studies to prevent overestimation of microplastic concentrations due to misidentification (Yang et al., 2021), although digestion is not yet standardized (Prata et al., 2019a). Some studies eliminate this step altogether (e.g. Hurley et al., 2018).

Freshwater fluvial samples are likely to contain more plant material, so it is more appropriate to use H_2O_2 than KOH, which is more efficient for digesting animal tissue (Prata et al., 2019a). Fenton's reagent (H_2O_2 and an iron (II) catalyst) may also be used to increase digestion efficiency (e.g., Prata et al., 2019a). Due to stronger reactions of polymers with higher concentration of H_2O_2 through bleaching and size and weight loss, it has been recommended to use 10% H_2O_2 for 18 hours (Frias et al., 2018). Greater exposure times do not significantly impact digestion efficiency (Prata et al., 2019a).

This study initially tested organic matter digestion using 10% H_2O_2 for at least 12 hours, following the method of Frias et al. (2018) to identify the efficacy of digestion. However, bleaching of organic matter was exhibited, and not all organic matter was completely removed. This was also experienced by Hurley et al. (2018), who also commented that digestion would increase the amount of organic material resembling microplastics, as digestion concealed organic structures. This study therefore does not use organic matter digestion during pre-treatment. Instead, strict criterion was followed to reduce misidentification (see Section 3.4).

2.6. Laboratory processing: density separation

As sediments have higher densities than plastics (0.8–1.6 g/cm^3) (Table 1), density solutions can be used to separate plastics from the sediment. A saturated salt solution with a known density (Table 3) is mixed with the sediment, allowing the sediment to separate from the plastics, and the supernatant containing microplastics is then collected (Frias et al., 2018).

	Density (g cm^{-3})	**Amount added to 1 litre of H_2O**
Sodium chloride (NaCl)	1.2	337
Sodium iodide (NaI)	1.3	494
	1.5	1000
Zinc chloride (ZnCl2)	1.3	500
	1.5	972
	1.8	1800

Table 3. *Amount of salts needed to be added to 1 litre of deionised water to achieve their associated densities. Table adapted from Coppock et al. (2017).*

In literature, three density solutions are commonly discussed and used to separate out microplastics from sediments, NaCl (1.2 g/cm^3), NaI (1.5 g/cm^3) and $ZnCl_2$ (1.5 g/cm^3) (Table 3). NaCl is most commonly solution used in literature (Prata et al., 2019b) as it is less expensive than NaI and $ZnCl_2$ (Coppock et al., 2017; Hidalgo-Ruz et al., 2012), easily available and environmentally non-toxic (Quinn et al., 2017). NaCl is also recommended by the NOAA (Masura et al., 2015). However, compared to NaI and $ZnCl_2$, NaCl is unable to density separate plastics with a density greater than 1.2 g/cm^3, such as polyvinyl chloride (PVC, 1.16–1.58 g/cm^3), polyethylene terephthalate (PET, 1.37–1.45 g/cm^3 – often used in textiles and making plastic bottles) and polyoxymethylene (POM, 1.41–1.61 g/cm^3) (Table 1) (Coppock et al., 2017; Yang et al., 2021). Therefore, using NaCl would underestimate the amount of microplastics found (Coppock et al., 2014; Nuelle et al., 2014), with the lowest recovery rate (85–95%), compared to NaI (94–98%) (Quinn et al., 2017), and $ZnCl_2$ (92-98%) (Coppock et al., 2017).

During microplastic recovery, a density of 1.5 g/cm^3 is recommended over 1.8 g/cm^3, as the higher density solution is able to keep fine sediment in suspension, precluding efficient separation of microplastics from sediment (Coppock et al., 2017). A density of 1.5 g/cm^3 is high enough to recover denser plastics such as PET and PVC, whilst preventing suspension of fine sediments (Coppock et al., 2017). Although $ZnCl_2$ is cheaper than NaI (Coppock et al., 2017), it is the most environmentally toxic of the other two density solutions and requires recovering and reuse (Prata et al., 2019b) and must be disposed properly. $ZnCl_2$ was therefore not used. The recovery rate of microplastics when using NaCl was found to be the lowest at 85–95%, compared to NaI (94–98%) (Quinn et al., 2017), and $ZnCl_2$ (92–98%) (Coppock et al., 2017).

NaI is the preferred density solution in previous literature, as it is environmentally safe, unlike $ZnCl_2$, and can extract higher density plastics that NaCl cannot (Prata et al., 2019b). Although it is the most expensive solution out of of NaCl and $ZnCl_2$ (Coppock et al., 2017), it can be recycled and reused multiple times (Prata et al., 2019b). However, NaI reacts with cellulose fibres commonly used in laboratory filters, turning them a red-black and can hinder visual identification (Prata et al., 2019b). An example of the filters being dyed by NaI can be seen in Figure 5.

Similar to Hurley et al. (2018), two density solutions were therefore used on each sample (NaCl (1.2 g/cm^3) and NaI (1.5 g/cm^3)) to enhance the recovery and extraction of microplastics. The use of both NaCl and NaI to increase efficacy was similarly employed by Nuelle et al. (2014).

Chapter 3: Methodology

3.1. Field collection method

The field collection methods were different between the Rio Bermejo and the River Wear, which will be discussed in this section. Samples from Argentina were taken from the water column (water sampling) and from riverbank sediments. Durham samples were taken only from fine channel bed sediment, which is discussed in Section 3.1.1. A simplified flow chart of the methodology is depicted in Figure 4.

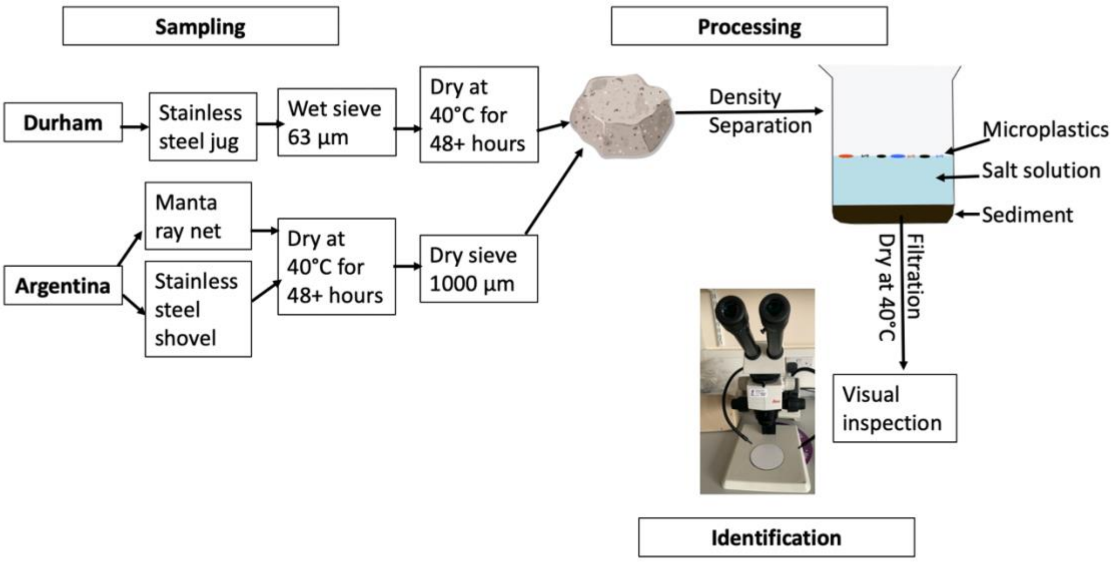


Figure 4. *Schematic flow diagram of the methodology, showing field sampling, sample processing and sample identification for Durham and Argentina samples. The process and visual inspection processes were the same for both Durham and Argentina, however different methods of field sampling were carried out for each locations.*

3.1.1. Durham

Fine channel bed sediment samples were collected using a bulk sampling collection method similar to Woodward et al. (2021) and Hurley et al. (2018) to ensure reproducibility and maintain comparability between studies within the UK. Samples were collected in baseflow conditions between October 2021 and July 2022.

Samples were collected by isolating an area of the channel bed by inserting an aluminium cylinder (height: 600 mm; diameter: 420 mm) into the bed sediment at a depth of 100 mm to sample the biotic zone. The bed sediments isolated in the cylinder were brought into resuspension by agitation using a piece of timber for 20 seconds, disturbing the bed-sediment matrix as described in Lambert & Walling (1988). This technique was carried out at three locations within a 10 m^2 area of the channel bed at each sampling site and combined to reduce spatial variability and better represent the sampling site. The water and water suspended sediment mixture were collected with a 1-litre stainless-steel jug and decanted into a clean 25-litre high density polyethylene container. The stainless-steel jug was rinsed using river water between sample collection. Samples were transported into the laboratory and processed the same day. The 25-litre polyethylene container was thoroughly rinsed following sample processing with tap water and left to air dry. See image Appendix B1 for examples of the sampling locations in Durham.

A preliminary sample collection method was initially tested before using the current methodology. The preliminary method involved using a stainless-steel scoop to obtain sediment samples from the channel bank at a depth of ~10 cm. Sediment samples were stored in transparent plastic bags. There was no specified distance away from the river channel, rather based on ease of access. The laboratory processing methodology however was identical to this current study. The microplastics observed were not included in this study due to differences in field sampling methodology, but example results can be seen in Appendix B3.

3.1.2. Rio Bermejo, Argentina

Samples from the Rio Bermejo were taken on behalf of this study by the German Research Centre for Geosciences, Potsdam (GFZ Potsdam). 14 sediment samples from 6 locations along the Rio Bermejo, including 1 location in the Rio San Francisco, 15km from the confluence, were collected. At each location, surface suspended sediment samples and riverbank sediment were collected on the same day, between March 2017 and March 2020.

Surface suspended sediment was collected by volume-reduced water sampling using a neuston net with a 300 µm mesh size and 15 cm diameter funnel opening. The neuston net was lowered from a bridge into the Rio Bermejo, with the net opening point facing against the flow of the river. The neuston net was lowered just beneath the surface of the river to sample the superficial layer of the water column (the top ~30 cm of the surface), similar to Dris et al. (2015). After 10 minutes, the neuston net was removed from the river, and the sediment samples were decanted into clean glass bottles. 10 minutes was a sufficient amount of time to obtain a representative sample volume, similar to that of Dris et al. (2015). The river velocity between sample sites ranged between 0.1–0.7 ms^{-1}. After each sample collection, the neuston net was thoroughly rinsed with river water to avoid contamination between samplings. The samples were then transported to the laboratory to be dried on the same day.

Riverbank sediments were collected using a stainless-steel scoop to sample the sediment surface at an approximate depth of 10 cm, similar to that of Horton et al. (2017). The stainless-steel scoop was rinsed thoroughly with river water between sample locations to avoid contamination. Sediment samples were placed into paper bags to be transported into the laboratory on the same day to be dried.

In the laboratory, surface suspended sediment and riverbank samples were decanted onto aluminium-foil lined metal trays and were dried in an oven for 48 hours at 40°C. The dry sediment samples were then decanted into 1-litre amber glass bottles, covered with an aluminium-foil lined plastic screw cap and stored at room temperature. The dry Rio Bermejo sediment samples were delivered and received at the Department of Earth Sciences, Durham University, in September 2021 for sample processing to take place.

In total, 16 jars each containing a 1-litre volume of sediment were received, including 2 jars of overfill from 2 different sample locations. Of the 16 jars, 7 broke on transit, and glass pieces were therefore mixed within the sediment samples. However, mixing between samples was negligible and sediment samples were contained in their respective jars. The sediment samples were first decanted into lidded clean paint pot tins to prevent airborne contamination and mixing between sediment samples, and any large glass pieces visible by eye contaminated in the sediments were picked out using stainless-steel tweezers prior to any sample processing.

3.2. Laboratory processing

All equipment used in the laboratory were rinsed with deionised water to avoid contamination. Blanks were carried out at each processing stage to account for any contamination. White cotton laboratory coats were worn at all times, and blue, purple or white nitrile gloves were used when handling chemicals. The colour of the gloves were recorded in case of contamination.

3.2.1. Filtration of sediments

Following the collection of Durham field samples, samples were wet sieved using a 63 μm stainless steel sieve to sort the sand fractions from the silt and clay (Lambert & Walling, 1988). 63 μm therefore represents the lower size limit of microplastics recorded (Prata et al., 2019b). The retained sand fraction was decanted onto an aluminium-lined metal tray and oven dried at 40°C for at least 24 hours, until dry. A temperature of 40°C was used to prevent changes in physical characteristics of the plastic, which can occur at temperatures above 60°C (Nuelle et al., 2014). No microplastic contamination was identified in blanks.

For Rio Bermejo samples, due to broken glass contamination in the samples, all samples had to be dry sieved using a 1 mm stainless steel sieve to remove larger glass pieces and any large organic debris. A lower limit filtration (as used for wet sieving in the Durham samples) was not used for the Rio Bermejo samples as the samples were dry and therefore unnecessary. However, 300 μm would represent the lower limit of microplastics found in suspended sediment due to the mesh size used during sediment collection. As microplastics are defined as being smaller than 5 mm (Hanke, 2013), the analysis of the Argentina samples may not completely represent the total microplastic concentration. All dry sediment samples were then transferred into blue polypropylene containers for storage, stored at room temperature, until processing for density separation.

3.3. Density separation

To make density solutions, specified weights of salt (Table 3) were added to 1-litre of deionised water, and stirred with a glass rod until no more salt would dissolve, to achieve the specified densities. The solution was transferred and stored in a 1-litre high density polyethylene bottles at room temperature until required for use.

Ten grams of dry sediment was decanted onto a clean, white polystyrene weighing boat using a stainless-steel spatula. A digital laboratory balance, accurate to <1 mg, was used and recalibrated after each sample was weighed, to account for any changes in the weighing scale. Weighing boats were cleaned using methanol and laboratory wipes after each use.

The 10 g of dry sediment were then decanted into 50ml centrifuge tubes for density separation. The first density solution, 1.2 g/cm^3 NaCl, was added to the 50 ml line and then covered. For two Durham samples, Cocken Road and Holliday Park, there was not enough sediment to reach the 10 g weight for analysis, with 4.2 g and 9.9 g respectively. The results of these samples were extrapolated accordingly to reach 10 g to maintain comparability amongst samples. The mixture was manually shaken for 3 minutes and was allowed to settle for at least 4 hours or until the solution was clear (similar to Woodward et al. (2021) and Hurley et al. (2018)). Samples were allowed to settle for longer amounts of time if the solution was not clear after 4 hours.

3.4. Collection of the supernatant

As organic matter digestion was not used for the fine channel bed sediments, some of these samples contained high amounts of organic matter that collected in the supernatant during the density separation. This made it difficult to filter out using the typical filtration system as described below. An additional step was provided to collect the supernatant, whereby the supernatant was initially filtered using a 70 μm metal sieve (smallest mesh size available for a small metal sieve close to the original mesh size used during wet sieving) to remove as much of the supernatant as possible. The supernatant was then decanted onto a translucent plastic petri dish and dried in an oven at 30–40 degrees for 24 hours or until dry.

The remaining supernatant was then collected using a plastic 5 ml syringe and then filtered using a metal filtration system and 25 mm diameter filter paper (Whatman Filter

Paper 1 (cellulose, pore size 11 μm). All equipment was rinsed between samples to avoid contamination. The filter paper was then transferred onto a foil-lined metal tray using metal tweezers and covered with aluminium foil, and dried in an oven at 30–40 degrees for 24 hours to dry. The dried filter paper was then stored in a lidded plastic container until required for microscopic identification.

A second extract using a higher density solution (NaI, 1.5 g/cm^3) was then repeated on the samples, based on the method of Hurley et al. (2018). As NaI is expensive, the filtered NaI solution was collected in a glass beaker and recycled. However, following filtration of the supernatant and drying, NaI experienced significant crystallization on the filter paper than NaCl, obscuring identification and often crystallized above the particles recovered. NaCl did not experience this issue, and did not dye the filter paper, allowing maximum contrast. Further, NaI coloured the filter paper to a red-black, as noted by Prata et al. (2019b), which made it difficult to identify microplastics, particularly darker coloured particles, and inhibited accurate determination of microplastics. An example of the dyed filter paper can be seen in Figure 5.

3.5. Visual inspection

Identification of microplastics were carried out using a 6x lens magnification light Leica M80 stereomicroscope. Visual inspection was carried out directly on the filter paper or petri dish (whichever was used during drying) to prevent loss during transfer (Yang et al., 2021). See Appendix B2 for an example of the set up during visual inspection. The criteria for identifying microplastics is strict and standardized, to reduce misidentification and underestimation, as summarised by Yang et al. (2021) and described below:

1) Dimension is <5 mm

2) Microplastic shapes are categorized as: fibre, pellet, foam, film and fragment. Microplastics must have a uniform homogeneous thickness
3) Coloured particles are homogenously coloured
4) No visible cellular or organic structures

However, these criteria may lead to misidentifying microplastics due to its limited nature. More strict criteria were therefore used within this study to increase identification accuracy (Nor and Obbard, 2014):

1) Fibres are equally thick along their entire length and should not taper at the end and should not be segmented or appear as twisted flat ribbons (Nor and Obbard, 2014)
2) Unnatural, homogenous colours compared to the majority of other colours in the sample (e.g. bright blues, reds), with a homogenous texture (Horton et al., 2017)
3) Unnatural shape (e.g. perfectly spherical: Horton et al., 2017)
4) Flexible with no brittleness (Horton et al., 2017)

Using these criteria together can also help to reduce misidentifying algae (Alam et al., 2019), which was a common issue during this study. Additionally, strict criterion is important when more accurate techniques cannot be used, such as FTIR analysis (Higaldo-Ruz et al., 2012).

Limitation

The highest magnification that the microscope was able to use was 6x, which meant that there was a visual diameter scope of 2 mm in total. This meant that it was difficult to determine whether small microparticles (smaller than ~0.5 mm) were microplastics. This limitation has been noted in previous studies (Hidalgo-Ruz et al., 2012; Yang et al., 2021). To reduce misidentification, fibre-shaped particles smaller than 0.5 mm were identified as synthetic microfibres based on colours that appeared inorganic (e.g. red or blues) (Horton et al., 2017) and a uniform homogenous thickness (Nor and Obbard, 2014). However, the lack of greater magnification and certainty may have underestimated the amount of microplastics smaller than 0.5 mm due to human bias (mistaking small dark coloured fibre-like shapes for environmental debris). Previous studies have also shown a trend of greater misidentifying microplastics as size of the particle decreases (Yang et al., 2021).

Additionally, there is a human bias when characterizing the colour of microplastics under the stereomicroscope. Stereomicroscopes can alter a particle's true colour with greater magnification. For example, black particles to the naked eye may appear navy/indigo, and green colours of algae often appeared blue. To avoid this, the magnification was reduced when a suspected microplastic was identified, and the colour that the particle occupied when zoomed out was recorded if the particle met the criteria in Chapter 3.5. Additionally, brighter coloured particles are generally more recognisable, compared to transparent, white or darker coloured particles, which may be mistaken for biological material (Dris et al., 2015). Transparent and white coloured particles were harder to observe in this study, as it was difficult to identify translucent particles against the white coloured filter paper. Salt crystals, particularly when using NaI, were also prominent, making it difficult to identify transparent microplastics compared to salt crystals.

During visual inspection, fly ash was commonly identified in the supernatant. Fly ash is easily identified from microplastics due to being a shiny grey-black in colour and more angular in shape. Fly ash is common in sediments in Durham due to the predominance of coal fields.

FTIR and Raman Spectroscopy Analysis

FTIR and Raman spectroscopy are common in previous studies (e.g. Horton et al., 2017) to identify and confirm the type of plastic (Hidalgo-Ruz et al., 2012). Raman Spectroscopy was not carried out in this samples due to having no access to equipment, and FTIR analysis was not able to be used due to the majority of the microplastics found being too small for analysis. Although identifying microplastic particles under visual inspection was carried out by a strict criterion, without using FTIR and Raman spectroscopy the lack of confirmation of an anthropogenic source may be a limitation; in previous studies, as much as 7% and 5% of suspected microplastics were found to be organic through Raman Spectroscopy (Horton et al., 2017; Alam et al., 2019).

Chapter 4: Results

4.1. Introduction

This section will separately discuss microplastics and their physical characteristics observed in the Rio Bermejo and River Wear. Microplastic abundance, shape, size, and colour will be summarised for both locations. Microplastic particle shapes classified in this study are categorized as fibre, film, fragment or other. This section will discuss and compare the microplastic shapes observed in Rio Bermejo and Durham samples, and its significance. Examples of microplastic particles observed in this study can be seen in Figure 5.

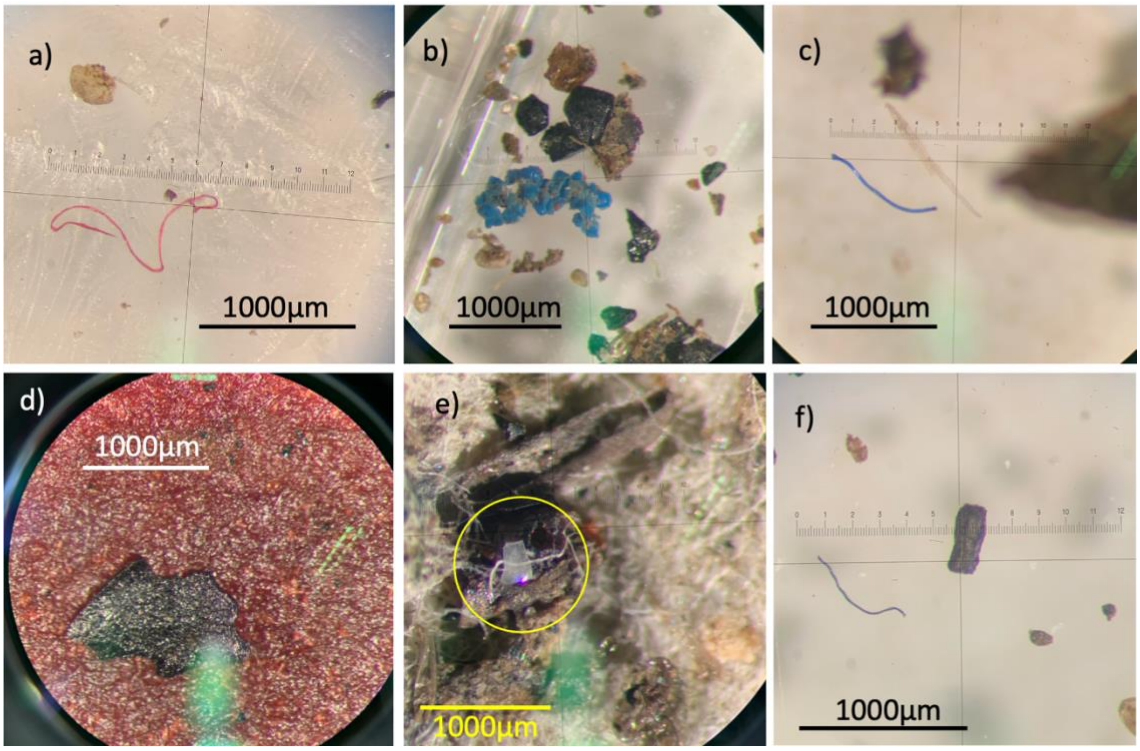


Figure 5: *Examples of identified microplastics from Durham and Argentina samples, viewed under a 6x lens magnification Leica M80 stereomicroscope. Images taken on a mobile phone camera. a) red fibre b) blue fragment c) blue fibre d) black fragment (viewed on NaI filter paper, hence dyed red) e) transparent fragment (circled) f) black fibre.*

Blanks carried out in the laboratory did not contain any microplastic particles when examined under the stereomicroscope and therefore there is no need to take microplastic contamination into account. Microplastic contents in each sample are expressed as the number of microplastic particles per 100 g of dry sediment to ensure representative comparability between sites: this is a standard technique in microplastic studies (e.g. Horton et al., 2017; Peng, G. et al., 2018; Alam et al., 2019).

4.2. Rio Bermejo, Argentina

4.2.1. Microplastic abundance

Visual identification was carried out on processed sediment samples to identify microplastic particles for both riverbank sediments and surface suspended sediment. Microplastic particles were found in all sites in Argentina in both suspended sediment and riverbank sediments, with the exception of the Reserva Natural Formosa site (Table 4). The study site of El Colorado had the greatest amount of microplastic particles found in suspended sediment, with an abundance of 70 particles per 100 g (Table 4). Puerto Lavelle had the greatest amount of microplastic particles in riverbank sediments, with an abundance of 50 particles per 100 g (Table 4). Average combined microplastic abundances in sites in the Rio Bermejo in suspended sediment were comparatively greater than that of riverbank sediment (Table 4). This study observed a mean (±standard deviation) microplastic concentration of 35.0 ± 25.9 particles per 100 g of dry surface suspended sediment (n=6), and 21.7 ± 18.3 particles per 100 g of dry riverbank sediment (n=6) (Table 4).

				Abundance/100 g		Percentage (%) of shape type in suspended sediment	Percentage (%) of shape type in riverbank sediment		
	Site	Latitude	Longitude	*Suspended sediment*	*Riverbank sediment*	*Fibre*	*Fibre*	*Film*	*Other*
Upstream	**Rio San Francisco**	-23.249116	-64.138283	40	10	100	0	0	100
	Embarcacion	-23.355918	-64.182774	60	30	100	66.7	33.3	0
	Reserva Natural Formosa	-24.3048	-61.83518	20	0	100	0	0	0
	Puerto Lavalle	-25.651642	-60.137531	10	50	100	80	20	0
	El Colorado	-26.33225	-59.36058	70	30	100	100	0	0
Downstream	**General Mansilla**	-26.66009	-58.63266	10	10	100	100	0	0
			Mean ± standard deviation	**35.0 ± 25.9**	**21.7 ± 18.3**				
			Total percentage (%)			**100**	**76.9**	**15.4**	**7.7**

Table 4. *Abundances of microplastics within suspended sediment and riverbank sediment, weight corrected to particles per 100 g of sediment for sites across the Rio*

Bermejo, Argentina. Rio San Francisco represents the most upstream site, and General Mansilla represents the most downstream site. The percentage of each microplastic particle shape type for each site in Argentina is also shown, alongside calculated percentage of each shape type for all combined samples from all sites in the Rio Bermejo. Refer to Appendix A2 for the complete dataset showing each microplastic shape.

4.2.2. Microplastic shape

In surface suspended sediments, 100% of microplastic particles identified in each site were fibres (Table 4), and no fragments, films, beads, or other shapes were identified. Therefore, all microplastics in surface suspended sediments were primary. In riverbank sediments, fibres were the dominant shape type in each site, apart from the site Rio San Francisco, where 100% of the particles were classified as other (Table 4). Films and others were proportionately less common in riverbank sediments for all sites apart from Rio San Francisco (Table 4). No microplastic fragments or beads were found in riverbank sediments at any sites. There was no specific trend in variation in microplastic shapes between sites for riverbank sediment. When riverbank samples are combined, 76.9% of microplastic particles observed were fibre, 15.4% were film, and 7.7% were classified as other (Table 4).

4.2.3. Microplastic size

Microplastic particles identified in surface suspended sediment and riverbank sediment had a size range of 167–2004 μm (mean: 623 μm) and 67–1169 μm (mean: 647 μm) respectively (Figure 6). Although the size range of suspended sediments were larger than riverbank sediments, the mean size of microplastics were similar in both, with surface suspended sediment being more positively skewed towards smaller microplastics than riverbank sediment (Figure 6). Differences in sample collections (using a 300 μm mesh size when collecting surface suspended sediment, vs not using a net in riverbank sediments) could explain why the smallest particle size in surface suspended sediment was larger than riverbank sediment. In both riverbank sediments and surface suspended sediment, the size range of 67–500 μm had the greatest proportion of microplastic particles (Figure 6). The greater the size range, the lower the proportion of microplastic particles were found for both sediment types (Figure 6). However, particles smaller than 500 μm had an increased risk of misidentification due to visual identification using a light microscope (see Section 3.4). Although this should be noted as a limitation, the use of a strict and standardized criteria, as mentioned in Section 3.4, will help to reduce misidentification.

As during water sampling a 300 μm mesh size manta trawl net was used, the lower limit of the microplastic found should be 300 μm for surface suspended sediment. However, particles smaller than 300 μm were found following visual inspection, up to 167 μm. Additionally, as the sieve size during laboratory processing was 1000 μm for both surface suspended sediment and riverbank sediment (see Section 3.2.1), particles greater than 1000 μm would have been filtered out and discarded, but during visual inspection, particles greater than 1000 μm in length were identified (Figure 6).

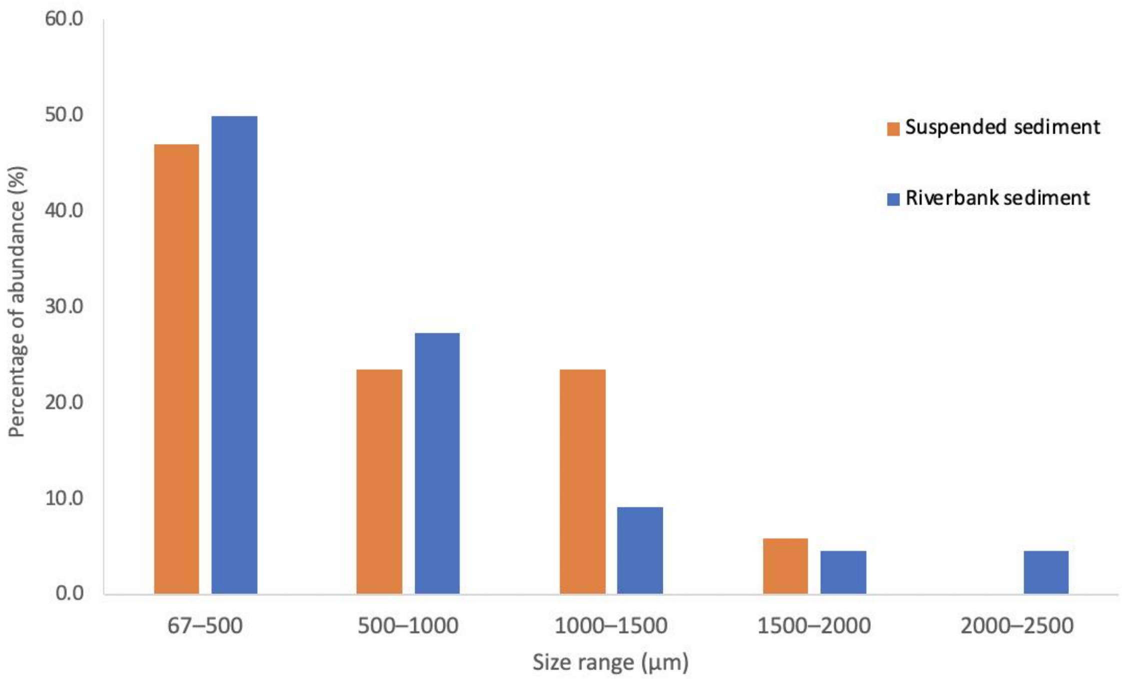


Figure 6. *Total percentage abundance of size ranges for microplastic particles identified in surface suspended sediment (n=22) and riverbank sediment (n=13) for Rio Bermejo microplastic samples. Refer to Appendix A2 for complete dataset showing size data.*

4.2.4. Microplastic colour

Microplastics identified in Argentina samples exhibited a variety of colours, including black, red, blue, green and translucent (Figure 7). Black was the predominant microplastic particle colour type, found in similar proportions with 62% and 61% of black particles in surface suspended sediment and riverbank sediment respectively (Figure 7). No transparent coloured microplastics were observed in surface suspended sediment (Figure 7a) but were observed in riverbank sediment (Figure 7b).

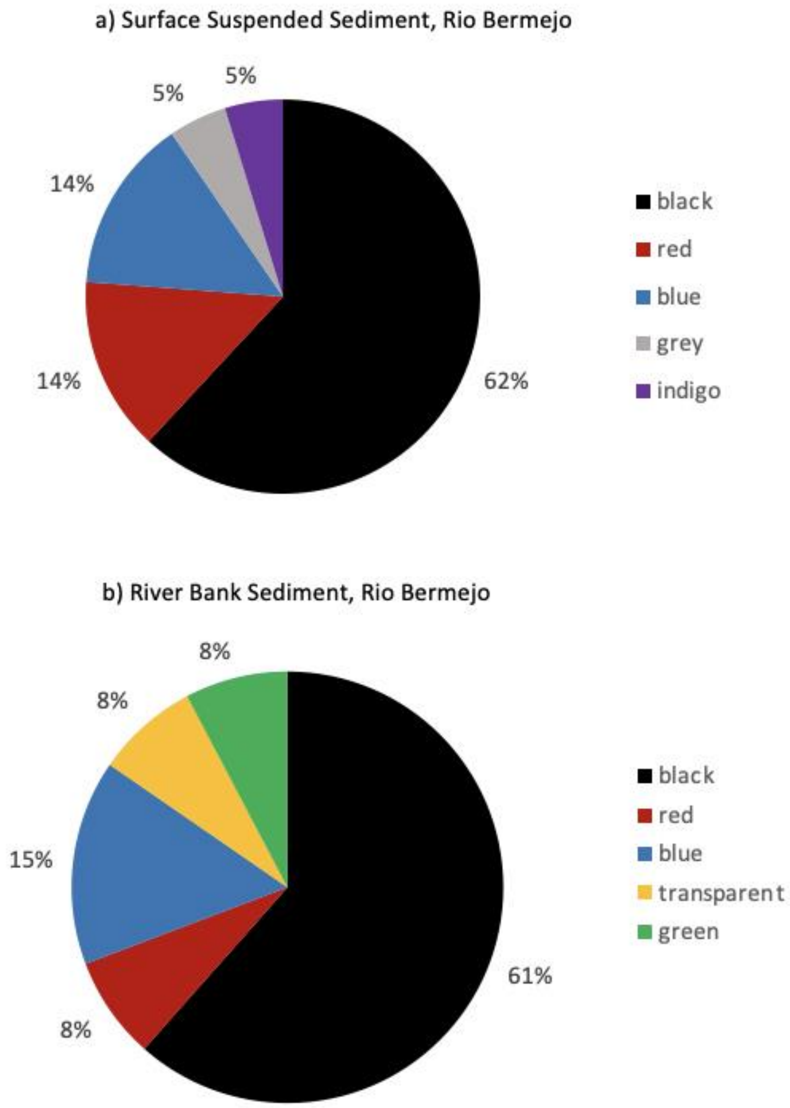


Figure 7. *Proportional colours of microplastics in the Rio Bermejo in combined sediment samples of a) surface suspended sediment (n=22), b) riverbank sediment (n=13). Refer to Appendix A2 for complete dataset of microplastic colours.*

4.3. River Wear, England

4.3.1. Microplastic abundance

Microplastics were observed in all sites across Durham. The least amount of microplastics were observed at site Riverside Wildlife Area, with an abundance of 100 particles per 100 g of dry sediment (Table 5). The greatest amount of microplastics observed were at site Cocken Road, with 574 particles per 100 g (Table 5). The mean concentration (± standard deviation) of microplastics across all sites was 208.4 ± 157.5 particles per 100 g of dry sediment (n=8) (Table 5). The high standard deviation reflects the anomalously large abundance (574 particles per 100 g) at Cocken Road (Table 5).

					Percentage (%) of shape type in fine river bed channel sediments				
Site	Latitude	Longitude	River	*Abundance per 100 g*	*Fibres*	*Film*	*Fragment*	*Bead*	*Other*
Batts Village Terrace	54.667989	-1.679039	River Wear	110	100	0	0	0	0
Jubilee Nature Area	54.703844	-1.677594	River Wear	260	88.5	7.7	0	0	3.8
Deerness Valley Nursery (River Deerness)	54.773309	-1.650432	River Deerness	140	92.9	0	7.1	0	0
Holliday Park (River Browney)	54.762773	-1.605076	River Browney	203	94.8	0	0	5.2	0
Cocken Road	54.818854	-1.565602	River Wear	574	95.8	0	0	4.2	0
Riverside Wildlife Area	54.84091	-1.56092	River Wear	100	100	0	0	0	0
Chester Le Street Park	54.854903	-1.562532	River Wear	170	88.2	0	5.88	5.9	0
Washington	54.88098	-1.50776	River Wear	110	90.9	0	9.1	0	0
			Mean ± standard deviation	**208.4 ± 157.3**					
			Total percentage		**93.7**	**1.2**	**3.0**	**1.5**	**0.6**

Table 5. *Abundances of microplastics within fine riverbed channel sediments, weight corrected to particles per 100 g of dry sediments. Sites are shown in order from upstream (Batts Village Terrace) to downstream (Washington). See Figure 2 for sample site locations. Calculated average mean of abundance is also shown. The percentage of each microplastic particle shape type for each site is shown, alongside calculated percentage of each shape type for all combined samples from all sites in the River Wear. Refer to Appendix A1 for the complete dataset of each microplastic shape.*

4.3.2. Microplastic shape

Overall, for all Durham samples combined, fibres, and hence primary microplastics, were the most dominant type of microplastic (93.7%), followed by fragments (3.0%) (Table 5). The least abundant shape overall was 'other', making up 0.6% (Table 5). Fibres were the most dominant in each site, and the proportion of fibres were similar in each site (Table 5). 'Films' and 'other' were only observed in Jubilee Nature Area (Table 5). The assemblage of microplastic shapes is seen to vary from study site, but there was no specific trend in variation in microplastic shapes between sites along the River Wear, or from upstream to downstream (Table 5).

4.3.3. Microplastic size

For all Durham samples, the smallest microplastic particle size observed was 83.5 μm, and the largest was 3750 μm. Two particles found were above the defined maximum microplastic size limit of 5000 μm (Hanke, 2013), both with a size of 6000 μm. The lowest size range corresponds with the sieve size used during sample processing (63 μm), as no microplastics were found smaller than this value. The size class of 0–500 μm had the greatest percentage abundance, at 35.5%, followed by 500–1000 μm, at 34.4% (Figure 8). Class size 3500–4000 μm had the lowest percentage abundance (0.6%) (Figure 8). Durham samples exhibited a trend similar to that of Rio Bermejo samples (Figure 6); a general increasing in the abundance of microplastics with a decrease in size range (Figure 8). A greater size range was exhibited in Durham samples (83.5–3750 μm) compared to Rio Bermejo samples (suspended sediment (167–2004 μm); riverbank sediment (67–1169 μm)) (Figure 6 and 8). This could be a result of the sieving method used during laboratory processing, where an upper limit mesh size of 1000 μm was used for samples in the Rio Bermejo.

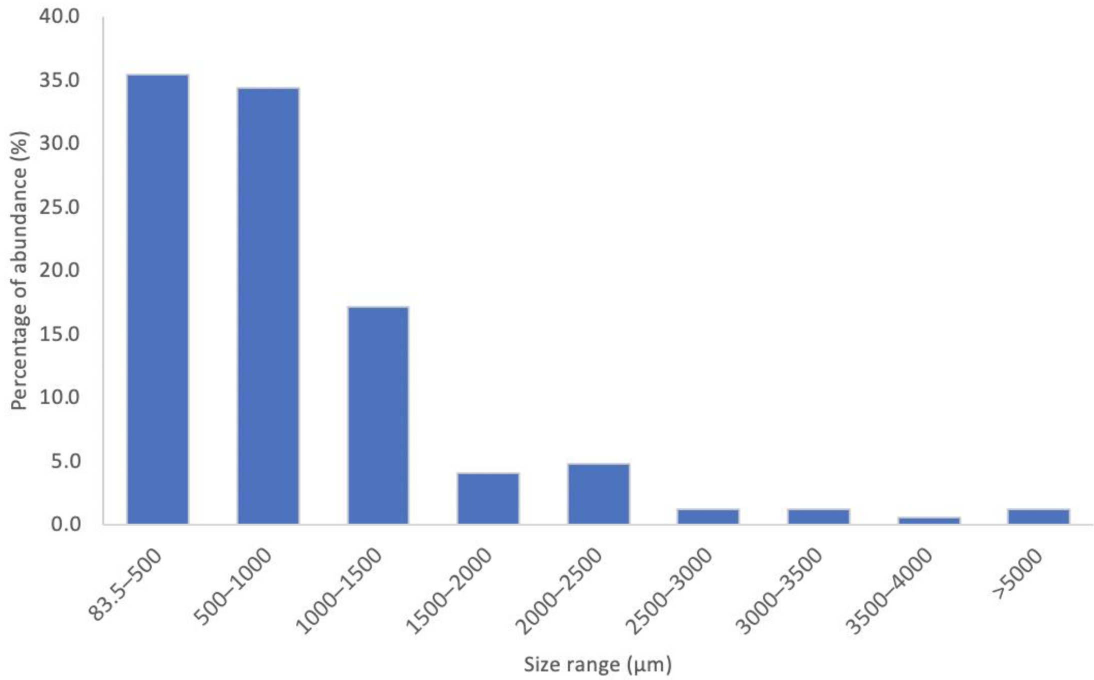


Figure 8. *Total percentage abundance of size ranges for combined observed Durham microplastic particles. 2 particles were observed to be larger than 5000 μm. Refer to Appendix A1 for the complete dataset of each microplastic size.*

4.3.4. Microplastic colour

Microplastics identified in Durham samples (Figure 9) exhibited a greater variety of colours compared to Argentina samples (Figure 7a and 7b), including black, red, blue, indigo and transparent. Black was the dominant microplastic particle colour type (46%), whereas white and orange were the least common (both 1%) (Figure 9). Durham samples exhibited a lower proportion of black coloured microplastics (Figure 9) compared to Rio Bermejo samples (62% and 61% in surface suspended sediment and riverbank sediment respectively) (Figure 7a and 7b). Durham also exhibited colours that were not observed in Rio Bermejo samples, including transparent (6%), white (1%) and orange (1%) (Figure 9). However, no green coloured particles were observed in Durham samples, which were observed in riverbank sediment in Rio Bermejo (7%) (Figure 7b and 7c).

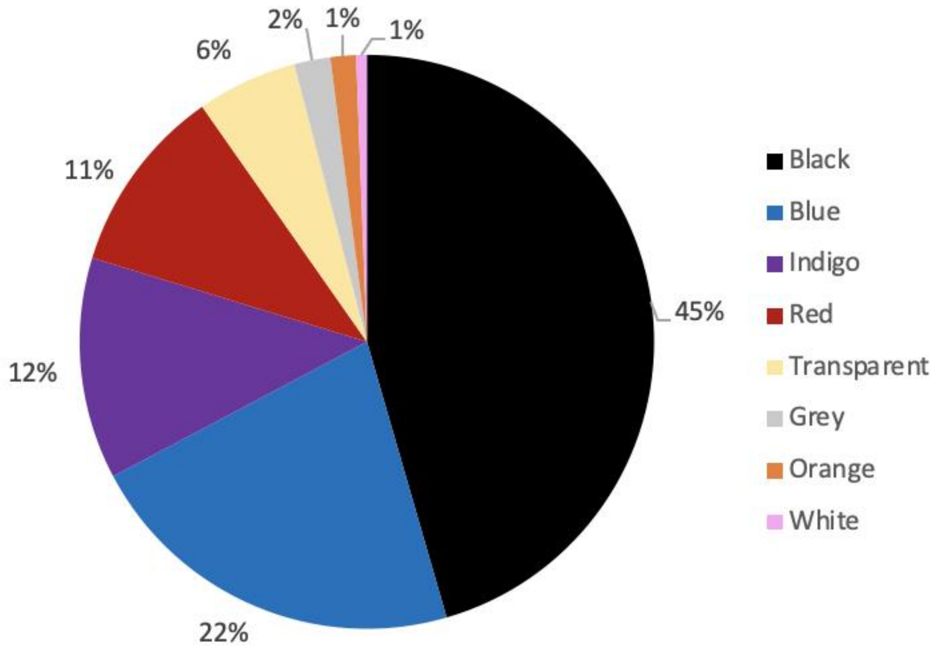


Figure 9. *Proportional colours of microplastics in combined sediment samples in fine channel bed sediment, River Wear (n=133). Refer to Appendix A1 for the complete dataset of each microplastic colour.*

Chapter 5: Discussion

5.1. Rio Bermejo

The Rio Bermejo region provides an ideal location to understand the distribution of sediments and therefore, microplastics along a river course due to receiving no tributary inputs (Repasch et al., 2021). Providing unequivocal interpretations for the microplastic abundance and assemblage at each sample site is difficult due to a variety of complex numbers involved, such as river dynamics (Eerkes-Medrano et al., 2015), but references based on urbanisation and population at sites can be made to help understand the influence anthropogenic activity has on microplastics in freshwater environments.

The abundance of microplastic particles in both riverbank sediment and suspended sediment in the Reserva Natural Formosa is found to be much less compared to the relatively more upstream, urban study sites of Rio San Francisco and Embarcación (Table 4). This is likely an indicator of the decrease in population and a change from urban to rural land. Study site Reserva Natural Formosa is a rural area with no major settlement nearby, and has the lowest population compared to the other sites. Additionally, the major town of Orán is within close proximity to the study sites Embarcación and Rio San Francisco (Figure 3), and therefore a higher population has a significant influence for these upstream study sites. Hydrodynamics may also help to explain the lower concentrations of microplastics at the study site Reserva Natural Formosa, an area with expansive floodplains. Low velocity environments, such as floodplains and lakes, are thought to be a sink for fine grained sediments and hence microplastics (Tibetts et al., 2018; Rolf et al., 2022). During high velocity, flooding events, microplastics are remobilised from channel bed sediment (Hurley et al., 2018), and can be deposited in lower velocity environments on floodplains (Tibetts et al., 2018). Additionally, previous studies in the River Tame, Greater Manchester, UK, observed that microplastics in overbank floodplain deposits are dominantly microbeads (84%), providing evidence that the microplastic assemblage are partitioned during a flood event, with fibres being flushed downstream (Woodward et al., 2021). Therefore, floodplains act as a preferential sink for microbeads. This may explain why zero microbeads were observed in site Reserva Natural Formosa in neither suspended or riverbank sediment.

Study sites Rio San Francisco, Embarcación, and El Colorado had higher amounts of microplastics found in suspended sediment compared to the other sites (Table 4), which may be a result of the relatively higher population and anthropogenic activities in these areas. Although El Colorado has less commercial and recreational fishing activities compared to study areas Embarcación and Rio San Francisco (see Section 1.9.2), other anthropogenic activities, such as textile laundering, may contribute to the addition of microplastics, particularly fibres, in the river (Alam et al., 2019). Interestingly, these study sites did not exhibit proportionally similar abundances in riverbank sediments (Table 4), with the study site Puerto Lavalle containing the highest abundance of microplastics. Since external factors such as channel topography, river flow velocity, and microplastic properties (density, shape, and size) affects the transport and distribution of microplastics in the freshwater environment (Eerkes-Medrano et al., 2015), it is not expected for the proportions of suspended sediment to be similar to riverbank sediment. This reflects how sampling different mediums can provide a unique interpretation for microplastics, and how standardization of field sampling is needed to ensure the interpretation of microplastics is best reflected in their sampling medium.

Study site Puerto Lavelle had the greatest amounts of microplastics in riverbank sediments in comparison to all other study sites in the Rio Bermejo (Table 4), which could be because the sample is located on the inner bank of a meander, where sediment is deposited, and the proximity to an active recreational campsite nearby. As previous studies estimate, sections of the river with low flow velocity are significant hotspots of accumulating microplastics in sediments (Nizzetto et al., 2016; Tibetts et al., 2018; Yang et al., 2021). Recreational activities in the campsite such as fishing and boating occur, which likely is a source for microplastics in riverbank sediment. Fibres derived from the air can also be a source of microplastics (Dris et al., 2015), for example, fallout from clothing and from recreational swimming, may also be a source of microplastics at this study site. Puerto Lavalle had a greater microplastic shape assemblage in riverbank sediment, compared to other rural study sites at the Reserva Natural Formosa and General Mansilla, where 20% of microplastics were film-shaped (Table 4). As microplastic shapes can allude to its origin (see Section 1.6), the presence of film, a secondary microplastic, is suggestive that an input of microplastics is locally derived at this study site (Horton et al., 2017). This could be due to the degradation of plastic material in the camp; for example, food packaging from litter (Horton et al., 2017). Microplastic fibres derived from clothing from recreational activity can also be deposited by terrestrial run off. It should however be noted that more data, such as identifying the type of plastic material is required to accurately determine the source of plastic.

Secondary microplastics derived from terrestrial runoff can also be suggested in other study sites in the Rio Bermejo. At site Rio San Francisco, 100% of microplastics in riverbank sediment were classified as ‘other’ shaped (Table 4). This may be representative of being in an urban area, with a dominant input from terrestrial runoff of secondary microplastics (Horton et al., 2017). No microplastic fibres were observed in riverbank sediment, but contributed to 100% of microplastics found in suspended sediment (Table 4). This may be due to differences in the sampling medium (see Section 5.1.1). The study site, Embarcación is an urban area and contained 33.3% of microplastic film and 66.6% of microplastic fibres in riverbank sediment (Table 4). Presence of film, a secondary microplastic, reflects an input source of terrestrial runoff and the fibres from a source of textile laundering (Horton et al., 2017). Whereas the study sites El Colorado and General Mansilla, both with settlements had a microplastic assemblage of 100% fibres in riverbank sediments (Table 4). This would indicate that sewage effluent was the dominant input source of microplastics in these locations. Differences between the dominant input source along study sites can be affected by a variety of factors, for example, the urban nature of the study site and proximity of the study sites to storm drainage (Horton et al., 2017). Thus, it is difficult to predict the dominating input source in specific locations.

The increase in abundance in microplastics in suspended sediment from study site Puerto Lavalle to El Colorado (Table 4) may represent the change from a rural to urban area. Study site El Colorado represents the urban settlement of El Colorado in the Formosa rovince (Figure 3), and so a greater abundance may reflect the higher population and anthropogenic activity. El Colorado had a microplastic abundance greater than the mean average for riverbank sediment (Table 4), supporting the influence of anthropogenic activity. A decrease in microplastic abundance in riverbank sediment from Puerto Lavalle to El Colorado may reflect changes in depositionary environment. As Puerto Lavalle represented a sampling site in the inner bend of a meander, it is possible that this is a hotspot for microplastic accumulation (Tibetts et al., 2018), compared to study site El Colorado, which would represent an area of lower microplastic accumulation. Since the deposition of microplastics is controlled by a number of complex factors (Eerkes-Medrano et al., 2015), it is difficult to interpret subtle changes in abundance between sites.

The general decrease in microplastic abundances in both suspended sediment and riverbank sediment in study site General Mansilla (Table 4) may be a reflection of the lower population in this study site compared to El Colorado, a larger urban settlement. General Mansilla also has abundances lower than the mean averages, reflecting its lower population than other sites, and hence a lower anthropogenic influence. However, due to being the most downstream study site, complex physical river properties may also affect the transport and dispersal of microplastics (Eerkes-Medrano et al., 2015). For example, having a greater channel depth and width, reduced steepness, differences in flow velocity and meandering properties, may affect the distribution of microplastics (Eerkes-Medrano et al., 2015).

5.1.1. Comparison between suspended and riverbank sediment

In the River Bermejo, average microplastic abundances in suspended sediment were comparatively greater than that of riverbank sediment (Table 4) by ~61.2%. As suspended sediment typically contains fine inorganic clay or silt (<63 μm) or fine sands (63–250 μm) during high velocity conditions, it can be alluded that suspended sediment will also have an affinity for smaller microplastics. Within suspended sediments, there is a greater skew towards smaller-sized microplastics compared to riverbank sediment (see Chapter 4.2.3), it can be interpreted that the size of microplastics affects the abundance in different sampling mediums. Woodward et al. (2020) also observed that in water samples, fibres dominate. Additionally, as microplastics used within consumer products typically have a density between 0.8–1.0 g/cm^3 (Yang et al., 2021), lower density microplastics, will tend to float on the water surface (Eerkes-Medrano et al., 2015). Fibres from textiles are typically polyester (1.37–1.45 g/cm^3), acrylic (1.09–1.20 g/cm^3) and/or polyamide (1.02–1.05 g/cm^3) (Table 1) (Browne et al., 2011), and thus textile laundering material will have an affinity to be buoyant. Buoyant fibres are more likely to remain in suspension for a longer period of time than other shapes (Hurley et al., 2018). Such fibres are able to be transported much further than other microplastics (Su et al., 2016) and could be more widely distributed in the aquatic environment. Microplastic fibres have been found to be the most easily entrained shape and is the least likely to accumulate in sediment deposits (Hurley et al., 2018). The general abundance of microplastic fibres, alongside their buoyancy, ease of entrainment, and therefore greater spatial distribution in freshwater environments may explain why there is higher dominance and abundance of microplastic fibres in surface suspended sediment in all sites in the Rio Bermejo, in comparison to riverbank sediment (Table 4). This shows that riverbank sediments are more representative of the overall microplastic assemblage due to a greater variety (Table 4), agreeing with Woodward et al. (2021). Therefore, future studies should focus on sediment sampling compared to water sampling.

All study sites in the Rio Bermejo had a higher concentration of microplastics in suspended sediment than in riverbank sediment, apart from Puerto Lavalle (Table 3). Study site Puerto Lavelle had five times more microplastics in riverbank sediment than in suspended sediment. This is possibly due to study site Puerto Lavalle being located in the inner bend of a meander, representing a depositionary hotspot environment (Tibetts et al., 2018). Moreover, Puerto Lavalle was located near to a recreational campsite nearby, and so microplastics derived from human activity may significantly contribute, for example due to increased litter.

5.2. River Wear

The study site, Cocken Road had a significantly greater abundance of microplastics (574 particles/100 g of dry fine channel bed sediment) compared to the other sites in the River Wear (Table 5). Cocken Road had almost twice the abundance of Jubilee Nature Area

(260 particles per 100 g of sediment), the site with the next largest abundance of microplastics. Cocken Road is the closest site located downstream of Durham City, the most populated, urban settlement on the River Wear, and its suburbs, including Framwellgate Moor, and Pity Me. Cocken Road therefore represents a site influenced by the greatest amount of anthropogenic activity on the River Wear. This agrees well with McGuinness (2022), who observed an increase in microplastic abundance towards the more urban, populous Durham City. There are three WWTPs between Durham City and Cocken Road (see Figure 2), of which the closest to Cocken Road is approximately 3 km upstream. It can therefore be interpreted Cocken Road is influenced by the inputs from WWTPs upstream. Previous studies have identified that WWTPs contribute to the abundance of microplastics in freshwater environments (Browne et al., 2011; Kay et al., 2018; Woodward et al., 2021).

Jubilee Nature Area had the second highest abundance of microplastics (260 particles per 100 g). This study site represents the site just after Willington Village and immediately downstream from a WWTP (see Figure 3). The close proximity of the sampling site to the WWTP may affect the abundance of microplastic particles found, where it is also possible that more microplastic fibres are found close to the point source (Woodward et al., 2021). Although population size and proximity to WWTPs can help to predict the abundances of microplastic particles in river systems, predictions are complex due to other external factors previously discussed. Moreover, the amount of microplastics retained in WWTPs can vary due to differences in their treatment, before being released as sewage effluent (Tibetts et al., 2018). Furthermore, UK policy allows untreated wastewater to be released from WWTPs (DEFRA, 2012). These factors therefore may affect how much microplastics are released (Tibetts et al., 2018), and highlight the unpredictability of the amount released into freshwater environments.

In comparison to previous overall microplastic abundances recorded in the River Wear (Durham City) (153.7 particles/100 g sediment), microplastic abundances in this study were greater (208.4 particles/100 g sediment) (Table 2). This is interesting as it is expected that more microplastics would be observed in the River Wear (Durham City) due to more localised sampling in an urban area with a higher population density. A potential explanation could be that study site Cocken Road may record an anomalously high abundance (574 particles/100 g of sediment) in this study (Table 5). Excluding Cocken Road from the mean average calculation in this study, the overall average abundance is 156.1 particles/100 g of sediment, similar to that of River Wear (Durham City). This again does not support the hypothesis. Differences in dates of sampling, temporal differences related to seasonal variations may therefore affect the overall abundances.

Microplastic fibres are the predominant shape in fine channel bed sediment in the River Wear (Table 4). The dominance of microplastic fibres is consistent with previous research (e.g. Horton et al., 2017; Turner et al., 2019). Cocken Road had the highest proportion of microplastic fibres of all sites in Durham (Table 4), making up 95.8% of the assemblage. This could represent that riverine microplastic inputs are proportionally more influenced from sewage effluent in Cocken Road than terrestrial runoff due to the higher proportion of fibres. Since there was no significant difference between the proportions of microplastic fibres between sample locations, or from upstream to downstream (Table 4), it is possible that WWTPs have a higher degree of influence than terrestrial runoff along the course of the River Wear. However, McGuinness (2022) observed a greater shape assemblage in the River Wear (Durham City), containing less fibres overall (55%), and more fragments (26%) than in this study (Table 2). This difference may be reflective of the impacts of higher population density in Durham City, resulting in more litter, road wear and hence terrestrial runoff (Eo et al., 2019), resulting in more secondary microplastics (Horton et al., 2017). Overall, McGuinness (2022) also identified that WWTPs were the most significant input source of microplastics in the River Wear. Taking into consideration the greater population size in Durham City, with a high proportion of the population connected to a WWTP (Boucher and Friot, 2017), it can be interpreted that WWTPs are the dominant source of microplastics in the River Wear. Terrestrial runoff also influences the input of secondary microplastics, particularly in Durham City (McGuinness, 2022). This shows that comparing microplastic assemblages is a better indicator to determine dominating input sources when comparing microplastic contamination between the River Wear and River Wear (Durham City), than comparing abundances (see above paragraph). Using microplastic abundance alone should therefore not be used to indicate the degree of microplastic contamination when comparing to other studies. This is particularly due to differences in sampling methodologies. Rather microplastic assemblage, particularly shape, should be used to help better understand microplastic sources during comparisons. This should be noted in future studies.

Fragments make up 3% of the total microplastic assemblage in the River Wear (Table 4), suggesting that terrestrial runoff had a much lower degree of influence than WWTP. Additionally, in the UK, as sewage sludge is allowed to be applied to arable land (DEFRA, 2012), there is a possibility that some microplastic fibres found were derived from terrestrial runoff (Horton et al., 2017). However, terrestrial runoff would not be the dominant input source due to the lack of secondary angular fragments in all sites (Horton et al., 2017). It can therefore be inferred that the dominant input source in all sites in the River Wear is likely from sewage effluent rather than terrestrial runoff, due to the dominance of primary microplastics.

A major input of microplastic beads into the freshwater system is from sewage effluent from WWTPs, released from cosmetic products (Tibetts et al., 2018). However, in the United Kingdom in January 2018, microplastic beads were banned from being used within cosmetic and personal care products (Environmental Protection England, 2017). The decline in use of microplastic beads may therefore represent the lack of microplastic beads found in the fine-channel bed sediment in the River Wear and its tributaries (Table 4). Furthermore, although river channel beds may act as a sink for microplastics (Corcoron et al., 2015), flooding events have been shown to remobilise microplastics in the channel bed and flush them downstream (Hurley et al., 2018). Flooding events and the date of sample collection is likely an explanation for the differences in concentration of microplastic beads from this study to previous studies. Hurley et al. (2018) observed 33% of observed microplastics to be microbeads during baseflow conditions in the Mersey/Irwell Rivers (Table 2), compared to 1.5% in the River Wear (Table 4). Hurley et al. (2018) carried out baseflow sediment sample collection between April and July 2015, hence, before the ban on microplastic beads on cosmetic and personal care products took place. Hurley et al. (2018) also observed that after a significant flooding event, microplastic contamination in the channel bed decreased by a mean average of 64%. It can therefore be interpreted that following the ban of microbeads, there has been a significant reduction in the amount of microplastic beads found in fine channel bed sediment in the UK. This is significant ecologically, knowing that some fish species feed selectively on shape and ingest only white-coloured plastic spherules (Carpenter et al., 1972) (see Section 1.5.1). However, other primary microplastics such as pellets are still used for industrial purposes such as in plastic manufacturing (Boucher and Friot, 2017). Pellets can then enter the freshwater environment if controls are not adequate in industrial facilities, for example through unintentional spills during transport or processing (Boucher and Friot, 2017).

As microplastic shape affects bioavailability, the high proportion of microplastic fibres observed is significant. A previous study identified that 87% of microplastics ingested by *Tubifex* worms were microplastic fibres, highlighting their affinity for microplastic fibres (Hurley et al., 2017). *Tubifex* worms are ingested by salmon and trout (Dunbrack et al., 1988), presenting a direct risk to human ingestion and transfer (Hurley et al., 2017) (see Section 1.5.3). The River Wear contains significant populations of salmon and trout (Environmental Agency, 2023), and recreational fishing activity, highlighting the risk of human level transfer.

5.3. Comparison between the Rio Bermejo and the River Wear

Average microplastic abundances in the Rio Bermejo in both riverbank sediment and suspended sediment are comparatively less than that in the River Wear and the River Wear (Durham City) (Table 2, 4 and 5) (McGuinness, 2022). Differences in abundance can be attributed to factors such as land use and socio-economic differences. As the Rio Bermejo has less urbanisation and a very low population density compared to the River Wear (see Section 1.9.2) (Kelly, 2001; Pedrozo et al., 1987), the lower anthropogenic activity reflects the lower amounts of microplastics released into the rivers. Additionally, technology efficiency can be attributed. South America has a relatively lower technology efficiency than Europe and therefore may increase the amount of microplastics released into the rivers (Boucher and Friot, 2017). However, using the IPAT formula to combine the influence of population and affluence with technology efficiency (see Section 1.8), South America is predicted to release less microplastics than Europe (Boucher and Friot, 2017), agreeing well with the microplastic abundances from this study. This implies that technology efficiency and processing capacity of WWTPs alone should not be used to interpret the amount of microplastics released and should be considered with population size and affluence. Moreover, the higher microplastic abundance in the River Wear compared to the Rio Bermejo can be attributed to industrialisation. The Rio Bermejo basin predominantly serves an agrarian economy, compared to the more industrialised River Wear basin. Therefore, industrialisation effects the abundance of microplastics, agreeing with Alam et al. (2019). The larger river basin and longer river length in the Rio Bermejo, compared to the River Wear, could also mean there is a greater distribution of microplastics in the basin and river, reducing the concentration of microplastics found in the river.

In the River Wear, River Wear (Durham City) and the Rio Bermejo, microplastic fibres are the dominant shape (Table 2, 4 and 5). In riverbank sediment in the Rio Bermejo, 76.9% of microplastics are fibres, compared to 93.7% in River Wear sediments. This implies that WWTPs are a significantly greater contributor of microplastics in the River Wear, compared to the Rio Bermejo, due to the greater abundance of fibres (Horton et al., 2017). 100% of microplastics in suspended sediment in the Rio Bermejo were fibres. However, the physical properties of fibres may skew the type of shape found in water samples towards fibres (see Section 5.1.1). Additionally, water samples generally have a dominance of fibres (Woodward et al., 2021), therefore shape comparisons are more accurate using river channel sediment.

A greater range of colours is seen in River Wear samples (Figure 9) compared to Rio Bermejo samples (Figure 7), with a dominance of black and blue coloured microplastics. The significance of blue coloured microplastics were similar to previous studies (Turner et al., 2019). Blue fibres, in particular, were the most abundant microplastic in an urban UK lake, making up 25% of all particles (Turner et al., 2019). As coloured microplastics are thought to be associated with consumer products with a longer time of usage (Yang et al., 2021; Shruti et al., 2019), it can be interpreted that the majority of microplastics found in the River Wear and Rio Bermejo originate from plastic items that are not single-use items. The low amount of transparent-coloured microplastics seen in the River Wear and the Rio Bermejo suggest that disposable single-use plastic items, have less of an influence on the overall course in both rivers (Yang et al., 2021). However, in the River Wear (Durham City), transparent microplastics were the most dominant colour (27%) (Table 2) (McGuinness, 2022). This can be interpreted that disposable, single-use plastics have a higher influence on the microplastic assemblage in the city, compared to the overall course of the River Wear. Interpretations made on the specific source of the plastic based solely on colour is ambiguous and out of this study's breadth (see Section 1.6). It is however important to note the colours of microplastics for future comparative references to aid in understanding the proportions and its ecological effects.

There is no obvious relationship between microplastic shape and colour found in this study. In surface suspended sediment and riverbank sediments in the Rio Bermejo, 100% and 76.9% of microplastic particles found were fibres (Table 3), of which 62% and 61% were black respectively (Figure 7a and 7b). In the River Wear, fibres made up 93.7% of the microplastic assemblage (Table 4), of which 45% were black (Figure 9). Blue coloured microplastics made up the second most common colour in both Durham (22%) and Rio Bermejo samples (14% and 15% in surface suspended and riverbank sediments respectively) (Figure 7 and 9). This indicates that the source of microplastics in both rivers come from a variety of plastic items and colours.

5.4. Global comparison and importance of findings

Previous studies typically focus on microplastic abundance and shape, with less data on size and colour (Table 2). This section will discuss this study's results in comparison to data from UK studies and globally (Table 2), focussing on microplastic abundance and shape. Putting this study's results into global context will help to elucidate any key differences. Comparing microplastic assemblages between global studies with different sampling methods may be a better indicator of microplastic contamination and their input sources than abundance alone, as noted previously in Chapter 5.2, therefore this section will focus more on assemblage.

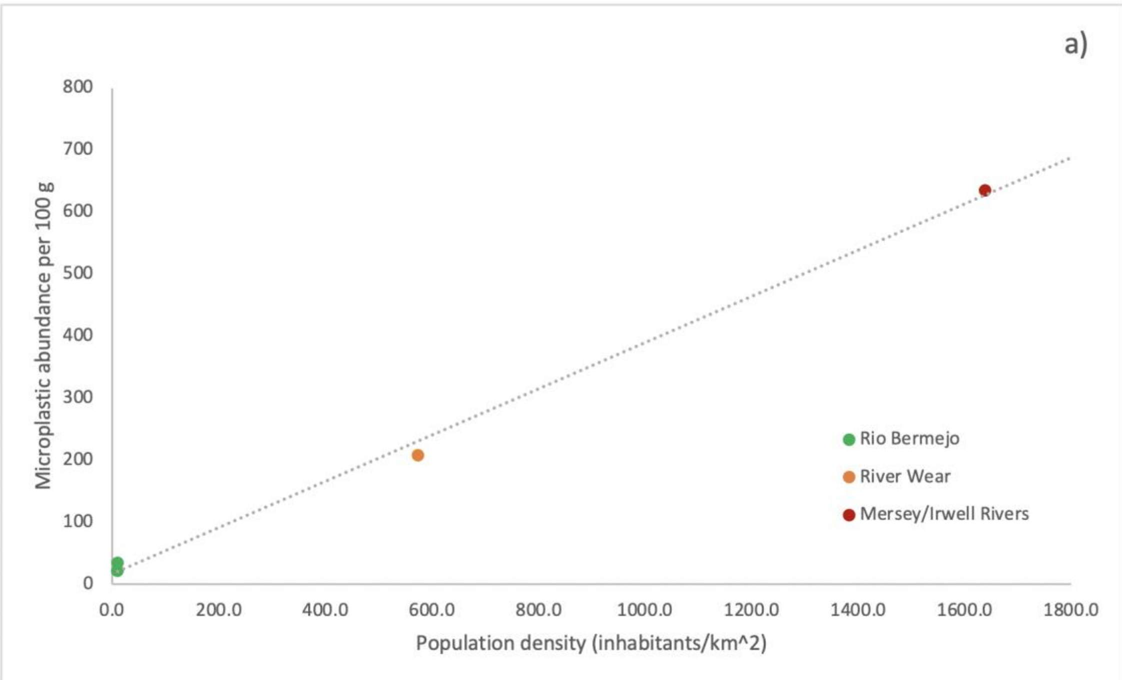
In comparison to data from other locations, the concentration of microplastics in the Rio Bermejo (Table 3) are comparably less than that of the River Thames (Horton et al., 2017) and Mersey/Irwell Rivers (Hurley et al., 2018) in the UK (Table 2). Globally, it is also much less in comparison to rivers in Shanghai, China (Peng et al., 2018) and Nakdong River, South Korea (Eo et al., 2019), but greater than that of Ciwalengke River, Indonesia (Alam et al., 2019) (Table 2). In comparison to previous UK data, average microplastic abundances in the River Wear were greater than that of the River Thames (Horton et al., 2017), but less than that of Mersey/Irwell Rivers (Hurley et al., 2018) (Table 2). Globally, the River Wear had greater average abundances than rivers in Shanghai, China (Peng, G. et al., 2018), the River Nakdong, South Korea (Eo et al., 2019) and Ciwalengke River, Indonesia (Alam et al., 2019) (Table 2). Differences in microplastic abundances may be due to differences in sampling methods, and therefore results may not be directly comparable. For example, Alam et al. (2019) carried out sediment sampling in the middle of the river channel, whereas Eo et al. (2019) does not specify the location. The location of river sediment sampling can affect the microplastic abundance (see Section 2.2) (Woodward et al., 2021). Areas of microplastic accumulation (hotspots) can also cause microplastic abundances to be unrepresentatively high in comparison to the overall river course (Tibbetts et al., 2018). Therefore, a standard sampling location will help to reduce anomalous results and provide a more accurate assessment of the microplastic contamination. The Ciwalengke River (Alam et al., 2019) observed the lowest microplastic abundances compared to every other study in Table 2, despite sampling a slum area with a high population density. A reason for this may be that Alam et al. (2019) dried wet sediment samples at 100°C for 48 hours during laboratory processing, which is a very high temperature that can cause microplastic distortion (Nuelle et al., 2014) (see Chapter 3.2.1). This may have resulted in an underestimation of microplastics during visual identification.

Globally, the three studies with the greatest abundance of microplastics are UK based (the River Wear in this study, River Tame, Greater Manchester (Woodward et al., 2021) and Mersey/Irwell Rivers (Hurley et al., 2018)) (see Table 2). Contrastingly, the River Tame, Birmingham, UK has the second lowest abundance compared to the other studies (Table 2), despite representing one of the most urbanised systems in the UK (Tibbetts et al., 2018). This may again be due to differences in field sampling methods, which was noted by Tibbetts et al. (2018), as well as in laboratory preparation. For example, during separation by density solution, Tibbetts et al. (2018) only allowed the solution to settle for 15 minutes, compared to 4+ hours in this study and Hurley et al. (2018) (see Section 3.3). A shorter time of settling may have reduced the amount of microplastics collected from the supernatant.

This study used a similar field sampling and laboratory processing methodology in River Wear sediments as Hurley et al. (2018), therefore closer comparisons can be made. Hurley et al. (2018) exhibited much higher overall abundances in the Mersey/Irwell Rivers, UK (635 microplastic particles per 100 g), than the River Wear (208.4 microplastic particles per 100 g) (Table 2). The Mersey/Irwell Rivers serve a population of 2.55 million (1637.2 inhabitants/km^2) (Hurley et al., 2018), compared to 620,000 in the River Wear basin

(574.1 inhabitants/km^2). A strong positive correlation was observed between population density and microplastic abundance between the Rio Bermejo, River Wear, and the Mersey/Irwell Rivers (Figure 10a): note, there are only three studies presented which may be influencing the strong correlation. Although field sampling methods for the Rio Bermejo were different to said studies, similar laboratory processing methods were used and so direct comparisons can be made. The Mersey/Irwell Rivers catchment is also relatively more urbanised and is the second most populated urban area in the UK. WWTPs in the Mersey/Irwell River catchment are operated by United Utilities, which have been known to release the highest amount of untreated wastewater and sewage in England (Laville et al., 2021). The River Wear basin catchment is under management by Northumbrian Water. In 2021, United Utilities had 113,940 incidents of untreated discharges and spills, compared to Northumbrian Water, which had 32,947 spills (Laville et al., 2021). This could suggest that the higher abundance of microplastics in the Mersey/Irwell Rivers could also be a result of the higher volumes of untreated wastewater released, compared to in the River Wear. It should be noted that 2021 does not represent the year of sampling that the Mersey/Irwell Rivers and the River Wear took place in. Despite this, policy in the UK has allowed untreated spills to be released into UK rivers for several decades (DEFRA, 2002; DEFRA 2012) (see Section 1.6.1), therefore highlighting the issue of untreated wastewater discharges. Untreated wastewater discharges also occur globally (Woodward et al., 2021), emphasising the global issue that untreated discharges have on microplastic contamination. Stricter legislations surrounding untreated water discharges should therefore be enacted to reduce the amount of microplastics released into the freshwater system. This suggests that population size and density, WWTPs and urbanization influence the abundance of microplastics, as also observed between the Rio Bermejo and River Wear (see Section 5.3).

A graph of results of microplastic abundance against population density from select previous studies and of this study was plotted (Figure 10) to identify any global relationships. Figure 10b indicates that the positive correlation between overall population density and microplastic abundance, as indicated in Figure 10a, is no longer apparent. No correlation between population density and microplastic abundance was also observed in Klein et al. (2015) and Tibbetts et al. (2018). This could, however, be due to the different sampling methods undertaken by the studies, causing differences in microplastic abundances. The strong correlation between this study's results and Hurley et al. (2018) (Figure 10a) emphasises that standardization of methodology is necessary for further direct comparisons to be made. This will allow unequivocal interpretations to elucidate the influence of various factors on microplastic assemblage.



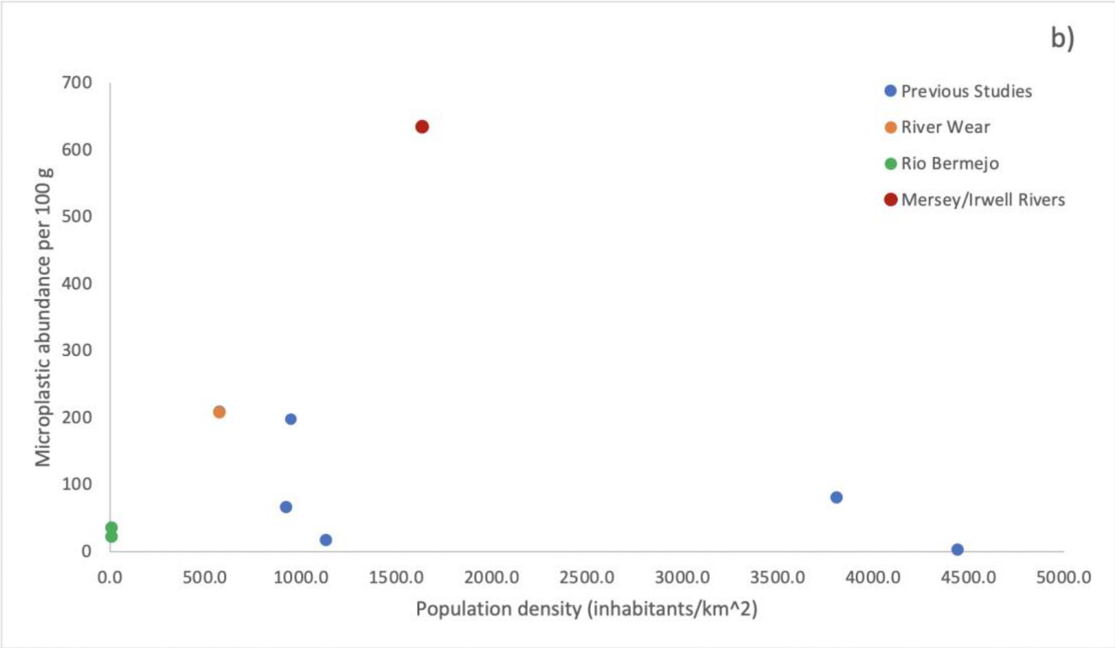


Figure 10. *Microplastic abundance in freshwater sediments against population density from this study and* ***a)*** *Mersey/Irwell Rivers (Hurley et al., 2018), segregated due to similar sampling methods, and* ***b)*** *select studies (n=9) shown in Table 2. Microplastic abundances were taken as an overall average from previous literature (see Table 2). Population density values were either taken directly from the studies, from values of population and catchment area provided in previous studies or from available data online. Data from the River Wear (Durham City) are not included due to the small sampling area in that study (McGuinness, 2022) and lack of representative population density value comparative to the River Wear overall. Mersey/Irwell Rivers are in the UK (Hurley et al., 2018), and Nakdong River is in South Korea (Eo et al., 2018). See Table 2 for complete results.*

Comparing upstream to downstream regions along the Rio Bermejo and the River Wear show no specific distribution or trend with microplastic abundance in any of the sampling mediums (Table 4 and 5). This was also observed in the River Wear (Durham City) (McGuinness, 2022), Ciwalengke River, Indonesia (Alam et al., 2019) and the River Ems, Germany (Eibes et al., 2022). These studies considered external influences, including population size, proximity to WWTPs, and location of river weirs, to influence the microplastic abundance (see Section 1.4.1) (McGuinness, 2022; Alam et al., 2019, Eibes et al., 2022).

Microplastic fibres were the most abundant shape in the River Wear (Table 5) and the River Wear (Durham City) (Table 2). However, compared to other riverine studies in the UK, fragments were the dominant shape in the Mersey/Irwell Rivers (57%) (Hurley et al., 2018), the River Thames (49.5%) (Horton et al., 2017), and the River Tame (49%) (Tibbetts et al., 2018) (Table 2). Fibres accounted for a lower proportion in these studies (Table 2). From the study by Boucher and Friot (2017), it was expected that the River Wear would have a higher proportion of secondary microplastics than fibres compared to the Rio Bermejo (see Section 1.8). These results suggests that the River Wear has a larger influence from WWTPs than other regions within the UK where terrestrial runoff has a larger influence (see Section 1.6). Moreover, the more varied microplastic shape assemblage seen in other UK studies, such as the Mersey/Irwell Rivers (Hurley et al., 2018) and River Tame, Greater Manchester (Woodward et al., 2021), may be a result of more spills of untreated wastewater released from WWTPs and combined sewage overflows. Woodward et al. (2021) observed that in sample sites proximal to a point source, the microplastic assemblage in riverbed sediment was proportionally similar to that in the untreated discharge released from the combined sewage overflow. As The Mersey/Irwell Rivers and River Tame, Greater Manchester are both managed by United Utilities, they experienced a higher number of incidents of spills of untreated wastewater compared to in the River Wear. This may explain why there is a greater microplastic shape assemblage, containing a lower proportion of fibres in these studies, compared to the River Wear.

Similarly, to the River Wear, microplastic fibres were also the most abundant shape in the Rio Bermejo (Table 4). Globally, fibres were also the dominant shape in the Ciwalengke River, Indonesia (91%) (Alam et al., 2019) (Table 2). However, in the Nakdong River, South Korea, and rivers in Shanghai, China, fragments (84%) and pellets

(89%) dominate respectively (Table 2) (Eo et al., 2019; Peng, G et al., 2018). This emphasises the varying degrees of influence of terrestrial runoff and WWTPs globally across different freshwater systems, suggesting that the River Wear and the Rio Bermejo has a larger influence from WWTPs than other regions within the UK and globally.

In general, the abundance of microplastics increased as the size of microplastics decreased, seen in both the River Wear and Rio Bermejo (Figure 6 and 8). This agrees with observations seen in the Nakdong River, South Korea (Eo et al., 2019), and the Ciwalengke River, Indonesia (Alam et al., 2019) (Table 2). Furthermore, the majority of microplastics in the River Wear and Rio Bermejo were smaller than 1500 μm (Figure 6 and 8), agreeing with global observations seen in Ciwalengke River, Indonesia (Alam et al., 2019), River Tame, UK (Tibbetts et al., 2018), rivers in Shanghai, China (Peng, G et al., 2018) and the Nakdong River, South Korea (Eo et al., 2019 (Table 2). This was also observed in Hampstead Pond, a lake in the UK (Turner et al., 2019).

This study's findings on size are important when considering the bioavailability of microplastics in freshwater systems. Previous research observed that the bioavailability of microplastics increase with a decrease in size range (see Section 1.5.1) (e.g. Wright et al., 2013). With a greater abundance of smaller sized microplastic particles in the environment, the risk of ingestion is greater. Considering the ubiquity of microplastics in the freshwater environments, this highlights the risks of microplastic ingestion by aquatic organisms. As fishing occur in both the Rio Bermejo and the River Wear, the movement of microplastics through the food chain and into humans, is also possible (see Section 1.5) (Wright and Kelly, 2017). Additionally, small microplastic particles (<200 μm) are less likely to be retained in riverbed sediments and are more likely to be transported to the marine environment than larger microplastics (Nizzetto et al., 2016).

5.5. Limitations and Future Research

Microplastic particles with dimensions smaller than the mesh size used during water sampling (300 μm) were observed in the surface suspended sediment, with the smallest particle found to be 167 μm. A potential explanation could be that some microplastic particles were trapped in larger organic material during sampling and hence not filtered out during sampling (Lindeque, 2020). Another potential explanation could be that clay minerals could interact with and adsorb microplastics (Corcoron et al., 2015). Additives and fillers, used to enhance properties of plastic, could interact with electrostatic forces on the silicate layers of clay (Corcoron et al., 2015). This could also be another reason for microplastics sinking and settling on the channel bed (Corcoron et al., 2015).

It should also be noted that data of WWTPs, including location and sewage release compliance, along the Rio Bermejo is not available, and therefore, it is difficult to accurately determine how WWTPs influence the microplastic assemblage in this study. However, understanding the dominant input source of an area can help to understand specific areas to focus on managing and limiting microplastic contamination in the future.

Differences in methodologies amongst studies, including field sampling, laboratory processing, and visual inspection, complicate direct comparisons between studies. Sampling methods may affect the outcome of microplastic assemblage. The dominance of fibres in suspended sediment may also be due to the short exposure time of the manta trawl net in the water, due to the high sediment yield in the Rio Bermejo, and therefore the limited breadth of sediment sampled, as noted by Dris et al. (2015). The lack of microbeads found may be a result of the mesh size influencing the types of particles found, where previous studies found that microbeads were only observed when using a mesh size of 100 μm (Lindeque et al., 2020). However, previous studies typically do not compare the abundance in suspended sediment as a unit of weight, but rather as volume (e.g. Alam et al., 2019; Dris et al., 2015). Moreover, it should also be noted that the number of microplastics detected during sampling may be underestimated, as only 10 g of sediment per sample site was used for analysis. This highlights the need for a standardised method of sample collection and analysis. Future studies should focus on standardizing methodology when researching freshwater microplastics.

Issues with visual inspection in this study may explain the relatively small percentage of translucent/white microplastic particles observed compared to previous studies (see Section 3.5). This may mean that this study's results of colours are not completely representative of the entire microplastic assemblage in the study sites. However, proportional comparisons of colour against Durham and Rio Bermejo samples can still be made, allowing links to ecological risks to be made for future references.

Due to the variety of factors that affect the transport and distribution of microplastics, such as flow velocity, water depth and bottom topography, the fate of microplastics in freshwater environments is complex to predict and more research is required on predicting the fate of microplastic particles (Eerkes-Medrano et al., 2015). The need for research is also highlighted by the fact that there were no significant differences between the proportions of microplastic found between sample locations, or from upstream to downstream, suggesting that sample location along a river does not affect the abundance of microplastics, but rather external factors. Future studies should consider seasonal variations, nearby land use, population densities and other inputs into freshwater systems, such as storm drains (Horton et al., 2017). Sampling a site located without a direct influence from WWTPs (e.g. upstream of any WWTPs) would also help to understand the significance of other external influences. For example, terrestrial runoff (Kelly et al., 1996), or atmospheric fallout (Dris et al., 2015). This was not possible in this study due to river accessibility issues.

This study highlights the ubiquity of microplastics in the terrestrial environment, and the challenges faced when carrying out research within microplastics. Standardization of methodology is required to be make more accurate comparisons between sites and site locations. This study identifies that anthropogenic activity influence the input of microplastics into the freshwater system, with factors such as population size and wastewater treatment plants influencing the amount and type of microplastics in the riverine system.

Conclusion

This is the first study to identify microplastics along the course of a river in Argentina, South America, and County Durham, Northeast England. Microplastics were quantified and characterised into shape, size, shape and colour to understand input sources, the factors that affect it and their degrees of influence. Comparisons were made between the River Wear and Rio Bermejo to address differences between the Global North and the Global South. These two river systems had differences in population density, urbanisation and technology efficiency. The data produced in this study helped to elucidate how these factors affected microplastic abundances and their physical characteristics. This study observed microplastic particles in all study sites across the Rio Bermejo and the River Wear, highlighting the ubiquity of plastics in freshwater environments. The River Wear contained a higher abundance of microplastics (208 microplastics/100 g) than the Rio Bermejo (35 microplastics/100 g and 22 microplastics/100 g in suspended sediment and riverbank sediment respectively), due to higher urbanisation and population density. A high abundance of microplastic fibres in the River Wear (93.7%) and the Rio Bermejo (100% and 76.9% in suspended sediment and riverbank sediment respectively) suggests that WWTPs were the dominant input source in both rivers. This highlights the need for better wastewater management techniques to prevent microplastic fibres from entering the freshwater environment. Microplastics <500 μm were the most common size range in both rivers. With a decrease in microplastic size, there was an increase in abundance of microplastics, highlighting the risk of microplastics in ecological ingestion. Providing unequivocal interpretations for microplastic sources is difficult due to the number of complex external factors that affect riverine microplastic distribution. Even if the results in this study are not completely representative of the entire microplastic assemblage and abundances, the results in this study help to understand the proportional differences of microplastic abundances and type between study sites along a freshwater system. Placing this study into a global context, it highlights the need for methodology standardization to ascertain the dominant input source compared to other regions: which ultimately affect future policies to mitigate microplastic contamination. Future research should assess how other factors can influence microplastic abundances and their characteristics, for example population density, land use and river forces and dynamics. Characterizing microplastics by density would help to understand how hydrodynamic forces affect the distribution of microplastics.

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Appendix A – Raw Data

Sample Number	Study Site	Shape	Colour	Size (μm)
1	Batts Village Terrace	Fibre	Black	251
2	Batts Village Terrace	Fibre	Black	251
3	Batts Village Terrace	Fibre	Red	167
4	Batts Village Terrace	Fibre	Black	334
5	Batts Village Terrace	Fibre	Black	167
6	Batts Village Terrace	Fibre	Indigo	251
7	Batts Village Terrace	Fibre	Red	835
8	Batts Village Terrace	Fibre	Black	334
9	Batts Village Terrace	Fibre	Indigo	1002
10	Batts Village Terrace	Fibre	Black	501
11	Batts Village Terrace	Fibre	Black	334
12	Jubilee Nature Area	Fibre	Black	251
13	Jubilee Nature Area	Fibre	Black	334
14	Jubilee Nature Area	Fibre	Red	668
15	Jubilee Nature Area	Fibre	Black	167
16	Jubilee Nature Area	Fibre	Black	418
17	Jubilee Nature Area	Fibre	Black	3000
18	Jubilee Nature Area	Fibre	Black	1002
19	Jubilee Nature Area	Fragment	Blue	1169
20	Jubilee Nature Area	Fibre	Black	501
21	Jubilee Nature Area	Fibre	Black	501
22	Jubilee Nature Area	Fibre	Black	668
23	Jubilee Nature Area	Fibre	Black	668
24	Jubilee Nature Area	Fibre	Black	501
25	Jubilee Nature Area	Fibre	Black	835
26	Jubilee Nature Area	Fibre	Indigo	668
27	Jubilee Nature Area	Fibre	Black	1002
28	Jubilee Nature Area	Fibre	Red	334
29	Jubilee Nature Area	Fibre	Black	835
30	Jubilee Nature Area	Fibre	Black	2004
31	Jubilee Nature Area	Fibre	Black	6000
32	Jubilee Nature Area	Film	Blue	1169
33	Jubilee Nature Area	Film	blue	167
34	Jubilee Nature Area	Fibre	Black	1002
35	Jubilee Nature Area	Fibre	Black	835
36	Jubilee Nature Area	Fibre	Blue	501
37	Jubilee Nature Area	Fibre	Blue	251
38	Deerness Valley Nursery	Fragment	Red	167
39	Deerness Valley Nursery	Fibre	Black	167
40	Deerness Valley Nursery	Fibre	Black	251
41	Deerness Valley Nursery	Fibre	Black	167
42	Deerness Valley Nursery	Fibre	Black	501
43	Deerness Valley Nursery	Fibre	Blue	835
44	Deerness Valley Nursery	Fibre	Black	835
45	Deerness Valley Nursery	Fibre	Blue	501
46	Deerness Valley Nursery	Fibre	Black	334
47	Deerness Valley Nursery	Fibre	Black	835
48	Deerness Valley Nursery	Fibre	Black	501
49	Deerness Valley Nursery	Fibre	Black	334
50	Deerness Valley Nursery	Fibre	Black	6000
51	Deerness Valley Nursery	Fibre	Black	668

52	Holliday Park	Fibre	Indigo	251
53	Holliday Park	Fibre	Black	2004
54	Holliday Park	Fibre	Black	167
55	Holliday Park	Fibre	Blue	835
56	Holliday Park	Fibre	Blue	1002
57	Holliday Park	Fibre	Black	919
58	Holliday Park	Fibre	Translucent	668
59	Holliday Park	Fibre	Black	334
60	Holliday Park	Fibre	Blue	668
61	Holliday Park	Fibre	Black	501
62	Holliday Park	Fragment	Translucent	334
63	Holliday Park	Fibre	Black	251
64	Holliday Park	Fibre	Red	167
65	Holliday Park	Fibre	Indigo	1670
66	Holliday Park	Fibre	Indigo	1670
67	Holliday Park	Fibre	Indigo	2004
68	Holliday Park	Fibre	Indigo	835
69	Holliday Park	Fibre	Indigo	1336
70	Holliday Park	Fibre	Indigo	1336
71	Holliday Park	Fibre	Grey	1336
72	Cocken Road	Fibre	Blue	1169
73	Cocken Road	Fibre	Blue	334
74	Cocken Road	Fibre	Blue	835
75	Cocken Road	Fibre	Grey	167
76	Cocken Road	Fibre	Red	1169
77	Cocken Road	Fibre	Blue	752
78	Cocken Road	Fibre	Red	334
79	Cocken Road	Fibre	Translucent	1002
80	Cocken Road	Fibre	Blue	668
81	Cocken Road	Fibre	Blue	501
82	Cocken Road	Fibre	Black	668
83	Cocken Road	Fibre	Black	167
84	Cocken Road	Fibre	Black	1086
85	Cocken Road	Bead	Orange	84
86	Cocken Road	Fibre	Red	251
87	Cocken Road	Fibre	Indigo	167
88	Cocken Road	Fibre	Black	334
89	Cocken Road	Fibre	Blue	418
90	Cocken Road	Fibre	Indigo	2004
91	Cocken Road	Fibre	Blue	2004
92	Cocken Road	Fibre	Red	501
93	Cocken Road	Fibre	Black	835
94	Cocken Road	Fibre	Black	501
95	Cocken Road	Fibre	Black	334
96	Riverside Wildlife Area	Fibre	Indigo	835
97	Riverside Wildlife Area	Fibre	Black	334
98	Riverside Wildlife Area	Fibre	Black	668
99	Riverside Wildlife Area	Fibre	Black	668
100	Riverside Wildlife Area	Fibre	Indigo	1169

101	Riverside Wildlife Area	Fibre	Translucent	1503
102	Riverside Wildlife Area	Fibre	Red	2672
103	Riverside Wildlife Area	Fibre	Blue	1169
104	Riverside Wildlife Area	Fibre	Translucent	835
105	Riverside Wildlife Area	Fibre	Black	501
106	Chester-le-Street Park	Fibre	Translucent	2004
107	Chester-le-Street Park	Fibre	Translucent	3000
108	Chester-le-Street Park	Fibre	Blue	418
109	Chester-le-Street Park	Fibre	Black	1002
110	Chester-le-Street Park	Fibre	Black	167
111	Chester-le-Street Park	Fibre	Black	334
112	Chester-le-Street Park	Fragment	Blue	251
113	Chester-le-Street Park	Fibre	Black	1002
114	Chester-le-Street Park	Fibre	Blue	835
115	Chester-le-Street Park	Fibre	Black	334
116	Chester-le-Street Park	Fibre	Black	585
117	Chester-le-Street Park	Fibre	Black	334
118	Chester-le-Street Park	Fibre	Indigo	668
119	Chester-le-Street Park	Fibre	Black	501
120	Chester-le-Street Park	Fibre	Blue	835
121	Chester-le-Street Park	Other	Blue	1169
122	Chester-le-Street Park	Fibre	Black	1169
123	Washington	Fibre	Indigo	1002
124	Washington	Fibre	Indigo	1002
125	Washington	Fibre	Blue	2004
126	Washington	Fibre	Red	835
127	Washington	Fibre	Black	2004
128	Washington	Fibre	Indigo	1086
129	Washington	Fibre	Black	919
130	Washington	Fibre	Black	251
131	Washington	Fibre	Translucent	2667
132	Washington	Fibre	White	3750
133	Washington	Fragment	Black	1670

Appendix A1. Complete dataset from Durham showing shape, colour and actual size of observed microplastics. Microplastics were obtained from 10 g samples of sediment. Note for Cocken Road, samples were obtained from 4.18 g and Holliday Park samples were obtained for 9.87 g. These samples were extrapolated to 10 g for later analysis.

a)

Number	Study Site	Type	Colour	Size (µm)
1	Rio San Francisco	Fibre	Red	1002
2	Rio San Francisco	Fibre	Red	668
3	Rio San Francisco	Fibre	Blue	418
4	Rio San Francisco	Fibre	Black	835
5	Embarcacion	Fibre	Red	167
6	Embarcacion	Fibre	Black	167
7	Embarcacion	Fibre	Black	251
8	Embarcacion	Fibre	Black	334
9	Embarcacion	Fibre	Black	835
10	Embarcacion	Fibre	Black	1837
11	Reserva Natural Formosa	Fibre	Black	334
12	Reserva Natural Formosa	Fibre	Black	251
13	Puerto Lavalle	Fibre	Blue	234
14	El Colorado	Fibre	Black	668
15	El Colorado	Fibre	Indigo	334
16	El Colorado	Fibre	Black	334
17	El Colorado	Fibre	blue	835
18	El Colorado	Fibre	Black	585
19	El Colorado	Fibre	Black	501
20	El Colorado	Fibre	Black	334
21	General Mansilla	Fibre	Grey	1002

b)

Number	Study Site	Type	Colour	Size (µm)
1	Rio San Francisco	Other	Blue	84
2	Embarcacion	Fibre	Black	67
3	Embarcacion	Film	Green	84
4	Embarcacion	Fibre	Black	2004
5	Puerto Lavalle	Fibre	Black	334
6	Puerto Lavalle	Fibre	Black	752
7	Puerto Lavalle	Fibre	Black	835
8	Puerto Lavalle	Fibre	Black	1002
9	Puerto Lavalle	Film	Translucent	1169
10	El Colorado	Fibre	Red	251
11	El Colorado	Fibre	Black	835
12	El Colorado	Fibre	Black	1002
13	General Mansilla	Fibre	Blue	334

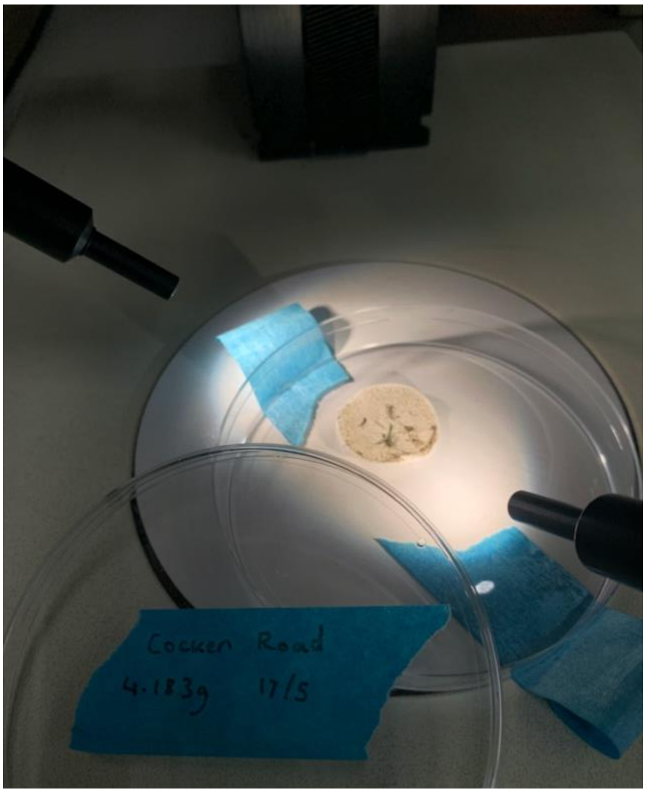
Appendix A2. Complete dataset from Rio Bermejo showing shape, colour and actual size of observed microplastics in **a)** surface suspended sediment **b)** riverbank sediment. Microplastics were all obtained from 10g samples of sediment.

Reference	Study area	Abundance (per 100 g of sediment)	Population density (inhabitants/km^2)
Horton et al., 2017	River Thames, UK	66	925.9
Hurley et al., 2018	Mersey/Irwell Rivers, UK	635	1637.2
Peng, G. et al., 2018	7 rivers and 1 tidal flat in Shanghai, China	80.2	3809.1
Alam et al., 2019	Ciwalengke River, Indonesia	3.0	4444.4
Eo et al., 2019	Nakdong River, South Korea	197	950.0
Tibbetts et al., 2018	River Tame, UK	16.5	1133.3
This study	River Wear	208.4	574.1
This study	Rio Bermejo (SUS)	35	9.7
This study	Rio Bermejo, (RBS)	21.7	9.7

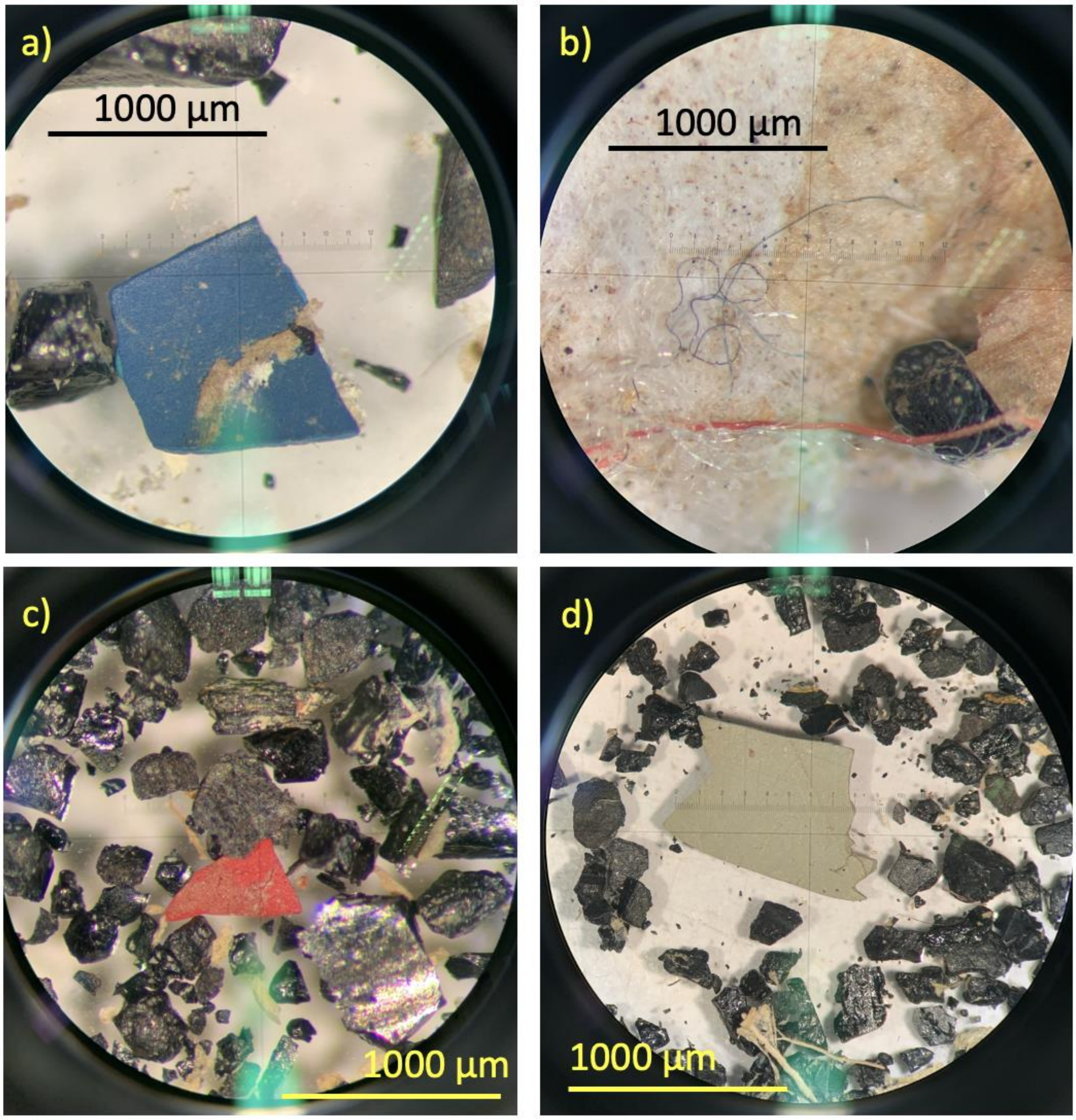
Appendix A3. *Table showing previous literature studies and their corresponding population density. Refer to Figure 10 for the graph.*

Appendix B – Images

Appendix B1. *An example of the sampling site locations in Durham.* ***a)*** *study site Holliday Park (River Browney). Image taken on the 13th May 2022* ***b)*** *The River Wear, image taken not at a specific site included in this study, but is a typical site in the middle-lower course of the river.*



Appendix B2. *Image showing the set up for visual inspection under the stereomicroscope. Filters containing the supernatant were stored in covered and sealed transparent plastic petri dishes. The seal was open only during visual inspection.*



Appendix B3. *Examples of microplastics observed in Durham samples from a preliminary sediment sample collection method that was later altered. These microplastics are not recorded in the final abundance count due to changes in field sampling methods. The methodology for laboratory preparation and density separation however was the same for the current study and these preliminary results. Note the abundance of coal ash in image* ***c)*** *and* ***d)*** *and their black, shiny and angular appearance.*